

# Atmospheric Deposition of Organochlorine Compounds to Remote High Mountain Lakes of Europe

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Bulk deposition samples were taken near three mountain lakes located in the Pyrenees (Estany Redó), Alps (Gossenköllesee), and Caledonian Mountains (Øvre Neådalsvatn) for evaluation of the atmospheric deposition load of organochlorine compounds (OC), namely, polychlorobiphenyls (PCBs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), and endosulfans, in the remote European high mountain areas. The compounds of present use in agriculture, namely, endosulfans and  $\gamma$ -HCH, exhibit large differences in mean deposition fluxes between the three sites. They occur in large amounts in Estany Redó (340 and 430 ng m<sup>-2</sup> month<sup>-1</sup> for endosulfans and  $\gamma$ -HCH, respectively), reflecting the impact of agricultural activities in southern Europe. This lake showed also the highest proportion of the more labile endosulfan isomers ( $\alpha$  and  $\beta$  = 82%) whereas only the most recalcitrant species, endosulfan sulfate, was found in Øvre Neådalsvatn. In contrast, the OC whose use is now banned exhibit a more uniform geographic distribution with deposition fluxes of 31–40, 30–100, and 1.4–15 ng m<sup>-2</sup> month<sup>-1</sup> for  $\alpha$ -HCH, PCBs, and HCB. Both compounds of present and past use exhibit a clear seasonal pattern, with higher deposition in the warm periods, which is consistent with enhanced volatilization at higher temperatures. In the case of the agricultural pesticides it may also reflect higher use during application periods. The OC distributions in the atmospheric deposition of the three sites are rather uniform and highly enriched in compounds with volatilities larger than 0.0032 Pa. However, more than 90% of these compounds are not retained in the lake waters

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or sediments. Comparison of OC composition in atmospheric and sedimentary deposition evidences a selective trapping of the less volatile compounds. Trapping efficiencies increase at decreasing air temperatures of the lacustrine systems.

## Introduction

Remote high mountain lakes can be defined as natural water bodies situated in mountain ranges, above the local tree line, far from pollution sites and not directly impacted by human activity. Their hydrology is often determined by precipitation, whereas water inputs from tributaries are negligible. Despite their remoteness, these ecosystems receive significant amounts of persistent organic pollutants such as polycyclic aromatic hydrocarbons (1,2) or organochlorine compounds (OC) (3–5), which are deposited after long-range transport through the atmosphere. As shown recently (3), the patterns of accumulation of some of these pollutants, e.g., the low-volatility OC, can be explained in the context of the global distillation model (6–8).

The occurrence of these pollutants in these lakes demands further understanding of the transport mechanisms from the atmosphere. Study of the atmospheric deposition constitutes a key factor for gaining insight into the uptake processes. For this purpose, deposition samples have been collected near three lakes, Redó, Gossenkölle, and Øvre Neådalsvatn, located in three main mountain ranges of Europe, Pyrenees, Alps, and Caledonian Mountains (Scandinavia), respectively (Figure 1, Table 1). Different annual average air temperatures are represented by these lakes, e.g. 3.6, 2.5, and 0.5 °C for Redó, Øvre Neådalsvatn, and Gossenkölle, respectively. Results will be described according to these temperature differences.

In the present paper, OC contents in atmospheric deposition are reported, namely, polychlorobiphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), endosulfans, 4,4'-DDE, and 4,4'-DDT. To the best of our knowledge this is the first study reporting deposition flux data of these compounds in high mountain lake systems (728–2417 m above sea level; Table 1). The results allowed us to determine seasonal and geographical trends. Comparison with previous OC data on these lakes such as water composition (5) or sedimentation rates (3) has yielded a better appraisal of the trapping mechanisms of these compounds into the lake systems and, therefore, of the accumulation processes involved in the global distillation model.

## Sampling and Analytical Methods

**Sampling.** Bulk atmospheric deposition samples were taken at 20–30 m from the shore of three remote lakes in Europe (Table 1). Sampling was conducted continuously over different periods depending on lake accessibility, monthly in Estany Redó (March 1997 to October 1998) and weekly in Gossenköllesee (October 1996 to October 1998). In Øvre Neådalsvatn, only samples from December 1997 and from April 1998 to August 1998 were available. Stainless steel samplers of different volume were used in each lake. In parallel to the bulk system, wet- and dry-only samples (WADOS) were collected at Estany Redó during the warm periods with a Model ARS 1010 sampler (MTX, Italy) equipped with two collectors and a moisture sensor. This sensor controls a motor-driven cover that switches between the buckets depending on weather conditions.

