Review of the manuscript ACP-2014-867

L. Zhang (Editor) Comments

This published ACPD version has been revised significantly based on the comments received from the first round quick reviews. While one reviewer posted more comments on this ACPD version, another review chose not to provide further comments. I have a few minor points for the authors to consider in the final version of this paper.

Reviewer comment. P3417, L23. Using "high solubility" instead of "low Henry's law constant" may be more straightforward. This is because different units are used in literature for Henry's law constant, and in some literature where a different unit is used than the one referred here, high H is equivalent to high solubility. In the main body of this paper where Henry's law constant is first used, the unit needs to be provided and a statement that "low H generally means high solubility" is preferred.

Response. We usually prefer to work with H because when referring to organic compounds, which show low solubility in water, speaking about high solubility may be confounding. H is more precise in the context of atmospheric deposition because it defines the capability of the compound to be deposited by wet and dry deposition as well as by air-water exchange. H takes into account two physical-chemical properties, volatility and solubility, that are both important in the atmospheric deposition of POPs. For example, pp'-DDT has a relatively low H (1.1 Pa m^3/mol) similar to α-HCH (0.741 Pa m^3/mol), but the water solubility of the two compounds is very different (0.149 mg/L for DDT and 96.85 mg/L for α-HCH).

In the revised version of the manuscript, we have provided the units of the H the first time that it appears (Page 7, Line 13)

Reviewer comment. P3418, L23. Some species have short lifetime, but can reemit from the surface after deposition and are then transported further down the wind (the so-called grass-hopper effect). Is this mechanism considered in this study?

Response. Actually the occurrence of the grasshopper effect has been confirmed and constitutes the base of our studies in high mountain areas (see for example: Grimalt et al 2001, ES&T, 35, 2690-2697, Arellano et al 2011, ES&T, 45, 9268-9675, among others). In our bulk atmospheric deposition devices, samples remained in the collectors during 15 or 30 days. In these conditions we assume that what was measured was the net amount of each compound that would be really deposited in these ecosystems during the considered sampling period, therefore, the influence of the grasshopper effect would be already included in our data.

Reviewer comment. P3420, L24. In general, bulk deposition collectors only collect a portion of dry deposition besides colleting all of the wet deposition. The magnitude of this collected dry deposition portion depends on species gas-particle partitioning, among many other factors (solubility, meteorological conditions, materials used in the collectors). Can the authors provide a brief discussion on how much portion the dry deposition was collected (should be species dependent)? Such information might be important, because in reality, dry deposition contributes more than wet deposition on annual basis for many pops (this is especially the case in non-snow season over vegetated surfaces).

Response. It is difficult to estimate the proportion of dry deposition collected by our bulk atmospheric deposition sampler. In initial experiments performed in 1997 in Redòn, we compared the efficiency of collection of our bulk deposition sampler with another sampler prepared for collecting dry and wet deposition separately. Focusing on the particle amounts, in some occasions the efficiency of the bulk deposition collector encompassed between 30 % and 50 % of the particles collected in the dry+wet deposition sampler, but in other cases the particle fluxes measured in the bulk atmospheric deposition samples were higher than those measured in the dry + wet samples.

Despite its limitations, bulk atmospheric deposition is considered a good approach to estimate total deposition of organic compounds. In the context of our study, it is not so clear that dry deposition contributes more than wet deposition (on annual basis) to the deposition of the studied compounds. It has to be taken into account that our sampling sites are located in remote mountain areas situated above the tree line, with low vegetation (catchment areas constituted basically by bare rock). Furthermore, they receive significant amounts of precipitation in form of snow and rain (more than in low altitude sites).

Reviewer comment. P3423, L16-22. Are these concentrations referred to ambient air concentrations? For all classes of POS, deposition and air concentration need to be discussed together to better explain the trends and patterns.

Response. No, they aren't. We have not measured air concentrations in this study. These are deposition fluxes calculated from concentrations measured in deposition samples. As it is explained in P3423, L3-6, atmospheric deposition fluxes (ng m^{-2} mo^{-1}) were calculated by multiplying the OC concentrations (ng L^{-1}) measured in each sample by the collected volume and dividing by the surface area of the collection funnel and the sampling time, around one month for most of the samples.

Reviewer comment. PP3425, L4. Also see a more recent and quantified study of snow scavenging (Zhang et al., 2015, ACP 15, 1421-1434)

Response. Thanks for informing us about the work by Zhang *et al*, from which we were not aware when submitting this manuscript. This work deals with different organic compounds than those considered in our study but confirms that snow is more efficient than rain for organic pollutants scavenging from the atmosphere. This reference has been added to the revised manuscript.

Referee 2.

Comments on “Increasing and decreasing trends of the atmospheric deposition of organochlorine compounds in remote areas” (ACP-2014-867) by Arellano et al.

This paper is a follow-up of authors’ another paper on PBDE deposition published on the same journal in 2014. The manuscript presents monitored POPs atmospheric deposition to several mountain areas across Europe. Authors investigated connections between spatial and temporal patterns of bulk deposition and environmental factors and elucidated potential mechanisms contributing to changes in deposition fluxes at different mountain sites where samplings were taken.

Reviewer comment. The title of the manuscript appears not really consistent with the major objectives of this paper.

Response. Although other results are discussed in this manuscript, we think that the most relevant outcomes of this study are the temporal trends observed in atmospheric deposition of OC in high mountain regions, and the fact that these trends are compound-dependent, with some compounds showing increasing concentrations, while other showed the opposite. This main result has been emphasized even more in the revised version published in ACP Discussions.

Reviewer comment. With limited ambient data collected by authors one cannot expect any statistical significant trend to be detected.

Response. Our results are statistically significant. Temperature, precipitation and total deposited particles have been described as the main factors governing POP deposition in previous studies. These parameters have been measured in the present study in all four sampling sites. Another main source of information for the understanding of the origin of the POPs deposited in remote sites are backwards air mass trajectories and these have been measured every two days during the whole sampling period (2 years in Gossenkölle, Redon and Skalnate Pleso and 2.8 years in Lochnagar). In each case, these measurements encompassed the reconstruction of the backwards air mass trajectories for the last 3 days at intervals of 6 hours using 12 end-points (longitude, latitude and altitude). These backwards air mass trajectories were representative of the air masses above the sampling sites. A total of 1900 air mass retrotrajectories were calculated which involved a considerable effort of computing and man-power. Concerning field work, one different team of sampling and field analysis had to be devoted to each of the sites. The conclusions of this study are based on the largest sampling and analytical effort ever performed in remote sites for the study of POPs considering the spatial coverage and the period of study. The work followed strict quality standards and it has provided reliable and statistically significant results for the evolution of POP deposition in Europe.

Reviewer comment. Some technique details of this paper relays to some extent on their previous paper on ACP, e.g., bulk atmospheric deposition sampler. Authors should state clearly that they collected wet and dry deposition flux.

Response. Yes, most of the technical details are given in our previous paper; however, in the present paper we included all fundamental details for the present study. For example, it is

mentioned throughout the manuscript that we analyzed bulk atmospheric deposition samples, which implies dry+wet deposition. This is clearly stated now in section 2.2 Sampling.

Reviewer comment. Air mass trajectories were also presented in their last ACP paper but only for the sampling period of 2004 through 2007. Present study also assessed POPs deposition fluxes for another two periods of time from 1997-98 and 2001-02. Are those backward trajectories collected in 2004-07 applied also in these two periods of time?

Response. No, the air mass trajectories discussed in this manuscript correspond only to those calculated for the time period between 2004 and 2007.

Reviewer comment. For instance, the strongest ENSO event over the last half century took place in 1997-98 which altered considerably the large scale wind pattern in Europe. The weak El Niño winter of 2006/2007 was unusually mild in Europe. All these would affect environmental fate and deposition of POPs in Europe.

Response. Certainly, these meteorological events could affect POP transport and deposition in Europe. However, the period chosen for sampling in our study ended in September 2006, before the weak El Niño event. In principle, this phenomenon should not have influenced our results. The strong ENSO of 1997-1998 could have influenced on the results of these previous studies that we were using for comparison. Nevertheless, this phenomenon will also have a great effect on other ambient variables like temperature and precipitation, which have also been taken into account in our temporal trend discussion. As mentioned in the text, no difference in mean annual temperature was observed between the time periods considered. In addition, the precipitation data indicate an increase in rainfall from 1997-1998 to 2001-2002 in Redon, but a decrease in 2005-2006 in this site as well as in Gossenköllesee.

Reviewer comment. Could authors explain further why HCB deposition was lowest, even lower than HCH? HCB is very stable with longest life time (aprox 2 yr) in air among those OCs investigated in this study. HCB is of higher Henry's law constant similar to PCBs and high volatility similar to a-HCH. Atmospheric level of HCB is still relatively higher as compared with PCBs and HCHs in the Northern Hemisphere (e., Hung et al 2010). Under the same meteorological conditions, the authors' result showed lower deposition with higher air concentration of HCB. This seems weird.

Response. Regarding the physical-chemical properties of HCB compared to the other OCs included in our study, we have performed a literature search to obtain comparable values among the wide range of constants published for these compounds. The main conclusion is that, in terms of volatility, HCB has a behavior equivalent to a high volatility PCB. It is more volatile than the most volatile congener considered in this study (PCB 28). This is also reflected in the H of HCB, which is the highest among the studied compounds. These two high P_L and H imply low tendency to deposit by any of the deposition mechanisms (dry deposition, wet deposition or air-water exchange), therefore the low deposition fluxes measured for this compound in our study are coherent with its physical-chemical properties.

Compound	P_L (Pa)	H (Pam^3/mol)
HCB	0.094	65
PCB 8	0.148	22.9
PCB 15	0.0575	13.49
PCB 28	0.0269	30.2
PCB 101	0.00245	24
PCB 153	6.03×10^{-4}	19.95
α-HCH	0.245	0.741
γ-HCH	0.0759	0.309

Values of HCB from Shen and Wania, 2005. Values of HCHs from Xiao et al., 2004. Values of PCBs from Li et al., 2003.

Paper from Hung et al 2010 mentioned by the reviewer (Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006) indicates an increase in the concentration of HCB in the Arctic air, which is consistent with the cold condensation theory predicting a selective accumulation of high volatility compounds like HCB in the polar areas, while moderately volatile OC would be deposited and accumulated in mountain regions. These results are also coherent with the low deposition fluxes of HCB measured in our high mountain sites.

