Università
Ca'Foscari
Venezia

Scuola Dottorale di Ateneo
Graduate School

Dottorato di ricerca
in Scienza e gestione dei cambiamenti climatici
Ciclo XXVI
Anno di discussione 2015

Emissions of anthropogenic pollutants and their environmental concentrations in Alpine areas:

Trends under Climate Change assumptions

SETTORE SCIENTIFICO DISCIPLINARE DI AFFERENZA: CHIM/12
CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI

Tesi di Dottorato di Tair Dolores Teran Guerrero,
matricola 955838

Coordinatore del Dottorato	**Tutore del Dottorando**
Prof. Carlo Barbante	**Prof. Antonio Marcomini**

Acknowledgements

I would like to express my sincere gratitude to my advisor Professor Antonio Marcomini. I would like to thank you for encouraging my research and for allowing me to grow as a research scientist. I would also like to thank my co-advisor Lara Lamon (PhD) for following and giving me your support and invaluable advice on both research as well as on my career have been priceless during my research. I would especially like to thank the members of my PhD external committee Professors Marco Vighi and Katrina Borga for your brilliant comments and suggestions.

Special thanks to Professor Frank Wania and Wania's Research Group at University of Toronto who gave me the support to continue with my research. Notable place is given to Johnny Westgate that always were very patient and gave me the advice in the right moment.

Also thank you to everyone at Marcomini's Research Group who helped the project and support my stay in Venice headquarters. Especially to Elena Semenzin (PhD), Alex Zabeo (PhD), Elisa Giubilato (PhD), Elisa Furlan, Sara Alba and graduate student Leonardo Grassi.

I gratefully acknowledge the funding sources that made my Ph.D. work possible. I was funded by the Ca Foscari University fellowship. My work was also supported by the CONACYT-Mexico PhD grants Program.

An exceptional thanks to my family. Words cannot express how grateful I am to my husband Miguel Angel who supported me in writing, and encouraged me to strive towards my goal and was always my support in the moments when there was no one to answer my queries, my daughters Nuru Constanza and Gaia Inés that always share your loving and well-understanding with your student-mommy. Especially to my mother Gloria Guerrero, I have experienced Your guidance day by day, I will be forever thankful for all of the sacrifices that you've made on my behalf. My sisters and brother Anizul, Daniela and Anuar who supported my dreams and my study. Thanks to my mother-in-law Maria de la Luz Castaneda for being a great grandmother during the early years.

Contents

Abstract

Evidence of climate change has been observed at both the global and local scales. The climate variables considered in this study include temperature, ice extensions, widespread changes and quantities of precipitation, ocean salinity, wind speed and incidents of extreme weather including droughts, heavy precipitation, heat waves and intensity of tropical cyclones.

These climate variables influence the status of the ecosystem and this may negatively influence the ecosystem services that benefit human beings obtain, such as water storage, groundwater recharge, storm protection, flood mitigation, shoreline stabilisation, erosion control and retention of carbon, nutrients, sediments and pollutants, affect human systems.

In this context, this Ph.D. Thesis aims at contributing to the assessment of the impacts of climate change in influencing anthropogenic pollutants' concentration, in particular persistent organic pollutants (POPs), in high-altitude regions, in order to identify how the atmospheric conditions due to climate change may affect the environmental concentrations of the selected pollutants.

First, we presented an exhaustive and critical review regarding the effects of climate change over the POPs' regulation efforts and monitoring programs driven towards decreasing or banning POPs' emissions in the environment.

Second, it was possible to collect relevant environmental data in an online database with chemical information useful for the subsequent application of a multimedia fugacity model named MountainPOP3.0 for the fate and transport of organic pollutants, with the aim of assessing the effect of climate change on POPs' environmental distribution in Alpine environments.

Giving the data available, the case study selected was the mountainous region of the high valley of Adda River (Valtellina) in the Northern Italian Alps, while the considered pollutants were HCB and α-HCH. We carried out a number of dynamic simulations considering two different scenarios, a current scenario (20CE) and a future one (RCP4.5). We performed a comparative analysis of the results of the simulations, as a tool for identifying the effects of climate change over the environmental behaviour of POPs.

Estratto

Evidenze dei cambiamenti climatici sul comportamento ambientale dei contaminanti organici persistenti sono stati osservati sia a scala globale che locale. Variabili climatiche considerate in questi studi includono temperatura, estensione dei ghiacciai, cambiamenti diffusi nel modello e quantità delle precipitazioni, della salinità degli oceani, dei venti e gli eventi meteorologici estremi compresi siccità, forti precipitazioni, ondate di calore e l'intensità dei cicloni tropicali.

Le variabili climatiche influenzano quindi lo stato dell'ambiente e questo può influenzare negativamente la fruibilità da parte dell'uomo, come lo stoccaggio di acqua, ricarico delle falde acquifere, protezione della tempesta, mitigazione delle alluvioni, la tutela dei litorali, il controllo dell'erosione e lo stoccaggio di carbonio, ecc.

In questo contesto, questa tesi di dottorato si propone di contribuire alla valutazione degli impatti dei cambiamenti climatici che influenziano le concentrazione degli inquinanti di origine antropica, in particolare gli inquinanti organici persistenti (POP), nelle regioni ad alta quota, al fine di individuare come il cambiamento climatico possa influenzare le concentrazioni ambientali di contaminanti selezionati. Innanzitutto viene presentata una relazione esaustiva e critica per quanto riguarda gli effetti dei cambiamenti climatici sui monitoraggi dei POP attraverso la riduzione o la messa in bando delle emissioni dei POP nell'ambiente. In secondo luogo è stato possibile raccogliere dati ambientali rilevanti in un database online con informazioni chimiche utili per la successiva applicazione del modello di fugacità MountainPOP3.0 per il trasporto e destino degli inquinanti organici al fine di valutare gli effetti dei cambiamenti climatici sulla distribuzione ambientale dei POP in ambienti alpini. In base alla disponibilità di dati il caso di studio individuato è l’alta valle del fiume Adda (Valtellina), i contaminanti considerati sono HCB ed α-HCH. Sono state fatte diverse simulazioni dinamiche considerando due diversi scenari climatici, uno presente (20CE) ed uno futuro (RCP4.5) e i risultati sono stati confrontati come indicatore dell’effetto climatico sul comportamento ambientale dei POP.

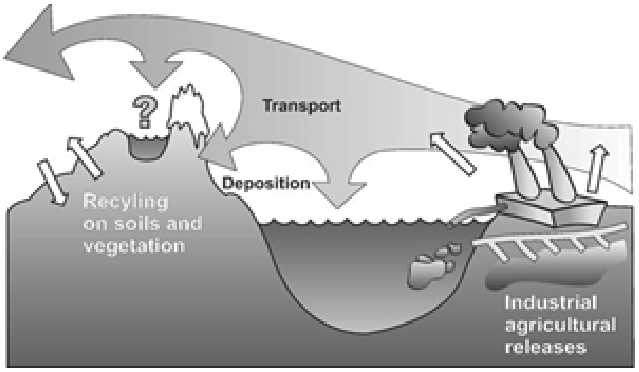
1. Introduction

1.1 Persistent Organic Pollutants and climate change

High-altitude mountainous ecosystems had been considered amongst the last pristine and ‘‘untouched’’ environments on our globe (Daly and Wania, 2005). However, these mountainous regions are often found in the vicinity of densely populated and industrialized regions, thus being important recreational areas (e.g., ski resorts, hiking), commonly used for extensive agricultural purposes (e.g., husbandry) and even as energy resources (e.g., as water supplies for hydropower plants) or as water reservoirs. For these reasons, the ecosystems of alpine areas (e.g., European Alps, Blue Mountains, Sierra Nevada, South American Andes, European Pyrenees, Himalayas, Australian Snowy Mountains, etc.) are already under substantial ecological pressure and have been the subject of particular attention and analyses of atmospheric studies(Guzzella et al., 2011; Kirstine et al., 1998; Calamari et al., 1991).

Persistent organic pollutants (POPs) are chemical substances that resist to environmental, chemical, physical and biological degradation (Hung et al., 2005). Because of their characteristic persistence, they are transported through air, water and migratory species across international boundaries and deposited far from their place of release, where they are accumulated in terrestrial and aquatic ecosystems (UNEP, 2001). Due to POP's long range transport potential, they have attracted scientific and political concern during the last decades (WHO, 2003), stimulating several conventions and initiatives, started in the past decades (UNECE, 1998; UNEP, 2001).

In the last 24 years, some studies have revealed that alpine environments, similar to the Polar Regions, are also affected by the deposition of POPs identified as sinks or receivers. In contrast, the tropical areas have been identified, mainly due to climatic and meteorological reasons, more as contamination sources (Kallenborn et al., 2007; Calamari et al., 1991). In special, Alpine regions are named as ‘‘early warning’’ sites with respect to global and medium-range transport, as well as for distribution processes for semi-volatile POPs (Kallenborn et al., 2007).



Notes: From (Kallenborn et al., 2007).

Figure 1.1. Principles of transport, deposition, and re-evaporation for persistent organic pollutants (POPs) into and from remote alpine regions.

Wania and Mackay, 1996 defined “global-fractionation” as the phenomenon that govern transport and behaviour of POPs at different latitudes, depending on environmental characteristics, mainly temperature gradient at latitudinal gradients. In this sense, Ccolder temperatures can favour greater absorption of POPs' into particulate matter in atmosphere and water, which then deposit on the surface and sediments. At colder temperatures, POPs remain more time into the environmental compartments and become more persistent. Besides, in cold ecosystems, POPs from water condense and move along different media from the atmosphere to the soil, ice and snow. For example, Gewurtz et al., 2006 reported differences between POPs accumulation rates in some fish species depending on where they live; in the Arctic region the POPs accumulation is more readily than in temperate region. On te other hand, POPs fluctuate along a temperature or latitudinal gradient: with low concentrations in the tropics at warm temperatures and high concentrations in the polar regions at colder temperatures. On a smaller scale, mountains achieve climatic gradients in an altitude gradient.

Daly and Wania, 2005 have pointed out that mountain regions are ideal settings to study contaminant transport and behaviour along gradients of climate and surface cover; especially with organic contaminants, its concentration on air, water bodies and biota is dynamic.

Due to their topography, mountain ranges have lower temperature averages than the surrounding lowlands, as well as increased precipitation. These specific meteorological conditions may increase a substance overall persistence, because degradation is slower at lower temperatures and the degradability of many substances is lower in surface media than in air (Wegmann et al., 2006). The “cold condensation effect” could increase POPs deposition rates and surfaces, favouring these regions as secondary emitters for POPs. These compounds are then available for transport from source regions to more pristine regions such as the Arctic, under favourable flow patterns associated with global climate variations.

Evidence of CC has been observed at both the global and the 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. CC influences the status of the ecosystem that may accordingly be affecting human systems.

The climate system is constituted by several components or compartments: atmosphere, water systems, living organisms. These elements determine various climate factors that govern the climate. The interactions between climate system’s components drive temporally and spatially averaged exchanges of heat, momentum, and water vapour that ultimately determine growth, recruitment, and migration patterns of POPs (Lamon et al., 2009; Daly and Wania, 2005).

Climate change assessment dictates a global perspective and time horizons that could cover periods from decades to centuries (Rogelj et al., 2012). A research approach is to integrate modelling of climate scenarios that represent an image of the future climate, and multimedia environmental models (MMM) that are tools oriented to study POPs fate and transport. This integrated assessment gives the opportunity to simulate POPs behaviour under climate change assumptions that help the identification of which and how climatological conditions will affect the fate and transport of POPs in the future. Such knowledge may finally be applied in the regulatory context, for instance for estimating the Predicted Environmental Concentration in Risk assessment (Daly and Wania, 2005; Klánová et al., 2011; Wegmann et al., 2009).

1.2 Motivations and objectives

The integration of climate change assumptions on this environmental behavioural modelling has required a major effort, not only in computational resources but also in a better understanding of the scientific basis on both the climate system and environmental behaviour of chemicals. Therefore, the main objective of this thesis is to assess the impacts of climate change effects on anthropogenic pollutants' concentration, in particular POPs, in high-altitude regions. In particular, the present work aims: 1) to identify the effect of climate change in the POPs fate and transport as a benchmark between current and future international regulatory framework; 2) to collect POPs under Stockholm Convention and Aarhus Protocol in order to reduce the gap between monitoring data and modelling of POPs behaviour in alpine environments; 3) to adapt and apply a fugacity model for mountainous region under climate change assumptions, focusing on the integration of climate variables in a dynamic mode as a novel analysis approach of climate change impacts on POPs behaviour at the regional scale. This is done through the following goals: a) identifying the data available in order to define a mountain case study in European Alps; b) using a fugacity model to study the behaviour of selected POPs in European Alps; c) fixing different climatic scenarios for observing and analysing the POPs behaviour under specific climatic conditions. All this, in order to identify how climate variables could affect the source-to-sink relationship in mountainous regions, such as the European Alps.

The structure of the thesis is presented in the next section.

1.3 Description of the work

The present study of the environmental behaviour of the selected chemicals in alpine environment and their trends in concentration changes due to climate change, and its results are presented as follows:

Chapter 2 presents the state of the art on climate change effects on POPs environmental behaviour with a scientific perspective for future regulatory actions. This chapter puts forward a critical literature review on the POPs regulation efforts driven towards decreasing POPs behaviour through reducing or banning POPs emissions in the environment. In order to identify how POPs-related regulation may take into account climate change in managing current or future POPs sources. This objective was achieved by reviewing scientific studies on climate change related effects on POPs environmental behaviour in order to distinguish how climate change is influencing POPs fate and transport. The contents of this chapter come from the paper published during the Ph.D. (Teran et al., 2012)

Chapter 3 shows in deep a review of reported data and information needed in the environmental pollution by POPs in Alpine areas. The main goal was the collection and integration of available reported data in the literature in a novel POPAlp database. Besides, a comparison and validation of quality assurance and quality control (QA/QC) were made between the different monitoring surveys. This chapter is a novel software application development that can be protect by international Intellectual property organization such as copyright and used online by the research community.

- **Chapter 4** is the scientific core of this research and elucidates the adaptation and application of MountainPOP3.0, a multimedia environmental model, aimed at the study of the environmental behaviour of alpha HCH and HCB in Valtellina Valley and their trends in concentration changes due to global climate change over the period 1971 to 2050. Climate change is represented by two scenarios: A) 20CE represents the present scenario and assumes no changes in the actual climate conditions; B) RCP4.5 represents a future scenario (Meinshausen et al., 2011). Both scenarios differ in three climate variables: temperature, precipitation and wind speed. This chapter will bring out the dominance of the landscape parameters when 20CE scenarios are used. This chapter emphasizes the close relationship between temperature changes and the environmental parameters that favour the exchanges between air and soil trhough wet the deposition effect of chemical partitioning between environmental compartments when the RCP4.5 scenario is used.

Finally, this work presents a general conclusions (**chapter 5**) regarding the research topic, and elucidates some suggestions as future work in this theme, which opens the door to further research about the application of another techniques for identifying the sources points or regions of POPs that put at risk vulnerable zones such as high mountainous regions.

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2. Climate change effects on POPs environmental behaviour. A scientific perspective for future regulatory actions

Tair Teran, Lara Lamon, Antonio Marcomini

Published in "Atmospheric Pollution Research" (2012), vol. 3, issue 4, pp 466-476, DOI 10.5094/APR.2012.054

Abstract

Since the adoption of the United Nations Framework Convention on Climate Change international efforts were aimed at limiting global change, and at managing and reducing the inevitable impacts of climate change. The growing concern on climate change related issues lead to create international agreements such as the Kyoto Protocol, and to establish the Intergovernmental Panel on Climate Change aimed at studying climate evolution and at defining common actions through the adoption of joint climate change mitigation and adaptation measures.

From the time when international Task Forces, projects and programs were shared in order to deal with the reduction of environmental exposure to persistent organic pollutants (POPs), international organisations have also been committed to estimating how climate change may affect POPs environmental behaviour and distribution.

In this review paper we report the track of POPs regulation efforts driven towards decreasing POPs environmental concentrations through reducing or banning POPs emissions in the environment. We also report scientific studies on climate change related effects on POPs environmental behaviour in order to feature how climate change is influencing POPs fate and transport. Our final aim is to identify how POPs-related regulation may take into account climate change in managing current or future POPs sources.

We find that in several case studies on this topic climate change is considered to contribute to enhance POPs long range transport and that remote areas are likely to be considered most impacted by POPs pollution under a climate change perspective. Our findings consider also that continuous monitoring programs oriented towards the observation of secondary POPs sources *and the enhancement of inventories reporting primary and secondary POPs emissions are useful in dealing with POPs exposure under climate change scenarios. We also suggest how communication between science and regulation should be driven towards considering climate change effects into chemicals' legislation.*

Keywords

Persistent organic pollutants, climate change, regulation, monitoring programs, multimedia modelling

2.1 Introduction

2.1.1 Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) are chemical substances that resist to environmental, chemical, physical and biological degradation; because of their characteristic persistence, they are transported through air, water and migratory species across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems (UNEP, 2001). POPs inputs in the environment can be distinguished in primary and secondary sources. Primary sources are those with direct fluxes into the environment and secondary sources are already contaminated environmental compartments that can release POPs in a time subsequent to their use or production (UNEP/AMAP, 2011; Hung et al., 2010). Due to their wide distribution, ability to bioaccumulate, and potential harmful effects such as immunotoxicity, neurotoxicity, developmental toxicity, carcinogenicity, mutagenicity, and endocrine disruption potentials, POPs have drawn scientific and political concern during the last decades (WHO, 2003).

POPs undergo long-range transport (LRT), meaning that they are transported to areas that are remote if compared to the source regions. In order to manage the harm posed by POPs, several conventions and initiatives were started in the past decades. The first national regulations and regional agreements, dealing with POPs management were introduced in the late '70s and aimed at banning or limiting the use and production of some POPs (e.g. dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyl -PCB, and in the same period some monitoring programmes were also established.

More recently, the European Parliament adopted a legislation on the Registration, Evaluation and Authorisation of Chemicals (REACH) (ECHA, 2008; EEA, 2007; EU, 2006), that was enforced in 2007. It aims at collecting information on the large amounts of chemicals that entered the European market without appropriate information on the hazards that they may pose to human health and the environment. This is done through the definition of new procedures for the registration of chemicals marketed in Europe and through the identification of a framework for assessing chemicals' impacts on human health and on the environment in order to minimize and avoid future harms caused by exposure to chemicals (ECHA, 2011). Under this framework, a procedure for special approach regarding Persistent, Bioaccumulative and Toxic chemicals (PBTs) and very Persistent and very Bioaccumulative chemicals (vPvBs) that are including POPs (ECHA, 2008) providing assessment on persistence, bioaccumulation and toxicity of marketed chemicals was proposed. This procedure requires the characterisation of the substance and related emissions, the definition of human and environmental exposure and risks associated with the subsequent uses, collecting information on chemicals' persistence, bioaccumulation and toxicity, assessment of exposure and impact on population or environmental stocks, evaluation of the economic value of health and environmental impacts, and an analysis of the positive or negative changes on health or environmental effects (ECHA, 2011). REACH legislation is currently seen as the European contribution to the Strategic Approach to International Chemicals Management (SAICM). The adoption and implementation of the SAICM's goals are related with the linkages between chemicals management, environment, and sustainable development organized under the auspices of the United Nations Economic Commission for Europe (UNECE). The REACH strategy may lead to classification of a substance as either persistent or not, or it may indicate the need for further testing and represents a substantial improvement of testing strategies and interpretation of results from biodegradation tests, maximizing the use of existing data, using multimedia models to identify and prioritize the most important environmental compartments, using this information to help determine the types of persistence data that would be most useful. Similarly, the implementation of international conventions and bodies such as the Mediterranean Action Plan for the Barcelona Convention (MAP) (UNEP, 1978) and the Arctic Monitoring and Assessment Programme (AMAP), clearly established that long range atmospheric transport is one of the main routes by which POPs are deposited in remote regions (Arctic Council, 1991).

2.1.2 Climate Change and its effects on POPs environmental behaviour

In 1980 the World Climate Research Programme (WCRP) was established by the joint action of the International Council for Science (ICSU) and the World Meteorological Organization (WMO) with the goal to determine how predictable the climate is and to assess the effect of human activities on climate.

Several studies reported evidence of current and past climate warming from sea surface temperature (SST) and land surface temperature (LST) observations (Brohan et al., 2006; Hansen et al., 2010; Smith et al., 2005), showing a more rapid temperature increase at higher latitudes than in the global average air and ocean water (Rummukainen, 2010; Solomon et al., 2007). Some consequences related to the increasing temperature are the faster rate of ice melt in the Arctic Sea, in Greenland and Antarctica, and the reduced area covered by ice caps and glaciers (AMAP SWIPA, 2011), and global sea level rise (Rummukainen, 2010; Solomon et al., 2007).

The IPCC Fourth Assessment Report (Solomon et al. 2007) addressed the scientific progress in climate science (Rummukainen, 2010; The Royal Society, 2010), and reports recent observations of particular relevance for the vulnerable regions, such as the Arctic (AMAP SWIPA, 2011), Antarctic (Chen et al., 2009), Greenland and the Alps (EEA, 2007).

When dealing with observed climate change, anthropogenic forcings are taken into account (e.g. anthropogenic emissions of greenhouse gases, land use change) together with environmental factors contributing to climate change (e.g. solar variability and volcanic eruptions) (Rummukainen, 2010; Forster et al., 2007). Climate change induced faster changes from the Earth system response in several regions, consisting for instance in higher summer temperatures in the Arctic that are suggesting that the warming rate over the last 50 years is nearly twice that for the last 100 years (Solomon et al., 2007), and in the changes in net accumulation and melt of Greenland ice sheets (AMAP SWIPA, 2011; Jansen et al., 2007).

Environmental variables such as temperature, wind speed, precipitation, and solar radiation influence directly or indirectly POPs environmental fate and transport. Thus, climate warming is likely to influence the environmental behaviour of POPs by enhancing the volatilisation from primary and secondary sources, by influencing their partitioning between soil, sediment, water and atmosphere, including air-surface exchange, wet/dry deposition, and reaction rates (Armitage et al., 2011; Noyes et al., 2009). In addition, climate change also encompasses the alteration of other important processes that influence POPs fate and transport, such as snow and ice melting (Bogdal et al., 2008), biota lipid dynamics (Matz, 2011), and organic carbon cycling (Nizzetto et al., 2010), changing chemicals’ fugacity capacity in environmental compartments (Armitage et al., 2011; Lamon et al., 2012; Noyes et al., 2009). Moreover, climate variability may induce interannual variations of POPs re-volatilisation that could undermine global efforts aimed at reducing environmental and human exposure to POPs (Klánová et al., 2011; Ma et al., 2011).

Each climate variable is associated to its variability and to the uncertainty related to the projected climate change scenario (IPCC, 2005). This uncertainty needs to be taken into account in POPs multimedia modelling together with the uncertainties related to physical chemical properties.

In this paper, a review of the literature concerning POPs environmental behaviour affected by climate change and some suggestions on possible future regulatory actions is presented in order to contribute to: 1) better understand how global warming could undermine global efforts to reduce environmental and human exposure to POPs; 2) highlight climate change effects increasing POPs environmental mobilization, exposure and transfer; 3) emphasize how regulations could address new POPs, assuming that environmental processes driven by climate change may affect temporal and spatial exposure to POPs; and 4) highlight the importance of screening for new or potential POPs assuming that temporal and spatial patterns of POPs may be affected by various processes driven by climate change.

2.2 State of the art on POPs regulation

POPs are the main focus of several national and international regulatory efforts aiming at reducing their emissions because of their high potential for LRT, persistence, and potential for bioaccumulation and their adverse effects on human health and the environment (TF- HTAP, 2010; Wania, 2006; NCP, 2003; Breivik et al., 2002; Arctic Monitoring and Assessment Programme, 1998).

2.2.1 International treaties on POPs

Transboundary air pollution is one of the most concerning environmental issues that attracted International Communities' efforts in the last 40 years. POPs are considered a global concerning issue and several efforts were done in the past decades to eliminate their emissions through the adoption of international agreements and conventions, as we anticipated before.

High exposure to POPs in remote regions, observation of POPs high concentrations in boreal biota from marine, freshwater and terrestrial ecosystems (Meyer and Wania, 2008; MacDonald et al., 2002; Wania, 1999) are examples of the high international concern on POPs toxicological effects.

Past studies proved the partial effectiveness of control actions by POPs regulations. In Japan, for instance, Kumar et al. (2005) highlighted the evidence that the reduction of some POPs is apparent since some were detected in both the organisms and in the environment, notwithstanding the ban of those substances 30 years ago. Similarly, Shunthirasingham et al. (2010) found that pesticides' concentrations show different trends in different world regions. For instance, following regulatory restrictions, the levels of HCB, HCH and chlordanes declined in most world regions, while some others, like a-endosulfan, chlorothalonil and trifluralin were reduced only for some regions such as Europe. However, some other regions, such as India, showed high concentrations of organochlorine pesticides (OCP).

The first internationally legally-binding instrument to deal with air pollution on a broad regional basis was the Convention on Long-range Transboundary Air Pollution (CLRTAP). Its main objective is to reduce and prevent long-range transboundary air pollution through the knowledge of transfer pathways between countries, promoting monitoring, modelling and prevention of pollutants' emissions into the environment (http://www.unece.org/env/lrtap/lrtap_h1.html).

Although CLRTAP was originally ratified in 1983 to address sulphur emissions in Western Europe, and its respective resulting acidification of the Scandinavian lakes, Canada´s Federal Government prepared and presented just in 1989 a report on POPs in the Arctic to the CLRTAP Working Group on Effects and the convention's Executive Body. Following preliminary studies demonstrating clear evidence that actions to address POPs should be warranted, in 1998 the Aarhus Protocol was drafted and signed with the objective to control, reduce or eliminate discharges, emissions and losses of a list of 12 POPs, including pesticides, industrial chemicals, and by-products. The protocol banned the use of some of them, while others were scheduled for future elimination.

After the official recognition that POPs emissions are affecting remote regions and that atmosphere is the dominant pathway, in 1995 the Governing Council of UNEP invited the Intergovernmental Forum on Chemical Safety and other international bodies to assess the 12 previously identified POPs. The "dirty dozen" were those chemicals that had almost certain adverse effects on human health and the environment; according to several studies on the effects caused by direct and indirect exposure to these substances were made in the past twenty years, in order to quantify their concentration in the environment and food and to prove their potential toxicity, persistence and bioaccumulation (Fürst, 2006; Schecter et al., 2003; Noren and Meironyte, 2000).

The resulting international legally-binding "Stockholm Convention" was finally signed in 2001 and entered into force in 2004, with the aim of addressing the identified list of POPs and of identifying additional candidate substances for future actions (UNEP, 2009). The first task of the UNEP Stockholm Convention since its adoption consisted in proposing a list of criteria for the identification of other POPs candidates. Following these criteria, the substance has to be persistent, bioaccumulative, toxic and have potential for long-range environmental transport, (UNEP, 2009). When a substance fulfils these requirements, then a risk profile is required in order to evaluate the effects of chemicals' emissions. This step involves a hazard assessment for the identified endpoint(s), including the toxicological interaction with multiple chemicals, the persistence and bio-accumulation, monitored data, and the definition of a value of local exposure. Finally, if the risk profile concludes that the substance is toxic and/or has environmental effects, a risk management evaluation is needed, reflecting socioeconomic considerations associated with possible control measures (UNEP, 2009). Amendments to the Stockholm Convention enlarged the list up to 22 POPs in 2011, as it is shown in Table 2.1.

Other POPs-related international efforts were carried out for monitoring biotic and abiotic environments over several decades such as the Convention for the Protection of the marine Environment of the North-East Atlantic (OSPAR) (OSPAR Convention, 1998).

2.2.2 POPs monitoring campaigns

Several attempts were made in the last two decades to monitor current emissions, to collect information for building emission inventories and to identify contributions of point and diffuse sources, in order to reduce the uncertainty related to model predictions (Klánová, 2009; Pozo et al., 2006; King and Adeel, 2002; IADN, 2000; Halsall et al., 1994) both at regional and global scales. The early approaches used to identify any particular substance and to reach a regional or global agreement for its elimination or restriction, stressed the importance of a programme for monitoring and modelling of long-range transport of air pollutants (Shatalov et al., 2001; Arctic Council, 1991; UNECE/CLRTAP, 1979; UNECE/EMEP, 1977). Pollutants emitted by primary sources have been commonly monitored (AMAP, 2003; Breivik et al., 2002), evaluated and modelled, with the aim of estimating temporal and spatial patterns, thanks to the global and regional monitoring programs reported in Table 2.2. Global monitoring programs are considered here as the ones covering areas in different continents or international waters. Monitoring programs are also reported in Figure 2.1.

Global POPs Monitoring Programs

POPs time trends have been investigated by collecting data through active sampling monitoring activities over long time periods, some lasting for more than a decade. For example, the Arctic Monitoring and Assessment Programme (AMAP) established in 1992, providing information on the status of the Arctic environment through data collection by high volume air samplers with sampling frequencies vary from site to site (from one sampling each year to one sampling each month). In addition, satellite stations were installed in the Arctic by AMAP, which were in operation at various times for periods ranging from 3 months to 2 years (Hung et al., 2010).

OSPAR also carries out monitoring activities in the area of interest as it is shown in Figure 2.1, as POPs are listed under the OSPAR list of hazardous chemicals.

Unfortunately, due to the high operational cost of high volume active samplers, POPs atmospheric monitoring programs have only been conducted at a reduced number of sites. To solve this problem, Passive Air Sampler (PAS) programs were initiated: the Global Atmospheric Passive Sampling (GAPS) network is a key global program for producing comparable global-scale data for POPs. This program started in December 2004 and considers three month sampling periods at more than fifty sites all over the world (Gusev et al., 2009; Pozo et al., 2006).

Regional POPs Monitoring Programs

Several attempts to integrate the components of global and regional monitoring networks were undertaken. Regional programs such as the European Monitoring and Evaluation Programme (EMEP, http://www.emep.int/), the Integrated Atmospheric Deposition Network (IADN) and the Northern Contaminants Program (NCP) provided relevant monitoring data to global programs like AMAP.

EMEP was established in 1977 with the objective of collecting, analysing and reporting emission data, measurement data and integrated assessment results. Many POPs monitoring sites from EMEP were (some of them still are) operated in support of already existing programmes, such as the Helsinki Commission or Baltic Marine Environment Protection Commission (HELCOM) (The Helsinki Commission, 2000) that aimed at protecting the marine environment of the Baltic Sea Area including the water-body and the seabed, their living resources and other forms of marine life. Furthermore, the National Monitoring Network in Europe (MONET) was designed and operated by the Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), aiming at collecting monthly samples at a number of EMEP sites to support relevant efforts for improving data consistency on air quality in most of Central and Eastern Europe, through capacity building and transfer of technology under the Stockholm Convention on POPs, GAPS and MONET also in support of EMEP. The MONET program consists of monitoring stations in Central, Southern and Eastern Europe (MONET-CEEC) (Klánová et al., 2011; Gasic et al., 2010), MONET in Africa (Klánová, 2009; Lammel et al., 2009) and MONET in Pacific Islands (MONET-PI) (Brebbia et al., 2011; Lal et al., 2009).

The table includes POPs that are listed in the Aarhus Protocol that has the objective to control, reduce or eliminate discharges, emissions and losses of POPs, including pesticides, industrial chemicals, and by-products. The protocol scheduled some of them for elimination (Annex 1), for restrictions on use (Annex 2), and for reductions in annual emissions from the level of the emission in a reference year (Annex 3). The table also shows the “dirty dozen” that were the initial POPs included before 2009 in both agreements.

IADN was developed as a sampling network around the Great Lakes in North America as a collaborative effort between Canada and the United States that was in operation since 1990 and aims at (i) determining atmospheric loadings and trends of priority toxic chemicals, (ii) acquire measurements, and (iii) helping in identifying POPs sources.

Table 2.1. List of POPs included in the Stockholm Convention and the Aarhus Protocol, with the aim of the elimination (Annex A), restriction (Annex B) the production, use, release and unsafe disposal of POPs and reduction (Annex C) and their unintentional releases (Annex C).

	Stockholm Convention			**UNECE POPs (Aarhus Protocol)**		
Chemical	Annex A	Annex B	Annex C	Annex I	Annex II	Annex III
Pesticides						
Aldrin	X			X		
Chlordane	X			X		
DDT (dichlorodiphenyltrichloroethane)		X		X	X	
Dieldrin	X			X		
Endrin	X			X		
Heptachlor	X			X		
Mirex	X			X		
Toxaphene	X			X		
Chlordecone	X			X		
alpha- HCH (alpha- hexachlorocyclohexane)	X			X	X	
beta-HCH (beta- hexachlorocyclohexane)	X			X	X	
Lindane (gamma- hexachlorocyclohexane)	X			X	X	
Pentachlorobenzene**$^{+}$	X		X	X		
Endosulfan and its isomers	X					
Industrial-chemical						
*HCB (hexachlorobenzene)***$^{+}$	X		X	X		X
PCB (polychlorinated biphenyl)$^{+}$	X		X	X	X	X
HBBP (hexabromodiphenyl)	X			X		
hexa-BD (hexabromodiphenyl ether) and hepta-BD (heptabromodiphenyl ether)	X			X		
PFOS (perfluorooctane sulfonic acid, its salts: perfluorooctane sulfonyl fluoride)		X		X	X	
Tetrabromodiphenyl ether and pentabromodiphenyl ether	X			X		
Industrial by-products						
PCDD (polychlorinated dibenzo-p-dioxins)			X			X
PCDF (polychlorinated dibenzofurans)			X			X
PAH- benzo(a)pyrene						X
PAH- benzo(b)fluoranthene						X
PAH- benzo(k)fluoranthene						X
PAH- indeno(1,2,3-cd)pyrene						X
Hexachlorobutadiene				X		
PCN (polychlorinated naphtalenes)				X		
Short-chain chlorinated paraffins				X	X	

Notes: Annex A: chemicals production and use must be eliminated; annex B: restrictions for production and use; annex C: reduce the unintentional releases.

Annex I: substances scheduled for elimination; Annex II: substances scheduled for restrictions on use; Annex III: substances scheduled for reduction in annual emissions from the level of the emission in a reference year.

** Pesticide and Industrial chemical, $^{+}$ by-product chemical

The "dirty dozen" are given in italics font and shaded on table.