TABLE 1. Sampling, Meteorological, and Morphological Characteristics of the Studied Areas

coordinates	altitude (m above sea level)	lake area (ha)	lake vol (10 <sup>6</sup> m <sup>3</sup> )	catchment area (km <sup>2</sup> )	sample type	sampling period	sampling frequency	mean prec <sup>a</sup> (mm/ year)	mean T (°C)
42°38' N, 0°46' E	2240	24	7.75	1.55	Estany Redó bulk dry + wet	Mar 97–Oct 98 Jun–Sept 97, Jun–Sept 98	monthly monthly	1500	3.6
62°47' N, 9°00' E	728	50	1.95	16	Øvre Neådalsvatn bulk	Dec 97, Apr–Aug 98	biweekly	1100	2.5
47°13' N, 11°1' E	2417	1.7	0.078	0.20	Gossenköllesee bulk	Oct 96–Oct 98	weekly	1100	0.5

<sup>a</sup> Average precipitation rate measured during the sampling period.

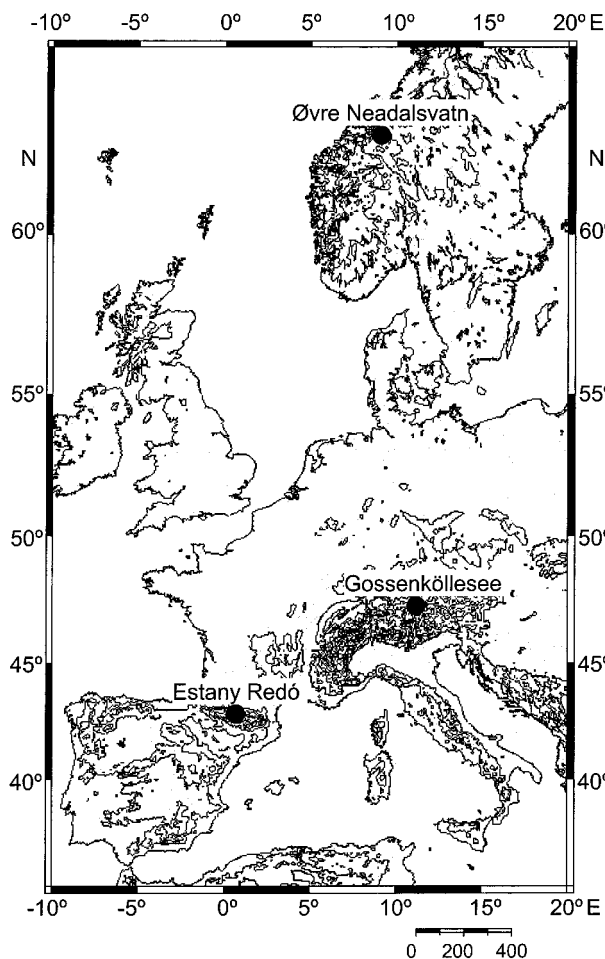


FIGURE 1. Map showing the location of the lakes in which atmospheric deposition was collected.

Automatic weather stations (AWS) located at each site (30 m from lake shore, sensors 6–10 m above ground level) provided data on temperature, wind direction and speed, solar radiation, relative humidity, air pressure, and precipitation every 30 min. The meteorological data were averaged for each sampling period.

Rain collection efficiencies calculated from the precipitation data measured by the AWS averaged 70% at Gossenköllesee and 77% at Estany Redó. The summer Redó samples reported in the study refer to the WADOS collector, which is the one providing higher rain collection efficiencies during this period (78%).

PCBs (seven congeners), pp'-DDE, pp'-DDT, HCB, HCHs ( $\alpha$ - and  $\gamma$ -isomers), and endosulfans ( $\alpha$ -,  $\beta$ -, and sulfate derivative) were determined in the bulk atmospheric depo-

sition samples. Samples were filtered on site through preweighed glass fiber filters (Whatman, GF/B, 45 mm diameter, 1  $\mu$ m pore size), and the filtrates were solid-phase-extracted with C18 Empore disks (47 mm diameter, 0.5 mm thickness) as described elsewhere (9). After water removal, bulk collectors were rinsed with Milli-Q water and the water volumes were filtered, solid-phase-extracted, and combined with the sample extracts. Milli-Q water was also added to the collectors when deposition was dry-only. These samples were then treated as in the previous case by filtration and solid-phase extraction. Glass fiber filters and disks were wrapped in aluminum foil and transported frozen to the laboratory. After sampling, each collector was carefully cleaned with Milli-Q water and acetone.