We have added a sentence in the revised manuscript to explain the physical-chemical reasons of the observed low deposition fluxes of HCB in pag 7, line 12: "In contrast, HCB exhibited the lowest deposition, generally in the range of few ng m^{-2} mo^{-1} according to its high volatility and Henry's law constant (P_L 0.094 Pa; H 65 Pam^3 mol^{-1}, Shen and Wania, 2005), which inhibit its removal from the atmosphere by any of the deposition mechanisms (air-water exchange or dry and wet deposition)".

Reviewer comment. Section 4.2. Authors should mention what data were used to estimate correlations between OC deposition flux and meteorological variables. Are these correlations from monthly deposition fluxes and monthly averaged temperature and precipitation?

Response. We obtained monthly deposition data for OCs, hence we standardized all meteorological data to a monthly basis. This is mentioned in the header of Table 4 and 5, and in the first paragraph of the 4.2 section.

Reviewer comment. Frankly, no matter how primary emission or secondary emission dominate, these chemicals always show higher level in warm season and lower level in cold season. This is a common knowledge. So such correlation analysis does not show added values to our knowledge.

Response. We are not sure if reviewer's comment referred to all OCs or only to those showing a positive correlation with temperature in this study. In fact, we observed this seasonality for endosulfans in the four sites (the current use pesticide), while in the case of PCBs it was only found in one of the sites, indicating that there are other factors controlling the concentration of these compounds in atmospheric deposition for the studied period in these sites. These results contrast

with those found in previous studies performed in Redon and Gossenköllesee in 1996, when all compounds showed higher level in warm season than in cold season.

In this sense, there are several studies reporting this lack of seasonality, mainly in remote sites such as Finokalia (Eastern Mediterranean Sea) (Mandalakis and Stephanou 2004, ES&T, 38, 3011-3018) or even the opposite, namely negative correlation between PCB concentration in precipitation and temperature (see for example paper on PCB in atmospheric deposition over the Baltic Sea by Agrell et al, 2002, Atmospheric Environ., 36, 371-383 and references herein). In view of the differences in seasonal behavior reported in the literature for these compounds, we think that is worth to perform this correlation analysis to study which factors have a greater influence in our specific case.

Reviewer comment. Given its short half-life in air, endosulfan (pg 15, line 13) would quickly be degraded after its application in summer.

Response. We couldn't find any reference to endosulfan in pag 15, line 13 in any of the versions of our manuscript; therefore we do not know what the referee wanted to state with this comment. In any case, several studies have shown the occurrence of endosulfans in remote areas far from its production/application areas which indicate the long range transport potential of this compound despite its half-life.

Reviewer comment. Pg 3, line 21, "…with limited atmospheric transport", not sure what does this mean.

Response. This means that pesticides with low vapor pressure and short half-lives in air have limited capacity for long-range transport. This is clearly described in Hageman et al. (2006), for instance.

Reviewer comment. Without or with limited atmospheric transport, where deposited or mountain tracked POPs come from?

Response. Well, this is one of the objectives of our study which has been addressed investigating the relationship between air mass trajectories arriving at each site and OC deposition fluxes. Our results showed no correlation for PCBs, which is consistent with diffuse pollution from unspecific sources as the predominant origin of these compounds in these remote sites. In contrast, significant correlations between current-use pesticides and air masses flowing from the south were observed in Gossenköllesee, Lochnagar and Redòn. In Gossenköllesee and Lochnagar, the relationship between pesticide concentration and southern air masses was univocal reflecting the impact of regions with intensive agricultural activities, whereas in Redòn, the correlation between air masses from the south and temperature did not allow to discriminating between these two determinant factors of pesticide deposition.

Reviewer comment. A recent study by Zheng and Nizzetto et al (Environ Popll 2014, 195, 115-112) showed that soil total organic carbon dominated PCBs accumulation and distribution in mountains, not cold-trapping associated with temperature.

Response. Thanks for quoting Zheng *et al*. We were not aware of this paper when submitting our manuscript. Actually, this study confirms the influence of the cold-trapping effect in the PCB distributions in mountain slopes. Zheng *et al* describe what it has been published in several papers, that is, the influence of soil organic matter (TOC) in the distribution and accumulation of persistent

organic pollutants (POPs), with high organic carbon content soils accumulating higher amounts of POPs (see for example, Meijer et al, ES&T, 37,667-672 (2003), Ribes et al ES&T, 36, 1879-1885 (2002), among others); however, once soil organic carbon has been taken into account, it is possible to study the influence of other environmental factors such as temperature, precipitation, etc. In fact, one of the main conclusions of the paper from Zheng *et al* is the occurrence of an altitudinal gradient in TOC normalized concentrations of PCBs at increasing altitude in 16 sites out of the 20 studied (see section 3.4. Distribution along the altitudinal gradient, pag 118). Similar results were reported for other areas once the concentrations of PCBs in soils were normalized by TOC (Ribes et al., 2002). Zheng *et al* indicate that this result confirms previous evidences of orographic cold trapping in Chinese high mountains and other regions of the world. Even more, these authors reported that temperature and wet deposition were the only variables significantly correlated with PCBs enrichment trends along the slopes, which is consistent with the altitudinal cold trapping theory.

Reviewer comment. Pg 4, line 13, "POPs were determined in bulk…", deposition cannot determine POPs. POPs environmental fate was determined in bulk atmospheric deposition?.

Response. The reviewer is correct. This sentence had a problem. We determined POP concentrations. We had changed this sentence in the new version of the manuscript published in ACP discussions as: POP concentrations were determined in bulk atmospheric deposition samples collected monthly in four mountain areas distributed throughout Europe between 2004 and 2006

Reviewer comment. Pg 4, line 21-24: the third and fourth objectives have no significant difference.

Response. These objectives were already modified in the final version of the manuscript: (iii) to determine which environmental variables control the atmospheric deposition fluxes of OCs and to quantify their influence, and (iv) to identify potential source regions of these compounds in high mountain areas of Europe

Reviewer comment. Pg 7, line 20-21 and other places of the paper for air mass trajectories: see my previous comment.

Response. We have indicated here and in other paragraphs (when suitable) that the air mass trajectories discussed in the manuscript corresponded to the period from 2004 to 2007.

Reviewer comment. Pg 8, line 19-20:

Response. We do not know which the referee's comment for these lines is.

Reviewer comment. Pg 13, line 19, 'in' should be 'on'.

Response. We have modified this sentence.

Reviewer comment. Section 4.4, see my general comment.

Response. See answers above.

Reviewer comment. Pg 17, line 23, PCB138 has greater long-range transport potential.

Response. According to the physical-chemical constants PCB 138 has not greater long-range transport potential than the other PCB congeners considered in this study. We observed that this congener showed the strongest increase in 2004-2006, in comparison to the time interval sampled in 1996-1998. For a more homogeneous comparison of the total PCB congener values between different time periods, we performed some calculations excluding this congener.

Reviewer comment. Pg 18, line 22-26, these statements are speculative.

Response. We agree with the referee that these statements are speculative, since we cannot demonstrate with our data that the PCB increase is related to the additional inputs due to the melting of glaciers; however our data matches with this "glacier hypothesis" in terms of the increase of the total PCB amount as well as in terms of changes in PCB composition (higher contribution of the less volatile congeners in comparison to the PCB mixtures found in 1996-98 and 2000-2001). Several studies have showed that, in these high altitude sites of Europe, environmental compartments, namely soils, aquatic organisms, sediments and snow, are enriched in less volatile PCB congeners in relation to what is found in the atmosphere. Moreover, recent studies have demonstrated that melting glaciers in high mountain regions can act as secondary sources of POPs released to Alpine lakes (Schmid et al., Environ. Sci. Technol., 45, 203-208, 2011;Blais et al., Ambio, 30, 410-415, 2001), especially for PCBs (Bogdal et al., Environ. Sci. Technol., 44, 4063-4069, 2010). Indeed, increasing concentrations of POPs have been observed recently in sediments of Lake Oberaar, a glacier-fed lake in Switzerland (Bogdal et al., Environ. Sci. Technol., 43, 8173-8177, 2009). Hence, although speculative, we think that these statements are plausible and may explain the temporal trend observed in PCB concentrations and composition in atmospheric deposition samples; however, this paragraph has been modified to clearly state that this is a hypothesis.

Reviewer comment. Figure 1, add more detailed information in figure captions.

Response. In the final version of the manuscript published in the ACP discussions we had changed Figure 1's caption by: Mean percentage contribution of PCB congeners considering all deposition samples (total) and for each study site.

Reviewer comment. Figure 4, define upper and lower panel as fig. 4a and 4b.

Response. Again, this was already done in the final version of the manuscript.

Increasing and decreasing trends of the atmospheric deposition of organochlorine compounds in European remote areas during the last decade

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Abstract

Bulk atmospheric deposition samples were collected between 2004 and 2007 at four high altitude European sites encompassing east (Skalnaté pleso), west (Lochnagar), central (Gossenköllesee) and south (Redòn) regions, and analysed for legacy and current-use organochlorine compounds (OCs), Polychlorobiphenyls (PCBs) generally showed the highest deposition fluxes in the four sites, between 112 ng m^{-2} mo^{-1} and 488 ng m^{-2} mo^{-1}, and hexachlorobenzene (HCB) the lowest, a few ng m^{-2} mo^{-1}. Among pesticides, endosulfans were found at higher deposition fluxes (11-177 ng m^{-2} mo^{-1}) than hexachlorocyclohexanes (HCHs) (17-66 ng m^{-2} mo^{-1}) in all sites except Lochnagar that was characterized by very low fluxes of this insecticide.

Comparison of the present measurements with previous determinations in Redòn (1997-1998 and 2001-2002) and Gossenköllesee (1996-1998) provided for the first time an assessment of the long-term temporal trends in OC atmospheric deposition in the European background areas. PCBs showed increasing deposition trends while HCB deposition fluxes remained nearly constant. Reemission of PCBs from soils or as consequence of glacier melting and subsequent precipitation and trapping of the volatilized compounds may explain the observed PCB trends. This process does not occur for HCB due to its high volatility which keeps most of this pollutant in the gas phase.

A significant decline of pesticide deposition was observed during this studied decade (1996-2006) which is consistent with the restriction in the use of these compounds in most of the European countries. In any case, degassing of HCHs or endosulfans from ice melting to the atmosphere should be limited because of the low Henry's law constants of these compounds that will retain them dissolved in the melted water.

Investigation of the relationship between air mass trajectories arriving at each site and OC deposition fluxes showed no correlation for PCBs, which is consistent with diffuse pollution from unspecific sources as the predominant origin of these compounds in these remote sites. In contrast, significant correlations between current-use pesticides and air masses flowing from the south were observed in Gossenköllesee, Lochnagar and Redòn. In the case of Redòn, the higher proportion of air masses from the south occurred in parallel to higher temperatures, which did not allow to discriminating between these two determinant factors of pesticide deposition. However, in Gossenköllesee and Lochnagar, the relationship between pesticide concentration and southern air masses was univocal reflecting the impact of regions with intensive agricultural activities.