Another monitoring activity on POPs in Canada was provided by the NCP, established in 1991, with the aim of reducing and possibly eliminating contaminants from the Arctic environment. NCP was responsible also for activities related to POPs modelling. Physical and chemical properties (i.e., toxicity, resistance to biological or chemical degradation, semi-volatility, lipophilicity) and environmental transport processes (e.g. advection by winds, marine currents, wet and dry deposition, particulate matter deposition) were combined into mathematical models to identify, understand and illustrate the connection between POPs sources in industrial and agricultural regions to the Northern Hemisphere and the contaminants' transport to remote regions of the Arctic (Hung et al., 2005; Macdonald et al., 2005; NCP, 2003).

In Asia in 1996 the project "Environmental Monitoring and Governance in the East Asian Hydrosphere -Monitoring of POPs" (EMGEAH) was launched as a joint collaboration between the United Nations University (UNU) and Shimadzu Corporation. It involves monitoring pollution from POPs land-based sources in marine and coastal environments (Wang et al., 2012; Iino et al., 2009; King and Adeel, 2002). The EMGEAH network has monitored POPs in water, sediment, soil and biota. These monitoring data provided a general overview of the levels of POPs in the Eastern Asia (Iino et al., 2009), contributing to the effective implementation of Stockholm Convention towards the production of an inventory of priority pollutants (Wang et al., 2012), starting the process of environmental risk assessment in some areas of the country (Wang et al., 2012, 2011).

The Western Airborne Contaminants Assessment Project (WACAP) (http://www.nature.nps.gov/) which operated from 2002 to 2007 was designed to determine the risk from airborne contaminants to ecosystems and food webs in western national parks of the United States, through conducting analysis of the concentrations and biological effects related to exposure to POPs. POPs were monitored in air, snow, water, sediments, lichens, conifer needles, and fish in watersheds in each of eight core parks in the Western United States, including Alaska (Landers et al., 2008). Results from WACAP highlighted existing strong correlations between the concentration of several chemicals (namely DDT, PAHs, chlordanes and endosulfans) in lichens and in conifer needles in areas located in proximity of intensive farming, indicating that in most cases high environmental concentrations are probably attributable to regional agricultural sources. On the other hand, the detection of banned contaminants at relevant concentrations in protected areas suggests that POPs re-volatilization is occurring from soils sources located in the neighbouring regions (Landers et al., 2008).

The same purpose as the previous program has been carried out by other alpine monitoring programmes: MonarPOP (Belis et al., 2009; Iozza et al., 2009; Offenthaler et al., 2009; Tremolada et al., 2009; Nizzetto et al., 2006) funded by the European Union in Austria, Germany, Italy, Slovenia and Switzerland, during 2004 to 2006; and Western Canadian Mountains Programme (WCMP) (Choi et al., 2009; Shen et al., 2004) funded by Canadian government in Western Canada during 2004 and 2005. The last Programme also compares its PAH's data with those from passive sampling in United States, Costa Rica, Belize and Mexico in order to estimate the continental long range transport from Southern to Northern (Shen et al., 2005). As the time series get longer and are more statistically robust, it is possible to discern how contaminant trends are affected by climate variability and possible changes in POPs exposure pathways (Macdonald et al., 2005; WHO, 2003).

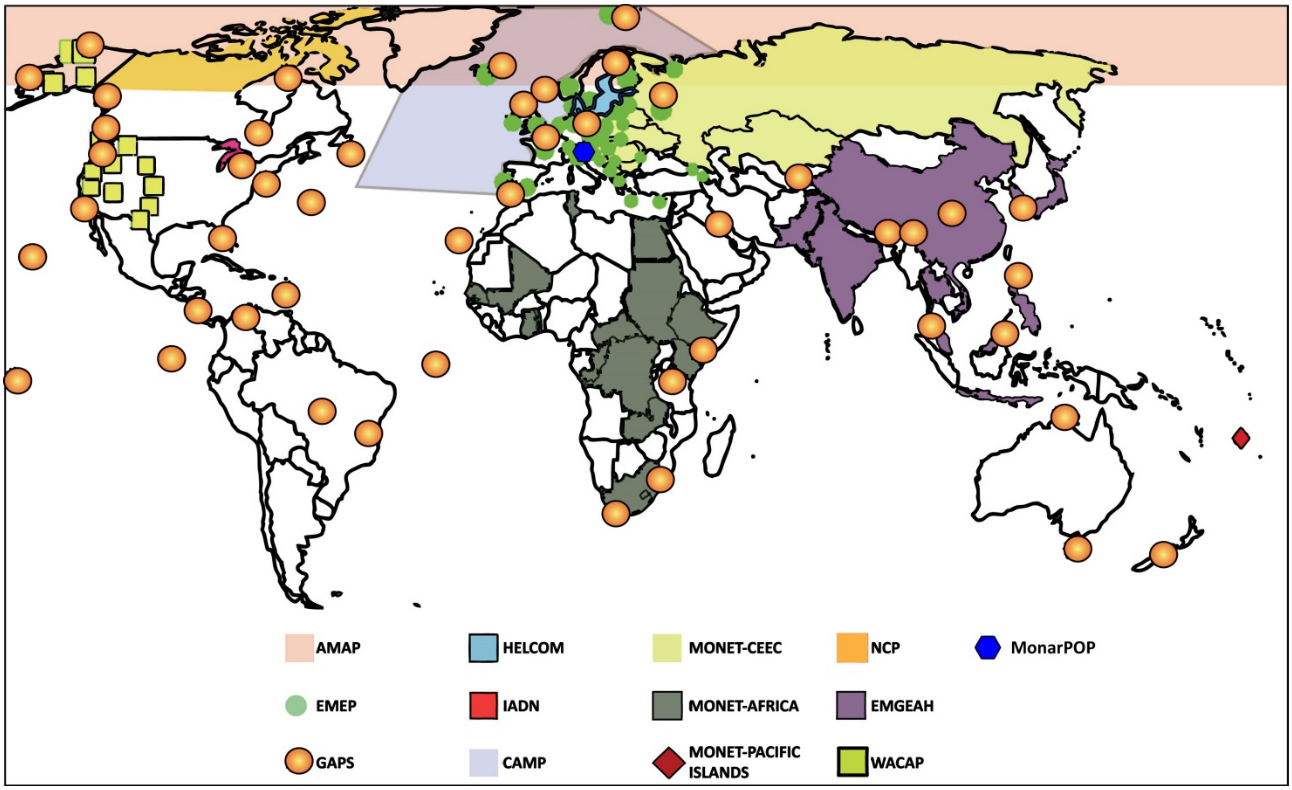

Figure 2.1. Global and regional international monitoring programmes. Geographical distribution of POPs global and regional monitoring campaigns. All the monitoring programs in the figure are also listed in Table 1.2. When possible, single sampling stations were reported.

Several studies aimed at improving our understanding of how global warming could undermine global efforts to reduce environmental and human exposure to POPs, demonstrating that the impacts of policy decisions on environmental levels will require continued monitoring of 'legacy POPs in both abiotic environments and in key biota. In the past few years a larger list of new chemicals detected in remote regions as the Arctic and mountain regions was observed. Measurement activity of new chemical has a great relevance for the Stockholm Convention and for other national assessments of chemicals such as REACH, and for the assessments of potential health effects on Arctic ecosystems and humans (Muir and de Wit, 2010; Wilson et al., 2009; Boethling et al., 2009).

2.3 Implications of environmental change on POPs fate and transport

As we introduced earlier in this paper, climate change involves changes in the mean value or changes in the variability of a climate property that persists for an extended time (Solomon et al., 2007). Starting from these alterations, climate change-oriented trends in POPs environmental fate and transport may also be identified. Climate variability forecasted by climate change scenarios presented by the 4th IPCC assessment report (Solomon et al., 2007) shows that atmospheric temperature is increasing globally, this leading to the loss of ice-cover in forms of permafrost and ice-cap in Alaska, according to previous results (Macdonald et al., 2005). Furthermore, it was shown that the variability in sea-ice motion was correlated to the variations in the wind by the Arctic Oscillation (AO). During winter wind anomalies associated with the positive AO index increases the advection of ice away from the North Pole (Eurasian and Alaskan coasts). Such advection enhances the production of thin ice, when the central pack ice moves away from the coastal ice creating a "flaw" in the ice surface (flaw leads) along the coast, and preconditions the sea-ice to be more prone to melt during the following spring and summer (Rigor and Wallace, 2004).

Since chemicals' environmental behaviour is driven by environmental variables, climate change may alter any aspect related to POPs environmental fate and transport from POPs emissions to the environment, to their transport and their degradation. The changes involved by climate fluctuations on POP's fate and transport are often investigated through the application of

Eulerian multimedia fate and transport models both at global and regional scales (e.g. Lamon et al., 2012; Lammel et al., 2009; Semeena et al., 2006; Gusev et al., 2005), or through the application of more complex Global Circulation Models (GCMs) (e.g. Stemmler and Lammel, 2011).

Climate fluctuations operate through climate variables such as temperature, wind speed, water and snow precipitation, solar radiation, atmospheric pressure, marine salinity, dry period, marine currents, ice cover, as well as interactions among these, like vegetation mass and type, organic carbon content, sediment re-suspension and deposition, and population dynamic (Gusev et al., 2009; Lamon et al., 2009). These variations drive temporally and spatially averaged exchanges of heat, momentum, and water vapour that ultimately alter re-volatilisation, transport and distribution patterns of POPs (Hung et al., 2005).

The Task Force on Hemispheric Transport of Air Pollution (HTAP) established by the UNECE for the planning and drafting the technical work necessary to estimate intercontinental transport of air pollution in the Northern Hemisphere, provides information to policy makers and international organizations on issues related to long-range and intercontinental transport of air pollution and to serve as a basis for future cooperative research and policy action also assuming climate change effects on POPs environmental fate and transport (TF- HTAP, 2010). The HTAP task force pursues these objectives through the application of global-scale multimedia mass balance models, that significantly improved scientific knowledge about how chemicals' emissions occurring in industrialized regions may affect contamination of pristine regions, such as the Arctic and mountainous regions (Dentener et al., 2010; Gouin and Wania, 2007; Wania, 2006; Hung et al., 2005). These models are a key component in understanding the environmental dynamics of POPs; in fact they combine information about emissions, chemicals' properties and interactions with the environmental compartments to be merged in final results which can be evaluated against observations provided by monitoring studies.

Temperature is one of the main climate drivers in determining POPs global distribution as it has a direct influence through affecting chemicals' half-life, partitioning, volatilisation and re-emissions, and indirectly, for instance through effects on hydroxyl radical formation process (Gouin and Wania, 2007; TF- HTAP, 2010; Wania, 2006).

Table 2.2. International agreements and POPs monitoring programs. The table shows a summary of existing monitoring programmes at regional and global scale, and international agreements and marine conventions; where existing, the relationship between conventions and the monitoring programs is also shown.

International Agreements			
Parties	Name	Description	
51 Parties from: European Union, North America, Eastern Europe, Caucasus and Central Asia	UNECE-LRTAP	United Nations Economic Commission for Europe (UN-ECE): agreement on a POPs protocol under the Geneva Convention on Long-Range Transboundary Air Pollution (LRTAP) from 1979. POPs Protocol (Aarhus Protocol) entered into force by the end of 2003	
177 Parties from United Nations	UNEP-Stockholm Convention	United Nations Environmental Program (UNEP): Stockholm Convention entered into force in May 2004	
Eight Arctic States: Canada, Denmark (including Greenland and the Faroe Islands), Finland, Iceland, Norway, Russia, Sweden and USA	Arctic Council	The Arctic Council is a high-level intergovernmental forum which addresses issues of sustainable development and environmental protection in the Arctic, formally established in 1996	
Marine Conventions			
Parties	Name	Description	
AMAP, EMEP	OSPAR	Protection of the Marine Environment of the North-East Atlantic: The parties are Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom since 1992	
AMAP, EMEP	HELCOM	The Helsinki Commission: Convention on the Protection of the Marine Environment of the Baltic Sea Area; intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden	
EMEP	MEDPOL	The Marine Pollution Assessment and Control Component of Mediterranean Action Plan; it is responsible for the follow up work related to the implementation of the LBS Protocol, the Protocol for the Protection of the Mediterranean Sea against Pollution	
Global POPs monitoring programs			

Parties	Name	Description	Type of sampling
Canada, UNEP-Stockholm Convention, Arctic Council, NCP	GAPS	Global Atmospheric Passive Sampling study; started in 2004. More than 65 monitoring sites on 7 continents	Passive sampling
UNEP-Stockholm Convention, Arctic Council, NCP	AMAP	Artic Monitoring and Assessment Programme for: Canada, Denmark (including Greenland and the Faroe Islands), Finland, Iceland, Norway, Russia, Sweden and USA. Established in 1992.	High volume active air sampling, biota and humans sampling
OSPAR	CAMP	Comprehensive Atmospheric Monitoring Program.	
Regional POPs monitoring programs			
Parties	Name	Description	Type of sampling
UNEP-Stockholm Convention, UNECE, Arctic Council	EMEP	European Monitoring and Evaluation Programme. Established in 1977.	High volume active air sampling and PUF foam
Canada, USA, UNEP-Stockholm Convention	IADN	Integrated Atmospheric Deposition Network around Great Lakes in North America. Started in 1990	Active air sampling, precipitation monitoring
Canada, AMAP, Arctic Council	NCP	Canadian Northern Contaminants Program coordinates Canada's action on northern contaminants, including Persistent Organic Pollutants (POPs), both nationally and internationally (Canada and Russia). Started in 1991.	Active air sampling, biota and human sampling
UNEP-Stockholm Convention, GAPS, WHO; Coordinated by RECETOX	MONET- Africa	National Monitoring Network in Northern Africa; long-term monitoring of air quality at background locations: Canary Islands, Congo, DR Congo, Egypt, Ethiopia, Ghana, Kenya, Mali, Nigeria, Mauritius, Senegal, South Africa, Sudan, Togo, Zambia. Started in 2008	Passive sampling
UNEP-Stockholm Convention, GAPS, WHO; Coordinated by RECETOX	MONET- CEEC	National Monitoring Network in Central and Eastern European Region; Long-term monitoring of air quality at background locations: Czech Republic, Bosnia and Herzegovina, Estonia, Latvia, Lithuania, Romania, Serbia and Slovakia. Started in 2005.	Passive sampling
UNEP-Stockholm Convention, GAPS, WHO; Coordinated by RECETOX	MONET-PI	National Monitoring Network Pacific Islands (2006-2007); Long-term monitoring of air quality at background locations: Fiji Islands	Passive sampling
United Nations University; Institute for Sustainability and Peace (UNU-ISP)	EMGEAH	Environmental Monitoring and Governance in the East Asian Hydrosphere (EMGEAH) - Monitoring of POPs. Coastal waters of nine East Asian countries, namely China, India, Pakistan, Indonesia, Japan, the Republic of Korea, Malaysia, Singapore, Thailand, Vietnam and Philippines	Biomonitoring and water monitoring
US- EPA	WACAP	Western Airborne Contaminants Assessment Project (2002 to 2007); the contaminant situation at 20 national parks from the Arctic to the Mexican border	Passive sampling

UNEP-Stockholm Convention, UNECE, EMEP, EU	MonarPOP	Five countries (Austria, Germany, Italy, Slovenia, and Switzerland) established a network to assess the POP load of the Alps. From 2004 to 2006	Active and passive air sampling, biomonitoring, soil, water
Canada	Western Canadian Mountains	22 sites along three transects (Revelstoke, Yoho, and Observation, 6–8 sites for each transect) in the mountains of Western Canada	Passive air sampling, soil and needles
UK, UNECE-LRTAP	TOMPs	The Toxic Organic Micro Pollutants Network operates since 1991, currently collects samples at six sites across England and Scotland.	Andersen GPS-1 samples
GEF-UNEP	GEF-UNEP	Global Environmental Facility (GEF): Capacity Strengthening and Technical Assistance for the Implementation of Stockholm Convention National Implementation Plans (NIPs) in African Least Developed Countries (LDCs). Supporting the Implementation of the Global Monitoring Plan. Enabling activities for the Stockholm Convention on Persistent Organic Pollutants (POPs): Development of a National Implementation Plan in Developing Countries. Started in 2006.	Passive and active sampling

The potential of higher temperatures to enhance secondary emissions from previously contaminated environments through enhanced volatility, more rapid degradation and altered partitioning between phases, play an important role in global distribution of POPs (Lamon et al., 2009b; MacLeod et al., 2005). These secondary sources will dominate the total inventories of POPs that were largely used in the past, especially in remote regions due to their own nature of diffusive sources (Lamon et al., 2012; Nizzetto et al., 2010; Ma et al., 2004). In a secondary source-controlled world, physical-chemical processes such as burial and storage in terrestrial subsurface layers during organic carbon transformation, riverine export in dissolved and particulate form, and export of particle-bound chemicals by settling to deep sediments are expected to represent the major active stores and sources of pollutants. Nizzetto et al. (2010) proposed that a better understanding of the evolution of anthropogenic and natural factors will enable the definition of future re-emissions of pollutants in the environment (Breivik et al., 2007).

Sea surface temperature (SST) and wind speed influence volatilisation rates, that will vary for different temperature and wind speed regimes, hence in different climatic zones and by climate change (Stemmler and Lammel, 2011). Wind speeds also play an important role in influencing POPs global fate and transport, as the enhanced intercontinental transport of POPs (e.g. PCBs) is also a result of increased wind speeds, as it was investigated in several studies (Lamon et al., 2012; MacLeod et al., 2005). Seasonal temperature cycles that induce the chemical to undergo one or more transport and deposition cycles (hops) are related to atmospheric pressure patterns. For instance, enhanced transport of some POPs (e.g. PAHs) to the Arctic was observed in winter, in conjunction with the high atmospheric pressure characterising the Siberian winter, originating the Arctic haze event together with higher emissions in Eurasia during this period. This has provided important basis for the qualitative prediction, control, and management of regional air pollution problems (Gusev A. et al., 2011; TF- HTAP, 2010).

Water and snow precipitation events involve washout, wet deposition of POPs from the atmosphere to surfaces (water and soil compartments). 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 (Tremolada et al., 2008; Daly and Wania, 2005). An increase in heavy precipitation events and in floods has been recently observed, while the total amount of precipitation may be considered unchanged, or decreasing (Lamon et al., 2009b; Lenderink and Meijgaard, 2008; Trenberth et al., 2007).

The fate of POPs in the ocean depends on key processes related to transport by ocean currents, air-sea exchange (volatilisation and phase partitioning), degradation in sea water and partitioning and deposition with suspended particulate matter (Lamon et al., 2012).

Changes in light conditions and radiation intensity, that influences photochemical degradation, may change transport patterns of POPs (UNECE 2010) also to the Arctic (Kallenborn et al., 2007), affecting POPs distribution, transformation and degradation processes (e.g., photochemistry) (Lamon et al., 2009).

2.3.1 Main findings

Several studies addressed climate change influence on POPs environmental fate and transport in order to elucidate the effects on their long-range transport. Mountain regions have been proposed as ideal sensitive places (Daly and Wania, 2005) besides Arctic region (UNEP/AMAP, 2011; Kallenborn et al., 2007), as long as these are not directly impacted by human activities, and are characterised by peculiar meteorological patterns, e.g., diurnal surface temperature change, precipitation rate and diurnal winds. Notwithstanding their remoteness from sources of pollution they still are contaminated by POPs. Alpine lakes also have been referenced to clarify the contribution of atmospheric long-range transport to the POPs contamination –specifically PBDEs, HBCD, PCNs PCBs and DDT- (Schmid et al., 2011; Bogdal et al., 2008). First, Schmid et al. (2011) compared historical trends of some POPs and found that those banned, after showing a declining trend after their ban, exhibit an unexpected increase in concentrations. Such increase was accompanied with accelerated adjacent glaciers' melting. In contrast, lowlands lakes presented steadily decreasing levels since the 1970's (Bogdal et al., 2008). These studies supported the hypothesis that a closer link exists between the glaciers' melting and the released pollutants in sediments in pro-glacial lakes, making the ice-melting an important secondary source of POPs. Furthermore, a relationship between the amounts of ice formed in a given period and the concentration of each pollutant: a relative small amount of ice formed at a period when environmental pollution was high can represent an important reservoir of contaminants, and results in an important release with ice melting. Other relevant secondary sources acting as POPs reservoirs are soil, vegetation, sediments (Nizzetto et al., 2010).

Several studies addressed the global POPs distribution, reporting temperature as one of the most relevant variables influencing both emission rates from primary and secondary sources, phase-particle partitioning, reaction rates (biodegradation, oxidation), air surface exchange (volatilisation), air soil exchange (deposition) and hydroxyl radical formation (Lamon et al., 2012, 2009b; Jurado et al., 2007; Gusev et al., 2005; Ma et al., 2004). Wind speed is another environmental variable that is associated with certain atmospheric POPs fluxes. Lamon, et al. (2009b) investigated the processes related to climate patterns and interannual variations of POPs concentrations. Their results show that climate change may affect emissions of POPs by enhancing volatilisation and re-volatilisation (Hung et al., 2005), and lead to increased atmospheric emissions especially in remote areas.

Other parameters related to POPs environmental distribution are quantity, quality and spatial variation of precipitations. These climate parameters associated with various climate patterns would also affect scavenging by absorption to snow and thence transport and deposition of organic pollutants (UNEP/AMAP, 2011; Gabrieli et al., 2010; Daly and Wania, 2005).

In recent studies it was possible to detect evidence of POPs re-volatilisation induced by regional warming (Ma et al., 2011). Increasing trends of HCB and PCBs that have been observed in Arctic air could be attributed to their tendency of volatilisation from water to air.

2.3.2 Possible next steps in regulating climate change effects on POPs environmental behaviour

In the previous paragraphs we reported several studies where climate variables influence Predicted Environmental Concentrations (PECs) for POPs.

The UNEP Stockholm convention addresses how to classify POPs by considering substances' physical chemical characteristics. Recently, the UNEP/AMAP expert group reported on climate change implications on the management of POPs and found that climate change may have a potential direct impact on present and future management of POPs, and is likely to enhance the exposure to POPs in some regions (AMAP and UNEP 2011). However, the way to go for obtaining an integration of climate change effects on POPs environmental behaviour in chemicals' regulation is still missing.

A thorough integration between the different international initiatives on the management of POPs would help to define a reference framework for POPs and other chemicals' assessment also taking in consideration climate change.

As described earlier in this paper, REACH is the reference guidance in Europe for the definition of procedures in the assessment of exposure to PBTs and vPvBs (ECHA, 2011), and thus providing assessment and analysis on chemicals' health or environmental effects (ECHA, 2011).

Chemicals' legislation may take into consideration climate change by giving more emphasis to the variability of environmental parameters that should be selected on the basis of sound studies on climate change effects on POPs environmental behaviour. Also, more emphasis should be given to uncertainty analysis in the definition of PECs.

When it is necessary to take into account climate change in estimating the environmental behaviour of chemicals, uncertainty plays a key role, and this could be one key aspect to be better addressed by regulation. Climate change scenarios are characterized by different typologies of uncertainties (IPCC, 2005), and these should be integrated with the uncertainties related to chemicals' modelling. A dialogue between scientists and regulators could be oriented towards the definition of probability distributions of input climate parameters in chemicals' multimedia models, and/or the definition of a sensitivity analysis where special attention is dedicated to climate parameters. This is still a challenging issue, as no guidance on how to estimate uncertainty in exposure modelling is existing, and it is actually difficult even to compare results and uncertainty estimates from similar models. For instance, the REACH regulation addresses how to deal with uncertainty estimation in the evaluation of the risk factor, but does not provide a detailed insight on the uncertainty estimation on PECs in exposure modelling. This may be the next step towards taking into consideration environmental variability and change in chemicals' regulation.

2.4 Conclusions

In the previous sections we have considered how POPs environmental distribution is influenced by emissions' spatial distribution, chemicals' physical-chemical properties, and global and regional atmospheric and oceanic circulation patterns (i.e. wind speeds, precipitation, interactions with the Earth's surface, ocean currents, organic carbon content, and biological pathways) (AMAP, 1998). Such variability is affected by climate change that in turn influences POPs environmental fate and transport.

From the case studies reported in this review paper, we can infer that variables with a pronounced effect on POPs environmental fate and transport are temperature, affecting also re-volatilisation from POPs reservoirs, wind speeds and spatial distribution of primary and secondary pollution sources in each environmental compartment. Since primary and secondary emissions play a key role in describing POPs mass balance it is necessary to collect information on POPs emissions and to build updated emissions' inventories taking into account historical emissions and performing simulations in order to define the location and the amount of future sources of pollution. This objective is to be considered partially achieved thanks to the activities organised under the Task Force on Emissions Inventories and Projection (TFEIP), consisting of the active involvement of public authorities and of the communication between policy makers and science experts.

Snow and ice melting effects on POPs deserve special consideration, as several studies report that mountain environmental quality is impacted by POPs transport in such remote environments that act as a sink similarly to the Polar Regions. For this reason, mountain regions can be identified as the most sensitive and important ''early warning'' sites to assess climate change effects on POPs fate and transport.

Continuous monitoring activities are important as they could push the identification of new and unsuspecting primary or secondary sources. Moreover, continued monitoring supports fate and transport modelling activities aimed at identifying and characterising long range transport episodes from industrial and agricultural emissions (Kallenborn et al., 2007).

Considering that several modelling exercises demonstrate that long range transport potential increases under a climate change perspective, policy actions should be more restrictive in managing production and use of POPs and POPs-like chemicals.

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3. Environmental pollution by POPs in Alpine areas: A review of reported data and information needs

Technical report

Abstract

Persistent organic pollutants (POPs) are organic substances of very high concern because they resist degradation, can persist for a long time and travel through international boundaries and be deposited far from their place of release. Environmental characteristics, such as temperature, precipitation, or circulation patterns are influencing such POPs behaviour, as shown by a number of modelling attempts in the literature. A special issue is the mountainous environment that may be considered as a multi compartment environment far from anthropogenic sources, where emissions sources have been identified at the bottom valley. Different programs have monitored the presence of POPs in high mountains, with special attention at the European Alps. In this paper we present the development of our POPAlp database as a valuable tool for the systematic incremental accumulation and organization of monitored data that may be useful for the study of POP´s concentration process in European Alps. For this version of the POPAlp database we collected and integrated available existing data reported in the literature. Additionally, as an application of POPAlp we present a data analysis that highlights the close relationship between POPs concentrations and an altitudinal profile over the alpine mountains in a temperate zone.

Keywords

POP, monitoring, mountain top, Alps, organochlorine pesticides, Stockholm Convention

3.1. Introduction

Persistent organic pollutants (POPs) are organic substances of very high concern because they resist to environmental, chemical, physical and biological degradation. They can persist for a long time and travel through air, water and migratory species across international boundaries and deposited far from their places of release, and being accumulated in terrestrial and aquatic ecosystems, and in the abiotic compartments (UNEP, 2001). Due to their high lipophilic characteristic, they can be accumulated in lipid tissue of humans and animals, through the ingestion, contaminated outdoor or indoor air, drinking water and direct dermal contact. As a result of their persistence and accumulative characteristics, POPs bio-magnify along food chains, causing health side-effects such as neurotoxicity and reproductive toxicity (Gioia et al., 2013; Bogdal et al., 2012; Smaranda and Gavrilescu, 2008).

POPs are emitted in the environment from various natural and anthropogenic processes, such as forest fire and volcanic eruption, but mainly due to anthropogenic emissions (Ravindra et al., 2008), by deliberated release in mining, industrial activities, oil fields; by accidental emissions during combustion, such as non-controlled waste disposal sites (Orta-García et al., 2014); or by spraying with agricultural or disease controlled purposes (Smaranda and Gavrilescu, 2008).

Organic pollutants are classified in well-defined functional groups, such as per-fluorinated compounds, hydrocarbons, chlorinated-benzenes (Mackay, 2001), all associated with chemical properties affecting their persistence, toxicity and (bio)accumulation. Characteristics like the resistance to transformation and degradation, the time of total removal after the phase out of the chemicals (POPs), the released quantity into the environment can affect the concentration and fate of POPs in the environment, as well as the environmental compartment of discharge. Moreover, POPs have a preferential route (fractionation effect) in water, soil or vegetation from atmosphere that acts both as source and sink, depending on the mechanism of partitioning, deposition, degradation or re-volatilization, among others (Bogdal et al., 2012; Semeena et al., 2006; Fernandez and Grimalt, 2003; Wania and Mackay, 1996).

Environmental characteristics, such as temperature, precipitation, or circulation patterns play an essential role on POPs behaviour: they enhance the evaporation near of the Tropics and the subsequent movements and condensation in high and medium latitudes. Moreover, at high altitudes, low temperature and an increased precipitation may enhanced the cold trapping effect (Westgate et al., 2013) that affects not only condensation but decomposition reactions of POPs. In addition, the environmental conditions favour the state partition from gaseous to non-gaseous phase: highly volatile POPs tend to remain airborne and migrate faster, while less volatile POPs will partition into water, snow, ice, soil or vegetation (Wania and Mackay, 1996).

Modelling attempts demonstrate a relationship between environmental characteristics and POPs behaviour (Armitage and Wania, 2013; Gouin et al., 2013; Westgate et al., 2013; Lamon et al., 2012; Fernandez and Grimalt, 2003). In particular, in Armitage and Wania (2013) the particulate organic carbon was modulated, in order to find out the effects on the organic pollutants availability in the water column that could reduce the exposure for marine organisms. Westgate et al. (2013) applied a specific model for mountainous regions and highlighted the resulting correlation between cold trapping effect in high altitude and wet deposition, as main parameters that control the presence and behaviour of POPs at high altitude. Lamon et al. (2012) analysed different environmental parameters such as temperature and circulation patterns in atmosphere and sea, precipitation and particulate organic carbon that can vary in a long time term due to climate change effects, in order to figure out the PCBs behaviour and their trends in the Adriatic Sea. Lamon et al. (2012) found a close relationship between these parameters and climate change, giving more weight to the historical emissions and partitioning to water from atmosphere and to sediment from water. Gouin et al. (2013) made an analysis of the effect of temperature and changes in emission trends through re-volatilization (internal energy vaporization), changes in circulation patterns (atmosphere and sea) and run off effect, at the global scale. Several works have investigated the role of the physical characteristics in remote lakes for better understand the global distillation effect related not only with latitude but also with high altitudes (Fernández et al., 2005; Grimalt et al., 2004; Fernandez and Grimalt, 2003; Carrera et al., 2002). They highlighted a close dependence between the temperature gradient and the presence of some POPs at high altitude's environmental compartments.

Concerns about the health effects of exposure to POPs initially emerge from studies of wildlife communities that showed reproductive, developmental, endocrine, immunologic and carcinogenic effects (Abelsohn et al., 2002). As a result of these findings, POPs have been subjected to regulation under the POP conventions at global, regional and local scopes. However in contrast to expectations, the concentrations of the POPs that were banned for production and usages (that are listed in the table 3.1) are despite, being reduced at a very slow rate after the phase out due to re-mobilization from old stocks and environmental sinks (Wöhrnschimmel et al., 2012; Denier van der Gon et al., 2007; Bailey, 2001; Li et al., 2000).

Table 3.1. List of POPs regulated by Stockholm Convention and UNECE POP Convention.

Stockholm Convention	UNECE POPs (Aarhus Protocol)		
Chemical	Elimination	Restrictions	Reduction
Pesticides			
Aldrin	X (2001/1998)		
Chlordane	X (2001/1998)		
DDT (dichlorodiphenyltrichloroethane)	X (2001/1998)	X	
Dieldrin	X (2001/1998)		
Endrin	X (2001/1998)		
Heptachlor	X (2001/1998)		
Mirex	X (2001/1998)		
Toxaphene	X (2001/1998)		
Chlordecone	X (2009/1998)		
alpha- HCH (alpha-hexachlorocyclohexane)	X (2009/2009)	X	
beta-HCH (beta- hexachlorocyclohexane)	X (2009/2009)	X	
Lindane (gamma-hexachlorocyclohexane)	X (2009/2009)	X	
Pentachlorobenzene**+	X (2009/2009)		
Endosulfan and its isomers	X (2011)		
Industrial-chemical			
HCB (hexachlorobenzene)**+	X (2001/1998)		X
PCB (polychlorinated biphenyl)+	X (2001/1998)	X	X
Hexabromodiphenyl	X (2009/1998)		
hexa-BD (hexabromodiphenyl ether) and hepta-BD (heptabromodiphenyl ether)	X (2009/2009)		
PFOS (perfluorooctane sulfonic acid, its salts: perfluorooctane sulfonyl fluoride)	X (2009/2009)	X	
Tetrabromodiphenyl ether and pentabromodiphenyl ether	X (2009/2009)		
Industrial by-products			
PCDD (polychlorinated dibenzo-p-dioxins)			X
PCDF (polychlorinated dibenzofurans)			X
PAH- benzo(a)pyrene			X
PAH- benzo(b)fluoranthene			X
PAH- benzo(k)fluoranthene			X
PAH- indeno(1,2,3-cd)pyrene			X
Hexachlorobutadiene	X (2009/2009)		
PCN (polychlorinated naphtalenes)	X (2009/2009)		
Short-chain chlorinated paraffins	X (2009/2009)		

Note: ** Pesticide and Industrial chemical, + by-product chemical; yyyy/yyyy year of regulation on elimination in Stockholm Conv/UNECE-POPs. Chemicals presented in POPAlp are in grey colour.

List in table 3.1 shows the classification in pesticides, industrial production and by-products of each organic pollutant that is currently under international regulation and the respective banning date.

Moreover, monitoring campaigns in remote sites such as the Arctic and high altitudinal mountains that are considered as pristine environments (EMEP, 2012; GAPS, 2004; NCP, 2003; HELCOM, 2000) showed that pollutants such as POPs have been found in high levels of concentration, attracting the concern on health effects on indigenous population. Actually, mountainous environments are view as ideal environments to study the effects of environmental patterns on the POPs behaviour (Shunthirasingham et al., 2013; Westgate et al., 2013; Wegmann et al., 2006; Daly and Wania, 2005). Different programs monitore the presence of POPs in high mountains worldwide. To cite, the WACAP program in western national parks of the United States, from 2002 through 2007 (Landers et al., 2008); the GAPS program in mountains and the Great Lakes in Northern, Central and Southern America (Shunthirasingham et al., 2013; Pozo et al., 2006); and the MONARPOP program in European Alps (MONARPOP, 2005). Particularly, European Alps nowadays receives special attention by addressing the persistence and cold trapping effect as part of global distillation effect, fact that may also explain the presence of POPs in places such as Arctic (Westgate et al., 2013; Semeena et al., 2006; Vighi, 2006; Daly and Wania, 2005). Consequently, several works have been collected by Mountain-Lakes.org 2009 with limnology, hydrobiology, and ecology data observations (e.g. biodiversity) (Charles University Prague, 2009; Marchetto and Rogora, 2004) during 15 years of monitoring programs: AL:PE 1 and AL:PE 2 (Mosello et al., 1995), MOLAR (Straskrabova et al., 1999), EMERGE (Fernandez and Grimalt, 2003) and EUROLIMPACS (Catalan et al., 2013). All these programs have monitored a large number of mountain lakes under global change assumption, for different parameters such as pollutants' concentrations, temperature, and acidification, among others. In this context, MONARPOP is the first alpine region multi-compartment monitoring program with the main purpose of evaluating the state of POPs in remote mountainous location (Offenthaler et al., 2009; MONARPOP, 2005). Another important regional attempt is RICLIC – WARM (Cavallin, 2007) that addresses an environmental assessment of the mountainous region at the Southern Alps in Lombardy, Italy. RICLIC – WARM includes monitoring campaigns of anthropogenic pollutants in water, soil/sediment and biota compartments, all within a global warming framework (Villa et al., 2011; Bizzotto et al., 2009a, 2009b).