**Analytical Procedure.** The analytical methods used are detailed elsewhere (4, 9). Briefly, freeze-dried glass fiber filters were weighed for measurement of total particle amount and extracted by sonication with dichloromethane/methanol (2:1). Compounds adsorbed in membrane extraction disks were eluted subsequently with methanol (5 mL), cyclohexane (5 mL), and dichloromethane (5 mL). A recovery standard mixture of PCBs 30 and 209 was added to the extracts. Then, they were vacuum-evaporated until almost dryness and fractionated with aluminum oxide as described elsewhere (1). The fractions were vacuum-evaporated again to 1 mL and transferred to vials where they were concentrated to small volumes by a gentle stream of nitrogen. Prior to instrumental analysis, fractions were spiked with an internal standard mixture of tetrachloronaphthalene and octachloronaphthalene.

Series of field and procedural blanks were performed periodically. The former included transport and storage. For field blanks, bulk and WADOS deposition samplers were filled with Milli-Q water, filtered, and solid-phase-extracted. The filtration and adsorption disks were then transported and stored together with the samples. Reported values are blank and surrogate recovery corrected.

**Instrumental Analysis.** Quantitative analysis of organochlorine compounds was carried out by gas chromatography coupled to mass spectrometry, operating in the selected ion monitoring (SIM) and electron impact modes. Detailed description of the chromatographic and spectrometric conditions has been reported elsewhere (5). Quantification of endosulfans, HCB, and PCB 180 was performed by gas chromatography-mass spectrometry in negative chemical ionization and SIM mode, with NH<sub>3</sub> as reagent gas as described elsewhere (10). Quantitative levels were determined by the internal standard method. PCB 209 was used as reference standard for all PCB congeners and endosulfans. HCHs and HCB were quantified by reference to PCB 30.

Method quantitation (MQL) and detection limits (MDL) were calculated from real samples. They were defined as signal-to-noise ratios of 5 and 3, respectively. For PCBs, MDL varied between 10 and 30 pg in the dissolved phase and

between 25 and 60 pg in the particulate phase. For HCB they were 12 and 80 pg for the dissolved and particulate phases, respectively. Finally, HCHs and endosulfans were detected only in the dissolved phase, with a MDL of 90–150 pg, depending on the isomer. For compounds not detected in any sample, MDL and MQL were approached to the instrumental detection and quantitation limits as calculated from standard mixtures (9). Compound concentrations were only considered if they exceeded MQL. Mean percentage analyte recoveries calculated from surrogate data were 41 (standard deviation 7,  $n = 61$ ) and 66 (SD 17,  $n = 93$ ) for PCB 30 and PCB 209 in the particulate phase, respectively, and 43 (SD 8.6,  $n = 68$ ) and 67 (SD 15,  $n = 80$ ) for PCB 30 and PCB 209 in the dissolved phase, respectively.

## Results

Sample volumes were variable depending on site, season, and sampling frequency. Generally, the total volume of rain or snow collected within one sampling period varied between 1900 and 5500 mL at Øvre Neådalsvatn (biweekly), 800 and 10 000 mL at Estany Redó (monthly), and 12 and 2300 mL at Gossenköllesee (weekly). Low volume samples, e.g., <100 mL, from this Tyrolean lake were combined prior to analysis.

Deposition samples were analyzed after pollutant fractionation between the dissolved and particulate phases for facilitating storage and transport and for a higher degree of precision and accuracy in the analyses (9). However, the observed dissolved and particulate phase partitioning does not necessarily reflect the pollutant distribution either in the original precipitation or during atmospheric scavenging, since samples remained in the collection buckets during the sampling periods. For this reason, the results are only reported and discussed as total, i.e., dissolved + particulate, deposition fluxes. Furthermore, the observed concentrations reflect the net deposition rates, that is, the difference between precipitation uptake and possible volatilization at the local temperature conditions during sample collection. In fact, this partitioning between precipitation and volatilization operates throughout the deposition process, e.g., there is already a partitioning according to the local air column temperature distribution.