1 Introduction

The persistent organic pollutants (POPs) encompass a group of organic compounds, such as polychlorobiphenyls (PCBs), hexachlorobenzene (HCB) and others that were banned in many countries during the 1970s and the 1980s because of their persistence, toxicity, long-range transport potential and food-web bioaccumulation (UNEP, 2001).

Anthropogenic activities are very limited in high mountain regions which therefore constitute the most pristine ecosystems in the continents. However, there is evidence that even these areas receive impacts of long-range atmospheric transported pollutants such as POPs (Blais et al., 1998; Wang et al., 2009; Estellano et al., 2008; Fernández and Grimalt, 2003; Fernández et al., 1999; Daly and Wania, 2005). As observed in the polar regions (Cabrerizo et al., 2012; Halsall, 2004), field studies in Europe (Grimalt et al., 2001), Western Canada (Davidson et al., 2003), South America (Grimalt et al., 2004a; Pozo et al., 2007) and the Tibetan Plateau (Liu et al., 2010) among others, have shown that mountains can act as cold-traps for POPs or even organic compounds with limited atmospheric transport, e.g. currently used pesticides (Hageman et al., 2006). These previous studies have documented the overall accumulation process but the mechanisms by which these compounds are transported through the atmosphere and accumulate in these environments are largely unknown.

Atmospheric deposition is the main pathway by which POPs are incorporated into pristine regions (Carrera et al., 2002; Fernández et al., 2003). Unfortunately, there are substantial gaps of knowledge concerning the specific transfer mechanisms occurring at these sites, such as the influence of the physical-chemical properties of the trapped compounds and the environmental factors that are relevant for the overall deposition efficiencies.

These aspects are relevant in the context of the regulatory measures for POP synthesis and use that have led to declines in the concentrations of these compounds in several environments (Brun et al., 2008; Holoubek et al., 2007). As atmospheric concentrations of POPs decrease following restrictions on their emissions from primary sources, revolatilization from terrestrial surfaces of previously deposited pollutants, e.g. secondary sources, becomes an important component of their global environmental cycling (Nizzetto et al., 2010; Li et al., 2010). These processes may be particularly significant in remote cold regions, since POPs accumulated in soils and snow/ice surfaces of these areas in the past (Grimalt et al., 2001; 2004b; 2009; Guazzoni et al., 2011). Indeed, recent studies have provided evidence that revolatilization has already begun in polar (Ma et al., 2011; Wong et al., 2011) and Alpine regions (Bogdal et al., 2009).

Full understanding of these aspects is important because the remote mountain regions are the areas of most pristine freshwater formation. The pollutants incorporated in the waters of these ecosystems define a quality ceiling from which water properties will decrease upon transport to lower altitudes, e.g. as consequence of the incorporation of more pollutants.

In order to gain insight into these questions, POP concentrations were determined in bulk atmospheric deposition samples collected monthly in four mountain areas distributed throughout Europe between 2004 and 2006. The sampling sites encompassed the south (Pyrenees), central (Alps), east (Tatras), and west Europe (Grampians). In each site, every 2 days during the sampling period, backwards air mass trajectories were calculated to reconstruct the last 72 h air mass locations at 6 h intervals (Arellano et al., 2014).

The POPs analyzed included both legacy, PCBs, HCB and hexachlorocyclohexanes (HCHs), and current-use compounds, endosulfans. The specific objectives of this study are: (i) to determine the current levels of organochlorine compounds (OCs) in bulk deposition samples from remote areas of Europe representing different climatic regions; (ii) to investigate seasonal, spatial and temporal trends in the atmospheric deposition of OCs in these areas; (iii) to determine which environmental variables control the atmospheric deposition fluxes of OCs and to quantify their influence, and (iv) to identify potential source regions of these compounds in high mountain areas of Europe.

2 Materials and methods

2.1 Chemicals

Isooctane, n-hexane, dichloromethane, cyclohexane, methanol and acetone were for trace analysis, (Merck; Darmstadt, Germany). Anhydrous sodium sulfate (analytical-reagent grade, Merck) and aluminium oxide were cleaned by Soxhlet extraction with dichloromethane:hexane (1:1, v/v, 24 h) and before use they were activated by overnight heating at 450ºC and 120ºC, respectively.

Glass fiber filters (47 mm diameter, 1 mm, GF/B, Whatman, Maidstone, UK) were kiln-fired at 400ºC for 12 h, weighted and wrapped into aluminium foil until use. Empore C_{18} extraction disks (47 mm diameter, 0.5 mm thickness) were from 3M Co. (St Paul, MN, USA).

PCB 142 (internal standard), PCB 30 and PCB 209 (recovery standards) and a standard solution of HCHs, PCBs, HCB and endosulfans were purchased from Dr. Ehrenstorfer (Ausburg, Germany).

2.2 Sampling

Bulk (dry and wet) atmospheric deposition samples were regularly collected at the four remote high mountain areas selected for study (Table 1) over different time periods: monthly (one sample for the whole month deposition) from 2004 to 2006 in Gossenköllesee, Lake Redòn , and Skalnaté pleso and biweekly (one sample for the whole two weeks deposition) from 2004 to 2007 in Lochnagar. Further information concerning sampling devices and conditions is reported in Arellano et al. (2014).

Samples were filtered on site using pre-weighed glass fiber filters. The filtrates were solid-phase-extracted with C_{18} disks as described in Carrera et al (1998). After sample removal, the bulk collectors were rinsed with Milli-Q water which was filtered, solid-phase-extracted, and the extracts combined with those of the corresponding atmospheric deposition sample. Glass fiber filters and disks were wrapped in aluminium foil and transported frozen to the laboratory. Meteorological parameters, namely air temperature and precipitation were provided by automatic weather stations (AWS) located at each site.

2.3 Extraction and clean-up

Glass-fiber filters were freeze-dried and weighed for measuring total particle content in bulk atmospheric deposition samples. OCs were extracted from the filters by sonication with dichloromethane:methanol (2:1) (3 x 10 mL, 20 min each). Pollutants adsorbed in the C_{18} disks were eluted sequentially with methanol, cyclohexane and dichloromethane (Carrera et al., 1998). Both filter extracts and C_{18} disk eluates were combined and purified by column adsorption chromatography with aluminium oxide after adding a recovery standard mixture of PCB 30 and PCB 209. Prior to instrumental analysis, samples were spiked with PCB 142 as internal standard.

2.4 Instrumental analysis

PCBs, HCB and HCHs were analysed by gas chromatography with micro-electron capture detector (GC-μECD) (Agilent Technologies 6890 N). The chromatographic conditions are reported in detail elsewhere (Carrera et al., 1998). Endosulfans (α- and β- isomers and endosulfan sulfate) were analysed by gas chromatography coupled to mass spectrometry in negative ion chemical ionization (GC-MS-NICI) and selective ion recording modes (Trace DSQ

Instrument Thermo Electron). This technique was also used for structural confirmation of all OCs.

For the GC-MS-NICI determinations, extracts were injected in a HP-5MS capillary column (30 m long, 0.25 mm internal diameter and 0.25 μm film thickness). Helium was used as carrier gas (1.2 mL/min) and ammonia as reagent gas (2.5 mL/min). The oven temperature program encompassed an initial temperature of 90ºC, which was held for 1 min, followed by a first increase to 130ºC at 8ºC/min and a final ramp to 325ºC at 5ºC/min with a hold time of 10 min. Injector, transfer line and ion source temperatures were 270ºC, 280ºC and 176ºC, respectively. The ions selected for compound identification and quantitation were m/z 406 (quantification), m/z 372 and m/z 161 for α- and β- endosulfan, and m/z 386 (quantification), m/z 372 and m/z 161 for endosulfan sulfate.

This technique was also used for quantification of the other OCs when the interferences in GC-μECD did not allow their determination.

2.5 Quality control and assurance

Quantification was performed by the internal standard method. Field and procedural blanks were obtained at each sampling site and processed together with the samples. For field blanks, Milli-Q water was filtered, solid-phase adsorbed, transported and stored for subsequent analysis in parallel to real samples. In general, blank values represent less than 10% of bulk deposition sample concentrations. These values were used to determine method detection limits (MDL) that were established as the average blank value plus 3 times the standard deviation. MDL for PCBs ranged between 0.17 and 1.6 ng depending on the congener examined, 0.20 ng for HCHs, 0.04 ng for HCB, and between 0.05 and 0.10 ng for the endosulfans. Efficiency of the analytical procedure was evaluated from recoveries of the surrogate standards, which varied between 51±18 % for PCB 30 and 85±25 % for PCB 209. All reported values were recovery corrected.

3 Results

3.1 OC deposition fluxes and spatial distribution

Atmospheric deposition fluxes (ng m^{-2} mo^{-1}) were calculated by multiplying the OC concentrations (ng L^{-1}) measured in each sample by the collected volume and dividing by the surface area of the collection funnel and the sampling time, around one month for most of the

samples. In Lochnagar, where each sample corresponded to two weeks, monthly deposition was obtained by summing the values of two consecutive samples. For sampling times higher than one month, a correction factor was applied in order to normalize all values at monthly basis. The mean deposition fluxes of HCHs (α- and γ-HCH), HCB, endosulfans (α- and β-endosulfan, and endosulfan sulfate), and PCBs (sum of PCB 28, 52, 101, 118, 153, 138, and 180) to each study site are summarized in Table 2. All studied compounds were found in the four sampling sites, with detection frequencies higher than 80 %, except for PCB 28 in Redòn (detected in 65% of the samples) and α- and β-endosulfans in Lochnagar (frequency of detection 61% and 68%, respectively).

The most abundant OC pollutants in all sites were PCBs, with fluxes ranging between 112 ng $m^{-2}mo^{-1}$ (Redòn) and 488 ng m^{-2} mo^{-1} (Skalnaté). In contrast, HCB exhibited the lowest deposition, generally in the range of few ng m^{-2} mo^{-1}, which is consistent with its high volatility and Henry's law constant (P_L=0.094 Pa; H=65 Pam^3 mol^{-1}, Shen and Wania, 2005), which inhibit its removal from the atmosphere by any of the deposition mechanisms (air-water exchange or dry and wet deposition). Among pesticides, endosulfans were found at higher concentrations (11-177 ng m^{-2} mo^{-1}) than HCHs (17-66 ng m^{-2} mo^{-1}) in all sites except Lochnagar, where endosulfans were found at very low concentrations. This difference likely reflects the phasing out of HCHs in the European countries.