Nonetheless all these efforts, the existing assessment of the exposure still presents a remarkable gap between monitoring programs and the feasibility of applying such measurements for applications in fate and transport modelling and exposure assessment. Considering the gap that exists between POPs monitoring programs and the spatial coverage in alpine regions, the present study focuses on updating the state of the art in environmental POPs data concentrations available in European Alpine region in a systematic and integrated framework. This goal is archived through (1) the collection of existing monitoring data available in European Alps, (2) the examination of spatial and temporal coverage of collected POPs environmental concentration measurements, and (3) the quality assurance and quality control (QA/QC) comparison and validation between different monitoring programs.

The main contribution of this work is the release of public database “POPAlp” that contains existing information of POPs data available from monitoring programs surveyed in European Alps during the period 1999 to 2012. POPAlp is a valuable method for the systematic incremental accumulation and organization of monitored data which may lead to a better understanding of the POP´s concentration process in European Alps. Finally, as an application which shows the utility of POPAlps we carried out a data analysis that highlight the close relationship between POPs concentrations and an altitudinal gradient across the area of European Alps.

3.2. Materials and Methods

We collected reported data from published POPs monitoring surveys available in the European Alps. In order to store, manage and analyse the reported existing information regarding POPs concentrations in European Alps, our “POPAlp” database collects available existing data that was published during the period 1999 to 2012. This database integrates POPs monitoring concentrations in the Alps in Austria, Germany, Switzerland, Slovenia, Italy and Czech Republic and has been designed for exchanging existing data on POPs contamination in the Alps, and as a tool for integrating new monitoring information from the scientific community. The POPAlp database is suitable to compile and organize comparable and incremental information data that may facilitate the analysis and understanding of the environmental factors that govern POPs environmental behaviour at high elevations. Besides, it may be relevant to identify the most impacted alpine zones and environmental compartments exposed to POPs. An important characteristic of POPAlp is the management of many datasets from monitoring campaigns, carried out in one or several environmental compartments air, soil, sediment, water, snow and ice. In addition, some others monitoring campaigns in vegetation and fauna were also included in the current database.

Furthermore, POPAlp is able to distinguish between active and passive air sampling and the monitored data of the contaminants defined by the Stockholm Convention and Aarhus Protocol (Teran et al., 2012).

Table 3.2. POPs monitored in the Alps environment published during the period 1999 – 2012.

Authors' reference	DDT	HCH	HCB	PCB	PAH	PCDD /PCDF	PBDE	Others OCs	Chlorinated Paraffins	Monitored period
(Villa et al., 2003)	X	X	X							1996, 2000
(Herbert et al., 2004)				X	X					2002
(Jaward et al., 2005)	X		X	X						2003
(Finizio et al., 2006)	X	X	X	X						2003
(Nizzetto et al., 2006)				X						2003
(Villa et al., 2006)	X	X	X	X						2000, 2002
(Tremolada et al., 2008)	X	X	X	X				X		2003
(Tremolada et al., 2009)		X	X	X						2007
(Bizzotto et al., 2009a)	X	X	X	X						2006
(Bizzotto et al., 2009b)	X	X	X	X						2006
(Guazzoni et al., 2011)				X						2008
(Tremolada et al., 2011)	X									2007-2008
(Villa et al., 2011)	X	X		X						2007
(Parolini et al., 2012)							X			2008
(Fernández et al., 1999)					X					1993-1998
(Carrera et al., 2001)	X	X		X	X					1997-1998
(Grimalt et al., 2001)			X	X						1993-1998
(Vilanova et al., 2001)	X	X		X				X		1996-1998
(Grimalt et al., 2009)	X	X		X						1997, 1998, 2005
(Iozza et al., 2009)									X	2004-2009
(Offenthaler et al., 2009)	X	X	X	X	X	X	X	X		2004-2007
(Quiroz et al., 2011)					X					2004
(Gabrieli et al., 2010)					X					2005

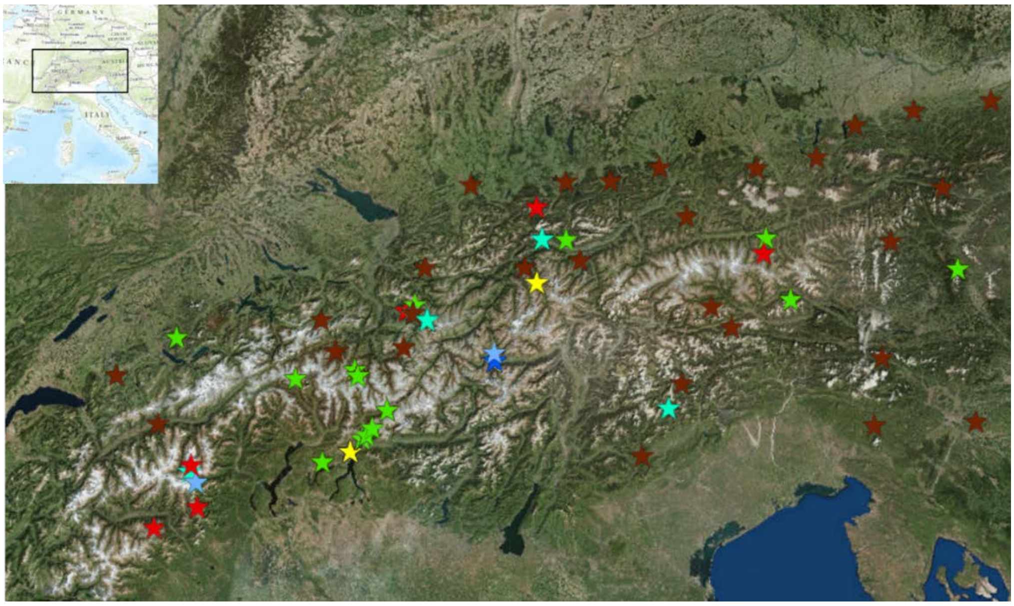
Table 3.2 lists the papers available that published data concentrations from monitoring campaigns in European Alps during the period 1999 to 2012, and that were considered in this paper for the initial version of our POPAlp database. We selected POPs studies depending on public availability of the datasets obtained in monitoring campaigns.

3.2.1 Definition of spatial and temporal coverage of monitoring campaigns

Monitoring data were organized by monitored compartment, substance, and monitoring period. All monitoring sites included on POPAlp database are located in figure 3.1. They are identified by colour depending on the monitored environmental matrix. Light green colour represents soil. Yellow colour represents sediment sampling. Blue colour in different tones represents water, snow and ice-core sampling sites. Brown colour represents humus, needles and pasture sampling sites. Fuchsia colour represents fauna sampling sites (micro and macro organisms). Particularly, fauna sampling category includes micro and macro organism as well as cow milk (Parolini et al., 2012).

Figure 3.1 includes MONARPOP sites for air, soil, humus, and needles (Offenthaler et al., 2009; MONARPOP, 2005). It is important to note that some monitoring sites are superposed into the figure, depending on how many matrixes have been monitored during the monitored survey.

The date reported for each monitoring datum is taken from each published study.



Note. Red stars represent air sampling campaigns (active, passive, and deposition). Light green stars represent soil. Yellow stars are sediment sampling campaigns. Blue stars in different tones represent water/snow/ice core sampling campaigns. Brown stars represent humus/needles/pasture sampling campaigns. Fuchsia stars represent fauna sampling campaigns (micro and macro organisms). (ARCGIS Explorer; Esri, USGS,NOAA).

Figure 3.1. Monitoring surveys included in POPAlp database.

3.2.2 Software and Database design

A system for managing and manipulating the collected POPs data was implemented. The system consists of two components: the database that stores and manages all the POPs data, and a Graphical User Interface (GUI) for user interaction and online data manipulation.

Once identified the main information elements consisting of matrices, monitoring campaigns and POP compounds, the conceptual analysis and modelling of the system for managing the database was carried out using UML (Unified Modelling Language) which is a general purpose modelling language, for the conceptual analysis and modelling of the system; and an Entity-Relationship Model (ER) for the specification of the database structure.

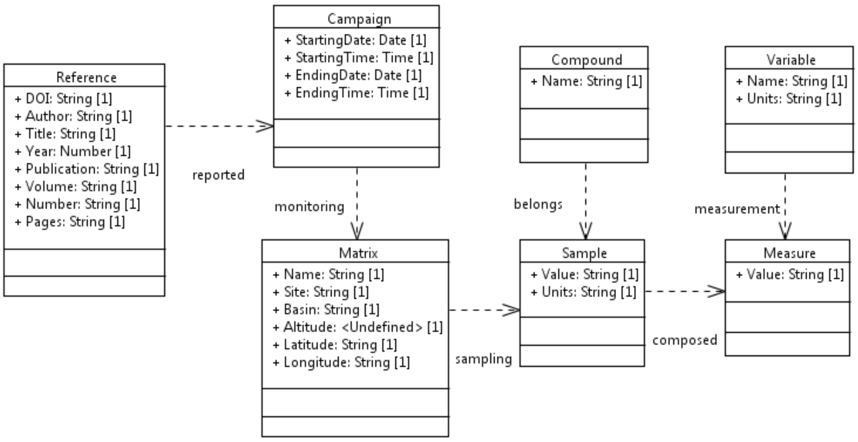
We developed an UML's Class diagram that represents the data structures for identifiying the main information data elements, its attributes and relationships, as shown in Figure 3.2a. In this conceptual model, a *matrix* element is characterised by its location, which was temporally monitored by a *campaign* reported in a the scientific literature by an specific *reference*, resulting in a set of *samples* of different POP *compounds,* where such samples may involve *measurements* of different *variables* (basic statistic descriptors such minimum, maximum, mean, SD values, among other values).

Next, a second data analysis phase was carried out, in order to define the database structure, resulting in the ER model of Figure 3.2.b, derived from the elements in the UML's Class diagram model.

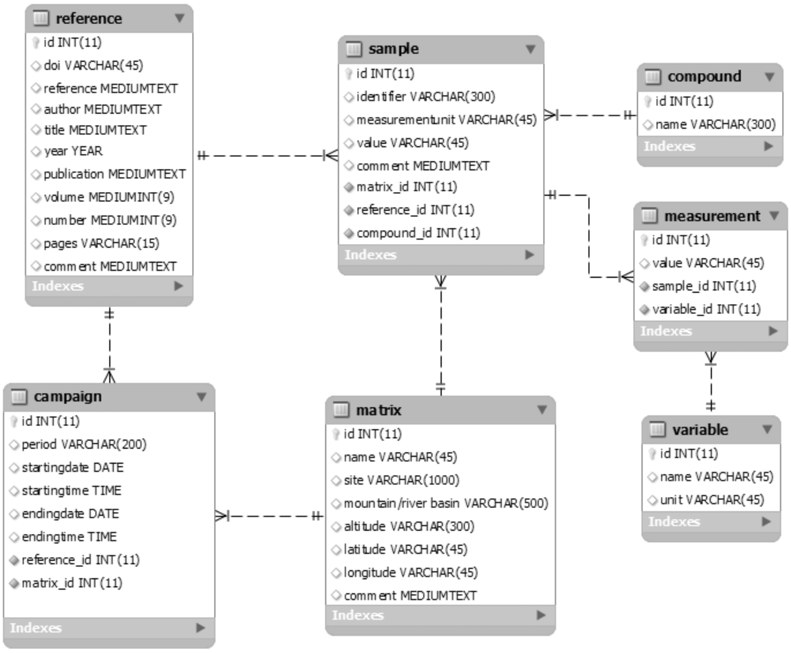
In the ER model the identified classes derived in data entities, where an entity represents a data set physically stored in a table in the database, while the links represent the logical relationships between data in the tables and define the data insertion/deletion rules and data consistency constrains (data types, data formats for numbers or dates).

For example, a data entry exists in *sample*, if such sample belongs to an existing *compound*, *matrix* and *reference* (where the relationship is due to the identification key composed by *compound_id, matrix_id, reference_id* fields), and that *sample* could not be deleted if is associated to one or more *variable* measurements.

The user's software for managing and consulting the POPAlp database was designed through a UML's Use Case diagram, which models the role, interactions and processes of the different users with the data.



(a)



(b)

Note: a) The Class diagram of the data structures of the data elements and the relationships between them. b) The Entity-Relational model that defines the database structure and logical relationship among data.

Figure 3.2. POPAlp' database design.

As illustrated in Figure 3.3, two user´s role profiles were identified: the data administrator and query users. Through the GUI, the administrator is able to define reported campaigns information and collect the associate monitoring data into POPAlp, which include the definition/manipulation of new matrices, POP compounds, and monitoring variables; while query users may perform customized queries and visualize the resulting data online. Figure 3.4 shows the resulting user's GUI, developed in Python programming language, downloadable as a stand-alone application from the CMCC site *http://www.cmcc.it/popalp*. The interface lets the user to perform complex multi-criteria queries, visualize the information with different ordering criteria and to export the results in simple tabular format for the post processing data analysis.

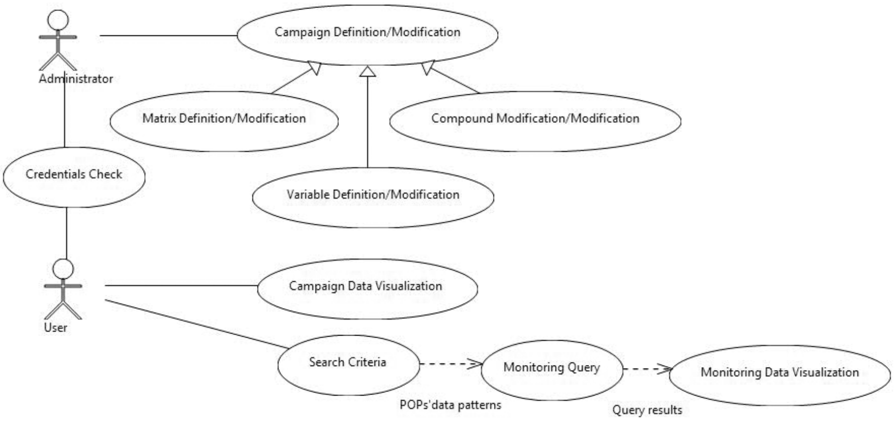


Figure 3.3. UML's Use Case diagram for modelling the user's role, interactions and processes with the POPAlp database.

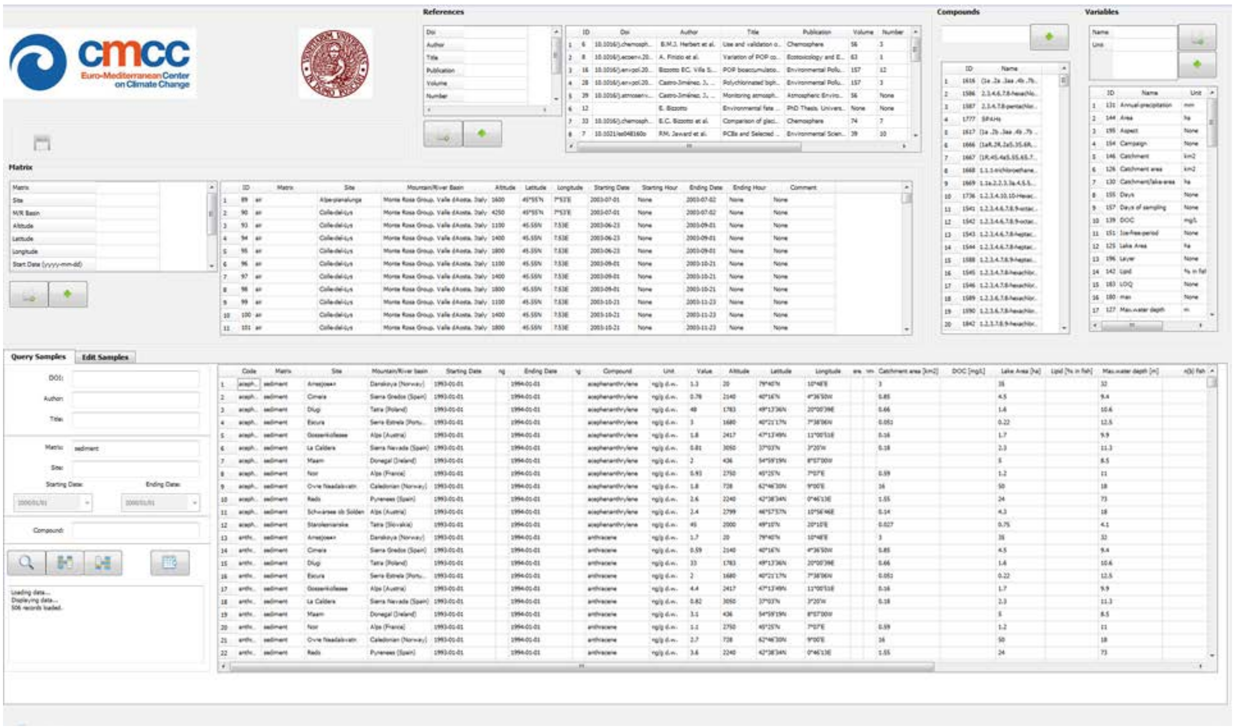


Figure 3.4. The Graphical User Interface for managing, collecting and data consulting of the POPAlp database.

3.2.3 Consistency between monitoring programs

The primary focus of the consistency between monitoring programs was the comparison of monitoring data on the presence of the POPs listed in table 3.1 (UNEP, 2007).

Some analysis methods and quality control for selected monitoring campaigns were evaluated in order to find consistency between monitoring programs throughout the sample collection, analytical methodologies, protocols for QA/QC, data archiving and accessibility (UNEP, 2007). Table 3.3 presents the sampling collection, analytical methods and QA/QC for each selected study.

3.2.3.1. Selection of samples

The criteria for selecting the different monitoring surveys in European Alps included in this work was to consider those which monitored POPs and reported data at high mountain sites located far from emission sources, in other words sources of POPs at local scale were rejected since European Alps was threatened as pristine region.

Air Sampling

In European Alps the combination of a number of active and passive sampling sites were presented in the selected surveys. As well, air bulk deposition sampling is usually fixed when the aim of the monitoring is recording the vegetation and rain effects in POPs’ deposition issue. Due to the low concentrations of some POPs (e.g. PCBs, HCHs, DDTs) in mountainous ambient air, large air volumes were collected with high and low volumes samples equipped for absorbing two phases: the gas phase and the particulate phase. Several different instruments were used to collect particulate matter, each with its own characteristic particle size range and flow rate range. During the monitoring studies the sampling frequency is based on short intensive measuring campaigns; two or more campaigns (summer and winter) were used to obtain information about the main seasonal changes (Offenthaler et al., 2009; Nizzetto et al., 2006), variations in concentration under different meteorological conditions and re-volatilization patterns (Finizio et al., 2006; Jaward et al., 2005).

Surface Water sampling

Stand-alone pumping and Van-dorn collection bottles were used (Villa et al., 2011; Bizzotto et al., 2009a; Vilanova et al., 2001) for liquid and particulate phases: dissolved organic compounds and suspended particles. Similar works reported environmental features, seasonal, biological, and meteorological events (U.S. Geological Survey, 2006). However, in such works the sampling frequency differs for each monitoring survey. For this reason, data was presented as monthly mean and standard deviation in order to obtain information about the main seasonal changes (Villa et al., 2011; Bizzotto et al., 2009a; Vilanova et al., 2001) with sampling rate uniformity.

Table 3.3. Methods and procedures reported from each monitoring survey in POPAlp

Author	Matrix	Sampling	Instrumental analysis		Quality Control		
			Fractionation	Identification	Identification		Quantification
					Blanks	Standard references	
(Jaward et al., 2005)	Air	Air passive sampling, Air active sampling	GC	MS (SIM mode)	Lab and field		MDL - derived from blanks
(Finizio et al., 2006)	Air	Air active sampling (high and low volume)	GC		Analysed periodically		MDL - instrumental detection limit and Sample detection limit
(Nizzetto et al., 2006)	Air	Bulk deposition sampling	GC	ECD	Field (every 6 samples)	Reference sample in order to validate the analytical procedure	DL defined as 3 times the blanks values
(Offenthaler et al., 2009)	Air	Air active sampling (High volume) Air active sampling (low volume) Bulk deposition sampling Passive air sampling	(HR) GC	HRMS for PCBs and PCDD/PCDF; HRMS (EI) for PAHs; EI -MS/MS for chlorinated paraffins; Trace GC -MS/MS for PBDEs;		1) According to EPA 1613 2) Relative response factors previously obtained from 3 standard solution injections 3) By means of the C12-labelled internal standards	
(Vilanova et al., 2001)	Water	stand-alone pump (filter and PTFE)	GC	MS-NCI		External standard method (using multilevel calibration mixtures)	
(Bizzotto et al., 2009a)	Snowmelt runoff	Collected by Van Dorn bottle	GC	MS (SIM mode)	Field blanks (n=5)		DL- for the analysis method were 35pgL-1 in May and 12pgL-1 in subsequent months
(Villa et al., 2011)	water	Collected by Van Dorn bottle	GC	MS (SIM mode)	Field blanks were generated All samples were blank corrected but not recovery corrected.		MDL - determined using the instrumental detection limit for the lowest concentration standard for each compound
(Fernández et al., 1999)	Sediment	Sediment coring	GC	MS	Field blanks (1 each 8 samples).		Standard reference material for calibration. External standard method EPAmix16
(Grimalt et al., 2001)	Sediment	Sediment coring	GC	MS-NCI	Field blanks.		LODs estimated. Validated by replicated analysis of reference sample (10 times noise ratio)
(Bizzotto et al., 2009b)	Sediment	Steel gathered instrumental	GC	MS (SIM mode)	Lab blanks (n=7) for each set of soxhlet extractions		DL - varied according to sample mass
(Villa et al., 2011)	Sediment	Grab sampler at 3 sites depths	GC	MS (SIM mode)	Field blanks were generated. Not recovery corrected.		MDL - determined using the instrumental detection limit for the lowest concentration standard for each compound

Author	Matrix	Sampling	Instrumental analysis		Quality Control		
			Fractionation	Identification	Identification		Quantification
					Blanks	Standard references	
(Tremolada et al., 2008)	Soil	Manually dug down	GC	MSD (SIM mode)	Field blanks		Calibration curves were performed
(Offenthaler et al., 2009)	Soil	Cores were extracted from each pit	(HR) GC	MS for PCBs and PCDD/PCDF; HRMS (EI) for PAHs; Trace GC -MS/MS for PBDEs; EI -MS/MS for chlorinated paraffins		Identification and quantification were done by isotope dilution method: According to EPA 1613	
(Tremolada et al., 2009)	Soil	Manually dug down	GC	MS (EI mode)	Blank every batch of 4 samples		LODs estimated by the signal to noise ratio (3:1). LOQs are not higher than 0.1 ngg-1 dw
(Tremolada et al., 2011)	Soil	Manually dug			Blank every batch of 4 samples using anhydrous sodium sulfate		LODs curve estimated by the signal to noise ratio. LOQs are not higher than 0.01 ng g-1 (dw)
(Quiroz et al., 2011)	Soil	Collected by 5cm stainless steel cylinder. triplicate soil samples	GC	MS	Procedural blanks 1 for each 9 samples.	Compound identification by comparison of the m/z profiles of the sample and external standards. Internal standard method.	Calibration curve were performed by each compound. MDL - based on signal to noise ratio (3:1)
(Guazzoni et al., 2011)	soil	3 cubes of soil were taken and separated into 3 layers	GC	MS (EI mode)	Procedural blank was run in parallel with every batch of 3 samples	Quantification was performed by external standard calibration curves.	LODs estimated by the signal to noise ratio (3:1). LOQs were not higher than 0.001ng/g dw
(Parolini et al., 2012)	Soil	ibid Guazzoni 2011	GC	MS (EI mode)	1 procedural blank was run every batch of 4 samples		LOD were quantified by the signal to noise ratio detection (3:1)
(Carrera et al., 2001)	Snowpack	Pre-rinsed stainless steel corer and filters	GC	MS	Field blanks (1 each 8 samples).	External standard method EPAmix16. Standard reference material for calibration	
(Villa et al., 2003)	Ice core	Electromechanical wire drill system - stainless steel shovel	GC	MSD (SIM mode) ECD for quality of analytical data	Blanks analysed periodically		MDL - instrumental detection limit
(Herbert et al., 2004)	Snowpack	snow can - aluminium sampler - low volume (7.5l) and high volume (50l)	GC	MS (SIM mode)	Lab and field		
(Villa et al., 2006)	Ice core	Firn-core depth 23.75m - electromechanical wire drill system	GC	MSD (SIM mode)	Blanks presented detectable compounds		MDL determined as the instrumental detection limit of the lowest concentration standard
(Finizio et al., 2006)	Snowpack	Snow samples	GC		Blanks analysed periodically		MDL - instrumental detection limit and Sample detection limit

Author	Matrix	Sampling	Instrumental analysis		Quality Control		
			Fractionation	Identification	Identification		Quantification
					Blanks	Standard references	
(Bizzotto et al., 2009a)	Snowmelt runoff	Water sample	GC	MSD (SIM mode)	Field blanks (n=5)		DL- for the analysis method were 35pgL-1 in May and 12pgL-1 in subsequent months
(Grimalt et al., 2009)	Snowpack	Hand cored (pre-rinsed stainless steel corers) (ibid Carrera 1998)	GC	MS (SIM and EI mode) (ibid Carrera 2001)	Field and procedural blanks of each sampling sites		MQ and DL - were calculated for each snow sample
(Gabrieli et al., 2010)	Snowpack	Plunging vertically with 50cm long aluminum core samples	HPLC	Fluorimetric detector	Blanks	External calibration	DL calculated as 3 times the standard deviation of the blank.
(Grimalt et al., 2001)	Biota	Fish collection	GC	MS-NICI			Q&DL aprox. 10pg/g w.w.
(Bizzotto et al., 2009b)	Biota	Macro-invertebrates surber net and subsequent catch stored in formaldehyde	GC	MS (SIM mode)	Lab blanks (n=7) for each set of soxhlet extractions		DL - varied according to sample mass and the lipid content was determined gravimetrically
(Iozza et al., 2009)	Biota	Spruce needles - collected, pooles and transferred	GC	EI-MS/MS	Blanks		MDL - the sum of the mean concentration and 3 times the standard deviation of 5 (needles) blank measurements and 6 (humus) blank measurements
		Humus - 30x30cm (depths 0.8 - 23.8cm) pooled and transferred					
(Offenthaler et al., 2009)	Humus	From rectangular sampling grid an entire humus layer within a 0.09 m2 square	(HR) GC	MS for PCBs and PCDD/PCDF; HRMS (EI) for PAHs; Trace GC -MS/MS for PBDEs; EI -MS/MS for chlorinated paraffin	Isotope dilution method: 1)According to EPA 1613		
(Villa et al., 2011)	Biota	Fish muscle tissue collected using standard procedures	GC	MS (SIM mode) SIA (stable isotope analysis)	Field blanks were generated All samples were blank corrected but not recovery corrected.		MDL - determined using the instrumental detection limit for the lowest concentration standard for each compound
		Plankton samples using nets of 50 and 200 micrometers mesh size					
(Parolini et al., 2012)	Biota	Vegetation was cut and wrapped in clean tinfoil	GC	MS (EI mode)	1 procedural blank was run every batch of 4 samples		LOD were quantified by the signal to noise ratio detection (3:1)
		Cow milk samples were collected during the pasture season					

Notes. Information extracted from each published study.

Soil Sampling

The samples were collected by manually dug, then homogenised and stored under similar conditions (Parolini et al., 2012; Guazzoni et al., 2011; Quiroz et al., 2011; Offenthaler et al., 2009; Tremolada et al., 2008, 2009, 2011). From the samples, the total organic carbon were determined by CHN elemental analyser.

Sediment Sampling

Sediment samples were collected through sediment coring, using a steel gathered instrumental and stored in tight glass bottles, in the deepest part of the lake (Grimalt et al., 2001; Fernández et al., 1999), in the upper part of the lake (Villa et al., 2011), and along water streams (Bizzotto et al., 2009b). In this case, the total organic carbon were determined by CHN elemental analyser.

Snow and Ice Sampling

Snow cores samples used aluminium and stainless steel cans (Gabrieli et al., 2010; Grimalt et al., 2009; Finizio et al., 2006; Herbert et al., 2004; Carrera et al., 2001) for dissolved fraction and particulate phases: particulate by filtration and dissolved fraction by absorption. Meteorological (temperature, snow events, back trajectories) and physical conditions (temperature, snow density and stratigraphic) were given.

Ice samples were obtained from electromechanical wire drill (Villa et al., 2003, 2006). Physical characteristics such as dating ice core, density profile and depth were given.

Biota Sampling

POPAlp includes some biota samples, even when the number of sampling data of this matrix is small in the databse. Mainly, spruce needles, pasture and humus were included in this category (Parolini et al., 2012; Villa et al., 2011; Iozza et al., 2009; Offenthaler et al., 2009). On the other hand, several fish and plankton samples (Villa et al., 2011; Bizzotto et al., 2009b; Grimalt et al., 2001) were included as complement data for water and sediment data available in POPAlp. Milk-cow samples complemented pasture data (Parolini et al., 2012). The concentration´s data were given in dry mass and the total carbon content was calculated by CHN elemental analyser.

QA/QC field blanks exposed to the same field and transport conditions were collected in all monitoring campaigns with different procedures and quantities (see table 3.3).

3.2.3.2. Standard reference materials

Reference materials (RMs) are samples that have been tested in many different laboratories or by several different analytical techniques and given a certified value with a reduced uncertainty (U.S. Geological Survey, 2006). Clearly, the external standard EPA 1613 were used for PCDD/Fs and EPA mix16 for PAHs by (Offenthaler et al., 2009; Carrera et al., 2001). Internal standards were used as a compound with similarities in physical and chemical properties to the analyte in the sample (Quiroz et al., 2011). For other compounds was not clear which were the external/internal standards used.

3.2.3.3. Chemical analysis

Analytical procedure

The determination of a specific organic compound distributed between the phases was obtained by fractionation using gas chromatography (GC) and high resolution gas chromatography (HRGC). The chemical identification was made by mass spectrometers in single ion monitoring (SIM) and by an electron-capture detector (ECD) that greatly increase the sensitivity. The ionization technique varied from electron technique (EI) and negative ion mode (NCI).

Samples were blank corrected with QA/QC laboratory blanks but not recovery corrected (Villa et al., 2011; Offenthaler et al., 2009).

Thresholds to evaluate the method detection limit (MDL) were calculated as 3 times the standard deviation of the n-blank.

3.2.4. Chemical selection and data comparison

We selected several POPs in order to make an inter-comparison with mean-concentration data over European Alps in specific environmental matrices. The aim of this inter-comparison over time was for assessing the spatial concentrations and for future modelling purposes. The main difficult in this comparison was managing the discrepancy of the frequency sampling rate of the reported data in the considered papers: monthly; weekly; 2-days and less than 24 hours (day and night) and the required time aggregation (annual) during large time trends.

The substances were grouped by family organic-chemical species: DDTs, HCB, HCHs, PCBs, PAHs, Organochlorine pesticides (OCPs), PCDD/Fs, chlorinated paraffin, PBDEs, PFOS.

3.3. Results and discussion

3.3.1. Information needs for monitoring POPs behaviour in European Alps

According to the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants (UNEP, 2013) air sample collection was considered as the main target environmental compartment for POPs and for their behaviour into environment. The primary objective during air sample is to obtain representative data for assessing baselines and changes over time and space and the regional and global transport of POPs (UNEP, 2013).

Table 3.4. Temporal and environmental matrix characteristics for mountainous monitoring surveys in European Alps**.**

Authors' reference	**Monitoring period**	**Matrix**						
Villa et al. 2003	1996, 2000	Snow						
Herbert et al. 2004	2002	Snow		Ice				
Jaward et al. 2005	2003		Air					
Finizio et al. 2006	2003	Snow	Air					
Nizzetto et al. 2006	2003		Air					
Villa et al. 2006	2000, 2002		Air	Ice				
Tremolada et al. 2008	2003						Soil	
Tremolada et al. 2009	2007						Soil	
Bizzotto et al. 2009	2006					Water		Biota (macro-invertebrates)
Bizzotto et al. 2009b	2006					Water		
Guazzoni et al. 2011	2008						Soil	
Tremolada et al. 2011	2007-2008						Soil	
Villa et al. 2011	2007				Sediment	Water		Biota (plankton and fish)
Parolini et al. 2012	2008						Soil	
Fernández et al. 1999	1993-1994				Sediment			
Carrera et al. 2001	1997-1998	Snow						
Grimalt et al. 2001	1993-1994				Sediment			Biota (fish)
Vilanova et al. 2001	1996-1998					Water		
Grimalt et al. 2009	1997, 1998, 2005	Snow						
Iozza et al. 2009	2004-2009							Biota (s. needles and humus)
Offenthaler et al. 2009	2004-2007		Air				Soil	Biota (s. needles and humus)
Quiroz et al. 2011	2004						Soil	
Gabrieli et al. 2010	2005	Snow						

Note. Dashed colour groups the different surveys according to chemical laboratories and analysis techniques used.