HCHs, namely,  $\gamma$ -HCH, exhibited the highest deposition fluxes (Figure 2). Endosulfans constituted the second major group. PCBs were found at significant lower levels but always above MQL in all samples analyzed from the three mountain lakes, while  $\alpha$ - and  $\beta$ -endosulfan were above MQL mainly in the spring–summer periods (Figure 3). HCB was one of the OC found in lower amounts but they generally occurred at concentrations higher than MQL. In contrast, 4,4'-DDE and 4,4'-DDT were only found occasionally at concentrations near to MDL, in particular at Gossenköllesee; for this reason they are not included in the study. Other OC were below MDL in nearly all cases.

**Hexachlorocyclohexanes (HCHs).** Bulk atmospheric deposition of total HCH isomers was 470, 150, and 340  $\text{ng m}^{-2} \text{ month}^{-1}$  at Estany Redó, Øvre Neådalsvatn, and Gossenköllesee, respectively (Figure 2).

Most HCHs corresponded to the  $\gamma$ -isomer, with values of 430  $\text{ng m}^{-2} \text{ month}^{-1}$  at Estany Redó, 120  $\text{ng m}^{-2} \text{ month}^{-1}$  at Øvre Neådalsvatn, and 305  $\text{ng m}^{-2} \text{ month}^{-1}$  at Gossenköllesee. The  $\alpha$ -isomer showed lower differences between lakes (fluxes of 40, 31, and 35  $\text{ng m}^{-2} \text{ month}^{-1}$ , respectively; Figure 2).

HCHs are mostly deposited in wet form (11) due to their high water solubilities of 1.6 and 7.4  $\text{ng L}^{-1}$  for the  $\alpha$ - and  $\gamma$ -isomers, respectively (12). The measured deposition amounts could therefore be transformed into volume-weighted means (VWM), in nanograms per liter, by considering the corresponding precipitation volume measured during each sampling period. Accordingly, values of 0.48,

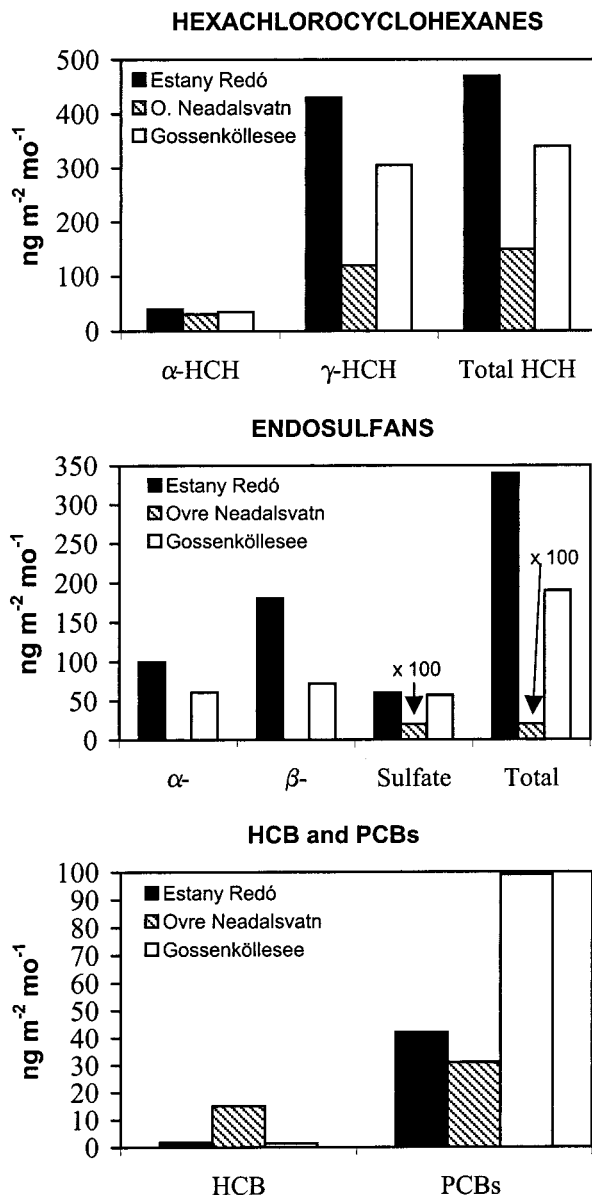


FIGURE 2. Mean monthly deposition of organochlorine compounds in European remote mountain areas. PCBs indicate the sum of all analyzed polychlorobiphenyl congeners, HCHs the sum of the  $\alpha$ - and  $\gamma$ -hexachlorocyclohexanes, and total endosulfans the sum of the  $\alpha$ - and  $\beta$ -endosulfanes and the sulfate derivative. The endosulfan values in lake Øvre Neådalsvatn are represented after 100 times amplification.