Skalnaté Pleso exhibited the highest deposition fluxes of all studied OCs generally followed by Lochnagar (Table 2). The lowest levels of legacy OCs (α- and γ-HCH, HCB, and PCBs) were found in Redòn. However, significant amounts of endosulfans (pesticides of current use) were observed in this site, which is in agreement with the influence of agricultural activities in the south of Europe. The higher concentrations of OCs, especially PCBs, in east Europe are consistent with the high historical use and production of these compounds in central Europe and the former Czechoslovakia until 1984 (Taniyasu et al., 2003; Holoubek et al., 2007). Similar spatial distribution of PCBs and HCHs in remote European air samples was observed elsewhere (Halse et al., 2011), with higher concentrations in east Europe and lower in the Iberian Peninsula, which was attributed to the prevailing wind regimes from west to east. Nevertheless, these authors also found low levels of these compounds in the atmosphere over the British Isles, which is not observed in the present study.

The differences between sites for the legacy compounds are low, within a factor of four at the most. The present fluxes of these compounds probably reflect emissions to the European atmosphere originating from secondary sources, e.g. soils. HCB exhibited a different spatial

pattern with similar fluxes in Lochnagar, Redòn and Gossenköllesee, and one order of magnitude higher in Skalnaté. The high volatility and atmospheric mobility of this compound has resulted in rather uniform air concentrations in remote areas (Jaward et al., 2004). In contrast, the spatial pattern observed in the present study suggests that there are emission sources of this pollutant near the Tatra Mts, likely as consequence of the production of organochlorinated solvents or application of HCB-contaminated pesticides, e.g. chlorothalonil (Hung et al., 2010).

Conversely, the endosulfans exhibit higher deposition fluxes in Redòn and Skalnaté, with differences between sites above one order of magnitude. These results are consistent with primary sources of this pesticide related to agriculture in southern and eastern Europe.

The PCB deposition fluxes found in Redòn and Gossenköllesee are in the range of those reported in remote or background sites such as the Baltic Sea, NE Atlantic, and eastern Mediterranean region (Table 3). In contrast, the higher fluxes in Lochnagar and Skalnaté are similar to those measured in urban areas of Chicago or Texas (Table 3). This unexpected result could reflect the influence of post PCB uses near these deposition sites, as described for HCB in Skalnaté. However, most of the previous studies on PCB levels in atmospheric deposition are focused on wet-only deposition, while the present work also includes dry deposition. In this sense, several authors have stated that particle scavenging was the dominant source of PCBs in rain despite the small fraction of these compounds associated to atmospheric particles (Dickhut and Gustafson, 1995; Poster and Baker, 1996). In addition, a significant fraction of the annual precipitation to these remote mountain sites is in form of snow, which has been reported to be more efficient than rain for organic pollutant scavenging from the atmosphere (Lei and Wania, 2004; Zhang et al., 2015). Both factors, contribution of dry deposition and snow scavenging efficiency may explain the relatively high deposition fluxes of PCBs found in Lochnagar and Skalnaté.

For the other studied compounds, the deposition fluxes were low, similar or even lower than the levels reported in remote regions (Table 3).

3.2 Compound Distributions

Polychlorobiphenyls. The congener distributions of these compounds were dominated by the lower molecular weight compounds with PCB 101 and PCB 52 as the most abundant congeners (Fig. 1), except in Redòn where PCB 138 predominates. This congener is also the main PCB of low volatility in all sites. The distributions are rather uniform regardless of location or season (differences not statistically significant at 95 % confidence level, ANOVA).

The congener distribution found in this study is similar to that reported in atmospheric deposition of other sites, with PCB mixtures dominated by congeners containing three to six chlorine atoms (Franz and Eisenreich, 1993; Agrell et al., 2002), but with somewhat higher contribution of less volatile PCBs than in background areas of eastern Mediterranean sea (Mandalakis and Stephanou, 2004) or in previous measurements on PCB deposition in high altitude mountain sites of Europe (Carrera et al., 2002). This shift towards more chlorinated PCB predominance could be related to emissions from mountain soils and glaciers which are likely enriched in these congeners as consequence of their selective accumulation by the cold-trap effect observed in high mountain areas from temperate latitudes (Grimalt et al., 2001; Carrera et al., 2001).

Hexachlorocyclohexanes. These insecticides were used in the past as technical mixtures, α-HCH, 60-70 % and γ-HCH, 10-15 %, with a α-HCH/γ-HCH ratio of 4-7 (Jantunen et al., 2008) or lindane, the γ-isomer (≥ 99%). Nowadays, the use of lindane ceased in the majority of the European countries (in France it was banned in 1998, in Germany in 2004) and Canada (Li and Vijgen, 2006; Becker et al., 2008).

In this study, γ-HCH was the major isomer found in the four sampling sites, representing between 66% of total HCHs (Lochnagar) and 81% (Gossenköllesee). Consequently, the α-HCH/γ-HCH ratios, 0.23-0.51, were far below the values measured in the technical HCH mixture (4-7). This result is consistent with the phasing out of technical HCH in Europe and the subsequent use of lindane. In addition, higher Henry's law constant of α-HCH than γ-HCH would enhance the predominant deposition of γ over α-isomer which will lower the ratio in relation to what is present in the atmosphere. A dominant usage of lindane has been reported in the western part of Europe, while the technical HCH tended to dominate in east Europe (Halse et al., 2011). This geographical difference is not reflected in the atmospheric deposition patterns of this study, since the α/γ-HCH ratios were consistently lower in the eastern and central European sites, Gossenköllesee and Skalnaté, than in Lochnagar and Redòn, situated in western Europe (Table 2).

Endosulfan. This is broad spectrum insecticide of global current use. USA and several countries in Europe have stopped its production which has resulted in declining concentrations in the northern hemisphere during the last years (Weber et al., 2010). Recently, May 2011, it has been included in the list of chemicals banned under the Stockholm Convention with some specific exemptions (Stockholm Convection, 2011). The endosulfan isomers in Gossenköllesee, Redòn and Skalnaté Pleso were dominated by β-endosulfan, with an α/β ratio ranging between 0.51 and 0.58. This composition contrasts with the relative proportion found in the technical mixtures,

ratios between 2 and 2.3. Several studies have reported higher concentrations of β-endosulfan in precipitation than α-endosulfan (Brun et al., 2008; Arellano et al., 2011; Sun et al., 2006b; Carrera et al., 2002) despite that concentrations in air followed the relative isomeric proportions of the commercial formulations. The lower Henry's law constant of β-endosulfan than α-endosulfan may result in the preferential deposition of the β-isomer by dry and wet deposition processes. In addition, higher concentrations of β-endosulfan have been observed in atmospheric particles (Brun et al., 2008) which may increase the concentrations of this isomer in deposition samples. In Lochnagar, endosulfan sulfate, a breakdown product of both α and β isomers, was the compound exhibiting highest values and the mean α/β ratio was higher than in the other sites, 1.3, but still lower than the values of the technical mixtures. The dominance of endosulfan sulfate is consistent with the low fluxes of the α- and β-isomers and suggests that the inputs of this insecticide arriving to this site were either from distant sources or very old spills.

4 Discussion

4.1 Influence of meteorological and atmospheric variables in the deposition fluxes of OCs

Pearson correlation coefficients of the log transformed OC deposition fluxes and particle concentration, monthly mean temperature, precipitation, and % of monthly air mass trajectories arriving at each site have been calculated. The statistically significant correlations found in each site at 95 % ($p<0.05$) and 99 % ($p<0.01$) confidence levels are reported ~~in~~ on Tables 4 and 5.

Endosulfan sulfate is the only compound found to correlate significantly with temperature in all four sites (Table 4), which results in a clear seasonal trend with higher deposition fluxes during the warm than in the cold periods (Figure 2). As mentioned in the previous section, this compound is generated by transformation of endosulfans which are widely used in agriculture. Accordingly, the positive correlation between endosulfan sulfate and temperature is reflecting the seasonal use of the precursors. Positive significant correlations of endosulfans and temperature are observed in Skalnaté and Redòn for the β-isomer and in Skalnaté and Lochnagar for the α-isomer. The seasonal pesticide trends in Skalnaté and Redòn have been related to increasing air concentrations as consequence of their field use during the warm period (Carrera et al., 2002; Brun et al., 2008; Aulagnier and Poissant, 2005; Carlsson et al., 2004). This trend is only observed for the degradation product in Gossenköllesee which may reflect significant degradation during transport to the highest altitude site among those considered in the present

study. The same cause is due to the significant correlation of γ-HCH and temperature in Redòn, Skalnaté and Lochnagar, the lack of correlation in Gossenköllesee may again be due to the high altitude of this site which dampen the inputs from the agricultural activity developed at lower altitude.

Significant temperature dependences are observed in Skalnaté for HCB and PCB 101, PCB 118 and PCB 153 (Table 4). This site is the one receiving highest deposition of these compounds (Table 2). The significant temperature dependence is probably related with emission from secondary sources reflecting past uses of these compounds (Carrera et al., 2002; Dickhut and Gustafson, 1995), e.g. influence of industrial spills from the Upper Sillesian or the black triangle industrial areas. The deposition of the PCB congeners with volatilities in the range of $3.2\ 10^{-3}$ Pa and $5.5\ 10^{-4}$ Pa in this elevated site (temperatures in the range of -9.2ºC and 9.0ºC, Table 1) suggest that the other PCB congeners are either too volatile > $3.5\ 10^{-3}$ Pa, e.g. PCB 28 and PCB 52, to show an increase in their concentration in deposition, or of insufficient volatility < $5.4\ 10^{-4}$ Pa, e.g. PCB 138 and PCB 180, to be re-emitted significantly to the atmosphere. In this sense, no relationship between PCB deposition to remote sites and temperature has been observed in the southern Mediterranean sea (Mandalakis and Stephanou, 2004), and even negative correlations have been reported between PCB deposition fluxes and temperature (Agrell et al., 2002, and references herein) which have been attributed to enhanced partitioning of these compounds to particles at low temperatures and increased scavenging efficiency of snow compared to rain.

Skalnaté is also the only site in which significant positive associations are observed between most compounds and particle deposition, e.g. α-HCH, γ-HCH, α-endosulfan, β-endosulfan, endosulfan sulfate, HCB, PCB 28, PCB 52, PCB 101, PCB 118 and PCB 153. In Redòn, there is nearly the same atmospheric deposition flux of particles (Table 1) and no association to any of these compounds is observed (Table 4). Thus, these associations are related to the high deposition fluxes of these compounds in this site (Table 2) as consequence of regional past spills of these pollutants and not to the high deposition of particles (Table 1).