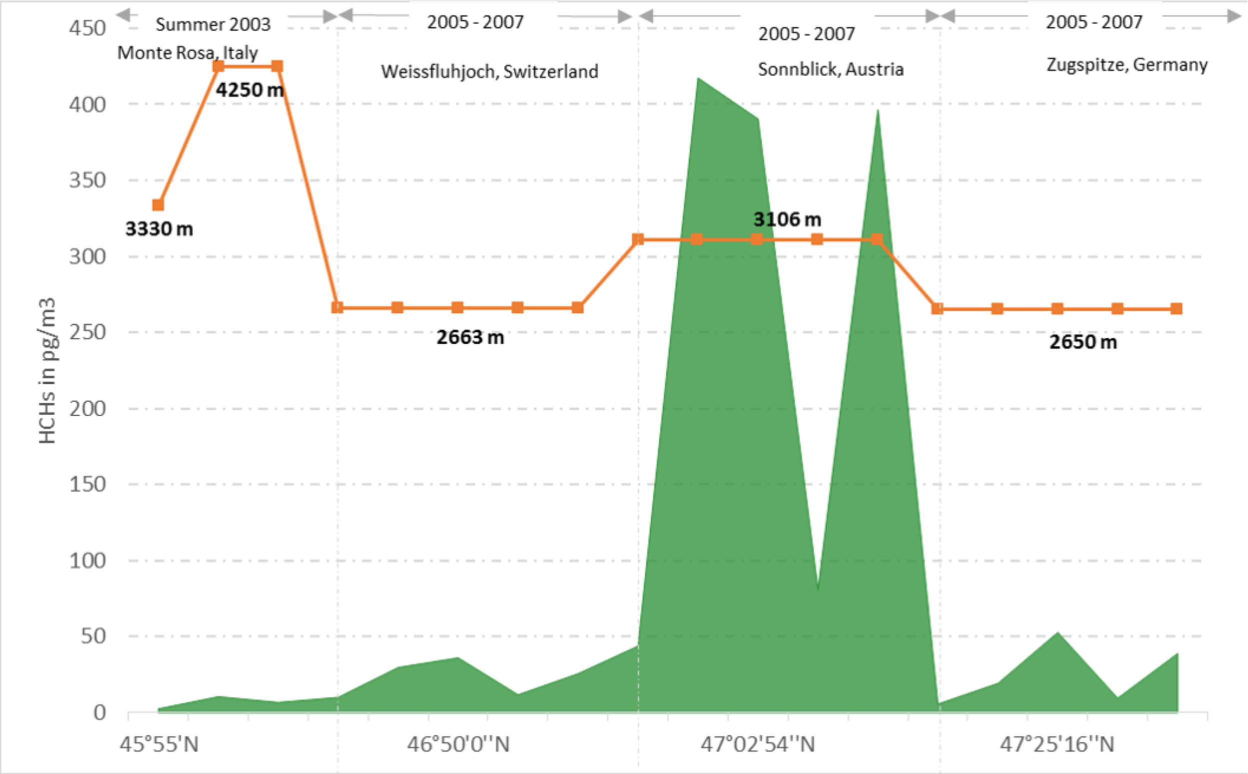
In European Alps, the regional assessment becomes of an exceptional interest, not only in air compartment, but also in water, sediment, soil, snow and ice, and biota compartments. On this regard, it is clear that there is a gap in the terrestrial coverage for monitoring campaigns derived to the high costs of these in the mountainous areas. Nonetheless, the public concentrations data available in literature shared a quality assurance and quality control between all attempts. The involved monitoring studies were careful to prevent photochemical reactions especially for snow and ice monitoring surveys (Gabrieli et al., 2010; Grimalt et al., 2009; Finizio et al., 2006; Villa et al., 2006; Herbert et al., 2004; Carrera et al., 2001). Besides, all studies reported preservation techniques of the sample between collection and analysis procedures. Several monitoring attempts were linked over time following the same sample and analysis procedures in order to compare their POPs concentrations' data, needed for both temporal and environmental matrix comparisons as table 3.4 shows.

The results reported by monitoring studies allow to refer spurious or contamination sources, such as seasonal, biological, and meteorological events, and (UNEP, 2013; U.S. Geological Survey, 2006).

3.3.2. POPs concentrations

POPs concentration data can assist the identification of source region of pollutants that are transported to an alpine area (Westgate and Wania, 2010). Their presence in a pristine regions, usually in the mountain top (up to 2000m a.s.l.) is linked with an industrial or residential zone, as a source point at the bottom of the mountain range. With the aim of carrying out an analysis of such concentrations, we used the integrated information referred in this paper and then we generated integrated reports using our PopAlp database. In particular we use a selection of alfa-HCH, DDTs, HCB and PAHs' particles bond according to the annex I, II and III of Stockholm Convention. These POPs have been phased out more than 20 years ago, and in some cases, such as DDT that were banned in Central Europe in the late 1980s, they were besides found in European Alps environments in particulate phase, and gas phase in air and liquid phase in air-precipitation and water bodies (e.g. lakes, rivers).

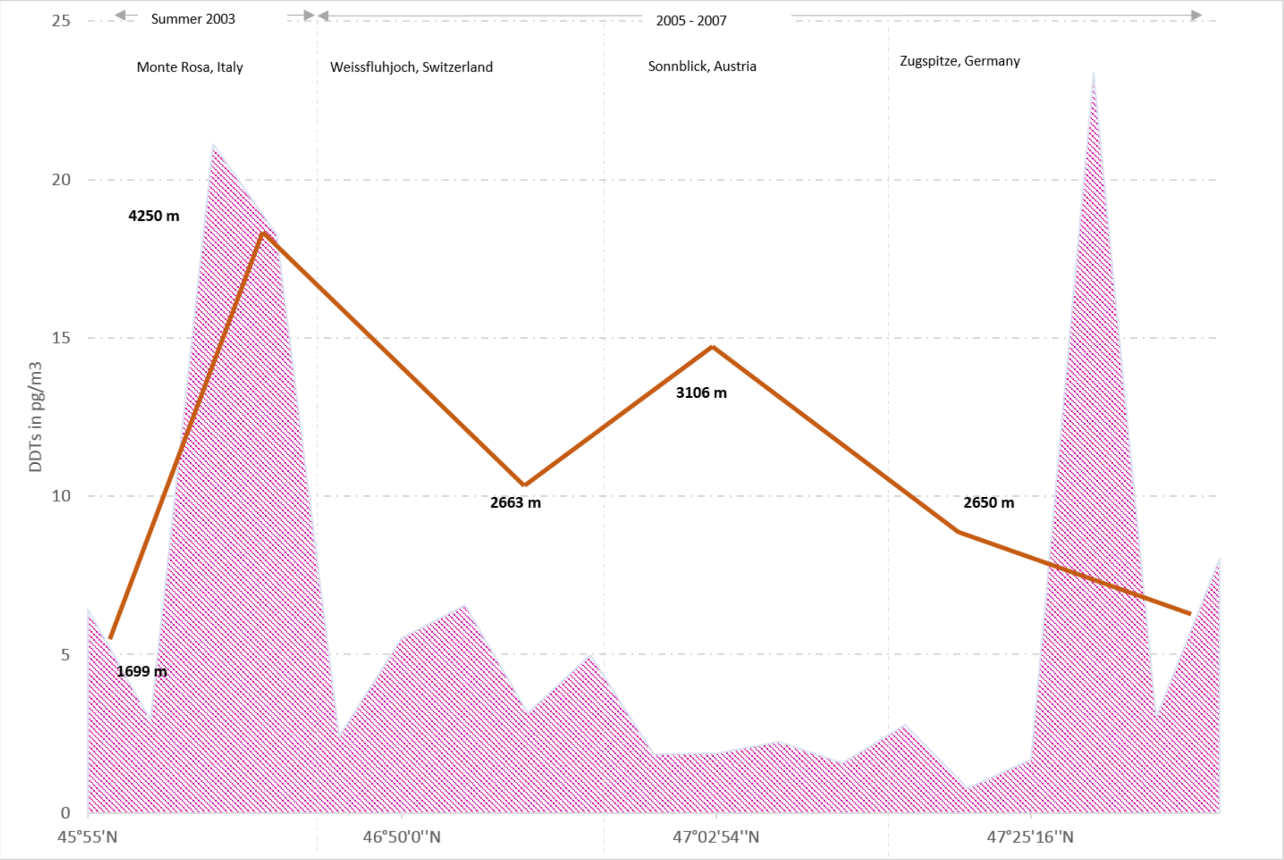
We analysed some organochlorine substances, specifically pesticides (OCP) and their by-products, which are POPs commonly used in agriculture and health control. Based on POPAlp, we first analysed the integrated data of the substance hexachlorocyclohexane (HCH), which has been identified as a monitored substance along European Alps and in more than one environmental compartment. HCH is available in two formulations: technical HCH and lindane (Li, 1999). The technical HCH forulation contains different proportions of the isomers: alpha-HCH (55 – 80%); beta-HCH (5 – 14%); gamma-HCH (8 – 15%); delta-HCH (2 – 16%) and epsilon-HCH (3 – 5%). On the other hand, the lindane formulation is gamma-HCH (lindane) and has been used mainly as a timber insecticide. Releases of lindane to water damage aquatic living species such insects and fishes, and can even persist and being accumulated in the fish's bodies. This ability to persist and accumulate in the environment means that lindane can travel long distances and have effects far from their original point of emission. Emissions of HCH occur through its manufacture, use, storage and transportation (EEA, 2013). In EU, more specifically in countries that share the European Alps mountain range, HCH was banned in 2009 but their production and use were stopped since 2004. In particular, dating ice-core lets to identify concentrations data during a long time period, from 1955 to 2005 (Villa et al., 2006). These data were monitored up to 4200 m a.s.l. with regional sources in the bottom of the mountain range, and the results from Villa et al. 2006 showed a peak in the early 1970s and a decreasing range during 1980s. Following the approach of Wania and Westgate (2008), this altitudinal distribution could be explained with the mountain cold trapping effect that was described as the temperature dependence of precipitation scavenging between bottom and mountain top (Wania and Westgate, 2008). Finizio et al., 2006 indicated HCHs concentrations data monitored during 2003. They found lower concentrations at high altitudes (up to 3300m a.s.l.) but after that, from 2005 and 2007, HCHs concentrations went up at Sonnblick, Austria (Offenthaler et al., 2009) which can be explained by the less efficiently scavenging due to precipitation, but an increase in snow scavenging due to air mass cools. Variations in concentrations can be linked directly with the historical use and distribution of lindane (gamma-HCH) and the subsequent differentiated release into the environment that result in differentiate concentrations, as can be observed in the graph in figure 3.5. The lower values can be explain due to the phase out of HCH as a result of the application of international agreement related to the chemical banned in the European region in the period 2003 to 2007 at different latitudes.



Notes. Sum HCH concentrations in air at different locations along European Alps. Green shape represents HCHs concentrations in air. Orange line represents an altitudinal profile. Data extracted from(Offenthaler et al., 2009; Finizio et al., 2006).

Figure 3.5. Concentrations of total HCH in European Alps air compartment (latitudinal profile)

Other considered OCP that was analysed is DDT, which has been produced and used for public health protection in all countries worldwide. DDT was definitely banned in UNECE region in 1998. However, DDT is still used in most African countries and some countries in Asia for controlling some diseases such Malaria vector, and also in agriculture. In Europe, its application was seasonal and its environmental behaviour still continue during the next years. The presence of DDTs in ice core presents a seasonal variation with the maximum in spring and minimum during autumn (Villa et al., 2003). This variation can be linked with re-volatilization during the summer period. The low volatilization and almost 30 years of release control are the reasons for low concentrations in air and the rapid losses of DDTs for 2003 (Finizio et al., 2006). Figure 3.6 presents the concentration data available from monitoring programs in Europeans Alps during 2003 to 2007 where seasonal variations for DDTs concentrations were found.



Notes. DDTs concentrations in air compartment at different altitudes in a latitude profile. (Finizio et al., 2006; Villa et al., 2003). Numbers next to brown line are altitudinal values. Red shade represents DDTs concentration data at specific locations.

Figure 3.6. Concentrations of total Sum DDT in European Alps air compartment (latitudinal profile).

Concentrations of Hexachlorobenzene (HCB) were compared using POPAlp. HCB in snow, ice-core and air environments shows continuous presence from 1955 to 2007. The use of this POP for industrial purposes and as by-products has an occurrence linked with urban zones. In particular HCB was extensively used as a seed dressing to prevent fungal disease on grains, but its use was discontinued in most countries in the 1970s.

The presence of HCB in snow and air shows that nowadays some diffusive sources remain as an important source of chemical into the environment. The amount of HCB continues to be released into the environment from several sources, including the use of some chlorinated pesticides, incomplete combustion, old disposal sites, as by-products, and waste material from manufacture of chlorinated solvents, chlorinated aromatics and chlorinated pesticides.

Additionally, it is possible that re-volatilization of 'old' HCB from soils would also occur and it is believed that no single source dominates current emissions (Barber et al., 2005). HCB´s concentrations in snow melt are very high and constant [100 ng/L] during 1990s (Villa et al., 2003). The plausible reason can be the high persistence and stability of HCB in the atmosphere that is its preferable transport route, as several authors have been pointed out (Shunthirasingham et al., 2013; Barber et al., 2005; Bailey, 2001). Meanwhile in (Finizio et al., 2006; Villa et al., 2006) presents the inverse case [0.0235ng/L]. HCB in (Villa et al., 2003) also presents constant trends along time. This occurrence could be due to the distance with sources and releases, probably because the industrial and residential zones are closer to the monitoring site than others ones analysed in this study.

Finally, we analysed POPs that were released as by-products of industrial and combustion processes, polycyclic aromatic hydrocarbons (PAHs). PAHs are presented in natural crude oil and coal deposits in significant amount and they are one of the most widespread organic pollutants. In addition to their presence in fossil fuels they are also formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, and incense (Ravindra et al., 2008; Fernandez and Grimalt, 2003). PAHs are less volatile, therefore they are found in the vicinity of their source (punctual and mobile). PAHs concentrations follow the occurrence pattern described before, by presenting elevated concentrations constrained by the presence of important industrial zones (Quiroz et al., 2011; Herbert et al., 2004). In contrast, (Gabrieli et al., 2010) presented lower concentrations during 2002, because of the high altitude (3260 m a.s.l) and the scarcity of diffusive source points from residential emissions in the interested area.

3.4. Conclusions

In this chapter we presented a method for the compilation and organization of monitored data of Persistent organic pollutants in mountains regions at the European Alps. Our resulting database POPAlp is able to systematically collect, store and manage monitored data of several POP's substances. With POPAlp is possible to obtain concentrations data in the environment available in European Alps. At this moment, we collected existing concentration data in the Alps in Austria, Germany, Switzerland, Slovenia, Italy and Czech Republic, from year 1999 to 2012, reported in the literature. POPAlp lets the user to update the database with the aim to maintain the effectiveness for assessing and evaluating purposes.

In a multiple campaign study (or if a large number of samples imposes the requirement to split up the data set and submitted as smaller individual batches), it may make sense to collect an extremely large volume of a single samples. When this is not possible for economic and management issues, the inter-program campaign becomes very useful to evaluate regional transport of POPs. Collection, analysis, and QA/QC data are performed in different laboratories following validated methods for volatile organic compounds (VOCs) (US EPA, 2014; UNEP, 2013; US EPA, 2012). When laboratories use validated methods, data are refined and this decrease drastically the information of contaminations which may led to differences in data that can drastically affect the interpretations and conclusions of studies (Su and Hung, 2010). The existence of a continuous monitoring program in high mountains is critical because of the vulnerability of the mountainous ecosystems in temperate zones.

During this inter-program comparison over sample collection, data procedures and QA/QC, we can conclude the pertinence of having a guiding tool for monitoring POPs and that allows to homogenise all necessary steps of data collection. This would help to produce reliable concentrations data for analyse long and medium time-lapse for baselines and assessing changes over time and space on a regional and global transport perspective of POPs (UNEP, 2013), not only in air, water and human tissues, also in sediment, soil, and snow/ice compartments for their rule as secondary sources of emissions

Total HCHs, DDTs, HCBs, and PAHs are selected in air as main target compartment and water, snow, soil as complement matrices monitored in European Alps. Mainly, the observed trends of some POPs in the environment are related with their chemical properties that let the chemical move from one media to another, or prefer some specific route. Moreover, chemical and physical properties are temperature dependent. Thus, mountainous environment has temperature and precipitation gradients that favour POPs follow specific behaviour until reach the top of the mountain. At the same time mountain top becomes a barrier and a privileged deposition place that could be a secondary source from re-volatilization, which enhanced the remobilization of those POPs. In this way, identifiying the possible correlations between long monitored data and climatological parameters may help the identification of climate impacts over POPs behaviour. On this regard, fate and transport models and atmospheric circulation models can assist in the integration of monitoring data and effectiveness of international regulation of POPs and their impacts into the environment including human health (UNEP, 2013; Buser et al., 2012; Bucchignani et al., 2011; Auer et al., 2007; Pozo et al., 2006).

Using POPAlp we observed that the importance of high altitudinal regions such as European Alps resides in their role as a secondary source from some chemicals that were phased out more than 20 years ago (UNECE/CLRTAP 1979b). For this reason, the temporal scale is a relevant variable to explain the POPs dynamic behaviour in mountainous environment. The obtained results and the observed trends show the usability of POPAlp as a valuable approach for integrating new monitoring information and monitoring data analysis, useful by the scientific community.

In the 1990’s Wania and Mackay (1996) indicated a classification scheme for POPs depending on their mobility in a global context. That study was reinforced for monitored campaigns done in a global scale, modelling POPs concentration at different latitudes. Since then, studies around the world have confirmed the presence and behaviour of POPs at global level. We propose the use of our POPAlp database as a suitable tool that can help to determine the POPs behaviour in mountainous region as a systematic task, useful for reducing the uncertainty in toxicological and screening studies not only for already known POPs, but for the new ones.

3.5. Acknowledgements

We acknowledge Miguel Angel Padilla Castaneda (PhD) from Scuola Superiore Sant'Anna di Pisa (IT) for his support in the design, development and management of database POPAlp.

3.6. References

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4. Climate change impact on the fate of persistent organic pollutants: a case study in the Italian Alps

Tair Teran-Guerrero, Lara Lamon, John Westgate, Edoardo Bucchignani, Myriam Montesarchio, Frank Wania, Antonio Marcomini

Abstract

High-altitude mountainous ecosystems are important areas used for recreational, extensive agricultural purposes and as energy resources. In the last 25 years, studies have revealed that alpine environments, similar to the Polar Regions, are affected by the transport of persistent organic pollutants (POPs). Several studies have reported the presence of high concentrations of POPs in mountainous regions in both biotic and abiotic media compared with those found near of source's sites at mountains' bottom or valley. In regard to explain the specific fate and transport of POPs in mountainous environment, dynamic fugacity model called MountainPOP3.0 has been adapted and applied in order to analyse the environmental behaviour of α- HCH and HCB in Italian Alps as function of climate variables (temperature, precipitation and wind speed). In order to analyse the effect of climate change in mountainous regime on POPs environmental distribution we made the comparison between two climate scenarios.

The application of MountainPOP3.0 reveals which environmental factors are the key factors that explain this mountain cold-trapping behaviour: 1) a high atmospheric organic particle load; 2) a notable gradient of precipitation increasing upslope; 3) and a large temperature gradient from the valley to the mountain-top.

Add a few lines on the main results related to the climate change effects. If you want you may also add some information (supporting results) from uncertainty analysis (not the other way around).

Keywords

HCH, HCB, mountain environment, fugacity model, climate change

4.1. Introduction

Environmental contamination by persistent organic pollutants (POPs) is an issue of global concern that is addressed by international agreements (UNEP, 2001, 2009) and other (inter)national legislations (HELCOM, 2000; OSPAR Convention, 1998; UNECE, 1998; Arctic Council, 1997). POPs are chemicals of concern because of their toxicity and their characteristic persistence, which is also related to their "remoteness" from emission sources that can influence, principally from two environmental mechanisms: the temperature dependence of chemical properties and atmospheric loss rates through OH radical reaction, also affected by environmental temperature gradients; the POPs distribution along spatial gradients into the environment (von Waldow et al., 2010). Because of the concern on the toxicological effects POPs may exert on human health and on the environment (AMAP, 2003; WHO, 2003; Abelsohn et al., 2002), extensive literature is available on multimedia fate and transport models (MMM) applications addressing the transfer of POPs chemicals to the poles, especially to the Arctic (de Wit, 2010; Muir and de Wit, 2010; Braune et al., 2005; Wania and Dugani, 2003) that is subject to impacts from exposure to POPs despite its distance from pollutants emissions.

POPs physicochemical properties such as chemical stability, semi-volatility, and affinity with organic carbon in soils, combined with the atmospheric latitudinal temperature gradient, generates a net transfer of such pollutants from low-medium to high latitude regions. Significant concentration increments at higher latitude have been observed for several POPs (Armitage et al., 2013; Wöhrnschimmel et al., 2012; Kallenborn et al., 2007; Semeena et al., 2006; Su et al., 2006), in remote areas, if compared with the emission regions.

Because POPs undergo long range transport and their environmental distribution is affected by temperature dependent air-surface exchange, mountain environments may receive POPs through the cold trapping process (Westgate et al., 2010) thus recalling latitudinal transfers to polar regions as observed in global redistribution studies (Grimalt et al., 2004; van Drooge et al., 2004). Westgate et al. (2010) recognize precipitation rate and amount and atmospheric temperature as relevant environmental variables affecting the environmental fate of POPs in mountain cold trapping.

Furthermore, they identify aerosol concentration and nature (that is related to the altitude) as a relevant environmental parameter and scavenging ratio as an important environmental process. Climate change is defined in the last IPCC Assessment Report as an alteration in the climate condition that can be identified by changes in the mean value or variability of a climate property that persist in time (Stocker et al., 2013). Since the mid-20th century anthropogenic forcings have likely made a substantial contribution to surface temperature increases; furthermore, there has been an anthropogenic contribution to the very substantial Arctic warming since the mid-20th century. Regarding climate change-related observations in mountain areas, measured vertical temperature profiles of mountain glaciers or ice sheets show that climate was warming over recent decades. According to observations, the Arctic and European Alps have experienced the greatest mass losses per unit area in the last four decades.

Considering that environmental variables are affecting chemicals fate and transport and assuming observed climate change, several authors have investigated so far the impact of climate change on environmental POPs concentrations. This was done through the application of multimedia environmental fate models (MMM) assuming present climate and future scenarios data as environmental variables inputs. Global scale simulations showed that POPs transport to the Arctic is enhanced under a climate change scenario (Lamon et al., 2009). Furthermore, regional scale simulations showed that remote emissions play a more important role if compared with regional emissions when assuming a climate scenario characterised by higher temperatures and wind speeds (Lamon et al., 2012).

The objectives of this work were: 1) to identify a case study area to make a chemical's mass balance considering emissions and environmental characteristics; 2) to apply a climate change scenario to evaluate the influence of climate variables on POPs environmental fate and concentrations in mountain areas; 3) to consider if whether and how climate change impacts POPs fate and transport in high mountain environments.

4.2. Materials and Methods

4.2.1. Chemicals selected as case studies

In this research chemicals were selected depending on 1) available POPs concentration data on European Alps (*POPAlp Database* (version 1.0) 2014) and 2) available information on environmental emissions. POPs measured concentrations were collected by consultation of the POPAlp database (http://www.cmcc.it/popalp/) reported in the last chapter of this thesis. POPs emission estimations were reviewed for the chemicals that were selected depending on monitoring information. Then finally, α-Hexachlorocyclohexane (α-HCH) and hexachlorobenzene (HCB) were selected as case studies for the simulation in high mountain environments, as the information was more complete and concentrated in a consistent time period. The monitoring sites and the number of samples considered are reported in Table 4.1.

Table 4.1. Data extrapolated by POPAlp database

http://www.cmcc.it/popalp/ (*POPAlp Database* (version 1.0) 2014).

Substance	Matrix sample	Place/Site	Starting date (dd/mm/yyyy)	Ending date (dd/mm/yyyy)	Data records	Reference
a-HCH	Soil	Mount Legnone, Sondrio, Lombardy, Italy	01/08/2003	01/08/2003	1	(Tremolada et al., 2008)
a-HCH	snow - ice melting	Ortles Cevedale to Lake Como, Lombardy, Italy	05/06/2006	05/07/2007	10	(Bizzotto, 2008)
a-HCH	water	Ortles Cevedale, Lombardy, Italy	05/06/2006	05/10/2006	22	(Bizzotto et al., 2009)
HCB	soil	Mount Legnone, Sondrio, Lombardy, Italy	01/08/2003	01/08/2003	1	(Tremolada et al., 2008)
HCB	snow - ice melting	Ortles Cevedale to Lake Como, Lombardy, Italy	05/06/2006	05/07/2007	15	(Bizzotto 2008)
HCB	water	Ortles Cevedale - Frodolfo Glacial, Lombardy, Italy	05/06/2006	05/10/2006	19	(Bizzotto et al. 2009)

The most representative isomers of technical HCH are the α-HCH, β-HCH, and γ-HCH (Xiao et al., 2004), and lindane as a purified γ-isomer (Li, 1999). HCHs were applied globally as pests control and as seed protection, poultry and livestock treatment, and household vector control for decades since 1942, when insecticidal properties of the γ-isomer were discovered. All the HCH isomers exhibit acute and chronic toxicological properties (Willett et al., 1998). It was included in Annex 1 of the Stockholm Convention (UNEP, 2001).

Hexachlorobenzene (HCB) was used as a fungicide and is also obtained as a by -product in industry in the production of chlorinated solvents, compounds and pesticides (ATSDR, 2013). It was banned by the Stockholm Convention, but it is still released in the environment due to ongoing use in developing countries, or to improper storage or disposal in developed countries, and as a by-product in waste streams of chlor-alkali plants and wood preserving plants and in fly ash and flue gas effluents from municipal incineration (ATSDR, 2013). Toxic effects of HCB on the reproductive system have been reported in several studies (Eggesbø et al., 2009; Alvarez et al., 2000).

Physical chemical characteristics of the selected substances are reported in Table 4.2, and were used as input values in the model simulation.

Table 4.2. Chemical properties of α-HCH and HCB at 25° C

Chemical inputs				
Name	***α-HCH***		***HCB***	
logK_{OW}	3,94	a	5,64	H
logK_{OA}	7,46	a	7,21	H
logK_{AW}	-3,52	a	-1,57	
dUow (kj/mol)	-5,1	a	-24,4	H
dUoa (kj/mol)	-61,9	a	-75,5	H
dUaw (kj/mol)	56,8	f	47,7	H
Molecular Mass (g/mol)	290,85	a	284,8	H
Second order OH Reaction Rate In Air (h^{-1})	3,58E-10	e	4,57E-11	e
[OH·] in air (cm^{-3})	9,70E+05	e	9,70E+05	e
HalfLife in Soil (h)	14000	b	44688	I
HalfLife in Water (h)	2920	c	22344	I
Activation Energy in Air (kj/mol)	11,2	e	24,3	E
Activation Energy in Soil (kj/mol)	30	d	30	I
H (Pa/m^{3}mol)	1,239	a	30	J

a. (Xiao et al., 2004)
b. (Wöhrnschimmel et al., 2012)
c. (Ngabe et al., 1993)
d. (Breivik et al., 2002)
e. (Brubaker and Hites, 1998)
f. (Armitage et al., 2013)
g. (Spivakovsky et al., 2000)
h. (Li et al., 2005)
i. (Shen and Wania, 2005)
j. (McPhedran et al., 2013)

4.2.2. The case study area: the upper Adda river basin

When dealing with MMM applications on mountain areas, it is necessary to make assumptions on environmental settings and on the definition of the environmental burden of the case study. In (Wegmann et al., 2006) authors are interested in investigating the condensation effects on top mountains, and authors define a generic mountain environment by modifying the precipitation rate and annual temperature course in a northern temperate zone. Other authors when investigating POPs spatial distribution mountain environments, applied a model assuming a massif as it were a single mountain (Daly et al., 2007), by sampling air and soil at numerous sites. Considering the distribution of chemicals' monitored data, the most appropriate scale for the case study is the river basin of the upper Adda, also known as Valtellina. In the literature, other authors selected a river basin as a case study scale in chemicals MMM fate and transport applications (Paul et al., 2012). A river (sub-)basin is defined as the "area of land from which all surface run-off flows through a sequence of streams, rivers and, possibly, lakes into the sea at a single river mouth, estuary or delta (or to a particular point in a water course, as in our case)" in the Water Framework Directive (EC, 2000). Accordingly, the river basin scale is assumed as a comprehensive spatial scale, that includes all relevant regional emissions and fluxes that were took into account in our chemical fate study.

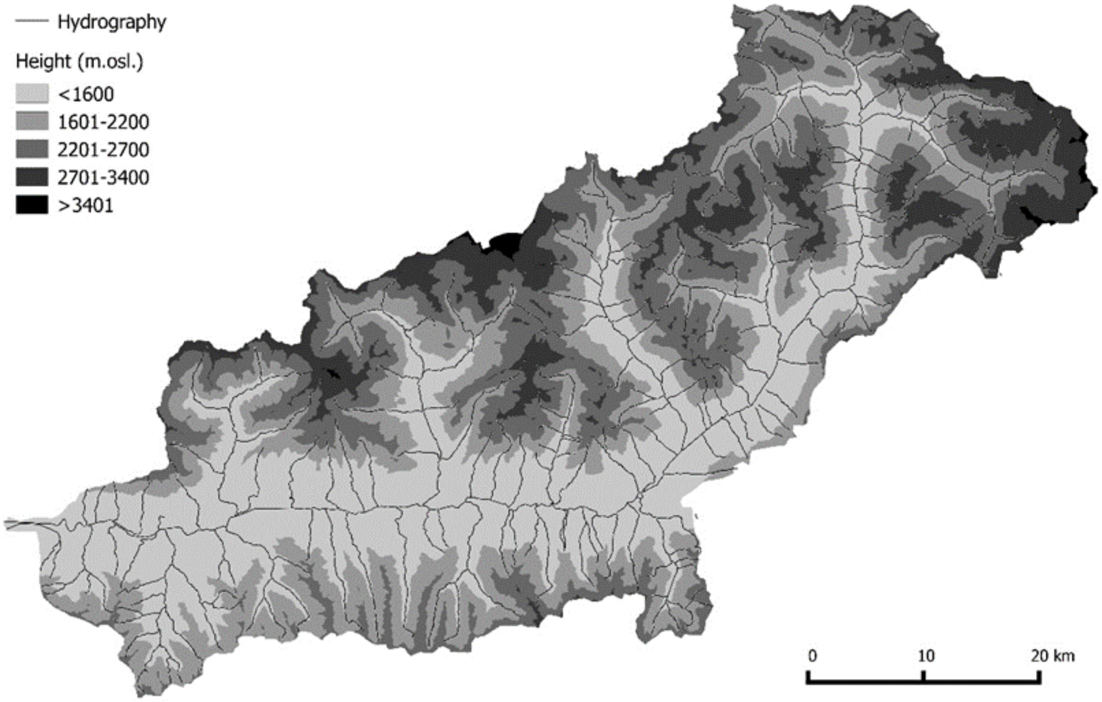

Figure 4.1. The case study area corresponds to the upper Adda river basin. The grey colour scale is related to the different altitudinal zones or isohypses[1] gradients, identified in order to make the model set up.

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[1] Lines that share the same elevation (m a.s.l.) on the terrain

An isohypses gradient map of the case study area is shown in Figure 4.1. It consists of a river sub-basin covering the course of the Adda River from its source in Val di Alpisella at the North-eastern to the river mouth in the Lake Como, located in the south-western part, and corresponds to the Valtellina orography. Its river length corresponds to 119 km, the top mountain included in the river basin catchment reaches 4050 m a.s.l., and the lowest elevation is at the river mouth at 198 m a.s.l.

4.2.3. The mountain multimedia model MountainPOP3.0

The applied model in this work, named MountainPOP3.0, is an update of the mountain multimedia model version MountainPOP by (Westgate and Wania, 2013), inspired to the first model by (Daly et al., 2007). MountainPOP is a fugacity based dynamic multimedia model where a mountain is described by a series of five altitudinal zones in sequence, from the largest to the top smallest zone. Each zone is parameterised by dimensions (soil depth and height, water depth and surface area, atmosphere height, fraction of soil organic matter), climate variables (temperature, precipitations, wind speeds) and environmental processes (deposition fluxes, partitioning between air and surface, air advection, water runoff, organic carbon content). Our updated model version that was applied in this study consists of three environmental compartments (air, soil and river water as added environmental compartment), considers the effect of temperature on physical chemical parameters of selected substances, and background air concentrations plus emissions in air, water and soil. These enhancements were done in order to perform a realistic simulation of the mass balance of the selected chemicals. The river water compartment was deemed important in this application as monitoring data were available at the river basin scale, and this requires take into account the river system. More information on the definition of the water compartment is given in the Supporting Material (SM1).

As (Westgate and Wania, 2013) pointed out, MountainPOP2.0 allows the user to isolates the mountain model from its surroundings assuming that the inflow concentrations are zero. For the Valtellina simulation MountainPOP3.0 the inflow concentrations are added to the model structure following the approach by CoZMo-POP2.0 model (Wania, 2006); the inflow concentrations in atmosphere are treated as advective inflow concentrations and are simulated by (Wöhrnschimmel et al., 2012; Li et al., 2000) as well as initial concentrations in soil and water, both treated as initial concentrations at time 0.

4.2.4. Model parameterization

Chemical partition coefficients along with environmental characteristics determine the Fugacity capacity (Z-value [mol*m-3*Pa-1]) of a medium, that is the capacity of a substance to run away from one environmental compartment to another.

The fugacity capacity of bulk compartments is calculated from the sum of the volume-fraction-weighted fugacity capacities of the constituent phases (Mackay, 2001; McKone et al., 1996).