0.39, and 0.30  $\text{ng L}^{-1}$  were obtained for  $\alpha$ -HCH and 5.6, 1.5, and 2.8  $\text{ng L}^{-1}$  for  $\gamma$ -HCH at Estany Redó, Øvre Neådalsvatn, and Gossenköllesee, respectively. This transformation is useful for comparison with recent measurements reported in the literature. The  $\alpha$ -HCH levels are similar to or slightly lower than those found in south Norway (1.9  $\text{ng L}^{-1}$  or 170–330  $\text{ng m}^{-2} \text{ month}^{-1}$ ), in the west coast of Sweden (30–47  $\text{ng m}^{-2} \text{ month}^{-1}$ ), in Denmark (1.2–3  $\text{ng L}^{-1}$ ; 1992) (13 and references therein), and in the Great Lakes area (1.2–2.6  $\text{ng L}^{-1}$ ; 1991–1995) (14) but higher than those reported from Lake Malawi in South Africa (0.13  $\text{ng L}^{-1}$ ) (15). These values are also higher than the annual average fluxes found in the free tropospheric zone of the eastern north Atlantic ocean, 7.9  $\text{ng m}^{-2} \text{ month}^{-1}$  (11).

$\gamma$ -HCH exhibits levels in the range of those found in southern Norway (4.4  $\text{ng L}^{-1}$ ) (13) and the Great Lakes region (0.7–2.7  $\text{ng L}^{-1}$ ) (14). Higher levels have been reported in