Skalnaté is also the site in which atmospheric deposition of most OCs is related to wet precipitation (Table 4). The high number of significant positive correlations as consequence of the regional spills which involved high emissions from secondary sources. The effect of wet precipitation is also noticed in the correlation with atmospheric deposition of the PCB congeners of lowest volatility, e.g. PCB 180 ($1.3\ 10^{-4}$ Pa), which probably are associated to suspended particles that are carried down with rain events. These rain events are also significant in the

atmospheric deposition of Redòn and Lochnagar but not in Gossenköllesee, the highest site 2413 m (Table 1), where least rain was recorded (1722 mm, Table 1).

As already mentioned for PCBs, correlation between deposition fluxes and precipitation, temperature or particle deposition has been observed for most of the study compounds in Skalnaté. Examination of the correlation between independent variables shows interdependences, involving that 26% of the particle deposition variance and 37% of the precipitation variance are explained by temperature, which makes difficult to establish the main factor controlling OC deposition fluxes in this remote site.

Multilinear regression analysis using all independent variables (Table 5) indicate that for some PCB congeners and HCB, the factor accounting for most of the variance is precipitation (HCB, PCB 118, and PCB 180) and particle deposition (PCB 101 and PCB 153) as sole independent variables. For pesticides, the combination of precipitation and temperature for HCHs and particle deposition and temperature for endosulfans accounted for 70% and 64-80% of the variance, respectively (Table 5). Based on the standardized coefficients in multilinear regression analysis, precipitation is the main factor controlling HCH deposition fluxes to this site, whereas in the case of endosulfan isomers, both variables, temperature and particle deposition, have similar influence. Finally for endosulfan sulfate, temperature is the dominant factor.

4.2 Influence of air mass origin

Further insight into the factors determining OC deposition in these remote sites can be obtained by investigation of the relationship with the main air mass trajectories arriving at each sampling site (Arellano et al., 2014). No statistically significant correlations between PCB deposition fluxes and air mass origin in Gossenköllesee and Lochnagar have been observed (Table 6), which is consistent with a diffuse pollution from unspecific sources, likely related to secondary emissions, as the main origin of PCBs arriving to these remotes sites. In contrast, significant correlations of PCB fluxes and prevailing air masses have been observed in Redòn and Skalnaté. In Redòn, significantly higher deposition fluxes of PCB 101, PCB 118 and PCB 138 were found to be associated to air masses flowing from the west North Atlantic, while in Skalnaté a significant decrease of fluxes of some PCB congeners is found in conjunction with air masses coming from the west (Table 6). Significant correlations between these air mass trajectories and meteorological variables have also been found in both sites. Thus, in Redòn the west North Atlantic air masses are significantly associated to higher precipitation fluxes, while negative correlations between % air masses from the west and temperature or particle deposition were

observed in Skalnaté (Table 6). Given these results, the observed variations in PCB fluxes associated to certain air masses could reflect an indirect consequence of the aforementioned relationship between PCB deposition fluxes and meteorological variables. In fact, no statistical significance of the percent contribution of west air masses as independent variable was found in the multilinear regression analysis of the deposition fluxes in Skalnaté (Table 5).

Higher deposition fluxes of HCHs and endosulfans were associated to air masses coming from the south in Redòn (Table 6). In addition, a decrease in α/γ-HCH ratio was also observed related to this air mass trajectory, indicating significant contributions of lindane coming from southern Europe. However, the correlation found between temperature and % contribution of backwards air mass trajectories from the south in Redòn does not allow ruling out temperature as the main factor controlling HCH and endosulfan levels in this site.

For Gossenköllesee, statistically significant correlations were found between β-endosulfan and endosulfan sulfate and percent of air masses from the North Atlantic, involving lower concentrations at higher contribution of air masses from this origin. Conversely, positive correlations were found between total endosulfans and back-trajectories coming from the south (north Africa, Mediterranean sea and/or Iberian Peninsula) in this site as well as in Lochnagar, which is consistent with the potential emission sources of this pesticide from areas of intensive agricultural activities. In addition, back-trajectories from the central/east Europe corresponded to higher α/γ-HCH ratios in Gossenköllesee according with the prevalent use of technical HCH in eastern Europe (Halse et al., 2011) and the impact of air pollution transported from the east in this site (Kaiser, 2009).

4.3 Long-term trends of atmospheric deposition of OCs to remote sites

In addition to the data reported in the present study, OC deposition fluxes were also measured in 1996-1998 in Gossenköllesee and 1997-1998 in Redòn (Carrera et al., 2002). Moreover, OC monthly deposition samples were measured in Redòn between July 2001 and June 2002. The combination of these series provides a deposition database over one decade, which despite its discontinuities allows us to assessing the long-term temporal trends of atmospheric precipitation of these pollutants in the European background sites. As indicated above, the previous studies showed a seasonal trend in OC deposition fluxes, with higher values during warm seasons. In view of this, we have calculated mean monthly deposition fluxes for complete annual periods to avoid the influence of this seasonality when comparing between different time periods (Table 7).

Concerning the studied pesticides, HCHs and endosulfans deposition fluxes decline significantly ($p<0.001$) both in Redòn and Gossenköllesee, involving decreases of up to one order of magnitude (Table 7, Fig. 3). In previous studies, HCH deposition to Redòn and Gossenköllesee was characterized by background levels with several peak fluxes during the warm season following their application in the fields. In the present study, the HCH deposition fluxes showed more uniform values throughout the year (Fig. 3), which were consistent with inputs from diffusive pollution by re-evaporation of past usages. The declines are observed for both α- and γ-HCH, although they are more pronounced for the latter as inferred from the increase in α/γ-HCH ratios observed in both sites (Table 7). These differences between isomers can be explained by volatility differences but also by the higher environmental persistence of the α- than the γ-isomer. In this sense, the conversion of γ-HCH to α-HCH in air by photoisomerization and the lower degradation rate of α-HCH than γ-HCH by reaction with hydroxyl radicals in the gas phase have been reported (Brun et al., 2008).

Closer examination of the pesticide concentrations in Redòn indicates that the main decline in deposition started after 2001-2002, which is consistent with the general phase-out of HCHs as well as the discontinuation of endosulfan production that took place in most of the European countries between 2000 and 2004 (Weber et al., 2010; Li and Vijgen, 2006). Significant declines were also observed in α-HCH and γ-HCH concentrations in atmospheric precipitation and air from different sites in Norway, Denmark and Sweden during 1996-2009 (Torseth et al., 2012), in the Arctic atmosphere (Brun et al., 2008), and in wet deposition and air in the Czech Republic for the period 1996-2005 (Holoubek et al., 2007).

In contrast, the PCB deposition fluxes measured during 2004-2006 are higher than those found in 1996-1998 (155 and 125 ng $m^{-2}mo^{-1}$ versus 99 and 42 ng $m^{-2}mo^{-1}$, in Gossenköllesee and Redòn, respectively (Table 7)), although the differences were only statistically significant in Redòn ($p<0.05$). Similar differences have been observed in Redòn in relation to the samples taken in 2001-2002. Mean PCB deposition fluxes during this period, 110 ng $m^{-2}mo^{-1}$, were higher than the levels measured in 1997-1998, and lower (but not statistically different) than those found in 2004-2006 (Table 7).

PCB 138 is the congener showing a strongest increase in the last period measured, 2004-2006, by reference to the time interval sampled in 1996-1998 (Table 7). No interferences in the determination of this congener have been observed; however, in order to avoid the influence of an overestimation of PCB 138 concentrations in temporal trend analysis, this congener was removed from the total PCB data set. Calculation of the atmospheric deposition differences

excluding this compound also shows an increase of PCB deposition between these two time periods (Table 7). As shown in Fig. 4, the deposition increases are more pronounced in Redòn than in Gossenköllesee and for the high chlorinated PCBs than for the more volatile congeners.

Average local air temperatures show small decreases, from 0.2ºC to -1.4ºC in Gossenköllesee station, and no defined trend, 4.1ºC and 4.0ºC in Redòn, during the sampling period (Table 7). Thus, the increase in atmospheric deposition cannot be attributed to deposition by precipitation trapping of volatilized PCBs from nearby sources. Furthermore, water precipitation did not change in Redòn, from 88 to 89 mm mo^{-1}, and decreased in Gossenköllesee, from 112 to 57 mm mo^{-1} (Table 7). Precipitation changes cannot, therefore, explain the increase in PCB deposition. In fact, the precipitation decrease in Gossenköllesee may perhaps have counteracted the trend towards higher PCB deposition and for this reason the observed increases in deposition of these compounds are stronger in Redòn.

A priori, an increasing trend of PCB deposition fluxes in remote regions is not expected since the global production of these compounds strongly decreased in the 1970's and was stopped in the eighties. In fact, declines in PCB air concentrations as consequence of the ban of these compounds have been reported (Holoubek et al., 2007; Halse et al., 2011; Schuster et al., 2010). However, in remote areas such as Svalbard (Norway) and Canadian Arctic (Hung et al., 2010) increases of PCB air concentrations have been observed, being attributed to the remobilization of these compounds from Arctic reservoirs like waters, soils and snow/ice as a result of sea-ice retreat and rising temperatures induced by climate change (Ma et al., 2011). Analogously, melting of glaciers in high mountain regions have been suggested as potential secondary sources of POPs released to Alpine lakes (Schmid et al., 2011; Blais et al., 2001), especially for PCBs (Bogdal et al., 2010). Indeed, increasing concentrations of POPs have been recently observed in sediments of Lake Oberaar, a glacier-fed lake in Switzerland, and the trend was attributed to glacier melting and remobilization of ice trapped compounds (Bogdal et al., 2009). Taking into account that high European mountain regions are enriched in more chlorinated PCBs due to selective accumulation in these cold areas (Grimalt et al., 2001; 2004b; 2009), we hypothesize that reemission of these pollutants as consequence of glacier melting could be responsible of the observed higher contribution of these congeners to the atmospheric deposition samples collected in 2001-2002 and 2004-2006 with respect to those collected in 1996-1998 and the increasing concentrations observed in their long-term temporal trends.

The Henry's law constants of PCBs, 31-53 Pa m^3 mol^{-1} (Bamford et al., 2000), can explain the transfer to the atmosphere of at least a portion of the trapped congeners upon ice melting. This is

not the case of the HCHs or endosulfans whose Henry's law constants, 0.74, 0.31 and 0.045-0.70 Pa m^3 mol^{-1} for α-HCH, γ-HCH and endosulfans, respectively (Shen and Wania, 2005; Xiao et al., 2004), tend to retain these compounds dissolved in water after ice melting. Thus, besides influences related with the changes in use of these compounds during the sampling period, their physical-chemical constants do not allow their transfer to the atmosphere in significant proportion upon ice melting and therefore decreases in atmospheric deposition were observed (Table 7).