Z value and BulkZ values are listed in table 4.3a

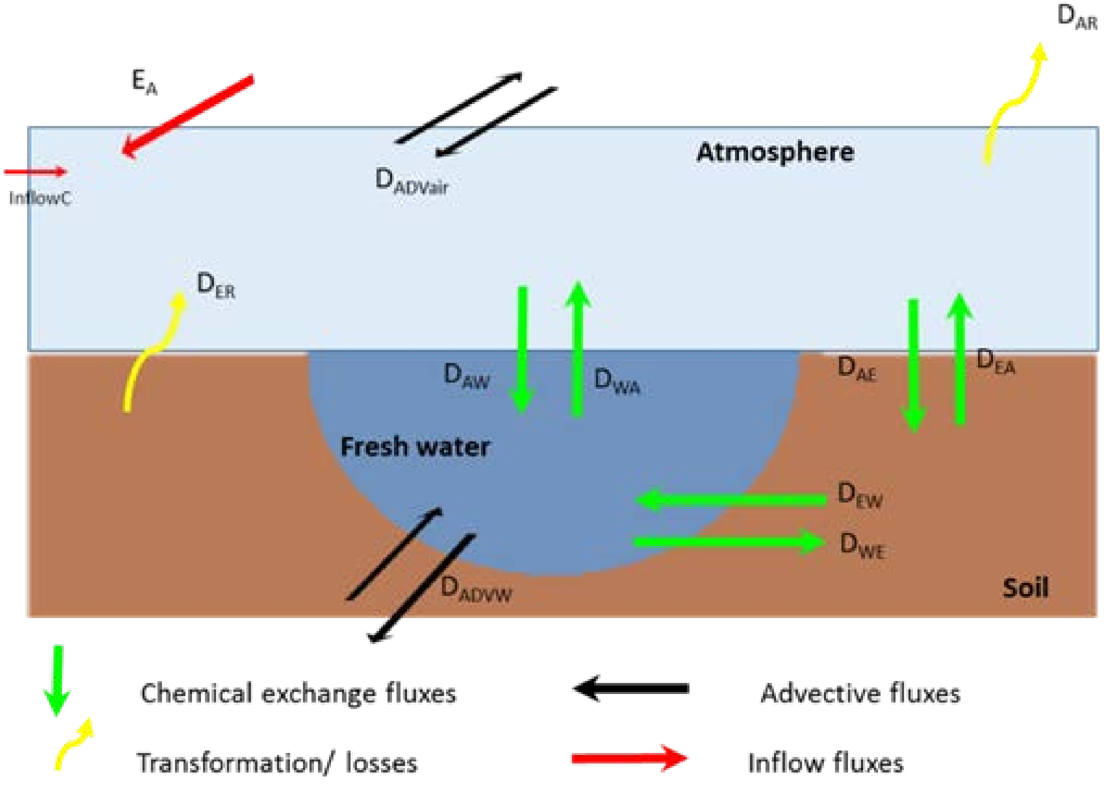


Figure 4.2. Schematic representation of the environmental compartments and contaminant fate processes in MountainPOP3.0

Table 4.3a. Fugacity Capacity (Z) equations of MountainPOP3.0

Z-values	**Equations**
Fugacity capacity of pure air	$Z_A(T) = \frac{1}{RT}$
Fugacity capacity of the liquid phase in atmosphere (i.e. precipitation)	$Z_R(T) = Z_w(T) + r * Z_Q(T) * VF_S$
Fugacity capacity in soil	$Z_E(T) = Z_W * \rho_E * FT_{EOC} * {K_{OW}(T_T)}/{\rho_W}$
Fugacity capacity of pure water	$Z_W(T_W) = \frac{1}{H(T_w)}$
Fugacity capacity of organic carbon particles	$Z_{POC}(T_W) = Z_W(T_W) * FF_{OC} * K_{OW}(T_W)$
bulkZ-values	
Fugacity capacity of atmospheric particle matters	$Z_Q(T) = F_{OC} * (\rho_Q / \rho_O) * \left[{K_{OA}}/{RT_A} \right]$
Bulk fugacity capacity in soil	$BulkZ_E(T) = VF_{EW} * Z_W(T) + FT_{EA} * Z_A(T) + FT_{EOC} * Z_E(T)$
Bulk fugacity capacity of vegetation	$bulkZ_V(T) = Z_{needle} * V_{coniferous} + Z_{leaf} * \frac{V_{deciduous}}{\rho}$
Deciduous vegetation	$Z_{leaf} = \frac{K_{PA}}{RT}$
Coniferous vegetation	$Z_{needle} = \frac{K_{PA}}{RT}$
Bulk fugacity capacity in water stream	$\mathrm{Bulk}\ Z_W = Z_W(T_w) + \left[{C_{POC_W}}/{\rho_{POC}} \right]$

Notes: The values and definitions for chemical and environmental parameters are described in the Supporting Material (SM).

The transport, degradation and transformation mechanisms (D-values [mol*h-1*Pa-1]) are determined by $\mathrm{D} = \mathrm{G} \times \mathrm{Z}$ where G[m3*h-1] is an effective transport rate included in MountainPOP. Figure 4.2 shows the fluxes between different media in MountainPOP3.0.

D-values represents advection in atmosphere and water compartments, transfer by diffusion/volatilization, wet/dry deposition, degradation controlled by reaction with the hydroxyl radical and transformation due to PH in soil. Table 4.3 presents the inter-media transfer D-values equations.

Table 4.3. D-values equations of MountainPOP3.0

Compartment	Process	D values
Atmosphere (A) - water (W)	Diffusion	$D_{Diff} = A_W \left[1/k_{WA} * Z_A(T) + 1/k_{AW} * Z_W(T)\right]^{-1}$
	Precipitation dissolution	$D_{RW} = A_W * rain * Z_R(T)$
	Wet deposition	$D_{QWW} = U_R * A_W * Z_R(T)$
	Dry deposition	$D_{QDW} = A_W * V_{dry} * V_Q * Z_Q(T)$
		$D_{AW} = D_{diff} + D_{RW} + D_{QWW} + D_{QDW}$
		$D_{WA} = D_{diff}$
Atmosphere (A) – Soil*(E)	Diffusion	$D_E = \frac{A_E}{(k_{AE} * Z_A(T))} + \frac{1}{(k_{MA} * Z_W(T)) + (k_{MS} * Z_A(T))}$
	Precipitation dissolution	$D_{RE} = U_R * A_E * Z_R(T_A)$
	Wet deposition	$D_{QWE} = U_R * A_E * Z_R(T)$
	Dry deposition	$D_{QDE} = A_E * V_{dry} * V_Q * Z_Q(T)$
		$D_{AE} = D_E + D_{RE} + D_{QWE} + D_{QDE}$
		$D_{EA} = D_E$
Soil (E) - Water (W)	Soil Horton's overland flow	$D_{EWH} = G_{SWHorton} * Z_{POC}(T)$
	Water Horton's overland flow	$D_{WEH} = G_{WEHorton} * Z_W(T)$
		$D_{EW} = D_{EWH} + D_{WEH}$
		$D_{WE} = 0$
Reaction either bulk phase i or sum of atmosphere and soil phases		$D_{AR} = V_A * RR_{OH} * BulkZ_A$
		$D_{ER} = V_E * RR_{PH} * BulkZ_E$
		$D_R = D_{AR} + D_{ER}$
Advection bulk phase		$D_{ADVAir} = BulkZ_A * aG$
		$D_{ADVWater} = BulkZ_w * wG$

Notes: Ai is the area between media i and j; subscripts on 'Z' and 'D' are atmosphere A, soil E, stream water W, aerosol Q, and organic content's particles POC. * Soil is defined as [forested soil + non forested soil] = 1. Equations modified from (Wania, 2006; Mackay, 2001). The values and definitions for environmental parameters are described in the Supporting Material (SM1 and SM6).

4.2.4.1. Atmosphere

The atmosphere is a three-phase system (gas, particle and precipitation), with the mass exchange of substance between phases being controlled by instantaneous equilibria, i.e. air-water, particles-water and particles-air (Semeena et al., 2006; Wania, 2006).

The estimation of the phase partitioning between gas phase and atmospheric particle matter (aerosols), by either absorption into organic matter is empirically based on the octanol-air partition coefficients, K_{oa} (Finizio et al., 1997). The temperature dependence of the partition coefficients is described by van't Hoff equations; the complete expressions of phase partitioning use the fugacity capacity into the model's regions. Fugacity capacity equations (Z-values) are presented in table 4.3a.

In terms of chemical fate processes (D-values), an up/down advection process related with wind speed takes place in atmosphere besides, volatilization from soil and water, deposition processes (wet and dry) and degradation by OH reactions also takes place in atmosphere. In particular, OH degradation rate is constant (Brubaker et al. 1998). The wind speed is treated as downward/upward flux.

4.2.4.2. Soil

In MountainPop3.0, a single layer soil model is used, i.e. the top soil layer. The phase partitioning in soil is given by the relationship between three phases system (soil, air and organic carbon content) through the K_{OW} that is the partition coefficient of organic carbon in water.

MountainPOP3.0 has not explicit fluxes from particulate organic carbon. Fugacity capacity equations (Z-values) are presented in table 4.3a. The BulkZ_E includes the transfers between solid, liquid and gaseous phases;; D-value for volatilisation from soil occurs when the substance is evaporated from the pore space in the three phase system of pore space (solid gas and liquid). The solid phase is related with the particle absorbed phase (solid mass transfer coefficient in soil pore space: MTCs) (Meyer et al., 2005). The liquid phase occurs between air and soil in water phase (liquid mass transfer coefficient air-soil: MTC_W). The gas phase is defined as the relation between the mass transfer coefficient air-soil in air phase (MTC_A). Soil hydrology is described by the Horton's Overland Flux (Brown, 2011; Dunne and Leopold, 1979) that take into account evaporation, precipitation and infiltration as main environmental parameters that drive the hydrology in water stream and soil exchanges. The full description of this method is included in the Supporting Material (SM1.1).

Transformation in soil is due to chemical reaction with the half-life reaction rate on soil dependent on acidity/basicity (pH); temperature, chemical and organic matter content.

4.2.4.3. Vegetation

MountainPOP assumes a static portion of vegetation in soil compartment, which is variable between zones along the modelled mountain. A special zone is the mountain top that does not have any vegetation at all. The type of vegetation is defined as high altitude forest canopy, deciduous ($\boldsymbol{V_{coniferous}}$) and coniferous ($\boldsymbol{V_{deciduous}}$). Thus, the fugacity capacity of vegetation is presented by $\boldsymbol{bulkZ_V}$ in table 4.3a and it is related with $\boldsymbol{Z_{leaf}}$ $\boldsymbol{a}$nd $\boldsymbol{Z_{needle}}$ where the partitioning phases are calculated based on (Wania, 2006; Horstmann and McLachlan, 1998) using spruce needle (coniferous) air partition coefficient and leaf (deciduous) air partition coefficient, dependent of temperature and the volume fractions, whose weighted numerical values are $\boldsymbol{K_{PA} = M * {K_{OA}}^{N}}$ with M = 38 and N = of 0,69 for coniferous; and M = 14; N = 0,76 for deciduous, whose details are presented in the supporting material.

4.2.4.4. Water stream

The water compartment is modelled as a water stream (Adda River) that springs from the mountain top and goes down up until to reach the bottom zone at Como Lake in Valtellina Mountain. The phase partitioning is done between three phase systems (liquid, solid and gaseous) and the expressions for calculating the fugacity capacity in water is listed in table 4.3a. The interface transport includes water advection from water/water; run off and infiltration from soil/water; wet and dry deposition from air/water.

As part of soil hydrology, the runoff/infiltration is treated using the Horton's overland flux. This methodology is based on infiltration capacity of the terrain, that should be semi-arid or vegetation scarce, such as the soil type in high-alpine environments. Overland flow occurs when rainfall intensity exceeds infiltration capacity. When it happens, water accumulates above this layer and flows horizontally toward the stream (Dunne and Leopold, 1979).

Regarding the change of a chemical mass in MountainPOP, the mass balance equation under dynamic conditions is solved by finite difference approximation in each compartment as shown in table 4.4.

Table 4.4. Mass balance equations for each compartment.

Mass balance in each compartment	Equations
$\frac{df_A V_A Z_A}{dt}$ = mass balance in air	$\frac{df_A V_A Z_A}{dt} = \frac{E_A + backC_A + D_{ADV} * f_A - D_{ADV} * f_A - D_{EA} * f_E + D_{AE} * f_A - f_A * \left[+ D_{AR} * \left(1 - FR_{CH-Q}\right)\right]}{dt}$
$\frac{df_E V_E Z_E}{dt}$ = mass balance in soil	$\frac{df_E V_E Z_E}{dt} = \frac{E_E + backC_E + D_{AE} * f_A - f_E * \left[D_{EA} + D_{EW} + D_{ER} * \text{molecular\_mass}\right]}{dt}$
$\frac{df_W V_W Z_W}{dt}$ = mass balance in water	$\frac{df_W V_W Z_W}{dt} = \frac{E_W + backC_W + D_{ADVWater} * f_W + D_{EW} * f_E + D_{AW} * f_A - f_W * \left[D_{ADVWater} + D_{WA}\right]}{dt}$

Note: $FR_{CH\text{-}Q}$ is the fraction of chemical on aerosol; E_i are the emissions to each compartment; $backC_i$ are the inflow concentrations in each compartment. Where $f[Pa] = \frac{C}{Z} \frac{[M/m^3]}{[M/m^3 Pa]}$; C is the chemical concentrations and, Z is the fugacity capacity.

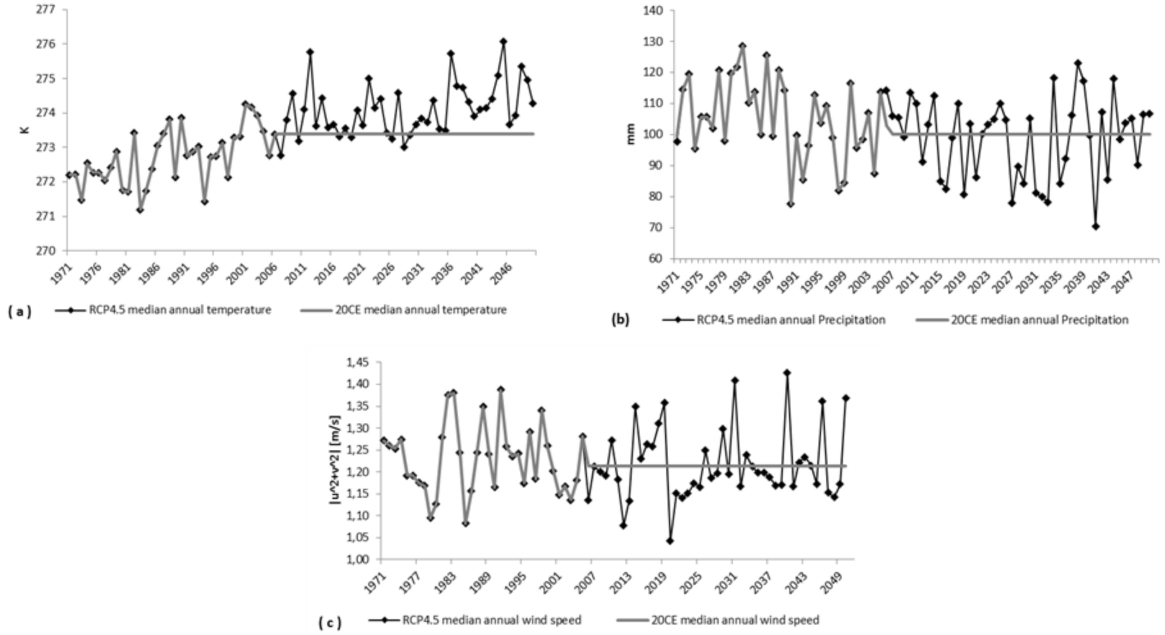
4.2.4.5. Climate data

Two different climate scenarios have been defined: the present scenario called 20CE and the future scenario from RCP4.5 (Meinshausen et al., 2011). Both scenarios were performed using climate input data obtained by the climatic simulations reported by (Montesarchio et al., 2014; Bucchignani et al., 2011), in particular temperature, precipitation and wind speed.

In both scenarios, there is a baseline made by the historical trend that runs from 1971 to 2005. The historical trend is the result of a regional climate modelling (RCM) simulation over the European Alps Region (Montesarchio et al., 2014; Bucchignani et al., 2013). During the climate simulation made by (Montesarchio et al., 2014) and (Bucchignani et al., 2013), a 35 years period (1971 – 2006) of observational daily data of two meter temperature and precipitation were compared with computational simulations by RCM COSMO-CLM (Rockel and Geyer, 2008) using ERA-40 Reanalysis, as boundary conditions, with an horizontal resolution of 0.0715◦ (8 km).

After that, the 20CE scenario was constructed by monthly average, taking the period from 1995 to 2005 that consequently defined the period from 2006 to 2050. On the other hand, the IPCC scenario RCP4.5 followed the approach based on RCP stands for Representative Concentration Pathways (Meinshausen et al., 2011); the RCP4.5 is characterized by a radiative forcing of about

4.5 W/m2 at stabilization after 2100 (Turco et al., 2013). Figure 4.3 shows both the 20CE and RCP4.5 scenarios used for the MountainPOP3.0 simulations carried out in this work.



Note: Climatic scenarios 20CE and RCP4.5: a) Temperature; b) Precipitation; and c) wind speed

Figure 4.3. Climate scenarios 20CE (grey continue line) and RCP4.5 (black continue line).

4.2.4.6. Model evaluation and uncertainty analysis

Environmental, chemical specific and landscape parameters were fixed as static variables and they were analysed using Monte Carlo uncertainty analysis (MacLeod et al., 2002).

The variance in output variables were analysed following the approach suggested by (MacLeod et al. 2002) using the confidence factor in the inputs (Cf_{input}) and outputs (Cf_{output}) as measures to comparison of the sensitivity of the model. Sensitivity analysis follows the equation: $\log Cf_{output} = |S| \log Cf_{input}$ where $|S| = \frac{\sigma_o}{\sigma_i}$ is the sensitivity of output (O) to changes in inputs (I). σ_O and σ_I are the standard deviations in input and output parameters. Medians (μ) and confidence factors (Cf_{input}) used in the Monte Carlo analysis are listed in SM6.

For climate data (temperature, precipitation and wind speed) that are dynamic variables, they were not considered in the uncertainty analysis, but rather compared at 20CE climate scenario against RCP4.5 (Wöhrnschimmel et al., 2013). Moreover, in Montesarchio et al (2014) authors tested the regional simulation and they concluded that good accuracy for superficial temperature with bias lower than 1.5°C at coarser resolution and lower than 0.7°C at finer resolution. Meanwhile, for precipitation data they calculated a bias lower than 30%, with pronounce seasonal variation (Montesarchio et al., 2014).

Emissions and inflow concentrations in atmosphere were also dynamic variables; they were treated as climatic variables in terms of model evaluation.

It means that present and future emission scenarios were constructed based on the effect of changes in temperature from 20CE and RCP4.5 scenarios. Furthermore, both chemicals are phased out and the contribution on the primary emissions is limited. Summing up, the analysis of emissions' contribution to the variability of the model was made by comparing the present and future simulations for both chemicals.

4.2.4.7. Emissions projections

4.2.4.7.1. Historical emissions (1971-2005)

Primary **α-HCH** emissions modelled with a global fate model were taken from (Wöhrnschimmel et al., 2012; Li et al., 2000). Primary emissions [g/h/km2] for α-HCH were assumed to occur in March and April in the Northern hemisphere. (Wöhrnschimmel et al., 2012) redistributed the total emissions into 5% air, 92.5% soil and 2.5% fresh water, and included assumptions on the effect of bans in certain countries like India, that in their appreciation were only poorly reflected in the original emission inventory.

The inflow concentration data were extracted ($backC_i$, where *i* = atmosphere, A; soil, E; water, W) from (Wöhrnschimmel et al., 2012; Li et al., 2000) interpolating their regional data to our specific zone.

HCB emissions (E) and inflow concentrations ($backC_i$) projections were constructed following (Gusev et al., 2009). Gusev et al. discussed about the most important sources and sinks of HCB and they pointed out that the atmosphere is the most important sink and source of HCB. Following the implications of that hypothesis and due to the scarce information of HCB emission from water and soil compartments, we assumed that HCB emissions are only relevant from atmosphere. For $backC_i$ we consider that HCB is very stable in the environment (Shunthirasingham et al., 2010). Thus, $backC_i$ are based on measures from the Central and

Southern Europe regions along the period 1971-2005 in all compartments (atmosphere, A; soil E; water stream W).

4.2.4.7.2. Emission's projections

In order to obtain the emissions projections only for our area of interest, we considered that chemical emissions in atmosphere, soil and water stream compartment are geographically well distributed, and the amount of emissions was weighted over the areas as defined in table 4.5.

Table 4.5. Superficial distribution for each zone in Valtellina Mountain.

Valtellina Valley	Area (km^2)	Altitude (m a.s.l.)
A	796,18	< 1600
B	702,63	1601 – 2200
C	689,90	2201 – 2700
D	371,17	2701 – 3400
E	20,54	> 3401
Total	**2580,42**	

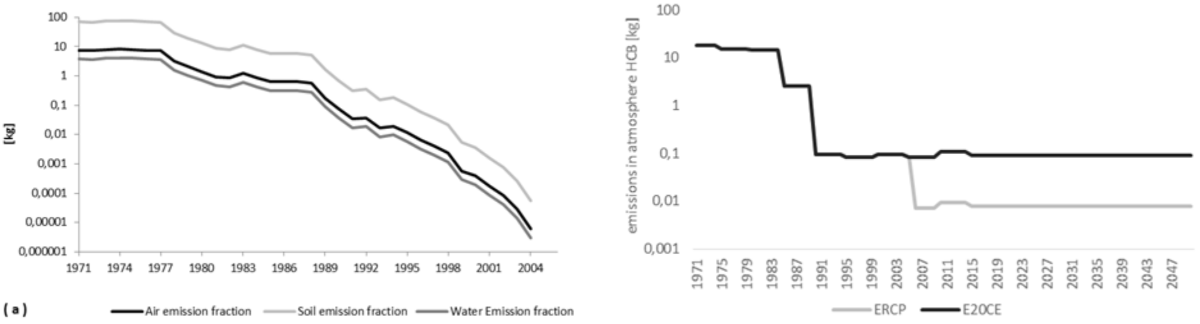
Emissions in soil are distributed in each zone while in water and atmosphere are focus only in the bottom (atmosphere compartment) /top (for water compartment) zone, from that the motion passes through the other zones by convective fluxes.

The α-HCH emissions for the present or "*business as usual*" projection were constructed for (i) atmosphere, (ii) soil and (iii) water stream compartment. They were integrated from Wöhrnschimmel et al (2012) data. Present and Future scenarios only have data from 1971 up to 2005, after that primary emissions vanish thanks to international agreements (UNEP, 2001; UNECE/CLRTAP, 1979) that banned the production, use and storage of this chemical substance, especially in Europe.

The HCB atmosphere emissions at present or "*business as usual*" projection includes data emissions from 1971 to 2050. The period between 1971 and 1989 was integrated with data that were interpolated from the Italian National Inventory reported by MSCE-CCC (Gusev et al., 2009). The period between 1990 and 2012 has the values published by LRTAP (EEA, 2013) and also they were interpolated from national inventory. Finally, from 2013 to 2050 the values were obtained with the monthly averages of the ten last years (2000 – 2010). For the whole period we used a fraction number of 0.28 extracted from the comparison of emissions data presented by

ARPALOMBARDIA at national and regional (ARPALOMBARDIA, 2012) that represents the contribution of Valtellina Valley (that contains Como, Sondrio and Lecco municipalities) to the Italian HCB emissions inventory. Even if HCB emissions have been reduced, the total elimination of its emissions is very difficult. Several authors have pointed out that the most important emissions are from secondary sources that are not anthropogenic but natural in environment (Breivik et al., 2006; Pacyna et al., 2003). In contrary, (Denier van der Gon et al., 2007) estimated that aluminium industry is the major source of the emission during the 2000-2020.

They calculated HCB emissions projections for 2020 based on national reported emissions on 2000 (EEA, 2013) and proposed some extra achievements to be included in the UNECE Protocol, in order to arrive a reduction up to 90% of national emissions: 0.16% reductions from industrial solid waste incineration; and 89.84% reductions from secondary aluminium production. They reported a good agreement with other studies (Denier van der Gone H.A.C. et al., 2006; Pacyna et al., 2003). During the construction of HCB projections used with MountainPOP we assume that in the vicinity of Valtellina valley is not a considerable aluminium industry and the present projection and the emissions are in good agreement with the mentioned past studies. The α-HCH and HCB emissions for each zone follow the trend showed in the figure 4.4.



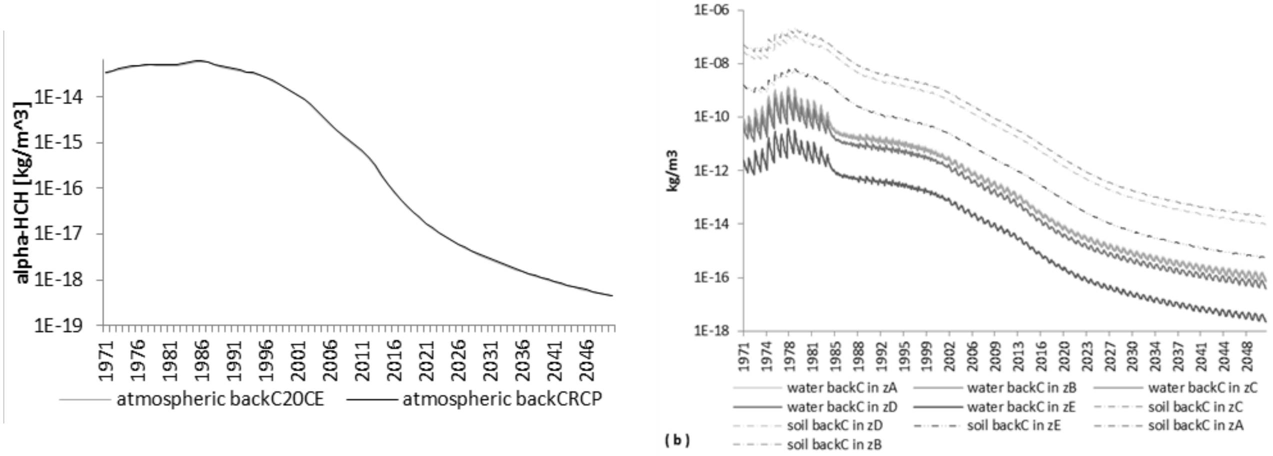
Note. (a) α-HCH emissions in each zone x compartment (atmosphere, soil and water) (b) HCB emissions in atmosphere per zone in Valtellina Valley during the period 1971–2050 for present and future emissions' projection. Adapted from (ARPALOMBARDIA, 2012; Wöhrnschimmel et al., 2012; Gusev et al., 2009; Barber et al., 2005).

Figure 4.4. Primary emissions projections for α-HCH and HCB.

The future projection for α-HCH and HCB were considered as follow: For α-HCH emissions' future projection is zero for the reasons described above (Wöhrnschimmel et al., 2012). For future projection of HCB emissions, dataset has been re-calculated based on present projection and the influence of the change in temperature of RCP4.5 climate projection, using the rate of volatilization (van t' Hoff expression) $\frac{E_{20CE}}{E_{RCP4.5}} = exp\left[\frac{\Delta U_{oa}}{R}\cdot\left(\frac{1}{T_{20CE}}-\frac{1}{T_{RCP4.5}}\right)\right]$ of chemical from primary sources and shown in Figure 4.4.

4.2.4.7.3. Inflow concentrations

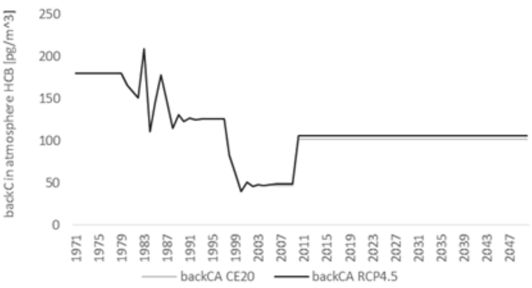
Inflow concentrations of α-HCH in atmosphere (Wöhrnschimmel et al., 2012) are introduced in the Valtellina Mountain along the whole simulation period (1971 – 2050). In atmosphere, the backC$_A$ are introduced in zone A. Meanwhile backC in soil and water stream are introduced at t=0 (1971) as backC$_i$ (where *i* = soil, *E*; water, *W*). Figure 4.5 shows the backC$_i$ for α-HCH.



Note: (A) α-HCH ***backC$_A$*** values are for the period 1971 – 2050. (b) α-HCH ***backC$_W$*** and ***backC$_E$*** are used only for 1971. Data are shown by compartment. Based on (Wöhrnschimmel et al., 2012).

Figure 4.5. Inflow concentrations (backC$_i$) for α-HCH in Valtellina Mountain.

Figure 4.6 shows the HCB backC$_i$ that are used in the same way as α-HCH: they are present only for the initial period (1971 y) in soil and water compartments. In atmosphere, background air concentrations were added during the whole period as advected polluted air from the base of mountain (zone A).



(a)

(b)

Area, time	Environmental Compartment	HCB	units	References
Po river, Italy, 1969	Water	1,7 (0,6 - 2,4)	ng/L	(Leoni and D’Arca, 1976)
Rome, Italy, 1971 – 1972	Soil	0,04	Ppm	(Leoni and D’Arca, 1976)

Notes: Initial HCB *backC_i* values in Valtellina Mountain for the period 1971 - 2050. (a) HCB *backC* in atmosphere compartment (zone A); dark continue line indicates the temperature correction follows the RCP4.5 scenario; (b) HCB *backC* in soil and water compartment for initial year (1971). Mean values (minimum – maximum).

Figure 4.6. Inflow concentrations (backC$_i$) for HCB in Valtellina Mountain.

4.2.5. Model Validation

With the aim of validating the modelling of Valtellina Mountain made by MountainPOP3.0 for α-HCH and HCB, we compare data from monitoring campaigns carried out in our area of study and well described in the literature, as presented before in section 3.3.2, with the concentrations and fugacity values calculated by MountainPOP3.0. Concentration data were monitored in soil and water compartments. All data were transformed to fugacity [f; Pa] in order to include in the same analysis the monitored data found in different compartments but at the same altitudinal zone.

For comparison purposes, we selected three baseline simulations of the 20CE scenario: a) the median simulation, it means, the one performed with the non-random median input values (reference simulation); b) the optimal simulation for the α-HCH chemical (the closer ratio to 1 global measured/modelled ratio) that best matched the available measured data from monitoring campaigns; c) the optimal simulation for the HCB chemical that best matched the available measured data from monitoring campaigns. While the first simulation was considered as the reference simualtion of the model, is important to remark that the other both optimal simulations for α-HCH and HCB chemicals, were obtained after the convergence analysis of the model from exhaustive simulations and experiments performed with the model, as detailed in the following section.

As comparison metric we employed the mean of the ratio of the measured versus modelled values of the corresponding date and monitored site (stream compartment at zones A, B and C), in a way that a value of 1.0 means a perfect matching.

4.2.6. Simulations and data analysis

We developed our MountainPop3.0 model in Java programming language using the NetBeans toolkit software, while the data analysis was performed using ad-hoc Python scripts for data reorganization, while Microsoft Excel, Matlab and SPSS v.16 as statistical analysis tools.

After computing the reference simulation (median simulation), we applied a series of exhaustive experimental simulations with MountainPop3.0 of the two scenarios 20CE and RCP4.5, each for both α-HCH and HCB, in order to identify the most important input variables, the uncertainty and sensibility, the stabilization and the final validation of the model, as follows:

In the first experiment we carried out four Monte Carlo simulations in order to perform a general data screening of the model and the identification of the most significant input and output variables, through principal component and input-output correlation analysis. For computational limits reason, each simulation consisted of 300 running trials with different input values for environmental and landscape parameters, all of them randomly generated within the range defined by the medians and confidence factors of the variables and assuming a log-normal distribution for all of them. Each simulation lasted approximately eight hours in a personal notebook PC computer with Windows Vista 64, for a total of 32 hours of computation. We additionally determined from these simulations the conditions in which the model generated convergent fugacity results.

After the parameters reduction and stabilization of the model, the second experiment consisted in series of simulations with variations of the most significant input variables, varying one single parameter per simulation, in order to evaluate the sensitivity of the model to single parameters and to identify the input parameters with the highest sensitivity, for all the combinations of 2 scenarios (20CE, RCP4.5) for α-HCH and HCB.

For the third experiment, we performed four new Monte Carlo simulations, following a 2 scenarios design, each one with 100 random variations of all the most sensitive input parameters, in order to estimate the global sensitivity of the model. In particular for both the α-HCH and HCH chemicals for the 20CE scenario, we evaluated the two values combinations of the most sensitive input parameter that best approximates the real observed data from monitoring campaigns. The evaluation was made by considering the two trials with the mean of the model vs measured values that best approximates to 1.0, one for α-HCH and one for HCB.

Finally, the fourth experiment, represents 4 simulations for the 2 scenarios each for α-HCH and HCB with the best identified input parameters of α-HCH and HCB, considered as our final reference baseline simulations. Then, we performed a comparative analysis in order to validate the model with respect to the available real data measurements. This fourth experiment we carried out considered the collected climate data of temperature, precipitation and wind speed, as explained in section 4.2.3 and the collected environmental, chemical specific and landscape parameters, as explained in section 4.2.4.

For more details of the considered input parameters and their ranges, see section 5.8 of the Annex.

4.3. Results

4.3.1. Uncertainty analysis of Monte Carlo simulation

For the Monte Carlo experiments, the considered input parameters (shown in SI4 of the Annex) were randomly varied assuming a log-normal distribution accordingly to their prescribed median (μ) and confidence factors (Cf). The concentrations (C) and fugacity (f) in the four compartments (atmosphere, waters stream and (non) forested soil) were chosen as output values. The variance (σ) in input and output parameters were collected, including chemical concentrations in air, soil, and water, and fugacity (Westgate and Wania, 2013) of α-HCH and HCB for each zone through a series of simulations' patterns. We assumed that output distributions are fitted with a log-normal distribution characterized by an output confidence factor (MacLeod et al., 2002).

4.3.1.1. Experiment 1: Data screening

As a preliminary data screening, in the first Monte Carlo experiment we computed 300 simulations, all covering 80 years (1971 – 2050) for the RCP4.5 and 20CE scenarios for both chemicals (α-HCH and HCB) using the parameters listed in table SM6, for a total of 1200 simulations.

Table 4.6. Zones and compartment scored by accumulated contributions over the six principal components.

compartment	zone	Accumulated* Rank	20CE Rank	RCP4.5 Rank
Soil Forested	A	1	4	3
Soil Forested	C	2	14	1
Soil NonForested	D	3	12	4
Soil NonForested	C	4	5	6
Soil Forested	B	5	10	5
Stream	A	6	1	12
Stream	C	7	6	15
Atmosphere	C	8	17	2
Soil NonForested	A	9	7	8
Stream	D	10	2	10

Note. *Due to the normal contribution of 20CE + RCP4.5 scenarios.

After the simulations, we carried out a principal components analysis of the variance over all the resulting output signals, in order to establish a preliminary evaluation of the compartment and zones variability behaviour. We scored the output values according to the accumulated contribution to the six principal components of the output variance over the four scenarios x chemical combinations. Next, we selected the 10 first more highly ranked component x zone combinations, presented in table 4.6, assuming that they explain at least the 65% of the total output variance of the model.

Once selected the 10 most variable zones x compartment combinations, we performed a correlation analysis between the resulting fugacities of these outcomes with respect of all the input variables, in order to identify the most significant parameters of the model. We applied a similar ranking, considering the weighted accumulative value of the correlations with respect of scenario x chemical combinations. Table 4.7 shows the ranked input parameters weighted by correlation factors when all the input parameters randomly vary at the same time. They were chosen for explaining up to 90% of the variance of the 10 selected outcomes due to their correlation.

Table 4.7. Accumulative correlation of input parameters using in Monte Carlo analysis.