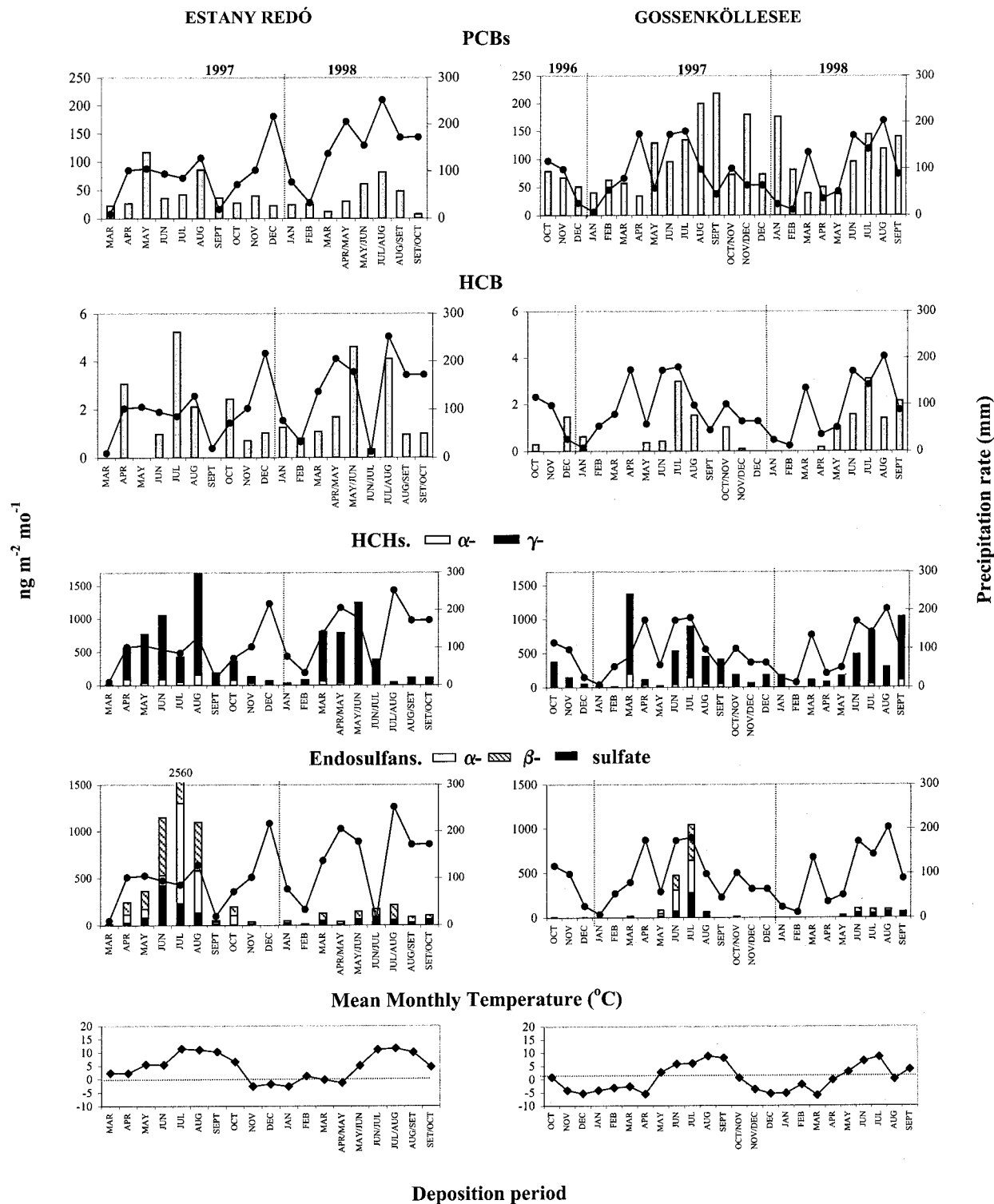


FIGURE 3. Temporal variation of precipitation (straight line, in millimeters), air temperature, and OC fluxes (bar units in nanograms per square meter per month) in bulk atmospheric deposition at Lakes Redó and Gossenkölle. Vertical dashed lines indicate different years.

coastal areas of Denmark ( $11\text{--}12\text{ ng L}^{-1}$ ) or close to regions where this pesticide is used, such as in Germany ( $117\text{--}171\text{ ng L}^{-1}$ ) and France ( $100\text{--}150\text{ ng L}^{-1}$ ) (13 and references therein). Lower values have been found in the free troposphere of the Canary Islands (2367 m above sea level),  $27\text{ ng m}^{-2}\text{ month}^{-1}$  (11), the lowest having been reported in Malawi Lake ( $0.15\text{ ng L}^{-1}$ ) (15).

**Endosulfans.**  $\alpha$ -Endosulfan,  $\beta$ -endosulfan, and the sulfate derivative (a main residue of the technical mixture) constitute the major second group of OC in the deposition samples of

Estany Redó,  $340\text{ ng m}^{-2}\text{ month}^{-1}$ , and Gossenköllesee,  $190\text{ ng m}^{-2}\text{ month}^{-1}$  (Figure 2). In contrast, at Øvre Neådalsvatn the amounts were 3 orders of magnitude lower, i.e.,  $0.2\text{ ng m}^{-2}\text{ month}^{-1}$ . The endosulfan composition at Estany Redó and Gossenköllesee is dominated by the  $\beta$ -isomer (Figure 2). Endosulfan sulfate is present in significant amounts at all three lakes and it is the only endosulfan species in Øvre Neådalsvatn. As these compounds are mainly present in the atmospheric gas phase (16), dry deposition is not expected to contribute significantly to their total atmospheric deposi-