HCB exhibits small decreases in deposition values during this sampling period (Table 7). However, air increases during 1995-2005 have been reported in the Czech Republic (Holoubek et al., 2007), as well as in Arctic air (early- to mid-2000s; Hung et al., 2010). Decreases in precipitation of this compound have been observed by the EMEP network (European Monitoring and Evaluation Programme) in several European sites (Torseth et al., 2012). HCB exhibits an elevated volatility, 6.3 10^{-2} Pa, and long atmospheric half-life, more than 700 days (Gramatica and Papa, 2007). These characteristics confer high atmospheric mobility and limited spatial variability of HCB in remote regions (Torseth at al., 2012). Therefore it would be difficult to observe significant changes in HCB levels in atmospheric deposition over a period of ten years.

The long-term trends of OCs found in this study suggest that regulatory efforts to decrease the emission of these compounds, e.g. pesticides, to the environment have been effective in a first stage but remobilization of some compounds, such as PCBs or HCB, previously accumulated in sink compartments may limit the effectiveness of these international control regulations.

Author contribution

L. A. carried out sample processing and OC analysis of the samples taken between 2004 and 2007 and performed the backward air mass trajectory calculations. R. F. analyzed samples from Redòn taken in 2001-2002. Sampling and other field work were designed and performed at each site by N. R. (Lochnagar), U. N. and H. T. (Gossenköllesee), E. S. (Skalnaté), and L. C. (Redòn). P. F. performed data interpretation and prepared the manuscript with contributions from all co-authors, especially J. G.

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Table 1. Sampling site location and meteorological conditions·

Sampling site	Mountain region	Latitude (N)	Longitude (E)	Altitude[a] (m asl)	T[b] (ºC)	Tw[c] (ºC)	Tsp[d] (ºC)	Tsu[e] (ºC)	Ta[f] (ºC)	Sampling period	T[g] (ºC)	Particle flux[h] (mg m^{-2} mo^{-1})	Precipitation[i] (mm)
Gossenköllesee	Tyrolean Alps (Austria)	47.22528	11.01390	2413	-0.9	-8.8	-2.0	6.6	0.6	June 2004-August 2006	-1.38*	132 (18-750)	1722
Redòn	Pyrenees (Spain)	42.64208	0.77951	2235	2.8	-4.5	0.7	10.9	4.0	May 2004-Sept. 2006	5.34	323 (14-2750)	2224
Lochnagar	Grampian Mts. (Scotland, UK)	56.95914	-3.23128	790	3.9	-1.1	2.6	9.6	4.5	June 2004-March 2007	5.09**	126 (14-1570)	4398
Skalnaté pleso	High Tatra Mts. (Slovakia)	49.18993	20.23422	1787	0.2	-9.2	-0.25	9.0	1.3	May 2004-May 2006	2.3	328 (43-1815)	3001

[a]Meters above sea level. [b]Annual average temperature. [c]Winter average temperature (December, January, February). [d]Spring average temperature (March, April, May). [e]Summer average temperature (June, July, August). [f]Autumn average temperature (September, October, November). [g]Mean temperature during the sampling period. [h]Average particle flux during the sampling period (min.-max.). [i]Total precipitation during the sampling period. *From October 2004 to August 2006 due to malfunctioning of AWS. **From June 2004 to November 2004 and October 2005 to March 2007 due to malfunctioning of AWS.

Table 2. Average atmospheric deposition fluxes of organochlorine compounds *(min.-max.)* in remote European regions (ng $m^{-2}mo^{-1}$).

	Lochnagar (n= 44)	Redòn (n= 22)	Gossenköllesee (n=18)	Skalnaté (n= 24)
∑7PCBs	305	112	168	488
	(78-876)	*(26-227)*	*(22-510)*	*(94-2340)*
α-HCH	19	5.7	4.6	16
	(3.2-93)	*(1.5-11)*	*(1.3-15)*	*(1.3-53)*
γ-HCH	37	12	20	50
	(6.2-130)	*(1.9-30)*	*(3.6-61)*	*(3.8-186)*
∑HCHs	56	17	25	66
	(12-199)	*(3.5-38)*	*(5.4-71)*	*(6.6-238)*
HCB	3.7	1.1	1.0	12
	(0.55-11)	*(0.13-6.5)*	*(BDL-8.1)*	*(BDL-86)*
α-Endosulfan	3.3	17	4.8	20
	(BDL-19)	*(BDL-93)*	*(BDL-19)*	*(BDL-119)*
β-Endosulfan	2.6	47	12	127
	(BDL-16)	*(BDL-205)*	*(BDL-39)*	*(0.35-637)*
Endosulfan sulfate	5.8	26	11	30
	(BDL-25)	*(BDL-148)*	*(0.66-34)*	*(0.71-118)*
∑Endosulfans	11	89	28	177
	(BDL-43)	*(BDL-446)*	*(0.66-77)*	*(1.3-832)*
α/γ HCH	0.51	0.50	0.23	0.32
	(0.0-0.93)	*(0.15-2.4)*	*(0.06-1.1)*	*(0.05-1.1)*
α/β Endosulfans	2.0	0.76	0.72	0.54
	(0.0-6.5)	*(0.0-4.9)*	*(0.0-2.4)*	*(0.05-5.8)*

BDL, below detection limit. ∑7PCBs, sum of PCBs 28, 52, 101, 118, 153, 138, and 180.

Table 3. Comparison of mean deposition fluxes of OC measured in remote European mountain regions with those reported in the literature.

Site/compound	Sampling period	∑PCBs	∑HCHs	∑endo.	HCB	Reference
Redòn[a]	Jul. 2004-Aug.2006	112	17	89	1.1	This study
Gossenköllesee[a]	Jun. 2004-Aug.2006	168	25	28	1.0	This study
Skalnaté pleso[a]	May 2004-May 2006	488	66	177	12	This study
Lochnagar[a]	Sept.2004-Mar.2007	305	56	11	3.7	This study
Eastern Mediterranean *(background)*	2000-2001	10-180[b]				Mandalakis and Stephanou,2004
New Jersey *(background)*	1997-2001	25-30[c]				Toten et al., 2004
New Jersey *(urban and suburban)*	1997-2001	330-1320[c]				Toten et al., 2004
Baltic Sea	1990-1992	36-168[b]				Agrell et al., 2002
Great Lakes *(remote sites)*		120-270				Hillery et al., 1998
NE Atlantic[a] *(remote)*	May 1999-Jul.2000	65[d]	35		7.2	Van Drooge et al., 2001
Natural Reserve, Hong Kong, China[a]	Aug.2002-Jul.2003		n.d.-3.9	n.d.-3.15[j]	1.8-20.3	Wong et al., 2004
Rio Janeiro, Brasil[a] *(industrial)*	2003-2004	510-9420				de Souza et al., 2007
Chicago, USA *(urban)*	1997-2003	252[e]				Sun et al., 2006a
" *(background)*		42[e]				
Galveston Bay, Texas *(urban)*	Feb.1995-Aug.1996	128[c]	136[g]		7.5	Park et al., 2001
Madison (USA)	1996-1998	217				Murray and Andren, 1996
Southern Ontario, Canada[a] *(background)*	May-Nov. 2002	26.5-903				Su et al., 2007
Lake Ontario, Canada *(rural)*	Sept.2002-Oct.2003		360[h]			Blanchard et al., 2006
Atlantic Canada *(background)*	1994-1999		112-182[i]	65.3-145[j]		Brun et al., 2008
			54.2-122[h]			
South Florida, USA *(agricultural)*	Jan.2003-Mar.2006			6070-6130		Potter et al., 2014
" *(background)*	Nov.2002-Aug.2006			49-76		
Flanders, Belgium	1997		1692	876		Quaghebeur et al., 2004
	2001			208		

New York-New Jersey	Jan.2000-May 2001		n.d.	51-127	Gioia et al., 2005
Chesapeake Bay, USA	Ap.-Sept. 2000-2004		93.3	382	Goel et al., 2005
Izmir, Turkey *(suburban)*	Not reported	401[f]	63.3	150	Odabasi et al., 2008

Otherwise note, levels from the literature were referred to wet-only deposition. n.d., not detected. [a]Bulk deposition. [b]Sum of 54 congeners. [c] Sum of more than 90 congeners. [d]Sum of 14 congeners. [e]Sum of 84 congeners. [f]Sum of 9 congeners. [g]Sum of 4 HCH isomers. [h] Lindane. [i]α-HCH. [j]Sum of α- and β-endo.

Table 4. Pearson correlation coefficients of OC deposition fluxes (ng m^{-2} mo^{-1}, log-transformed) and monthly mean temperature (T, ^{o}C), precipitation (Precip, mm mo^{-1}), and particle deposition (mg m^{-2} mo^{-1}, log-transformed) for the study sites.

	REDÒN			GOSSENKÖLLESEE			SKALNATÉ			LOCHNAGAR		
	Precip	T	Particles	Precip	T	Particles	Precip	T	Particles	Precip	T	Particles
α-HCH							0.612**	0.622**	0.510**	0.564**		
γ-HCH		0.560**					0.791**	0.692**	0.647**		0.437*	
α/γ-HCH										0.373*		
α-endosulfan							0.652**	0.687**	0.698**	0.526*	0.543*	
β-endosulfan		0.515*					0.636**	0.747**	0.729**			
Endo sulfate		0.744**			0.495*		0.712**	0.868**	0.634**		0.477*	
α/β-endosulf		-0.468*								-0.554*		
∑Endosulf		0.660**				0.486*					0.522*	
HCB							0.647**	0.438*	0.591**			
PCB 28									0.469*			
PCB 52									0.482*			
PCB 101	0.658**						0.520**	0.478*	0.763**			
PCB 118	0.594**						0.720**	0.582**	0.574**			
PCB 153							0.585**	0.546**	0.635**			
PCB 138	0.565**											
PCB 180							0.429*					0.410*

*Significance at 95 % confidence level. **Significance at 99 % confidence level.

Table 5. Linear regression analysis between OC deposition fluxes (ng m^{-2} mo^{-1}, log-transformed values), monthly mean temperature (T, ^{o}C), precipitation (Precip, mm mo^{-1}), particle deposition (mg m^{-2} mo^{-1}, log-transformed values) and % air masses flowing from the west in Skalnaté. Only compounds with statistically significant multilinear regression model are included.