	Input parameter	Units	Accumulative correlation (normalized)	Rank
	Fraction of forested soil solids which are organic matter		0.165	1
	Fraction of non-forested soil solids which are organic matter		0.317	2
	Width of Zone	km	0.417	3
	Length of zone	km	0.512	4
k_{MS}	Solid MTC over pore space soil	m/h	0.584	5
	Fraction of surface covered by streams		0.649	6
	Depth of soil	m	0.710	7
V_Q	Aerosol volume fraction		0.763	8
V_{dry}	Air-Soil Dry Deposition Velocity	m/h	0.813	9
	Snow scavenging ratio		0.859	10
k_{WA}	Water side MTC	m/h	0.902	11

From these results we observed that the inputs have different effects, as suggested by the different observed correlation values which varied depending on the zones, whose changes are shown in table 4.8. Chemical behaviour in 20CE scenario denotes high accumulate correlation up to 34.46% with landscape parameters for α-HCH and 31.38% for HCB, following by environmental parameters for water stream and soil compartments up to 65.54% for α-HCH and 68.62% for HCB. Instead in RCP4.5 scenarios, those environmental parameters related with the atmospheric compartment are more correlated with changes in concentration and fugacity in each compartment for α-HCH (91.38%) and HCB (91.67%).

Table 4.8. Input parameters with high correlation by climate scenario and by chemical.

20CE		RCP4.5	
α-HCH	**HCB**	**α-HCH**	**HCB**
Width of zone	Fraction of non-forested soil solids which are organic matter	Fraction of forested soil solids which are organic matter	Fraction of forested soil solids which are organic matter
Fraction of non-forested soil solids which are organic matter	Width of zone	Fraction of non-forested soil solids which are organic matter	Fraction of non-forested soil solids which are organic matter
Fraction of surface covered by streams	Fraction of forested soil solids which are organic matter	Air-soil dry deposition velocity	Air-soil dry deposition velocity
Length of zone	Fraction of surface covered by streams	Air side MTC	Solid MTC over pore space soil
Fraction of forested soil solids which are organic matter	Length of zone	Snow Scavenging Ratio	Length of zone
Solid MTC over pore space soil	Depth of soil	Length of zone	Snow Scavenging Ratio
Depth of soil	Water side MTC	Aerosol volume fraction	Aerosol volume fraction

Notes: cells in blue are related with landscape parameters; in blank are those environmental parameters.

Such results indicates that the zones and compartments more sensitive to the accumulated output variance in 20CE and RCP4.0 are the three lower zones of the forested soil compartment (A,B,C); the lower and intermediate zones of non-forested soil compartment (A,C,D). A possible interpretation is that (non)forested and forested compartments of soil are affected by the solid mass transfer coefficient (MTC) over pore space in soil and depth of soil, that may explain the volatilization/evaporation to atmosphere, in particular in zone C.

The fugacity at lower and intermediate zones of stream compartment (A,C,D) also showed to be significant sensitive to the input variability, specially for the 20CE scenario. This may be explained by the higher contribution of landscape parameters in 20CE than in RCP4.5, which is related to the streams dimension, and thus, the concentration and fugacity capacities of such compartment.

Regarding the atmospheric compartment, in particular at zone C, was affected more in the RCP4.5 scenario, suggesting that the chemicals tend to favour the movements from atmosphere to soil by wet deposition, for α-HCH and HCB. Particularly, evaporation from water stream to atmosphere for α-HCH is also a preferring route when RCP4.5 scenario is going on.

4.3.1.2. Model convergence

We observed from the results of experiment 1 an unstable behaviour of some output simulations, in special for the 20CE scenario, given the unconstrained growing of the stream compartment dimensions due to some landscape input values combinations. Thus, we add to the model two new input parameters, in order to define stream compartment dimensions more realistically, given real observation from monitoring campaigns (Grassi, 2014).

Table 4.9. Sensitivity of the model computed by individual inputs for Compartment x Mountain Zone.

	Atmosphere							**Non Forested Soil**							**Forested Soil**							**Stream**						
Zone	**Inputs**							**Inputs**							**Inputs**							**Inputs**						
	1	**5**	**6**	**7**	**25**	**30**	**31**	**1**	**5**	**6**	**7**	**25**	**30**	**31**	**1**	**5**	**6**	**7**	**25**	**30**	**31**	**1**	**5**	**6**	**7**	**25**	**30**	**31**
	20CE x aHCH																											
A	1.14	1	1	1	1	1	1	1.14	1.38	1	1.05	1	1	1	1.14	1.09	1.46	1.03	1	1	1	1.14	1.02	1.09	1.01	1	1.14	1
B	1.00	1	1	1	1	1	1	1.00	1.13	1	1.01	1	1	1	1.00	1.00	1.61	1.07	1	1	1	1.10	1	1.01	1.00	1	1.13	1.29
C	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.16	1.09	1	1	1	1.06	1	1.00	1.00	1	1.13	2.33
D	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.03	1	1	1	1	1.13	4.40
E	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.01	1	1	1	1	1.12	6.93
	20CE x HCB																											
A	1.00	1	1	1	1	1	1	1.01	1.07	1	1.00	1	1	1	1.01	1.00	1.29	1.03	1	1	1	1.09	1	1	1	1.04	1.01	1
B	1.00	1	1	1	1	1	1	1.00	1.02	1	1.00	1	1	1	1.00	1.00	1.35	1.06	1	1	1	1.07	1	1	1	1.06	1.01	1.02
C	1.00	1	1	1	1	1	1	1.00	1.06	1	1.00	1	1	1	1.00	1.00	1.26	1.11	1	1	1	1.02	1	1	1	1.02	1.01	1.01
D	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.01	1	1	1	1.29	1.05	1.15
E	1.01	1	1	1	1	1	1	1.01	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.00	1	1	1	1.35	1.07	1.34
	RCP4.5 x aHCH																											
A	1.35	1	1	1	1	1	1	1.35	1.25	1	1.07	1	1	1	1.35	1.04	1.45	1.04	1	1	1	1.34	1.01	1.09	1.01	1	1.33	1
B	1.00	1	1	1	1	1	1	1.00	1.26	1	1.01	1	1	1	1.00	1.02	1.15	1.08	1	1	1	1.44	1	1.01	1.00	1.00	1.31	1.15
C	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.15	1.03	1	1	1	1.27	1	1.00	1.00	1.00	1.31	1.64
D	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.12	1	1	1	1.00	1.29	2.61
E	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.03	1	1	1	1.02	1.31	4.16
	RCP4.5 x HCB																											
A	1.00	1	1	1	1	1	1	1.01	1.07	1	1.00	1	1	1	1.01	1.00	1.29	1.03	1	1	1	1.09	1	1	1	1.04	1.01	1
B	1.00	1	1	1	1	1	1	1.00	1.02	1	1.00	1	1	1	1.00	1.00	1.35	1.06	1	1	1	1.07	1	1	1	1.06	1.01	1.02
C	1.00	1	1	1	1	1	1	1.00	1.06	1	1.00	1	1	1	1.00	1.00	1.26	1.11	1	1	1	1.02	1	1	1	1.02	1.01	1.01
D	1.00	1	1	1	1	1	1	1.00	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.01	1	1	1	1.29	1.05	1.15
E	1.01	1	1	1	1	1	1	1.01	1.00	1	1.00	1	1	1	1.00	1.00	1.00	1.00	1	1	1	1.00	1	1	1	1.35	1.07	1.34

Inputs: 1-Zone Length; 5- Fraction of non-forested soil solids which are organic matter; 6- Fraction of forested soil solids which are organic matter; 7-Depth of Soil; 25- Water-to-Air Mass-Transfer Coefficient; 30-Stream Volume; 31- Stream volume decay rate.

Specifically, we introduced the input term ‘stream volume’ (input 30) which defines the quantity of water measured at zone A of the stream compartment (mean of 2.29E+08, Cf = 2.0); since we do not have any measured data of such volume for higher zones that A, we introduced a second term ‘stream volume decay rate’ (input 31) by the assumption that the stream volume suffers diminish proportionally to this term, up to higher zones at a mean rate = 0.43, Cf=2.0.

4.3.1.3. Experiment 2: Sensitivity analysis to single input parameters

In the experiment 2, we defined the sensitivity of the model, as suggested in MacLeod et al. (2002), in the form of single sensitivity analysis due to the random parameters variations of the selected inputs plus the two new introduced extra terms. The sensitivity of any single output given any input was defined as the relation of the output and input uncertainties as $|S| = {}^{\sigma_o}\!/_{\sigma_I}$, where σ_o and σ_I are the standard deviations of the outputs and inputs, respectively, while the relationship of the input and output confidence factors (*Cf*Cf_{input}, Cf_{output}) is given by $\log Cf_{output} = |S| \log Cf_{input}$.

Table 4.9 shows the sensitivity analysis of all the 20 combinations of zone x compartment for the six inputs that contributed to sensitivity’s changes (values other than 1), now computed to stable simulations due to the introduction of ‘stream volume’ and ‘stream volume decay proportion’. We executed 15 simulations per input variable, for 660 random simulations (15 simulations x 11 inputs x 2 scenarios x 2 chemicals). As expected, landscape parameters mostly affected the sensitivity of fugacity in steam compartment given the variation of the water streams. On the other hand, environment parameters have greater influence in soil compartments, being the forested soil compartment the more affected.

4.3.1.4. Experiment 3: Sensitivity analysis of the model

From sensitivity analysis of single inputs, we identified the inputs 1 (zone’s length), 6 (fraction of forested soil solids which are organic matter), 30 (stream volume) a 31 (stream volume decay proportion) as the most sensitive parameters of the model individually.

Then, with the aim to estimate the uncertainty of the full model, we carried out a new reduced Monte Carlo simulation randomly varying these four parameters in conjunction. The uncertainty of the model was calculated as reported in MacLeod et al. (2002) by

$$Cf_o = \exp[S_{I_1}^2(\ln Cf_{I_1})^2 + S_{I_2}^2(\ln Cf_{I_2})^2 + \cdots + S_{I_n}^2(\ln Cf_{I_n})^2]^{1/2}$$

Where Cf_o is the uncertainty of the model's output, giving the sensitivity S_{I_k} and the uncertainty of the model Cf_{I_k} of the input I_k, in this case over inputs *k={1, 6, 30, 31}*.

The resulting outputs uncertainty Cf_o and standard deviation σ_o of the model (Table 4.10) were estimated for all the four compartments, for the 4 combinations of 2 scenarios x 2 chemicals, after 100 simulations per scenario x chemical combination, for a total of 400 simulated mountains in this experiment. From Table 4.10 we observe that stream is the most sensitive compartment, followed by forested soil. From these two compartments is also possible to notice that the model is more sensitive to input variations at higher zones. In particular, the resulting growing trend in the stream compartment's sensitivity may be explained by the modelled volume decay law of the real stream volume measured at the lowest zone (zone A) up to higher zones, which suggests that the need of better future measuring campaigns of water flows.

Table 4.10. Sensitivity analysis of the model computed for Compartment x Mountain Zone.

	20CE x α-HCH							
	Atmosphere		**Non Forested Soil**		**Forested Soil**		**Stream**	
Zone	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o
A	1.642	0.2482	1.6894	0.2622	2.3136	0.4194	2.1834	0.3904
B	1.0369	0.0181	1.0433	0.0212	2.2218	0.3992	2.263	0.4083
C	1.0032	0.0016	1.0033	0.0017	2.2139	0.3974	3.9514	0.687
D	1.0013	0.0006	1.0015	0.0008	1	0	4.3421	0.7342
E	1.0179	0.0089	1.0255	0.0126	1	0	4.6476	0.7682
	20CE x HCB							
	Atmosphere		**Non Forested Soil**		**Forested Soil**		**Stream**	
Zone	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o
A	1.0287	0.0142	1.1272	0.0599	2.0513	0.3592	1.2018	0.0919
B	1.0258	0.0127	1.0292	0.0144	2.1524	0.3833	1.5502	0.2192
C	1.0198	0.0098	1.0211	0.0104	2.1148	0.3745	1.5466	0.218
D	1.0004	0.0002	1.0013	0.0006	1	0	1.9673	0.3383
E	1.1058	0.0503	1.1048	0.0499	1	0	2.4200	0.4419
	RCP4.5 x α-HCH							
	Atmosphere		**Non Forested Soil**		**Forested Soil**		**Stream**	
Zone	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o
A	1.6749	0.2579	1.7521	0.2804	2.2675	0.4093	2.3555	0.4284
B	1.0064	0.0032	1.012	0.006	2.0016	0.347	2.6586	0.4889
C	1.0019	0.001	1.002	0.001	1.7307	0.2743	3.0034	0.5499
D	1.0011	0.0005	1.0013	0.0006	1	0	3.1563	0.5747
E	1.0203	0.01	1.0364	0.0179	1	0	3.5566	0.6344
	RCP4.5 x HCB							
	Atmosphere		**Non Forested Soil**		**Forested Soil**		**Stream**	
Zone	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o	Cf_o	σ_o

A	1.0278	0.0137	1.1135	0.0538	2.0295	0.3539	1.2528	0.1127
B	1.025	0.0123	1.0292	0.0144	2.1041	0.3719	1.486	0.1981
C	1.0191	0.0094	1.0206	0.0102	2.0537	0.3598	1.5125	0.2069
D	1.0003	0.0002	1.0011	0.0006	1	0	1.8263	0.3011
E	1.1169	0.0553	1.1167	0.0552	1	0	2.1778	0.3892

As illustrated in Figure 4.7, is interesting to notice that HCB chemical exhibited a more stable behaviour than α-HCH in both scenarios, with fugacity oscillations of α-HCH against stable quicker decay of fugacity of HCB.

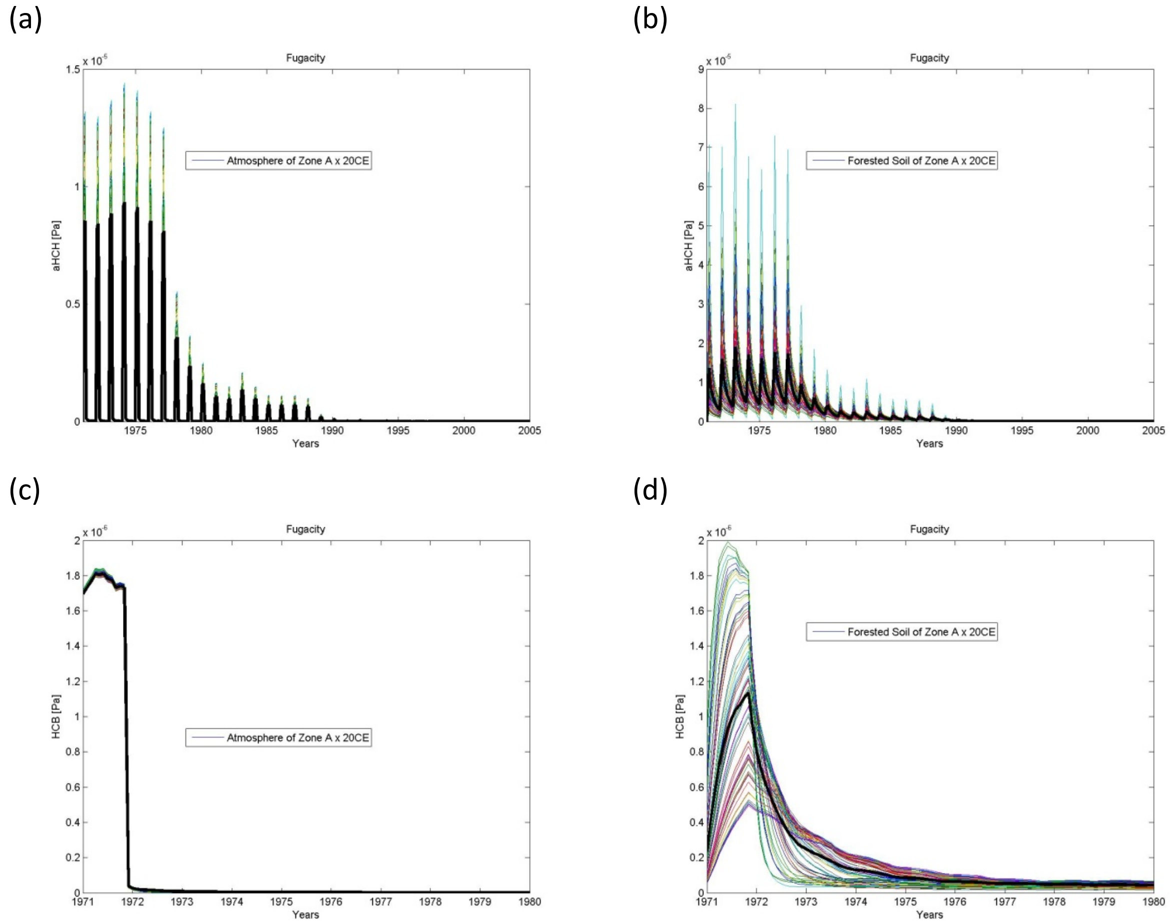
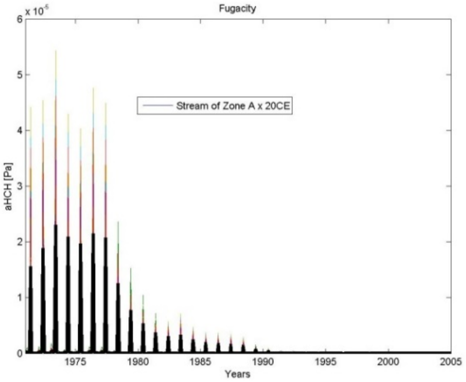


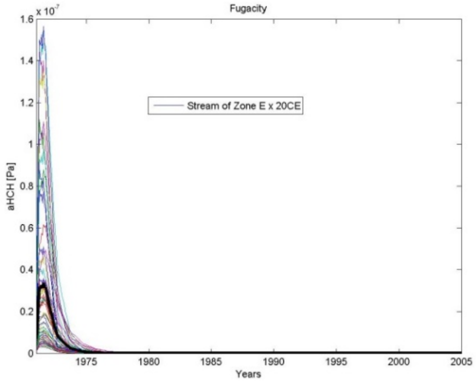
Figure 4.7. Modelled fugacity values from different compartments, showing different fugacity patterns between α-HCH and HCB chemicals in the 20CE scenario. (a) α-HCH fugacity from Zone A of Atmosphere compartment. (b) α-HCH fugacity from Zone A of Forested Soil compartment. (c) HCB fugacity from Zone A of Atmosphere compartment. (d) HCB fugacity from Zone A of Forested Soil compartment. The black cold curve represents the mean response of the Montecarlo simulations.

Figure 4.8 illustrates the effect of the random simulations over the fugacity of stream compartments, at the bottom (zone A) and the top (zone E) of the mountain, for the two scenarios and the two chemicals. Again, it can be observed a more stable with lower latency of chemical HCB than α-HCH, which on the other hand exhibit an oscillatory fugacity during the period of 1971-1980 due to stationary agricultural events; zone E shows an accumulation process of fugacity due to the transfer of HCH and α-HCH from zone A to E trough the time until their vanish.

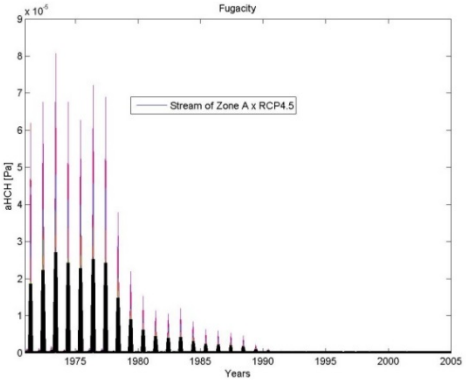
(a.1)



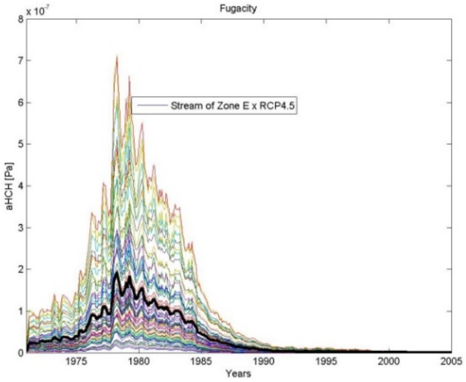
(a.2)



(b.1)



(b.2)



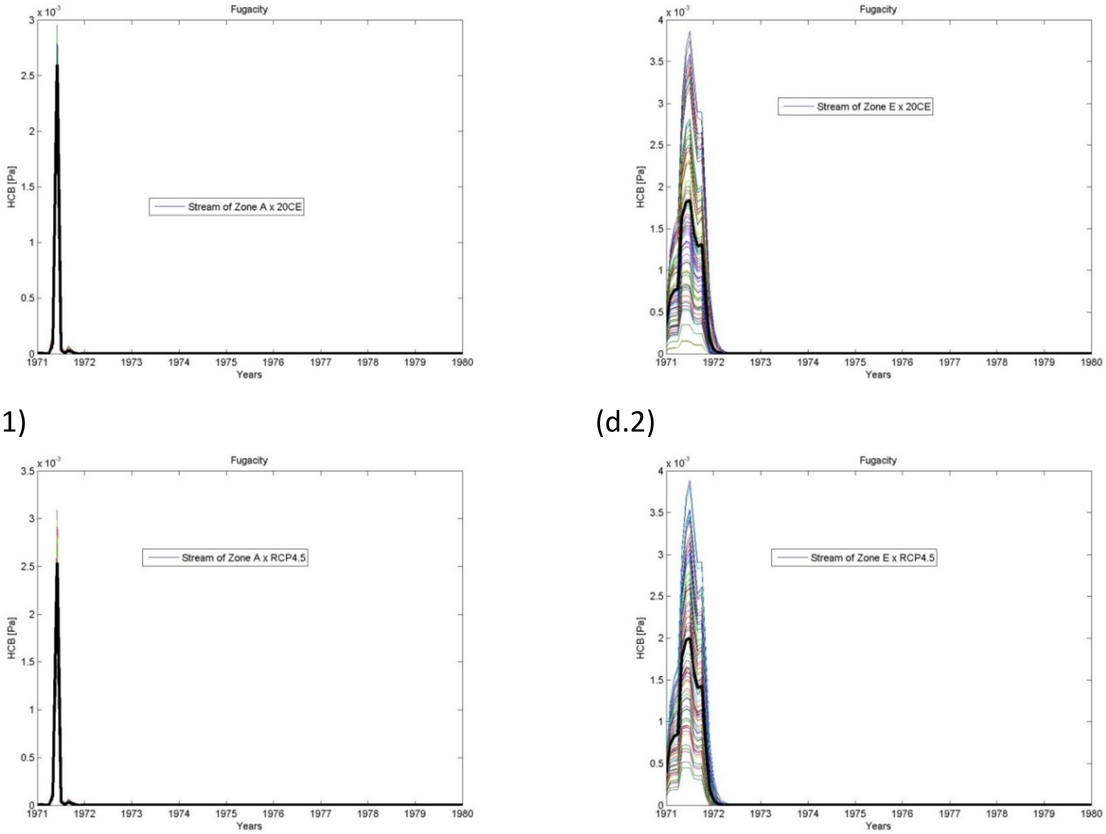


Figure 4.8. Modelled fugacity values of α-HCH and HCB, from zones A and E from Stream compartment for scenarios 20CE and RCP4.5. Difference in fugacity patterns can be observed for the α-HCH chemical between scenarios 20CE (a) and RCP4.5 (b), while less variation can be observed for HCB (c,d). The black cold curve represents the mean response of the Montecarlo simulations.

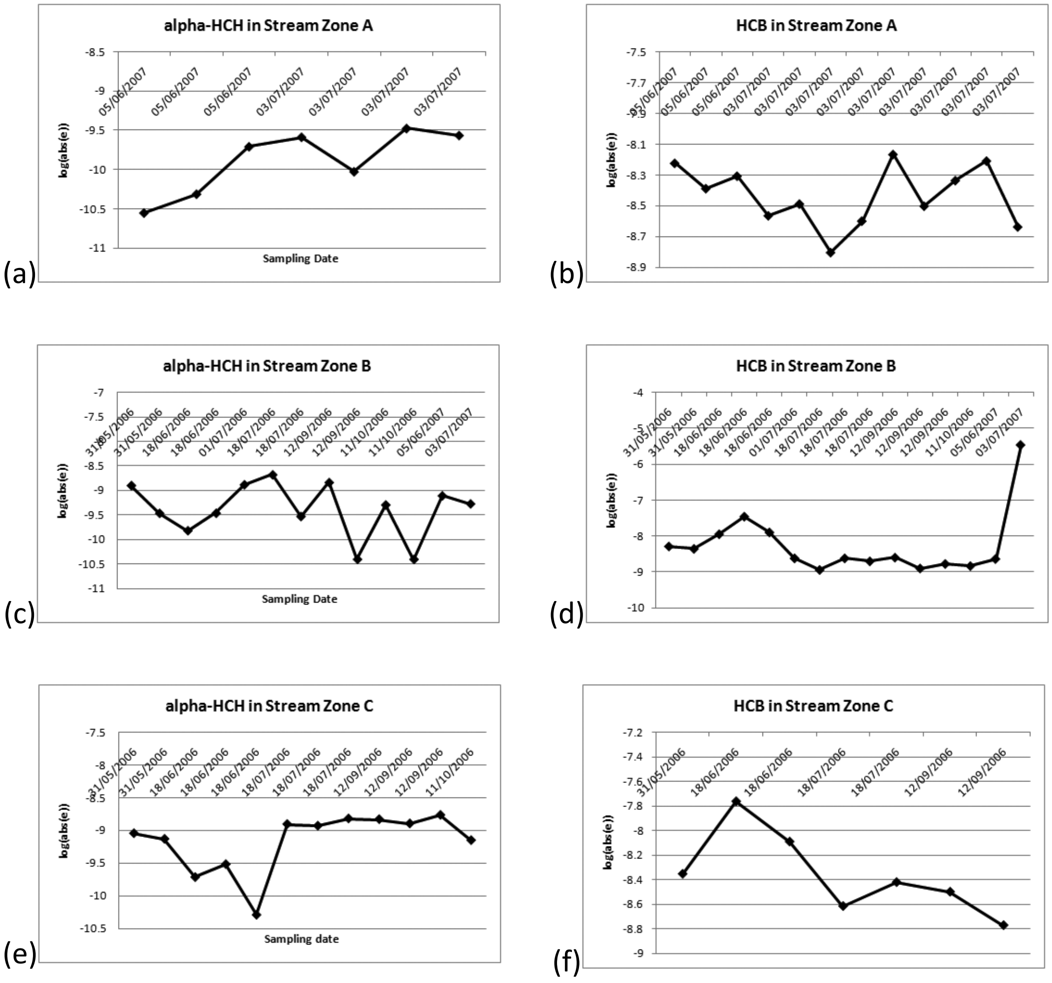
Table 4.11. Global Measured/Modelled Ratio of MountainPOP3.0 computed by the final Montecarlo random simulation of 20CE scenario.

α-HCH		HCB	
Concentration Ratio [modelled/measured]	**Fugacity Ratio [measured/modelled]**	**Concentration Ratio [modelled/measured]**	**Fugacity Ratio [measured/modelled]**
Median input values			
1.15E-12	6.59E+02	2.69E-09	1.33E+02
Optimal input values			
1.41E-03	8.12E+00	7.47E-04	1.42E+01

4.3.2. Model validation

Table 4.11 presents the summary of the comparing ratio value for the baseline median simulation and the best two simulation cases for α-HCH and HCB after exhaustive simulations, both compared in the 20CE scenario. The ratios indicates that the model matched acceptably the available real data of fugacity approximately within one to two orders of magnitude between, but tends to underestimate the concentration values at least three order of magnitudes.

Figure 9 shows the curves of the error between the modelled and measured fugacity data of α-HCH and HCB in water fluxes at different zones. The values represent the logarithmic value of the absolute error at specific sampling dates.



Note. (a), (c) and (e) α-HCH in Stream compartment at zones A, B anc C, respectively. (b), (d) and (e) HCB in Stream compartment at zones A, B and C, respectively.

Figure 4.9. Mean absolute errors (in logarithmic scale) between the modelled fugacity values and the real measured values in some sampling dates

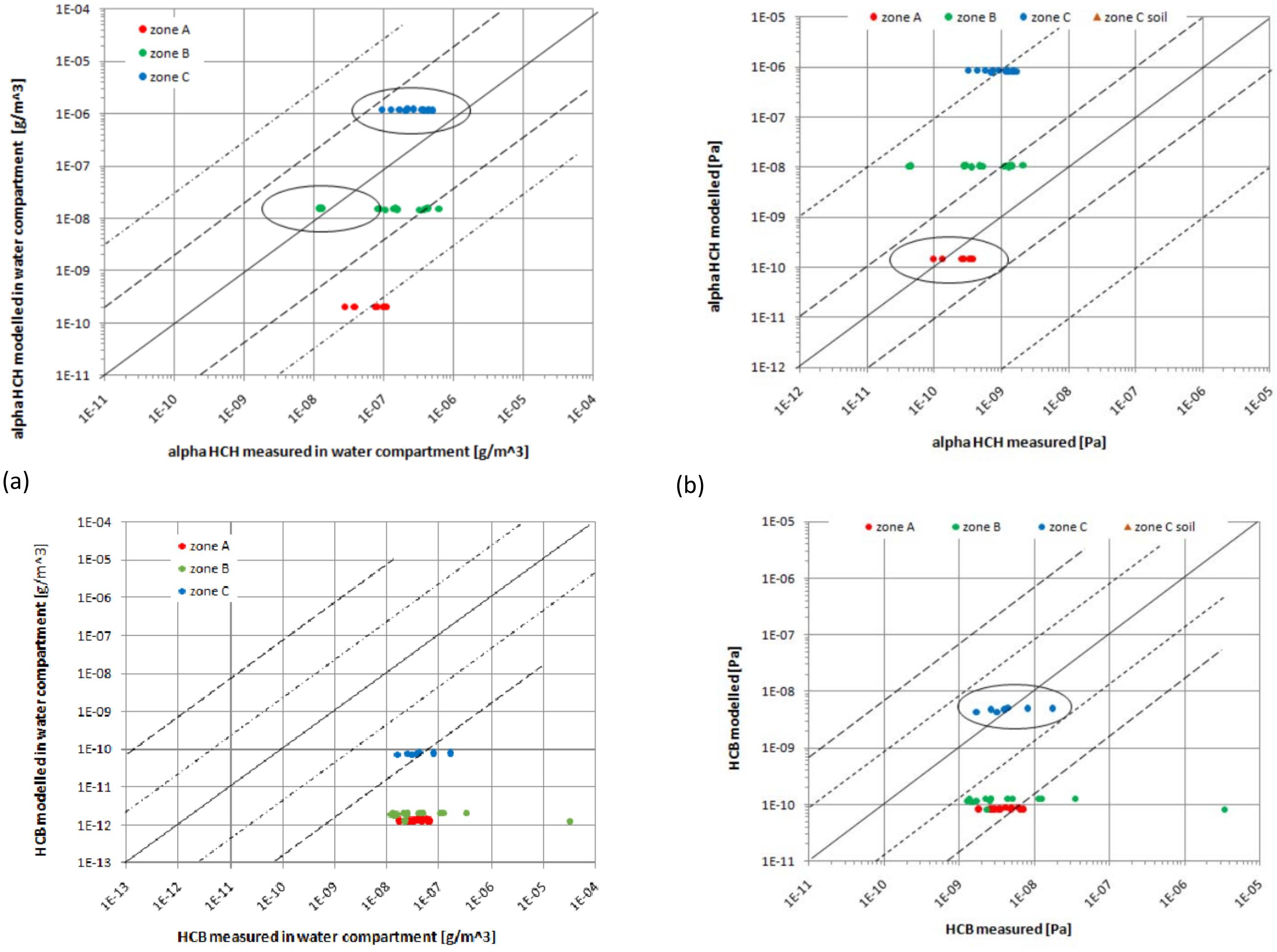
Figure 4.10 shows the comparison between the monitored and modelled data, with data transformed into fugacity values as indicated before. The agreement between most of the observed and modelled fugacity is within two orders of magnitude, and around 70% of the data of α-HCH lay within a factor of 10^2 for water compartment (Figure 4.10.a for concentrations and Figure 4.10.b for fugacity), while for HCB 100% of the fugacity data lay within a factor of 10^2 and 30% of concentrations (zone C) lay within a factor of 10^3 (Figure 4.10.c for concentrations and Figure 4.10.d for fugacity).

The case of soil data comparison between monitored and modelled is very weak since we only have one datum; for this datum from 2003 in zone B, MountainPOP3.0 overestimate fugacities with 10^2 orders of magnitude (which laid outside the graph ranges).

In general, the model presents a tendency to underestimate the concentrations in water stream compartment. This may occur due to the fact that the model does not take into account the contribution of melting glaciers, as a secondary source of contaminants materials that reaches the water stream. Another explanation is that the contribution of precipitation to the water stream does not follow the exact real conditions, overestimating the mass contribution in stream recharging. At this point, it is important to note that precipitation data for each zone does not follow the expected trend of increasing precipitation at high altitudes (Westgate and Wania, 2013). In particular, zone B features the higher precipitation than others mountains zones, during time. Other possibility may be attributable to the assumptions of the model regarding the modelled dimensions of the streams and the volume quantities of water through the mountain zones.

The comparison between measured and modelled data by MountainPOP3.0 for HCB in water compartment is in a good agreement (fig 4.10.b), with factor of 10^1 for data in zone A and C, and factor 10^2 in zone B. For the soil datum, the only comparison was underestimated with factor of 10^3.

This agreement could be explained if we note that HCB is very volatile and the preferential pathway is the atmospheric compartment; and due to its high persistence in environmental media, HCB presents a high environmental stability (Kannan et al., 1992), so the effect of underestimation in water compartment that we observed in α-HCH simulation does not play a big role in the simulated HCB behaviour with MountainPOP3.0.



(a) (b)

(c) (d)

Notes: Experiments results for α-HCH with monthly time step. (a) Comparison between α-HCH modelled and monitored concentrations, transformed in fugacity values in water and soil compartment. (b) Comparison between α-HCH modelled and monitored fugacity from water and soil compartment. (c) HCB Modelled vs monitored concentrations in water and soil compartment. (d) HCB Modelled vs monitored fugacity in water and soil compartment. Sloping with continue lines represent perfect agreement (100) and shaded lines represent an agreement within factors of 103, 102 and 101. HCB data from zone B is in grey circle. Monitored data from water are presented with black dots and soil are presented with black triangle symbols.

Figure 4.10. Comparison between MountainPOP3.0 modelled and monitored concentrations and fugacities in Valtellina, for the best cases within the final Montecarlo random simulation. (a) α-HCH concentrations. (b) α-HCH fugacities. (c) HCB concentrations. (d) HCB fugacities.