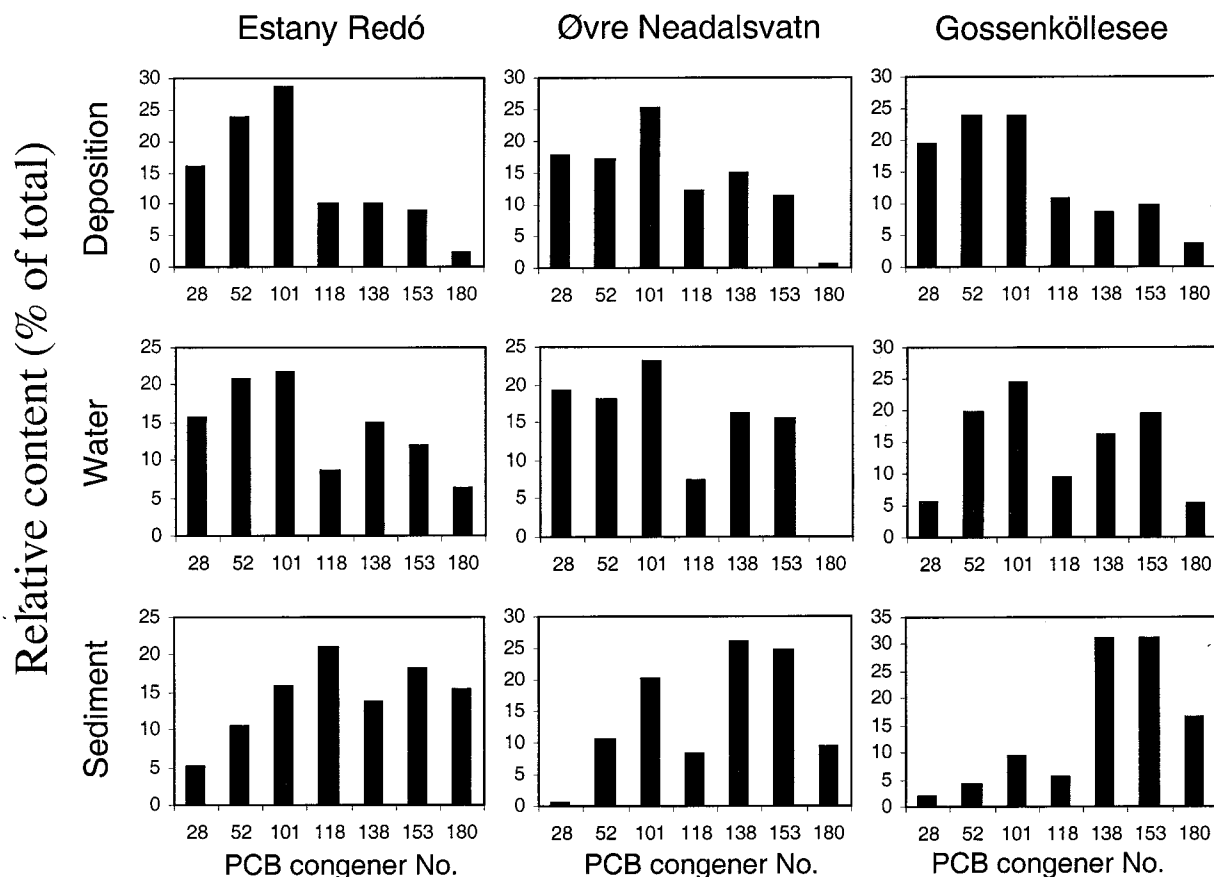


FIGURE 4. Comparison of the mean PCB congener distribution in bulk atmospheric deposition, water (dissolved + particulate phase) (5), and sediments (3) from remote high mountain lakes. Percent of total refers to the sum of the seven measured PCB congeners.

tion, and the deposition fluxes can be transformed into VWM as in the case of HCHs, i.e., <MDL (0.033), 0.37–45, and 0.003–11 ng L<sup>-1</sup> at Øvre Neadalsvatn, Estany Redó, and Gossenköllesee, respectively. Values of 0.036–7.9 have been reported in precipitation samples from the Sierra Nevada mountain range (USA) (17); these levels are similar to those detected at Gossenköllesee, clearly lower than the values found at Estany Redó, and higher than those at Øvre Neadalsvatn.

**Polychlorobiphenyls.** PCBs have been detected in all deposition samples. The congener distribution was dominated by lower molecular weight compounds (Figure 4). ANOVA shows that there are no consistent differences in the homologue distribution between lakes,  $p < 0.05$ . Similar PCB distributions have been reported in deposition samples from other sites in the USA (18, 19) and Europe (20).

The monthly mean deposition levels varied between 42 ng m<sup>-2</sup> month<sup>-1</sup> at Estany Redó, 31 ng m<sup>-2</sup> month<sup>-1</sup> at Øvre Neadalsvatn, and 99 ng m<sup>-2</sup> month<sup>-1</sup> at Gossenköllesee (Figure 2). The higher impact of PCB pollution at Gossenköllesee than at Estany Redó and Øvre Neadalsvatn is consistent with the results of other studies on PCB concentrations in snow (4), water (5), and sediment and fish samples (3) from these lakes.