		Linear regression coeff. (r)	Standardized coeff. (β)
α-HCH *vs*	T	0.622 (p = 0.001)	
(n = 25)	Precip.	0.612 (p = 0.001)	
	Particles	0.510 (p = 0.009)	
	% West	-0.570 (p = 0.004)	
	Prec. + % West	0.837 (p = 0.000)	0.646 (prec) / -0.364 (%west)γ-
HCH *vs*	T	0.692 (p = 0.000)	
(n = 25)	Precip.	0.791 (p = 0.000)	
	Particles	0.647 (p = 0.000)	
	T+ Precip.	0.834 (p = 0.000)	0.588 (prec) / 0.332 (T)
α-Endosulfan *vs*	T	0.687 (p = 0.000)	
(n = 24)	Precip.	0.652 (p = 0.001)	
	Particles	0.698 (p = 0.000)	
	% West	-0.506 (p = 0.012)	
	T + Particles	0.797 (p = 0.008)	0.470 (particles) / 0.447 (T)
β-Endosulfan *vs*	T	0.747 (p = 0.000)	
(n = 25)	Precip.	0.636 (p = 0.001)	
	Particles	0.729 (p = 0.000)	
	T + Particles	0.850 (p = 0.000)	0.508 (T) / 0.470 (particles)
Endo sulfate *vs*	T	0.868 (p = 0.000)	
(n = 25)	Precip.	0.712 (p = 0.000)	
	Particles	0.634 (p = 0.001)	
	% West	-0.430 (p = 0.032)	
	T + Precip.	0.898 (p = 0.024)	0.692 (T) / 0.289 (prec)
	T + Particles	0.896 (p = 0.029)	0.737 (T) / 0.258 (particles)

Multilevel regression coefficients indicated only if all considered variables in the model showed a significant correlation at least at 95% confidence level.

Table 6. Pearson correlation coefficients between OC deposition fluxes and % of air masses from different origins at the study sites.

	REDÒN				GOSSENKÖLLESEE			SKALNATÉ		LOCHNAGAR	
	Central/east Europe	South	N. Atlantic	N. Atlantic (west)	Central/east Europe	South	N. Atlantic	West	North Polar	North Polar	South
α-HCH								-0.411*			
γ-HCH	-0.456*	0.694**									
α/γ-HCH		-0.530*	0.560**	0.584**	0.478*						
α-endosulfan								-0.506*			
β-endosulfan							-0.647**				0.499*
Endo sulfate	-0.606**	0.602**					-0.480*	-0.430*			
α/β- endosulf			0.540*								
∑Endosulf	-0.569*	0.567*				0.455*					
HCB											
PCB 28								-0.452*			
PCB 52											
PCB 101				0.538*				-0.446*			
PCB 118				0.448*							
PCB 153								-0.456*			
PCB 138				0.447*					-0.426*	-0.454*	
PCB 180	-0.590**										
Precipitation				0.504*							
Temperature		0.805**	-0.608**					-0.411*			
Particle flux		0.498*						-0.428*	-0.414*		

*Significance at 95 % confidence level. **Significance at 99 % confidence level.

Table 7. Monthly mean deposition fluxes of organochlorine compounds (ng m^{-2} mo^{-1}) and pesticide ratios in Lake Redòn and Gossenköllesee at different periods.

Sampling site and period	T (^oC)	Precipitation (mm mo^{-1})	∑7PCBs[(a)]	∑6PCBs[(b)]	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	∑HCHs	∑Endo	HCB	α/γ-HCH	α/β-endo
Lake Redòn																
Mar 97-Feb 98[(c)]	4.1	88.0	42	37	4.5	10.1	11.2	5.0	4.9	4.5	1.1	430	473	1.5	0.22	0.54
Jul 01-Jun 02	2.8[(d)]	131	107	90	10.0	21	21	19	17	17	1.9	323	977	na	0.18	0.21
Mar 05-Feb 06	4.0	88.9	125	92	2.0	25	29	18	14	33	4.3	15.5	75	1.1	0.70	0.53
Gossenköllesee																
Oct 96-Sep 98[(c)]	0.2	112	99	92	28	19	21	8.4	9.3	9.2	3.7	340	190	1.8	0.10	0.70
Jun 04-April 06	-1.4[(e)]	57	155	122	10.2	28	43	19	17	33	5.2	21.9	28[(f)]	1.0	0.36	0.58

[(a)]Sum of all analysed congeners. [(b)]Sum of all analysed congeners excepting PCB 138. [(c)]Data from Carrera et al., 2002. [(d)]From January to December 2001. [(e)]October 2004 to Aug 2006. [(f)]Aug 2005-July 2006. na, not available.

FIGURE CAPTIONS

Fig. 1. Mean percentage contribution of PCB congeners for all deposition samples (total) and for each study site.

Fig. 2. Boxplots of several OC deposition fluxes during warm (red) and cold (blue) seasons at the study sites. Horizontal lines represent the median value. Atypical values (outside 1.5 times the interquartile range, IQR) are indicated by empty dots, while asterisks represent extreme values (outside 3 x IQR).

Fig. 3. Temporal trends of OC concentrations in bulk atmospheric deposition samples from Redòn. N/A, not available. ∑6PCBs, sum of PCB 28, 52, 101, 118, 153 and 180. ∑HCHs, sum of α-HCH and γ-HCH. ∑Endosulfans, sum of α-endosulfan, β-endosulfan and endosulfan sulfate.

Fig. 4. Percentage increase or decrease of atmospheric deposition fluxes of individual PCB congeners (A) and OCs (B) in Redòn and Gossenköllesee (GKS) during the study periods.

Fig. 1

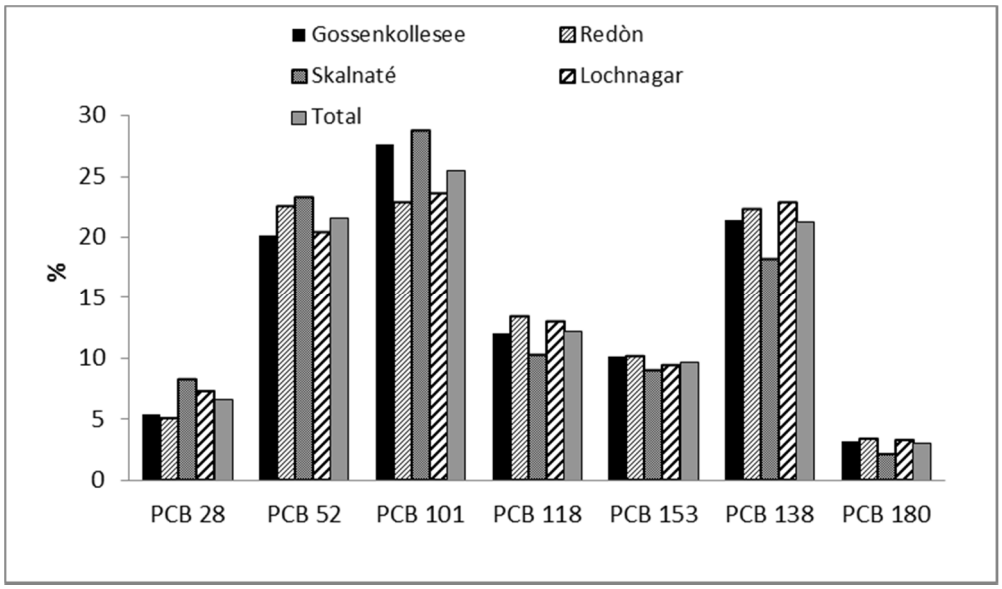

Gossenkollesee
Redòn
Skalnaté
Lochnagar
Total
30
25
20
15
10
5
0
%
PCB 28
PCB 52
PCB 101
PCB 118
PCB 153
PCB 138
PCB 180

Figure 2

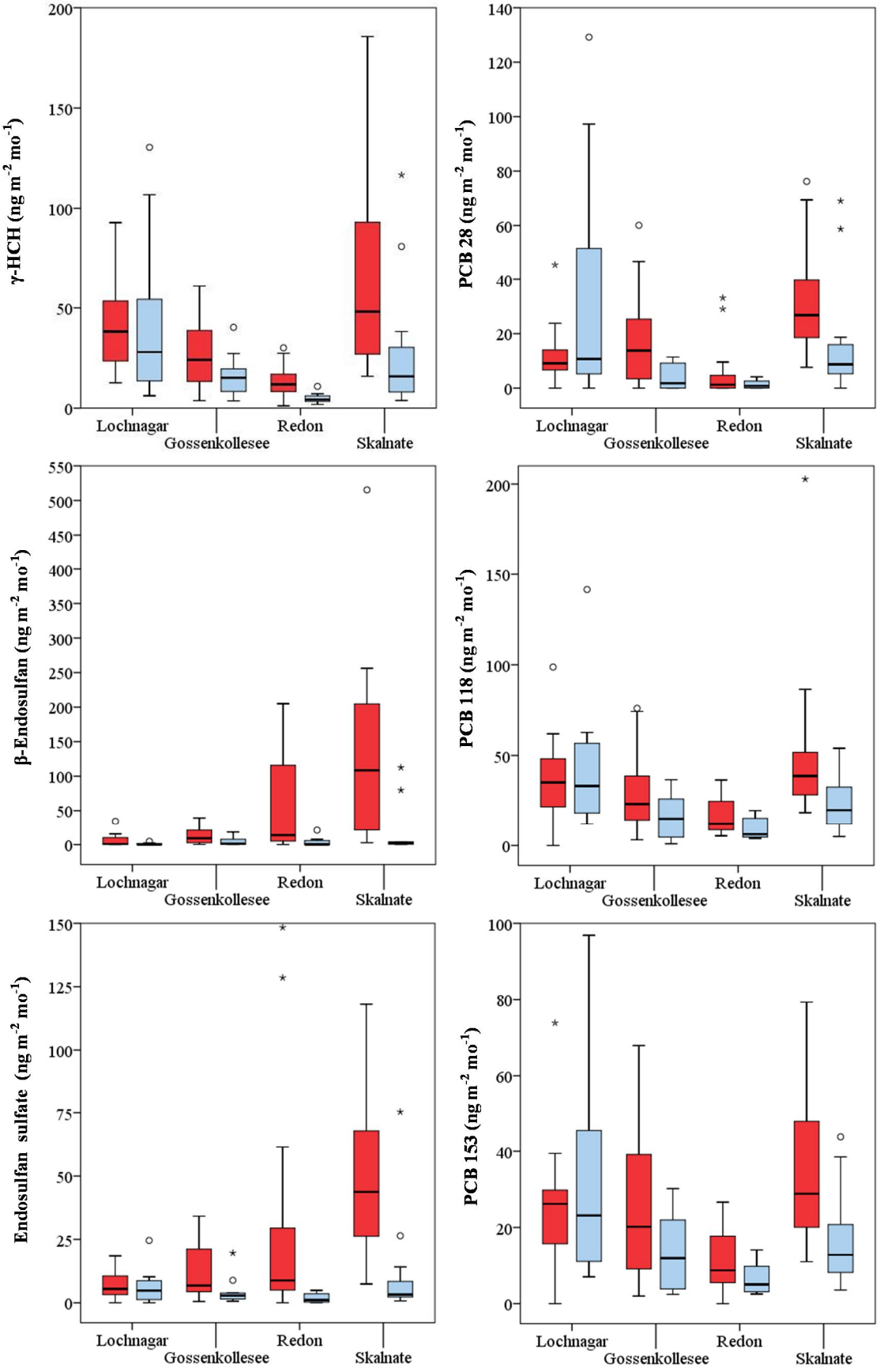

γ-HCH (ng m-2 mo-1)
PCB 28 (ng m-2 mo-1)
β-Endosulfan (ng m-2 mo-1)
PCB 118 (ng m-2 mo-1)
Endosulfan sulfate (ng m-2 mo-1)
PCB 153 (ng m-2 mo-1)
Lochnagar
Gossenkollesee
Redon
Skalnate