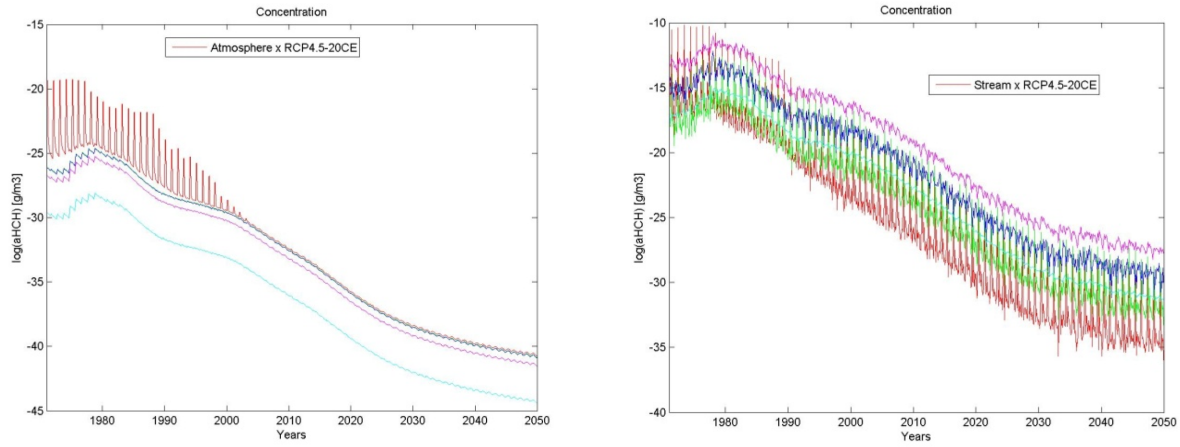
This observation may be reinforced if we point out that zone B has a higher precipitation trend than the precipitation trends of zones A and C.

4.3.3. Chemicals’ fate projections

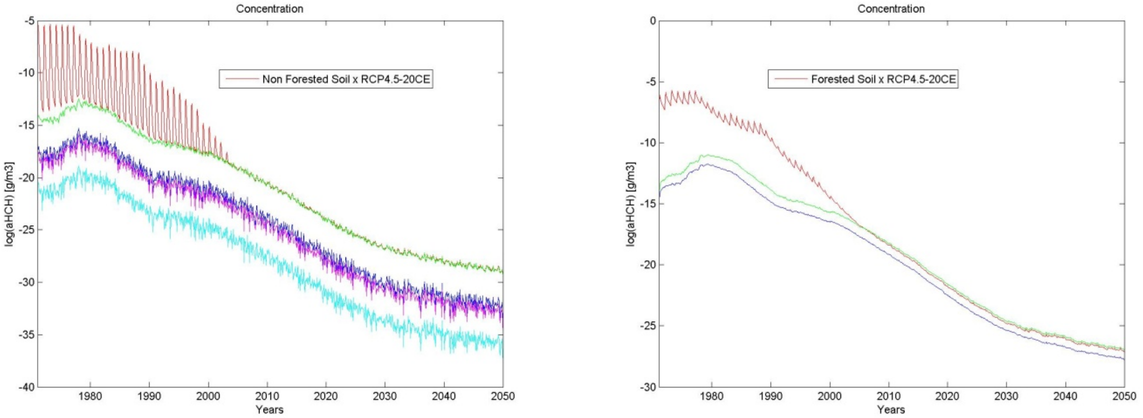
We performed several model experiments to compare the fate of α-HCH and HCB under the 20CE and the RCP4.5 climate scenarios. Chemical concentrations can be observed in figures 4.11 and 4.12 that show the results of the simulation of the climate change scenario RCP4.5. The results related to 20CE scenario are indicated in SM5.1.

4.3.3.1. α-HCH

We found that α-HCH concentrations are higher in forested soil than atmosphere and water (Figure 4.11). Concentrations in zone A are higher than in the other zones (except in stream compartment), but also more fluctuating in zone A. α-HCH is always present in the environment. The α-HCH concentration (C) decreases along the time period in all compartment for each zone. Bottom zones in atmosphere compartment (fig. 4.11a) have very similar concentrations, zone E is only lower from the others such 2 orders of magnitude. A concentration gradient decreases inversely to altitude ($C_A > C_B > C_C > C_D > C_E$).



(a) (b)



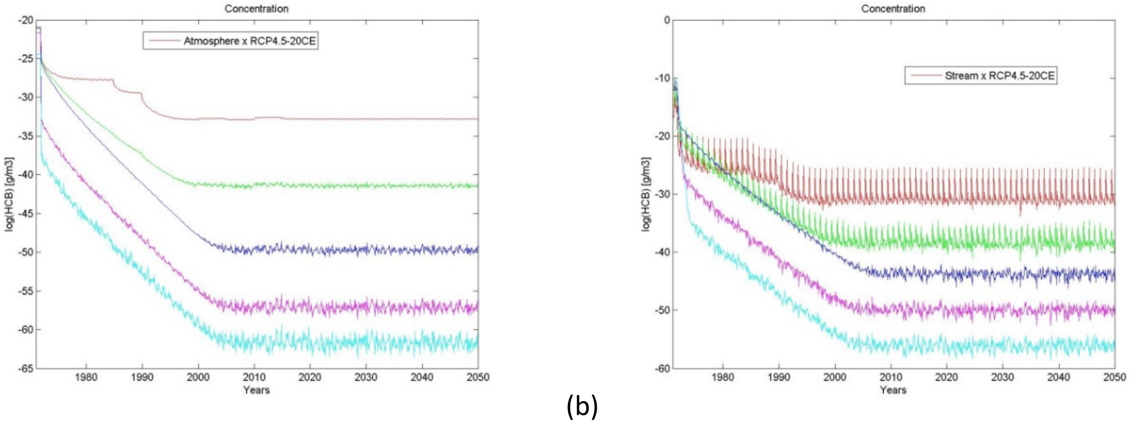
(c) (d)

Notes. α-HCH concentrations presented for each zone (A in red, B in green, C in blue, D in magenta, E in cyan)) in each compartment, (a) atmosphere; (b) water stream; (c) non-forested soil and (d) forested soil. Values are showing in log (10).

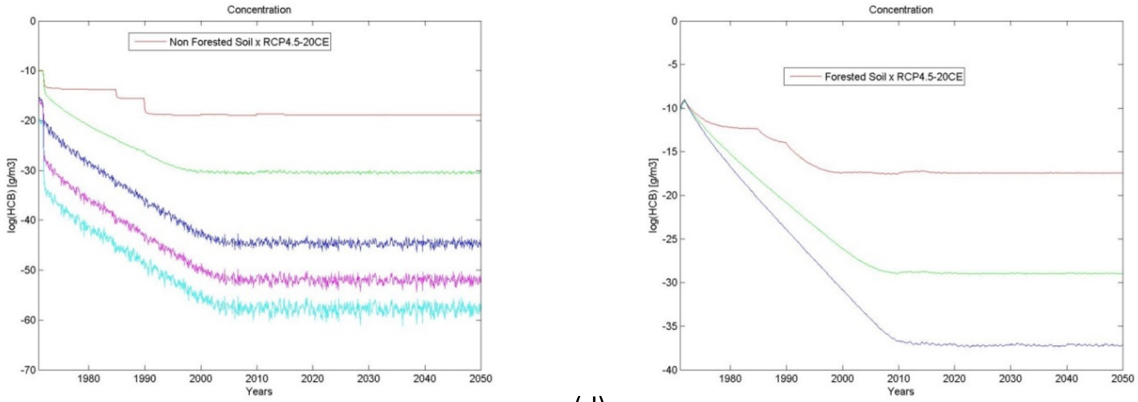
Figure 4.11. RCP4.5 scenario for α-HCH in Valtellina Mountain for the period 1971 – 2050.

4.3.3.2. HCB

HCB concentrations show more variability in water stream (fig 4.12.b) and but lower in forested soil (fig 4.12.d) compartments. The HCB concentrations decrease sharply in zone E in the water stream compartment. The concentration (C) stabilizes in (non)forested soil (fig 4.12.c), forested soil (fig 4.12.d) and atmosphere (fig 4.12.a), more in lower zones (zones A and B). Instead, and water stream compartments follow instability in all zones.



(a) (b)



(c) (d)

Notes. HCB concentrations presented for each zone (A in red, B in green, C in blue, D in magenta, E in cyan) in each compartment (atmosphere, water stream, non-forested soil and forested soil); values are showing in log (10).

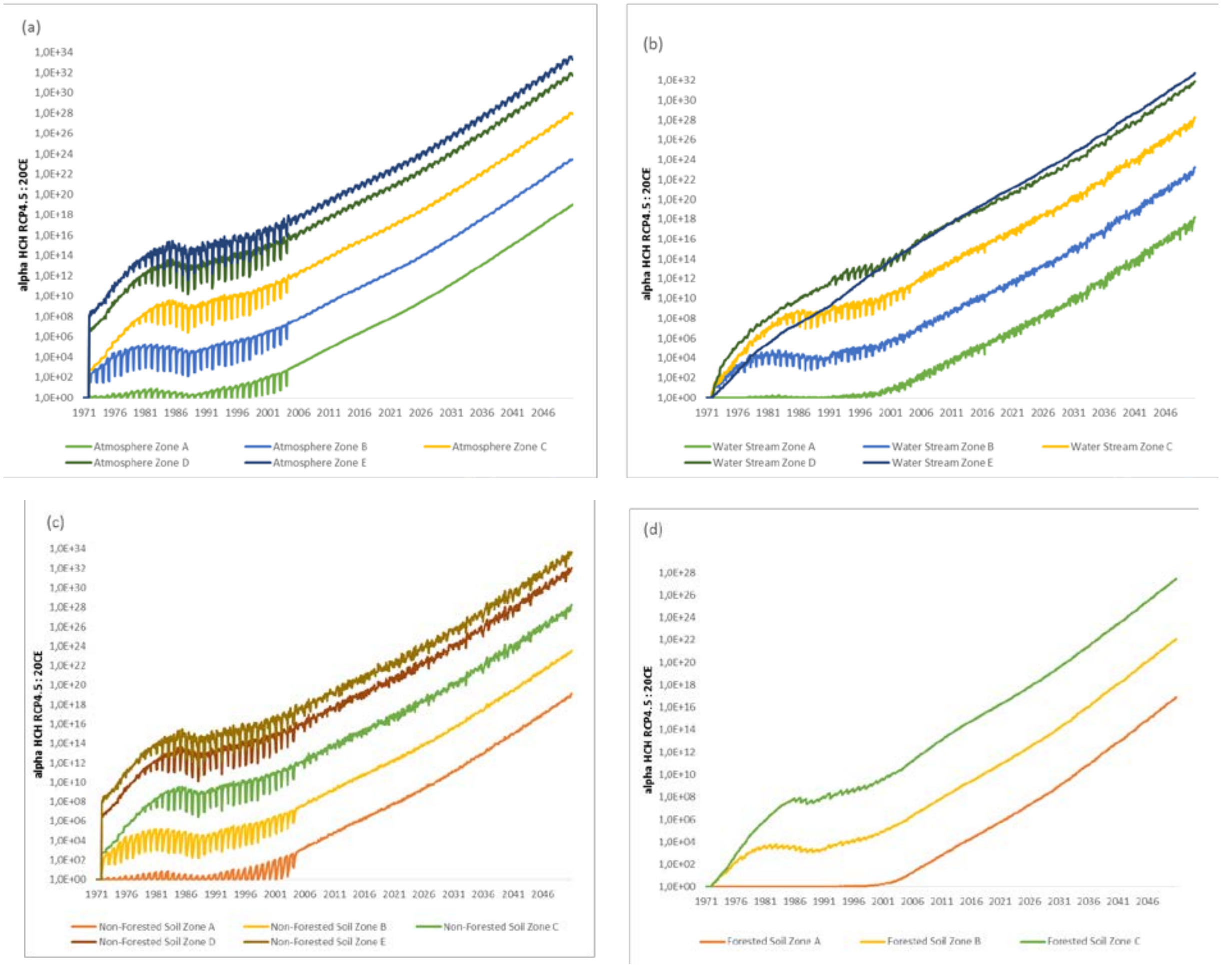
Figure 4.12. RCP4.5 scenario for HCB in Valtellina Mountain for the period 1971 – 2050.

4.3.4. 20CE and RCP4.5 Climate scenarios comparative analysis

We compared modelled concentrations and fugacities of a-HCH and HCB under the 20CE and RCP4.5 scenarios. This comparison between climate scenarios represents the ratio of change between the concentration values under different climate assumptions and was selected metric of values (Lamon et al., 2012). The results are reported in figures 4.13 and 4.14. Remarking that MountainPOP3.0 is a dynamic model and under the unsteady state conditions, the comparison was made for 80 years: 1971 to 2050. Particularly, figure 4.14 shows the ratio RCP4.5 and 20CE of HCB concentrations from 2006 to 2050 because the period 1971 to 2005 does not display any change between scenarios.

4.3.4.1. α-HCH

In general, α-HCH concentrations show higher increase in all compartments during the RCP4.5 scenario than 20CE. The trend in HCH concentrations is similar in all compartments although water stream compartment (fig.4.10.b) has a longer period of concentrations' stability in zone A (bottom zone) up to 2006, instead the other compartments show variations between climate scenarios since 2001.

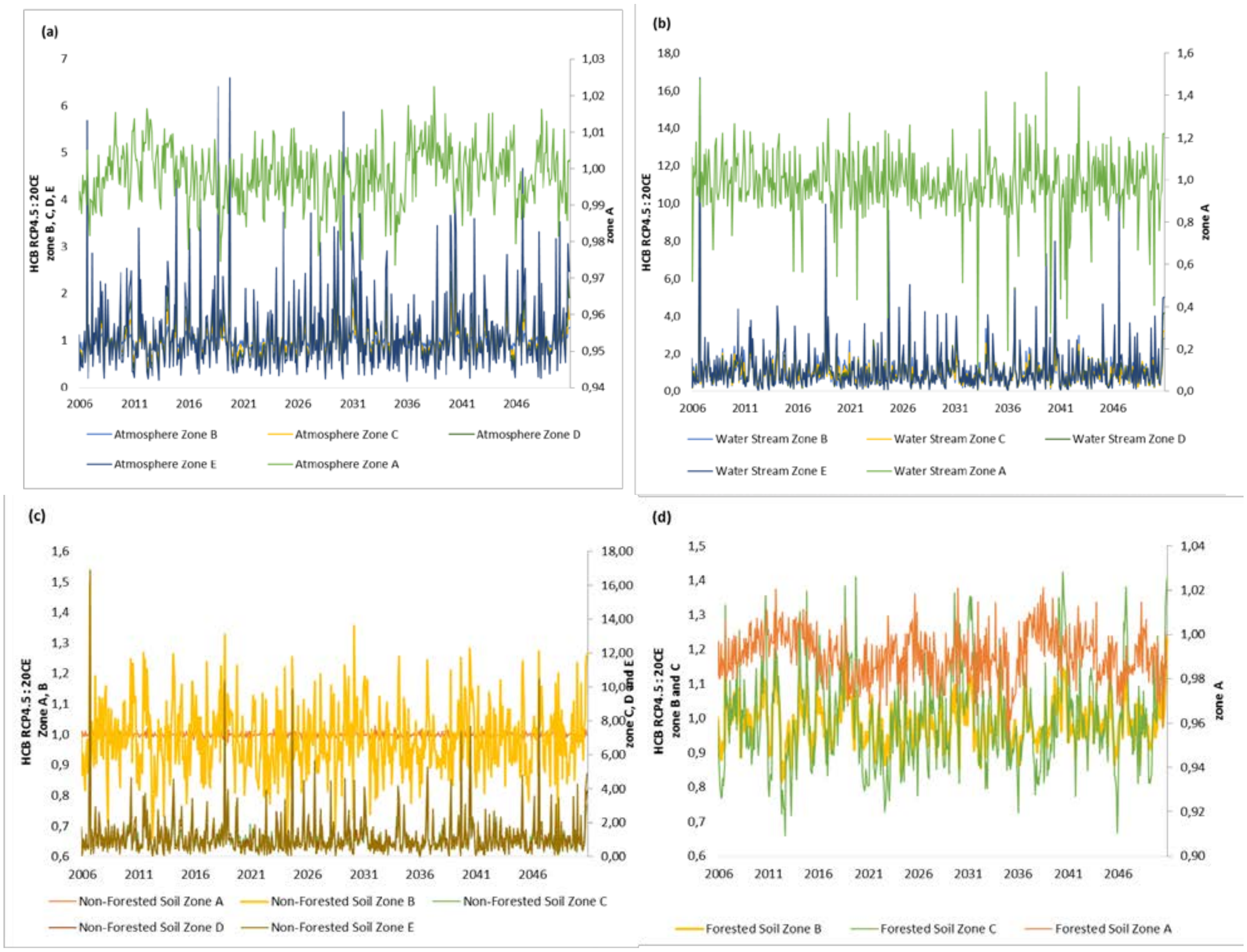


Note: (a) Ratio of modelled concentrations in atmospheric compartment for each zone; (b) Ratio of modelled concentrations in water stream compartment. (c) Ratio of modelled concentrations in non-forested soil compartment. (d) Ratio of modelled concentrations in forested compartment. Data are presented in log(10) scale.

Figure 4.13. Ratio of comparison for α-HCH modelled concentration between RCP4.5 and 20CE scenarios.

4.3.4.2. HCB

In general, the comparison of HCB concentrations between two climate scenarios in the atmospheric compartment (fig. 4.14.a) and (non)forested soil (fig 4.14.c and 4.14.d) shows similarity with no changes under two scenarios. HCB concentrations are more consistency along the time period (2006 – 2050) with greater concentration values at the top of the mountain. Water stream compartment varies between zones. Zone E (fig 4.14.b) shows an increment at the end of the period of HCB concentration in RCP4.5 scenarios respect to 20CE scenario. Contrary, always in water stream compartment but in zone C and D, concentrations decrease along the period for future scenario RCP4.5.



Note: (a) Ratio of modelled concentrations in atmospheric compartment for each zone; (b) Ratio of modelled concentrations in water stream compartment. (c) Ratio of modelled concentrations in non-forested soil compartment. (d) Ratio of modelled concentrations in forested compartment.

Figure 4.14. Ratio of comparison for HCB modelled concentration between RCP4.5 and 20CE scenarios.

4.4. Discussion

We reported a regional adaptation of MountainPOP3.0 model for α-HCH and HCB in Valtellina Valley localized in Italian Alps. The agreement between measured and modelled fugacities shown in figure 4.10 demonstrates that under the 20CE scenario the dynamic model can help to understand the variation between altitudinal zones and air, soil and water stream.

The sensitivity analysis of 20CE scenario conditions made possible the identification of the importance of landscape input variables in determining the environmental fate of our case study chemicals. Particularly, water stream compartment dimensions are govern by precipitation used in Horton's Overland Flow to calculate the dimensions of the stream. This finding lets the possibility to identify the effect of precipitation variable as a main source in the water mass balance in the model.

Under 20CE scenario, α-HCH concentrations shows a continuous decrease trend during the all period (figure SM1, from Annex). Meanwhile HCB shows slight fluctuations during the entire period. Due to its high persistence and its stability in gas phase, HCB is present in the atmosphere. Under climate change assumptions, HCB does not describe a reduction but a seasonal trend, with fluctuations between summer and winter periods. In atmosphere, HCB shows more stability (between 1.5) in the bottom than in the top of the mountain (zones C, D, E: factor of changes up to 5). During the uncertainty analysis for α-HCH and HCB simulation, the input variables that influenced more the chemical behaviour are: width (r = 0,34); fraction of solids in non-forested soil which are organic matter (r = 0,39); and soils emissions (r= 0,30). Particularly, it could be the reason of the instability in soil compartment found in the model simulation for HCB. Even when the effect of emissions uncertainty should be more important for environmental behaviour, landscape parameters, it means geometrical relationships between environmental compartments, seem to drive the chemical behaviour in MountainPOP3.0.

Results from the model experiments for the effects of climate change scenario RCP4.5 on modelled environmental concentrations of α-HCH and HCB become notable after the phase out for both chemicals: 2000s for α-HCH and less abruptly for HCB during 1990s (figures 4.11 and 4.12). When concentrations are compared between 2 scenarios (figures in 4.13 and 4.14), we can observe that concentrations fluctuate more during the primary emissions, when active. After 2004 that is the total phase out of α-HCH in the Central Europe, the concentrations are driven by secondary emissions such as re-volatilisation. In the course of the whole period concentrations declined in atmosphere (factor of 0,34) slower than in the other compartments: water stream (factor of 0,90): forested soil (factor of 0,92); and non-forested soil (factor of 0,79). This could be explained because α-HCH has a preferential pathway in atmosphere (Wöhrnschimmel et al., 2012) enhancing its presence in the atmosphere.

The modelled concentrations exhibit increments into environmental compartments (atmosphere, water, stream and (non) forested soil) during all period (1971 - 2050) even when other authors (Wöhrnschimmel et al., 2012; Roots et al., 2010; Barber et al., 2005; Li et al., 2000) have been noted the HCH primary emissions were stopped in 2004 in Central Europe, and that HCB has been decreased dramatically since 1970. This finding strengthen the importance of secondary emissions as a result of chemical remobilization from soil to atmosphere in mountainous environment.

At the end of the time period, α-HCH varies less in the bottom of the mountain than in the top, for all compartments. Forested soil compartment shows an increment in concentrations in climate change scenario RCP4.5 that can favour the volatilization to atmosphere over the evaporation transport. An analogous finding was reported by Wegmann et al., 2006 for a latitudinal averaged mountainous region, where the relatively high water solubility of α-HCH and, therefore, susceptibility to wet atmospheric deposition, is mainly responsible for this strong deposition in soil from mountainous region.

The climate change scenario (RCP4.5), where is assumed that temperature, precipitation and wind speed will vary dynamically by increasing and changing their spatial and temporal patterns, drives the chemical fate through the input from atmospheric wet deposition, and volatilization from water to atmosphere.

Results from MountainPOP3.0 experiments for the RCP4.5 climate change scenario identified secondary emissions, temperature, precipitation and fraction of solid organic matter in (non)forest compartment as the climate and environmental parameters affecting the distribution and fugacity of α-HCH and HCB in the study area, whereas wind speeds and dry deposition were less influential in changing modelled concentrations in the future climate scenario RCP4.5 (figures 4.11 and 4.12). These results are consistent with the sensitivity analyses (tables 4.7, 4.8). Wet deposition is the most important process in determining the increase in fugacity of soil compartment. Similar finding are reported in early version of MountainPOP3.0 by Westgate and Wania, 2013 where POPs were found at higher concentrations in a surface medium (soil, snow, foliage) high on a mountain, where it is colder, than in the same medium lower on the mountain.

During the experiment of data screening it was possible to establish a score of the accumulative contribution of environmental variables that contribute on compartment and zone variability behaviour (table 4.6). As a result of the accumulate contribution under principal component analysis, it was possible to identify not only how climate change affects chemical concentrations in each altitudinal zone but which compartment at specific altitudinal zone is more affected. Resulting forested soil at 2201 to 2700m a.s.l. (zone C) was the most affected environmental compartment under climate change assumption due to increasing of organic carbon content when temperature increases. While water stream compartment at the bottom of the mountain (zone A) was the most affected under 20CE scenario. The modelled concentrations under 20CE and RCP4.5 scenarios followed the altitudinal gradient in Valtellina Mountain. The greatest concentrations were found in the bottom of the mountain and the lower concentrations were found in the mountain top. The results of the model presented here provide some initial estimates of the possible effects of climate change on the fate and transport of α-HCH and HCB in Valtellina valley in Italian Alps, whilst becomes an ideal site to study HCH behaviour along gradients of climate variables. These specific meteorological conditions may increase the persistence, because degradation is slower at lower temperatures and the degradability of many substances is lower in surface media than in air, favouring these regions as secondary emitters for POPs.

This attempt should be seen as an effort on a realistic application of a dynamic fugacity model at regional scale under climate change assumptions and demonstrates that regional simulations can be a useful source of chemical behaviour information under climate change assumptions. Nonetheless, MountainPOP requires a very detailed parameterization of the environmental compartments, as well as the climate of the study area, making difficult the application. In addition, the lack of monitoring data in vulnerable areas such as high mountains reduces the effectiveness of model applications.

4.5. Acknowledgements

This paper was supported by the GEMINA project, funded by the Italian Ministry for the Environment, Land and Sea (MATTM). Tair Teran-Guerrero thanks funding from CONACYT-Mexico PhD grants Program. We furthermore acknowledge Leonardo Grassi for his support in the definition of the water balance in the case study areas.

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5 Conclusions

Climate change effects on POPs environmental behaviour in high altitudes

Climate change can influence POPs environmental fate and transport through the variability of global and regional atmospheric and oceanic circulation patterns (i.e. wind speeds, precipitation, interactions with the Earth's surface, ocean currents, organic carbon content, and biological pathways). This climate variability affects directly POPs environmental distribution through fluctuations in the emissions' spatial distribution and chemicals' physical-chemical properties.

The climate variables such as temperature, precipitation and wind speed have a pronounced effect on POPs environmental fate and transport, as well as the spatial distribution of primary and secondary pollution sources in each environmental compartment that play a key role in POPs behaviour. The (inter)national efforts on collecting information on POPs emissions and to build updated emissions' inventories must be strengthened in order to reduce uncertainty in describing POPs mass balance and performing simulations for defining the location and the amount of future sources of pollution.

This thesis contributes with the assessment of the impacts of climate change in influencing anthropogenic pollutants' concentration, in particular POPs, in high-altitude regions. In the second chapter, this thesis presented a comprehensive and significant review of the effects of climate change on POPs' behaviour in a national and international regulation perspective because of their adverse effects on ecosystems and human well-being.

In this regard, chapter 3 described a database called POPAlp developed as part of this thesis work and currently available online for the research community, that collects and manages information focused on the concentrations of POPs, useful for assisting in the identification and analysis of these organic pollutants which should not be present in pristine areas such as high mountains. Pristine areas don't have direct or indirect sources of POPs emissions, but they can act as an intermediate sink or deposition place on long range transport perspective.

POPAlp contains inter-program monitoring data and a QA/QC evaluation was implemented onto different methods of monitoring campaigns for collection, chemical analysis and statistical data management in order to find significant agreement between diverse studies. Data collected by

POPAlp can assist in environmental assessment of POPs' behaviour and long range transport to vulnerable areas such as high mountains environment.

Using POPAlp, alpha HCH and HCB were individuated because such pollutants fulfilled some requirements: they are POPs included in the annex A of Stockholm Convention, it means they are banned for over 10 years in international treaties. Moreover, they continue to be identified and measured in air, soil and water environmental compartments in mountainous regions localized far from primary sources of emissions.

These two compounds have different characteristics in their environmental performance; the most important is the great stability for HCB that allows to remain in circulation in the atmosphere for a long time, becoming the main emitter: the atmospheric air. Furthermore, alpha HCH emissions are governed by the direct application by spray to soil with agricultural purposes, releasing alpha HCH in higher amounts in soil compartment. For this reason, soil compartment is treated as the main alpha HCH emitter to the environment. High mountains have been recognized as one of the most vulnerable environments to climate change and POPs effects for the ecosystem. Mountain areas have also been recognized as ideal places to study long range transport and POPs' behaviour because they have well defined gradients of temperature, precipitation and wind speed that particularly affect the transport and behaviour of POPs.

Chapter 4 of this thesis was devoted to study the effect of climate change on POPs behaviour in mountainous environment through the adaptation and application of a fugacity model called MountainPOP3.0 under climate change assumptions, taking into account two climate scenarios, 20CE that represents the current climate conditions with no changes over the next 25 years; and RCP4.5 representing climate variation that would result from radiative forcing increases at 4.5 W/m2 relative to the pre-industrial era.

The fugacity model MountainPOP3.0 represents a mountainous environment divided in five zones and each zone consists of three compartments: air, soil and water and was adapted to simulate an alpine region called Valtellina Valley located in North-eastern of Italy in the European Alps. This area is marked by high altitude and includes the Adda River which springs in the highest elevation and runs down until reach the Como Lake at the bottom part of the valley. Therefore, the model was adapted not only to describe the behaviour of alpha HCH and HCB in Valtellina

Valley but also the chemical behaviour were analysed under the two different climate scenarios 20CE and RCP4.5.

In particular, the definition of a unique mountain represented a challenge since environmental conditions around the Valtellina Valley became a well-defined hypothetical high mountain with environmental conditions dynamically treated during the period 1971 to 2050.

The results of the adaptation and application of MountainPOP3.0 remarked that although the primary emissions of alpha HCH and HCB have stopped, both chemicals do not only remain in the environment but instead they are remobilized from secondary emissions that have been deposited and associated to organic carbon content in soils.

After the phase out of alpha HCH, the model results showed low levels of concentration (about 10E-18) that are impossible to detect with laboratory analytical equipment.

Under climate change assumptions, alpha HCH levels show a clear tendency to increase under RCP4.5 climate change scenario in the environment. Demonstrating the direct effect of climate change in parameters such organic carbon content, environmental temperature and precipitation, which can vary the behaviour patterns of POPs. For HCB, the effect of climate change is different because the temperature variations do not affect their chemical characteristics, making it much more stable into the environment.

During the model simulations, it was possible to identify not only how climate change affects chemical concentrations in an altitudinal gradient but which compartment at specific altitudinal zone is more affected. For climate change scenario RCP4.5 was done, forested soil at 2201 to 2700m a.s.l. (zone C) was the most affected environmental compartment. Under climate change assumption zone C experiments an increment in precipitation patterns, besides increment of organic carbon content when temperature increases. While water stream compartment at the bottom of the mountain (zone A) was the most affected under 20CE scenario.

This assessment of POPs' behaviour includes some landscape variables as an approximate average (e.g. water current velocity and maximum water volume), assuming constant values that are not representative of the study case at all. For this reason, this application of MountainPOP3.0 in Valtellina Valley provides some initial estimates of the possible effects of climate change on POPs behaviour, but it does not allow to use it in applications for international regulation, at least in its current state.

Nonetheless, MountainPOP allows to decisions-makers have more plausible perspective about the effects of climate change on POPs behaviour and their impacts in vulnerable zones such as European Alps. Based on Climate change studies, European Alps are on high risk according to changing in climate patterns not only in surface temperature, rainfall and wind patterns, but also due to the increasing risk on remobilization of POPs that were deposited in temperate zones during last decades. Therefore, POPs can continue their long range transport up to reach the Arctic.

MountainPOP requires a very detailed parameterization of the environmental compartments, as well as the climate of the study area, making difficult the application, as well the lack of monitoring data in vulnerable areas such as high mountains, which reduce the effectiveness of model applications. This attempt should be seen as an effort on a realistic application of a dynamic fugacity model at regional scale under climate change assumptions.

The successive steps of this study should be the integration of a transport pathway analysis, since the use of fugacity models such as MountainPOP3.0 can help into identify not only POPs behaviour, but the responsible actors of POPs emissions that affect pristine regions such as high mountains with high risk of re-volatilization of concern compounds that were banned and phase out during last decades.

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6. Annex

Supporting Material (SM) on climate change impact on the fate of persistent organic pollutants: a case study in the Italian Alps

Tair Teran-Guerrero, Lara Lamon, John Westgate, Edoardo Bucchignani, Frank Wania, Antonio Marcomini

6.1. MountainPOP3.0 equations

6.1.1. Design of Water compartment in MountainPOP3.0

Table SM1 lists the fluxes between water stream compartment, soil and atmosphere compartments. The water mass balance is calculated with the Horton Overland flow approximation (Brown, 2011). The water stream compartment receives precipitation as only net input of water. Evaporation is the main output from water and soil compartment. Meanwhile, precipitation and runoff from soil to water compartment are the input of water compartment. Runoff or Horton's Overland flows is determined by *SFC,* VF_{EW} and an empirical fitting factor *Runoff water stress*. If volume fraction of water reaches the saturation of the soil pore, all additional water reaches the water compartment as a surface flow. The rainfall intercepted from forest soil is function of the type of the forest canopy (deciduous) as a fraction dependent of the canopy volume.

The bulk water compartment can vary in depth, and therefore in volume (Brown, 2011) by altering empirical outflow fractions that determine the downstream flow of water based on the current volume of water (Brown, 2011).