Figure 3

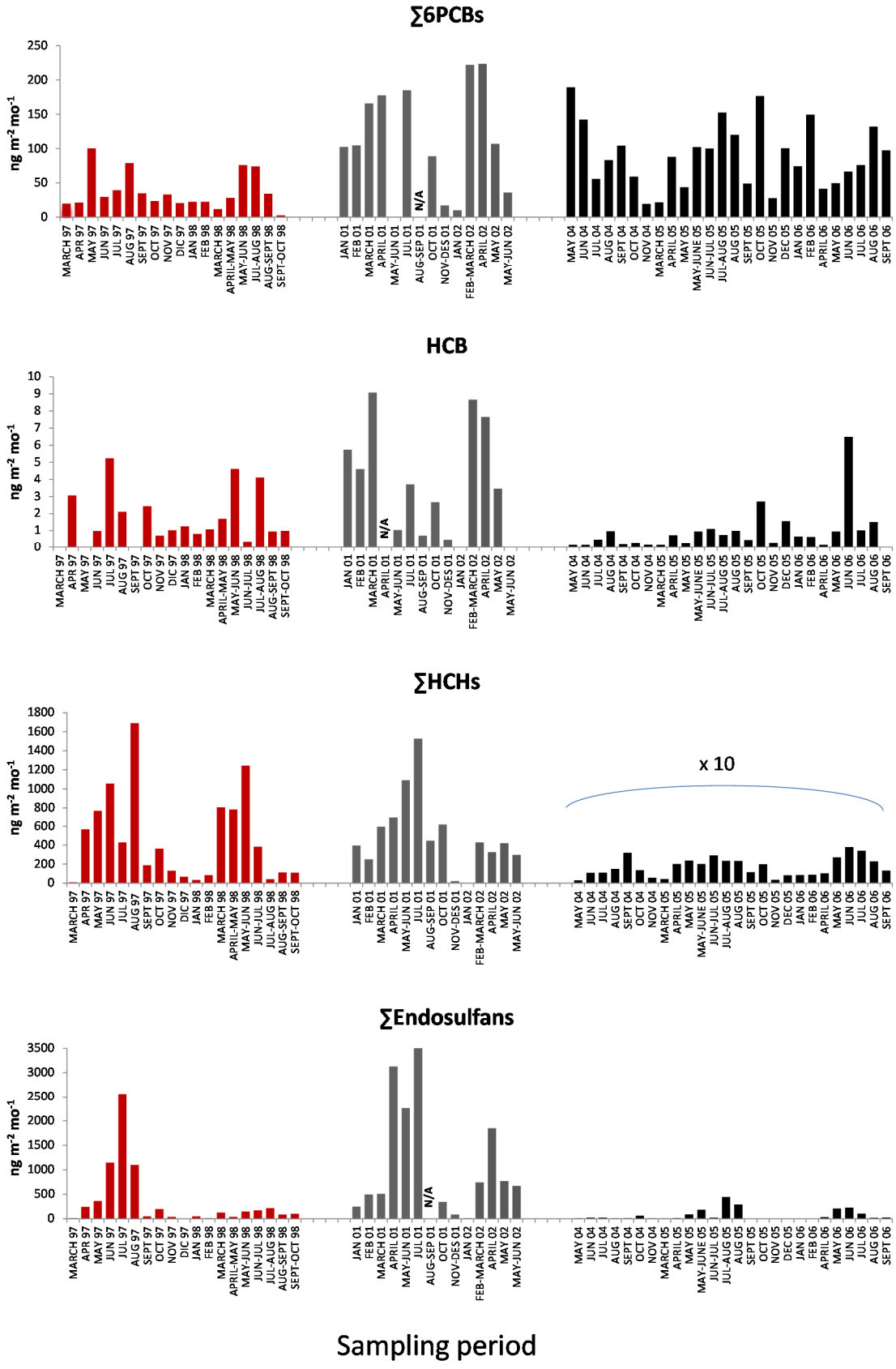
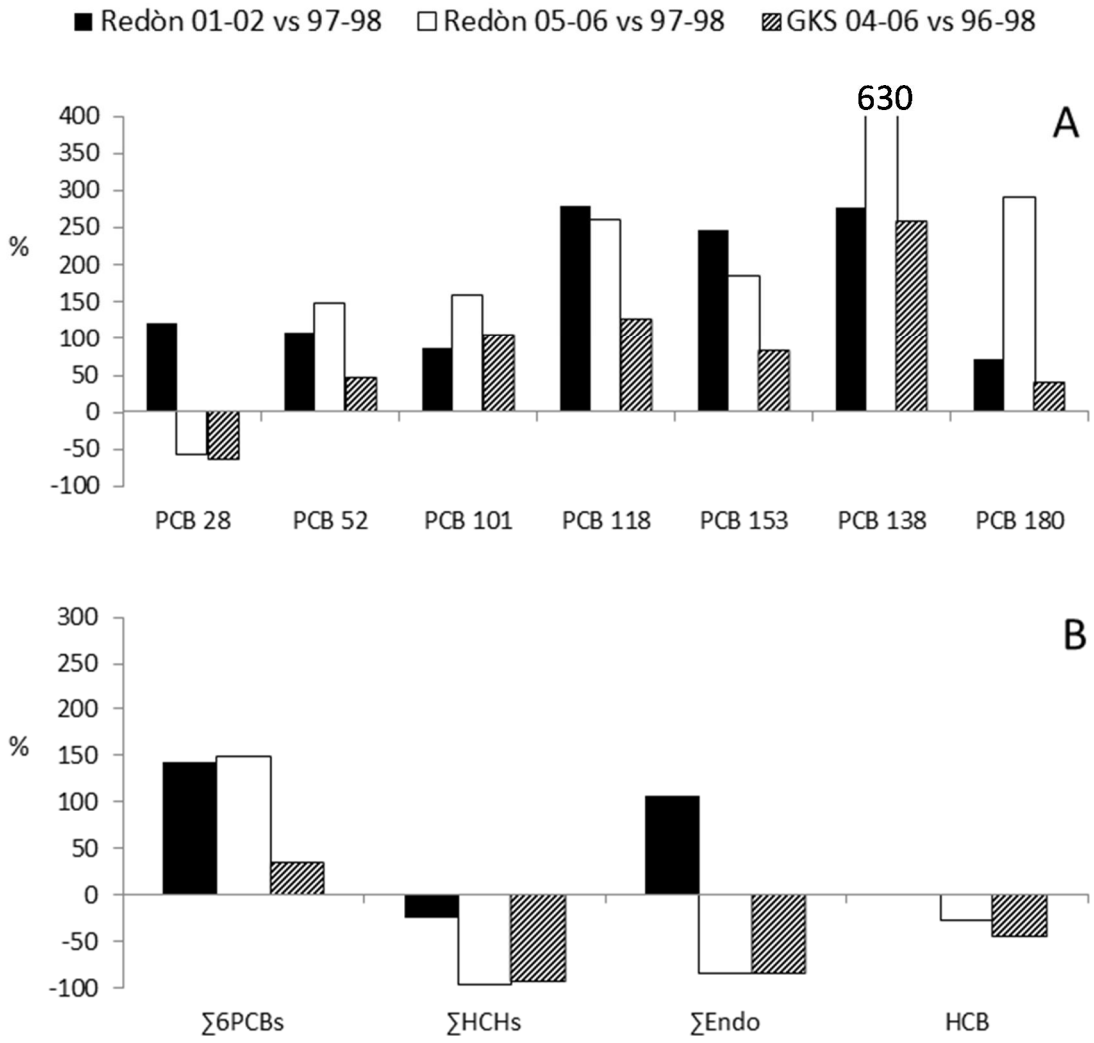

∑6PCBs
ng m-2 mo-1
250
200
150
100
50
0
N/A
HCB
ng m-2 mo-1
10
9
8
7
6
5
4
3
2
1
0
N/A
∑HCHs
ng m-2 mo-1
1800
1600
1400
1200
1000
800
600
400
200
0
x 10
∑Endosulfans
ng m-2 mo-1
3500
3000
2500
2000
1500
1000
500
0
N/A
MARCH 97
APR 97
MAY 97
JUN 97
JUL 97
AUG 97
SEPT 97
OCT 97
NOV 97
DIC 97
JAN 98
FEB 98
MARCH 98
APRIL-MAY 98
MAY-JUN 98
JUN-JUL 98
JUL-AUG 98
AUG-SEPT 98
SEPT-OCT 98
JAN 01
FEB 01
MARCH 01
APRIL 01
MAY-JUN 01
JUL 01
AUG-SEP 01
OCT 01
NOV-DES 01
JAN 02
FEB-MARCH 02
APRIL 02
MAY 02
MAY-JUN 02
MAY 04
JUN 04
JUL 04
AUG 04
SEPT 04
OCT 04
NOV 04
MARCH 05
APRIL 05
MAY 05
MAY-JUNE 05
JUN-JUL 05
JUL-AUG 05
AUG 05
SEPT 05
OCT 05
NOV 05
DEC 05
JAN 06
FEB 06
APRIL 06
MAY 06
JUN 06
JUL 06
AUG 06
SEPT 06
Sampling period

Figure 4


Redòn 01-02 vs 97-98
Redòn 05-06 vs 97-98
GKS 04-06 vs 96-98
630
A
%
400
350
300
250
200
150
100
50
0
-50
-100
PCB 28
PCB 52
PCB 101
PCB 118
PCB 153
PCB 138
PCB 180
B
%
300
250
200
150
100
50
0
-50
-100
∑6PCBs
∑HCHs
∑Endo
HCB