6.1.1.1. Mass balance of water (in terms of carrier phase G [m3h-1])

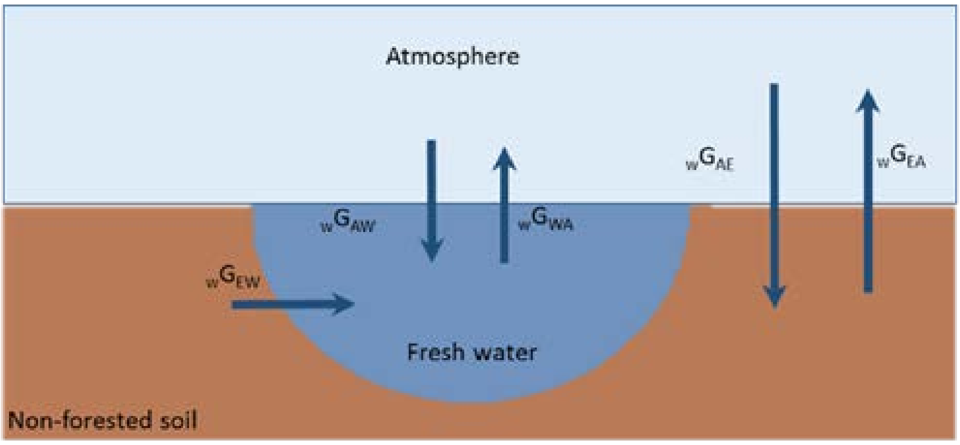


Figure SM1. Water fluxes between the compartments of MountainPOP3.0

Table SM1. Fluxes between water stream compartment and soil and atmosphere compartments

Fluxes [G]	**Equation**
${}_wG_{up}$ = advection ${}_wG_{up} = {}_wG_{down}$	${}_wG_{up}$ = streamflowrate $* A_w$ A_w = water surface area stream flow rate = stream (down/up) slope water flow [m^3/h]
${}_wG_{EW}$ = runoff (Horton's overland flux) / infiltration	Runoff fitting factor $= \frac{r_{MP}}{rws}$ Where r_{MP} = midpoint of rain rws = runoff water stress
${}_wG_{AE}$ = precipitation onto soil	Precipitation = A_E $*$rain, where A_E= soil surface area
${}_wG_{EA}$ = evaporation from soil	Evaporation = non forest fitting factor $*$ vapor pressure $*$ ews Where ews = evaporation water stress
${}_wG_{AW}$ = precipitation onto water	Precipitation = A_W $*$ rainfall
${}_wG_{WA}$ = evaporation from water	Evaporation = evaporation fitting factor $*$ vapor pressure $*$ wind speed

Table SM2. Empirical factors used in the water compartment fluxes

Empirical factors	**Value**
runoff fitting factor	$\frac{r_{mp}}{r_{ws}}$
Runoff water stress	$\left[\arctan(10 * VF_{EW} - SFC) + \arctan(10 * SFC)\right]^2$
evaporation soil - water stress	$\left[\arctan(10 * VF_{EW} - SFC) + \arctan(10 * SFC)\right]^3$
evaporation fitting factor	$\dfrac{\dfrac{r_{MP} * FR_{R-EV}}{wind\_speed}}{vapor\_pressure\left(\dfrac{T_{MP}}{ews}\right)}$

6.2. Glossary

Table SM3. Chemical and Environmental Parameters

Parameter	Symbol	dimensions*
Ideal gas constant	R	(J/molK)
Henry law constant	H	(T)
Density of aerosol (Q), octanol (O)	ρ_i	(kg/m3)
Fraction organic carbon in aerosol	F_{OC}	-
Solids volume fraction	VF_s	-
Rain scavenging ratio	r	-
Soil density	ρ_E	(kg/m3)
Total fraction of organic carbon (Daly et al., 2007)	FT_{EOC}	(kg/m3)
Water density	ρ_W	(kg/m3)
Partition coefficient of organic carbon	K_{OW}	-
Volume fraction soil-water	VF_{EW}	-
Total fraction of soil-air	FT_{EA}	-
Concentration of organic carbon particles	C_{POC_W}	-
Density of organic carbon particles	ρ_{POC}	(kg/m3)
Water side MTC	k_{WA}	(m/h)
Air side MTC	k_{AW}	(m/h)
Precipitation	rain	(mm)
Temperature	T	(K)
Precipitation rate	U_R	-
Dry deposition velocity	V_{dry}	-
Aerosol fraction	V_Q	-
Air side MTC over soil	k_{AE}	(m/h)
Gas MTC over pore space soil	k_{MA}	(m/h)
Solid MTC over pore space soil	k_{MS}	(m/h)
Horton over land flux	${}_{EW}G_{Horton}$	(mm/h)
Carrier phase in atmosphere	aG	(m3/h)
Carrier phase in water	wG	(m3/h)
OH Reaction rate	RR_{OH}	(1/h)
PH reaction rate in soil	RR_{PH}	-
Fraction of chemical on aerosol	FR_{CH-Q}	-

Note: MTC is mass transfer coefficient; * values for each parameter are shown in table SM6.1.

6.3. Definition of Valtellina Mountain's zones in MountainPOP3.0

The mountain has been constructed taking into account the altitudinal and morphological characteristics. Valtellina Valley is subdivided in five zones (A, B, C, D, E) accordingly to the relationship of their altitudinal characteristics such as altitude(E) > altitude(D) > altitude(C) > altitude(B) > altitude(A); and surface areas: Area(A) > Area(B) > Area(C) > Area(D) > Area(E) in order to construct an hypothetical mountain; the five zones are described as follows:

Table SM4. Values of each compartment in the five zones modelled in MountainPOP3.0.

	Id name	Altitude range (m a.s.l.)	Area (km^2)	Atmosphere height (km)	Width (km)	Depth of Soil (m)	Type of soil #	Type of vegetation $	Fraction* of OM#	Surface fraction of water stream	Mean current velocity x (m/s)
Zone A	Valtellina Mountain A	200 to 1600	796,18	763,65	28,22	1,3	entisols	coniferous forest	0,16	0,06	14,6
Zone B	Valtellina Mountain B	1601 to 2200	702,63	763,65	26,51	1,3	entisols	coniferous forest	0,16	0,01	1,5
Zone C	Valtellina Mountain C	2201 to 2700	689,90	763,65	26,27	1	inceptisols	alpine meadow	0,0038	0,006	0,1
Zone D	Valtellina Mountain D	2701 to 3400	371,17	763,65	19,27	1	inceptisols	alpine meadow	0,0038	0,005	0,001
Zone E	Valtellina Mountain E	up to 3401	20,54	763,65	4,53	0,02	cryosols	lichens	0,00057	0,06	0,0003

* In non-forested soil; # derived from (Sturani, 1992). Fraction of OM in forested soils is 0,45; x (Regione Lombardia, 2006); $ (Gironi, 2000)

The Adda River springs in zone A and follows a straight and proportional dimensions through all zones. The characteristic of soil and water stream for each zone are described in table 1. The a-HCH and HCB inputs come from the settlements found in the vicinity of Como municipality at zone A. Zone D and E don't have forested soil but non-forested soil.

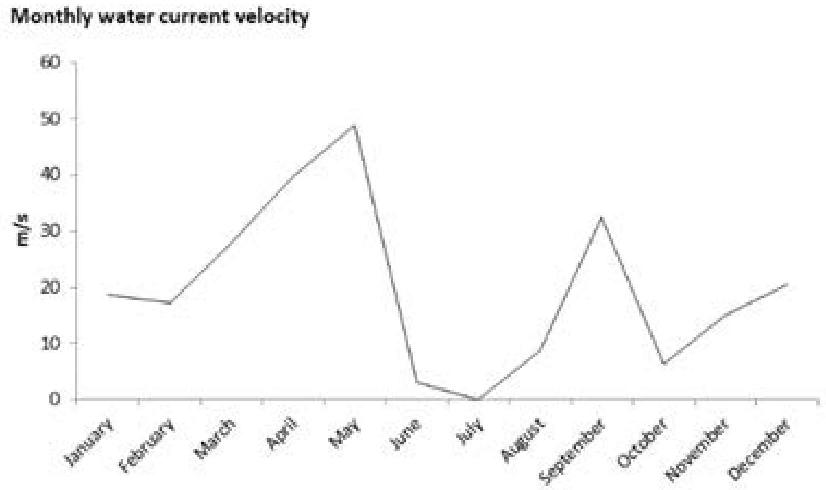


Figure SM2. Water current velocity (mean value). This value is the same for the water compartment in each zone along whole period. Based on (Regione Lombardia, 2006).

6.4. Climate scenarios analysis

6.4.1. Climate by mountainous zones

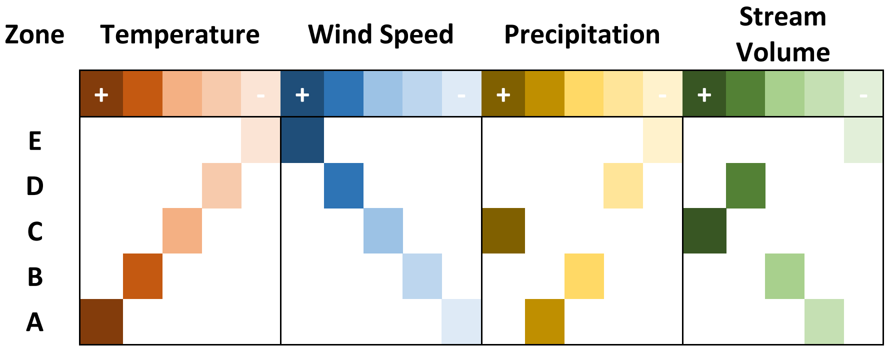
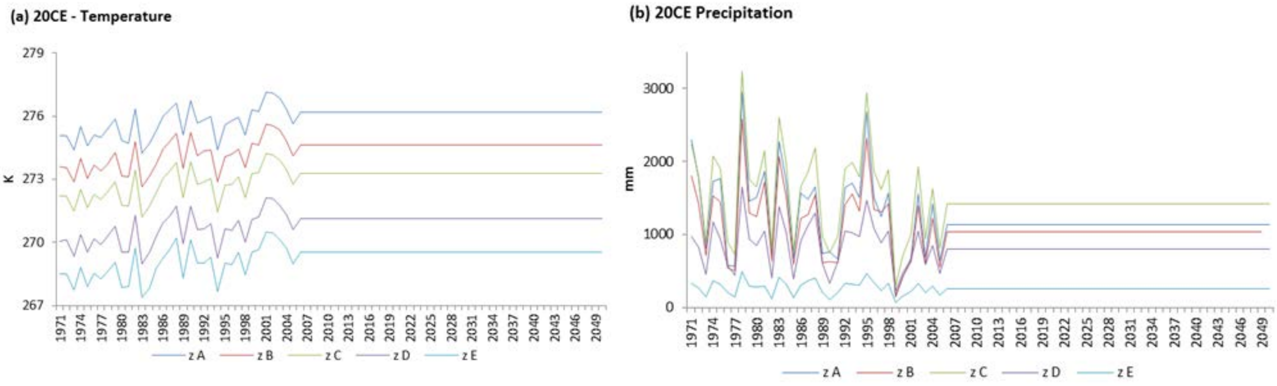


Figure 3. Gradient of variation for each climatic parameter in both scenarios 20CE and RCP4.5.

Climatic variables between zones don't follow strictly an altitudinal gradient. Temperature (T), follows the expected gradient, where zone A has the highest temperature during whole period of simulation; as well as wind speed (V) follows the expected gradient with high velocities in the top of the mountain, remembering that MountainPOP only takes into account a dairy wind direction, always from top to the bottom of the Valtellina Mountain. Precipitation is highest in zone C and lowest in zone A, as well spatial dimensions of the water stream (Adda River) are greatest for zone C. This is in agreement with precipitation trend that is the main parameter that drives the behaviour of water stream compartment.

6.4.2. 20CE scenario

20CE scenario is the present scenario. It is constructed in two parts: the first is the base line from 1971 to 2005 and the second part made with monthly averages, using the period 1995 to 2005 for calculate the averages. Figure SM2.2 presents the 20CE scenario for each zone of Valtellina Mountain.



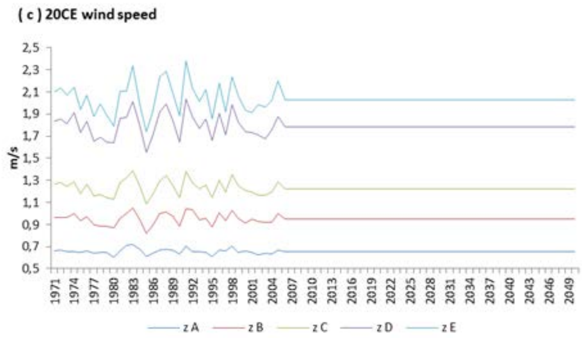


Figure SM4. 20CE scenario. Temperature (K); Precipitation (mm) and Wind Speed (m/s) used for each mountainous zone. Values are presented as annual averages.

6.4.3. RCP 4.5 scenario

Based on RCP4.5 projections **(Meinshausen et al., 2011)**, is composed in two parts: first part called historical trend from 1971 to 2005 and second part with values from climate modelling from **(Bucchignani et al., 2011)**. Figure SM2.3 presents the climatic projection for each Valtellina mountainous zones.

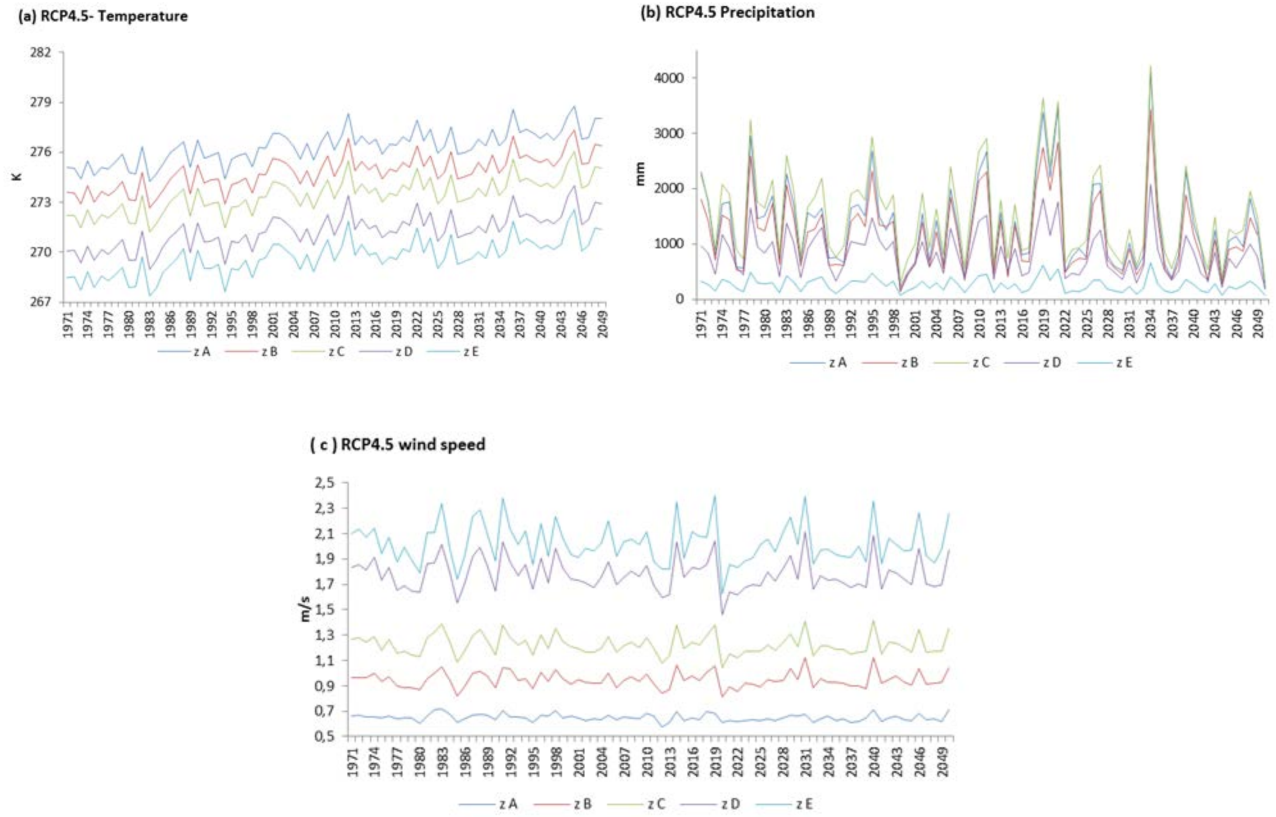


Figure SM5. RCP4.5 scenario. Temperature (K); Precipitation (mm) and Wind Speed (m/s) used for each mountainous zone. Values are presented as annual averages.

6.5. Emission scenarios

6.5.1.HCB

The construction of HCB emissions' projection was constructed based on data published by (Gusev et al., 2009; Denier van der Gon et al., 2007; Pacyna et al., 2003).

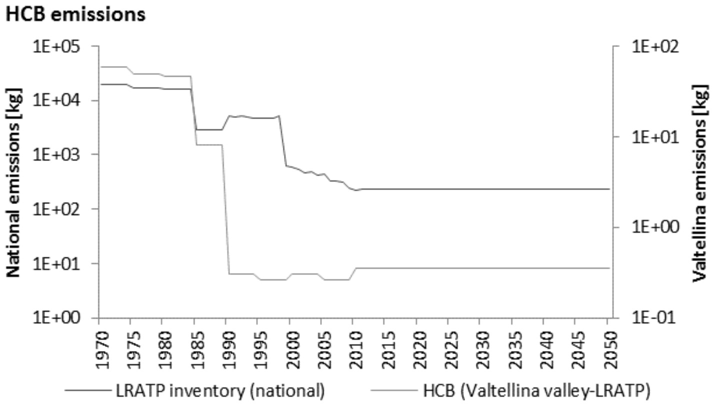


Figure SM6. HCB emissions' projection for Valtellina Mountain.

6.6. Inflow concentrations

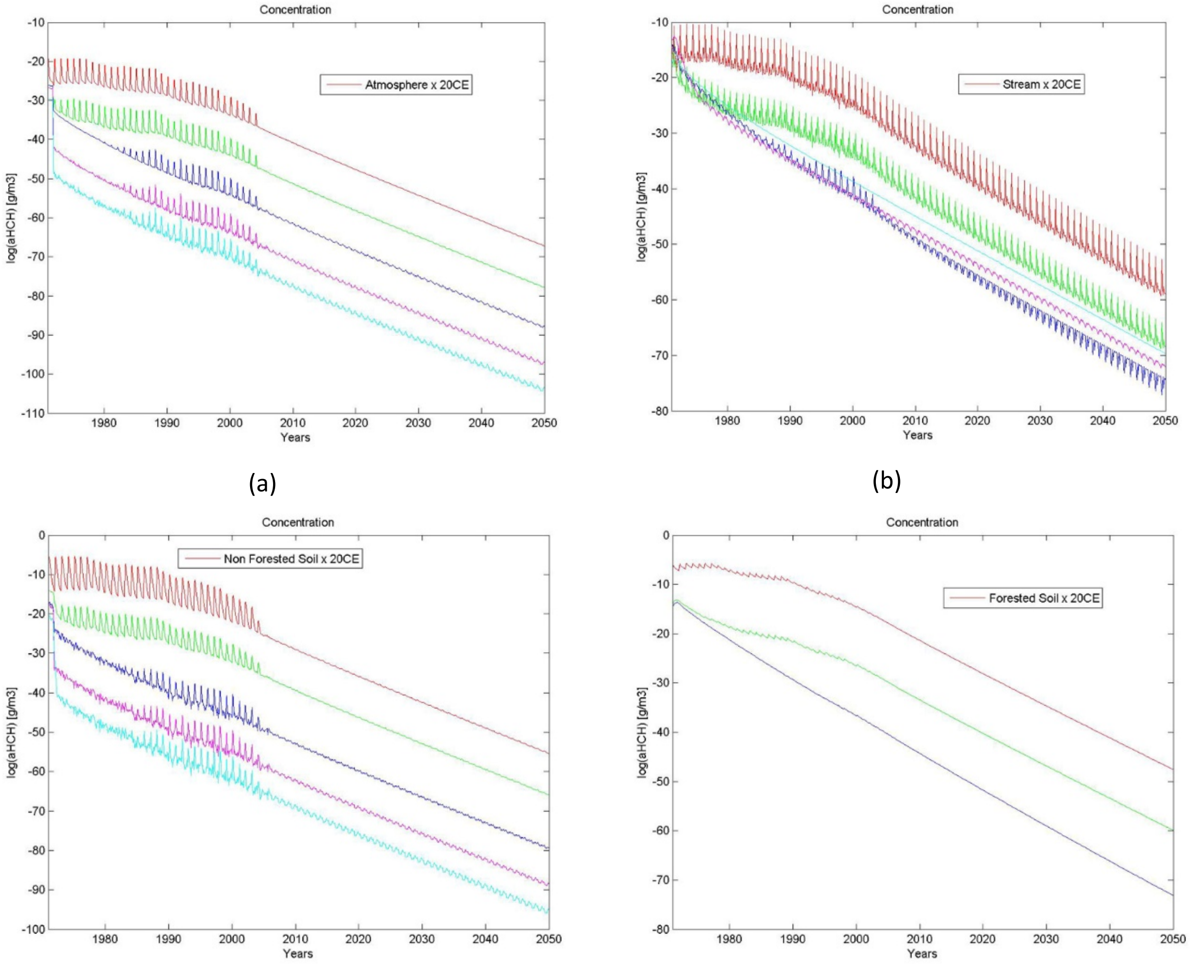
6.6.1. HCB

Table SM5 Publications references with values of HCB concentrations in different environmental compartments that were used to construct the baseline of HCB inflow concentration.

Author, Year	Monitoring place	Monitoring date	Environmental matrix	HCB	Measurement units
(Leoni and D'Arca, 1976)	Italy, Po river	1969	water stream	0,6 - 1,7	ng/L
(Greve, 1972)	Germany, Rhine river	1969 - 1972	water stream	0,01 - 0,52	µg/L
(Barber et al., 2005)	Canada	1986	ocean water	9 - 19	pg/L
(Kannan et al., 1992)	Baltic Sea	1971 - 1980	organisms	0,37 - 290	µg/g
(Kannan et al., 1992)	Baltic Sea	1981 - 1989	organisms	0,26	µg/g
(Billings and Bidleman, 1983)	USA	1977	air	0,18 - 0,29	ng/m^3
(Popp et al., 2000)	Germany	1998	air	51,6 - 123	pg/Nm3
(Jaward et al., 2004)	Italy	2002	bulk air	2,68 - 240	ng/sample
(Barber et al., 2005)	North Atlantic	2004	air	40	pg/m^3
(Shunthirasingham et al., 2013)	Switzerland	2010	air	102	pg/m^3
(Leoni and D'Arca, 1976)	Italy, Rome	1971 - 1972	soil	0,04	ppm
(Glooschenko et al., 1981)	Canada	1976	sediment	1,3 - 15,5	ng/kg
(Meijer et al., 2003)	Switzerland	1998	forested soil	680 (10 - 5210)	pg/g dw

6.7. Chemicals' fate projections

Concentrations of alpha HCH (Figure SM7) and HCB (Figure SM8) in Valtellina Mountain atmosphere, soil and water stream under 20CE scenario.

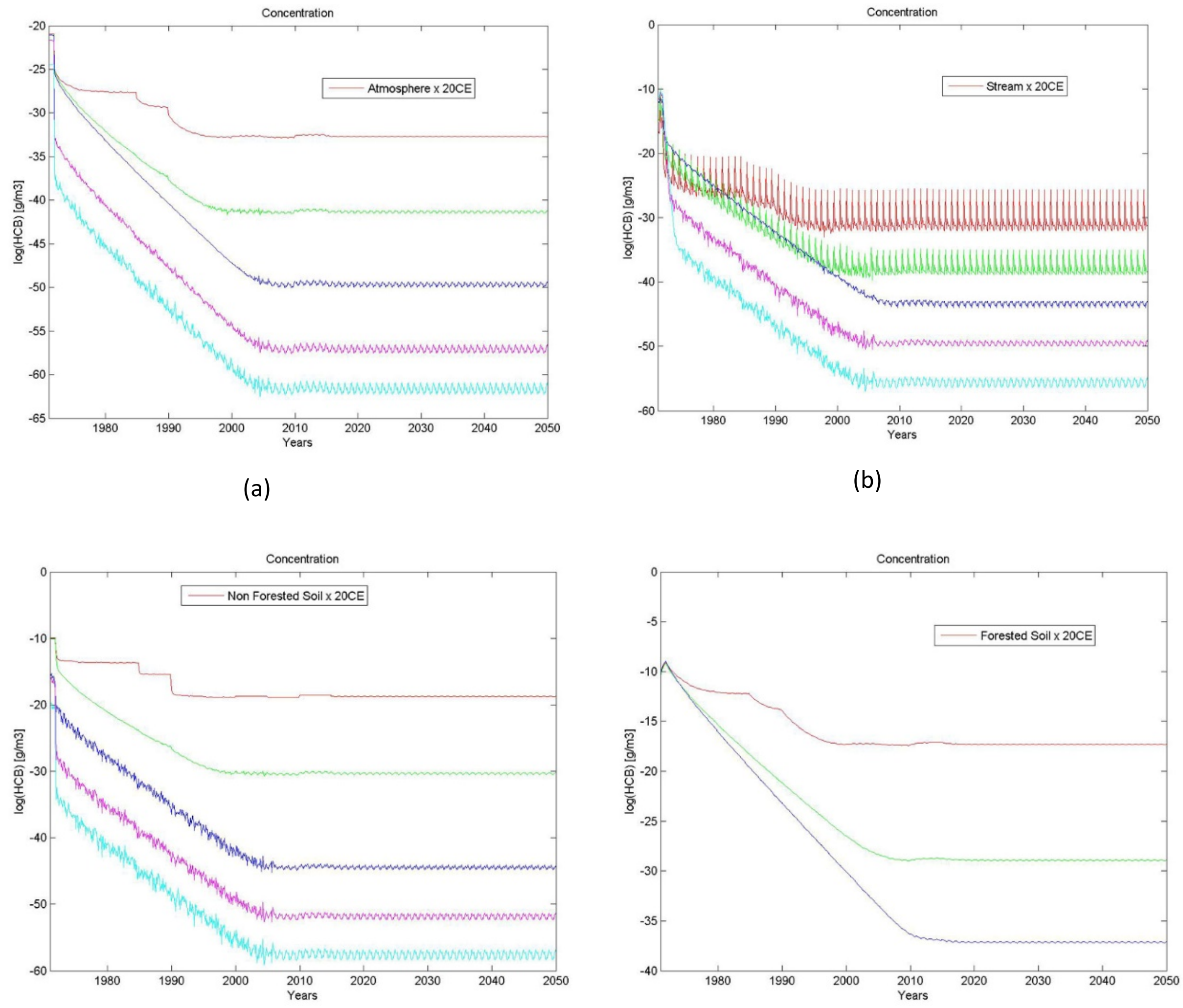


(a) (b)

(c) (d)

Notes. alpha HCH concentrations presented for each zone (A in red, B in green, C in blue, D in magenta, E in cyan)) in each compartment, (a) atmosphere; (b) water stream; (c) non-forested soil and (d) forested soil. Values are showing in log (10).

Figure SM7. 20CE scenario for alpha HCH in Valtellina Mountain for the period 1971 – 2050.



(a) (b)

(c) (d)

Notes. HCB concentrations presented for each zone (A in red, B in green, C in blue, D in magenta, E in cyan)) in each compartment, (a) atmosphere; (b) water stream; (c) non-forested soil and (d) forested soil. Values are showing in log (10).

Figure SM8. 20CE scenario for HCB in Valtellina Mountain for the period 1971 – 2050.

6.8. Uncertainty Analysis

Monte Carlo analysis gives support in the uncertainty analysis by identifying input parameters that most significantly contribute to overall model uncertainty (Lamon et al., 2009a; MacLeod et al., 2002; Slob, 1994).

6.8.1. Background

As MacLeod et al (2002) pointed out, Monte Carlo analysis is a technique for exhaustively simulating dynamic models through the application of stochastic generated values of the model inputs following a probabilistic distribution, in order to identify which ones most significantly affect the key outputs of the model. With Monte Carlo analysis is possible to accurately quantify the values (and associated uncertainties) of input variables that most strongly influence the model's predictions, and to test and set up scenarios that increase the model accuracy.

This technique is attractive because it is general and is unconstrained by the type of model that can be analysed or the selection of input distributions (Slob, 1994).

Monte Carlo analysis is characterized by:

1. It tends to be data intensive,
2. Requires the parameterization of the degree of uncertainty and
3. The shape of the input distributions appropriate to each individual input parameter for the specific conditions under examination.

6.8.1.1. Estimation of input parameter uncertainty

As discussed by Slob (1994), in cases in which uncertainty of the inputs of the model are estimated based on expert judgment, the choice of a log-normal distribution to describe uncertainty is both warranted and advantageous. The log-normal distribution can be better interpreted with the confidence factor (Cf) (MacLeod et al., 2002). A confidence factor of, e.g., 3 implies that 95% of all values in the distribution lie between 1/3 and 3 times the median, i.e., it defines the extent to which X might deviate from the median (μ) (MacLeod et al., 2002).

$$probability\left\{\frac{\mu}{Cf} < X < Cf * \mu\right\} = 0.95 \qquad (1)$$

The relationships between Cf and σ (variance) of a log-normal distribution are

$$\sigma = \frac{1}{2}\ln Cf \qquad Cf = e^{2\sigma} \qquad (2)$$

Table SM6.1 shows input confidence factors assumed for chemical properties and emission parameters in MountainPOP3.0 model (Wania and Westgate, 2008; Westgate and Wania, 2013). The confidence factors shown in Tables SM6.1 were used for the MountainPOP3.0 simulations using alpha-HCH and HBC in Valtellina Valley.

Table SM6. Medians (μ) and confidence factors (Cf) for selected input parameters (Westgate and Wania, 2013).

Variable Name	μ	Cf	Reference
Chemical property			
log Koa	7,46	1,1	(1)
log Kow	3,94	1,1	(1)
log Kaw	3,52	1,1	(1)
Environmental parameter			
air to water MTC (m/h)	5	3	(2)
water to Air MTC (m/h)	0,0875	3	(2)
rain scavenging ratio	10000	2	(2)
volume fraction of aerosols in air	10	3	(2)
air soil dry deposition velocity	2,00E-11	2	(2)
air -soil (water phase) MTC (m/h)	0,00001	3	(2)
air -soil (particle sorbed phase) MTC (m/h)	0,000001	3	(2)
air -soil (air phase) MTC (m/h)	0,02	3	(2)
Volume fraction of OC on aerosol	0,1	3	(4)
alpha-HCH half- life in soil (h)	14000	3	(2)
Fraction of non-forested soil solids which are organic matter (A)	0,160428	3	(2)
Fraction of forested soil solids which are organic matter (A)	0,45	3	(2)
Fraction of non-forested soil solids which are organic matter (B)	0,160428	3	(2)
Fraction of forested soil solids which are organic matter (B)	0,45	3	(2)
Fraction of non-forested soil solids which are organic matter (C)	0,003756	3	(2)
Fraction of forested soil solids which are organic matter (C)	0,45	3	(2)
Fraction of non-forested soil solids which are organic matter (D)	0,003756	3	(2)
Fraction of forested soil solids which are organic matter (D)	0,45	3	(2, 3)
Fraction of non-forested soil solids which are organic matter (E)	0,000568	3	(2)
Landscape parameter			
Fraction of forested soil solids which are organic matter (E)	0,45	3	(2)
Zone A surface area (km^2)	796,17668	1	(2)
Zone B surface area (km^2)	702,63465	1	(2)
Zone C surface area (km^2)	689,90545	1	(2)
Zone D surface area (km^2)	371,16738	1	(2)
Zone E surface area (km^2)	20,53676	1	(2)
Surface area of water compartment (A) (km^2)	1,6869501	1	(4)
Surface area of water compartment (B) (km^2)	0,3772552	1	(4)
Surface area of water compartment (C) (km^2)	0,1522878	1	(4)
Surface area of water compartment (D) (km^2)	0,0934303	1	(4)
Surface area of water compartment (E) (km^2)	0,2647984	1	(4)
Depth of soil (A) (km)	0,135	1	(4)
Depth of soil (B) (km)	0,135	1	(4)
Depth of soil (C) (km)	0,1	1	(4)
Forest soil area (D) (km^2)	0	1	(4)
Depth of soil (D) (km)	0,1	1	(4)
Forest soil area (E) (km^2)	0	1	(4)
Depth of soil (E) (km)	0,02	1	(4)

(1) (Lamon et al., 2012); (2) (MacLeod et al., 2002); (3) (Wania, 2006); (4) (Meyer et al., 2005)

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Estratto per riassunto della tesi di dottorato

Studente: Tair Dolores Teran Guerrero matricola: 955838
Dottorato: Scienza e gestione dei cambiamenti climatici
Ciclo: 26
Titolo della tesi: **Emissions of anthropogenic pollutants and their environmental concentrations in Alpine areas: Trends under Climate Change assumptions**

Abstract: Evidence of climate change has been observed at both the global and local scales. The climate variables considered in this study include temperature, ice extensions, widespread changes and quantities of precipitation, ocean salinity, wind speed and incidents of extreme weather including droughts, heavy precipitation, heat waves and intensity of tropical cyclones.

These climate variables influence the status of the ecosystem and this may negatively influence the ecosystem services that benefit human beings obtain, such as water storage, groundwater recharge, storm protection, flood mitigation, shoreline stabilisation, erosion control and retention of carbon, nutrients, sediments and pollutants, affect human systems.

In this context, this Ph.D. Thesis aims at contributing to the assessment of the impacts of climate change in influencing anthropogenic pollutants' concentration, in particular persistent organic pollutants (POPs), in high-altitude regions, in order to identify how the atmospheric conditions due to climate change may affect the environmental concentrations of the selected pollutants.

First, we presented an exhaustive and critical review regarding the effects of climate change over the POPs' regulation efforts and monitoring programs driven towards decreasing or banning POPs' emissions in the environment.

Second, it was possible to collect relevant environmental data in an online database with chemical information useful for the subsequent application of a multimedia fugacity model named MountainPOP3.0 for the fate and transport of organic pollutants, with the aim of assessing the effect of climate change on POPs' environmental distribution in Alpine environments.

Giving the available data, the case study selected was the mountainous region of the high valley of Adda River (Valtellina) in the Northern Italian Alps, while the considered pollutants were HCB and α-HCH. We carried out a number of dynamic simulations considering two different scenarios, a current scenario (20CE) and a future one (RCP4.5). We performed a comparative analysis of the results of the simulations, as a tool for identifying the effects of climate change over the environmental behaviour of POPs.

Estratto: Evidenze dei cambiamenti climatici sul comportamento ambientale dei contaminanti organici persistenti sono stati osservati sia a scala globale che locale. Variabili climatiche considerate in questi studi includono temperatura, estensione dei ghiacciai, cambiamenti diffusi nel modello e quantità delle precipitazioni, della salinità degli oceani, dei venti e gli eventi meteorologici estremi compresi siccità, forti precipitazioni, ondate di calore e l'intensità dei cicloni tropicali.

Le variabili climatiche influenzano quindi lo stato dell'ambiente e questo può influenzare negativamente la fruibilità da parte dell’uomo, come lo stoccaggio di acqua, ricarico delle falde acquifere, protezione della tempesta, mitigazione delle alluvioni, la tutela dei litorali, il controllo dell'erosione e lo stoccaggio di carbonio, ecc.

In questo contesto, questa tesi di dottorato si propone di contribuire alla valutazione degli impatti dei cambiamenti climatici che influenziano le concentrazione degli inquinanti di origine antropica, in particolare gli inquinanti organici persistenti (POP), nelle regioni ad alta quota, al fine di individuare come il cambiamento climatico possa influenzare le concentrazioni ambientali di contaminanti selezionati. Innanzitutto viene presentata una relazione esaustiva e critica per quanto riguarda gli effetti dei cambiamenti climatici sui monitoraggi dei POP attraverso la riduzione o la messa in bando delle emissioni dei POP nell'ambiente. In secondo luogo è stato possibile raccogliere dati ambientali rilevanti in un database online con informazioni chimiche utili per la successiva applicazione del modello di fugacità MountainPOP3.0 per il trasporto e destino degli inquinanti organici al fine di valutare gli effetti dei cambiamenti climatici sulla distribuzione ambientale dei POP in ambienti alpini. In base alla disponibilità di dati il caso di studio individuato è l’alta valle del fiume Adda (Valtellina), i contaminanti considerati sono HCB ed α-HCH. Sono state fatte diverse simulazioni dinamiche considerando due diversi scenari climatici, uno presente (20CE) ed uno futuro (RCP4.5) e i risultati sono stati confrontati come indicatore dell’effetto climatico sul comportamento ambientale dei POP.

Firma della studentessa