These PCB levels at the high mountain European lakes show intermediate values between those reported in remote areas such as the Arctic (17 ng m<sup>-2</sup> month<sup>-1</sup>) and lowland lakes close to pollution sources such as Esthwaite Water in England [mean bulk deposition over one year, 870 ng m<sup>-2</sup> month<sup>-1</sup> (sum of 52 congeners)] (20), Green Bay in Lake Michigan (183 ng m<sup>-2</sup> month<sup>-1</sup>) (21), or Chesapeake Bay, USA [115–130 ng m<sup>-2</sup> month<sup>-1</sup> (sum of 74 congeners)] (22). They are also similar to those reported in deposition samples collected at 2367 m above sea level in the free troposphere

of the eastern north Atlantic ocean, i.e., 65 ng m<sup>-2</sup> month<sup>-1</sup> (11).

Most of the deposition PCB data in the literature are given as VWM for wet-only deposition. Transformation of the PCB deposition fluxes gives values of 0.72, 0.32, and 2.8 ng L<sup>-1</sup> at Estany Redó, Øvre Neadalsvatn, and Gossenköllesee, respectively. These concentrations are expected to be higher than those only corresponding to wet deposition, since dry deposition of PCBs can contribute significantly to the levels measured in bulk deposition samples (11). In this respect, the values for Estany Redó wet-only samples collected during the summer periods, 0.39 ± 0.16 ng L<sup>-1</sup> (standard error calculated as described in ref 23), with bulk deposition levels for the equivalent period of 0.81 ng L<sup>-1</sup>, showing that about 50% PCB uptake at Estany Redó in summer is truly associated with wet deposition. This percentage may be lower in other lakes since they receive less water precipitation. In any case, these values are similar to those reported in the Great Lakes region (1.1–2.8 ng L<sup>-1</sup>; sum of 98 congeners) (14) and Chesapeake Bay (1.6 ng L<sup>-1</sup>) (18).

**Hexachlorobenzene.** No differences have been found between HCB deposition fluxes at Estany Redó and Gossenköllesee, with mean atmospheric deposition values in the range of 1.4–1.8 ng m<sup>-2</sup> month<sup>-1</sup>, although higher variability can be observed in Redó (Figure 3). HCB atmospheric deposition fluxes in Øvre Neadalsvatn are 1 order of magnitude higher than in these other two mountain lakes, i.e., 15 ng m<sup>-2</sup> month<sup>-1</sup> (Figure 2). No local pollution sources can explain this difference.

Values of HCB atmospheric deposition fluxes have been reported for few sites, for instance 7.2 ng m<sup>-2</sup> month<sup>-1</sup> in the free troposphere of the eastern north Atlantic ocean (11). Transformation into VWM yields values of 25–28 pg L<sup>-1</sup> at Gossenköllesee and Estany Redó and 215 pg L<sup>-1</sup> at Øvre

Neådalsvatn, allowing comparison with deposition samples collected over the Great Lakes,  $96 \pm 25 \text{ pg L}^{-1}$  (26–222  $\text{pg L}^{-1}$ ) (14); rural regions of Texas,  $400 \text{ pg L}^{-1}$  (24); and Lake Malawi,  $15 \pm 19 \text{ pg L}^{-1}$  (15). This transformation is approximate because HCB can also be partially incorporated in association with dry deposition (11, 25). In any case, comparison of these figures with the data from the literature shows that the concentrations found in Gossenköllesee and Estany Redó are similar to those found in remote sites whereas those in Øvre Neådalsvatn are 10 times higher than these levels.

## Discussion

**Geographic Distribution.** Endosulfans, one of the major OC detected in deposition samples, exhibit high levels at Estany Redó and Gossenköllesee and low levels at Øvre Neådalsvatn; the corresponding R:G:Ø ratio was 1700:950:1. These differences are in agreement with the endosulfan concentrations in lake water observed at these three lakes (5). This pesticide is in current use in agriculture in Canada, USA, and Europe. The differences in deposition levels observed in this study are consistent with higher applications in central and southern European areas and subsequent remobilization and transfer to more distant and remote northern sites.

In contrast,  $\alpha$ -HCH and PCBs had similar deposition fluxes at the three lakes, with R:G:Ø ratios of 1.3:1.1:1 and 1.4:3.3:1, respectively. These compounds are now banned from possible application; therefore, their fluxes may witness the levels of diffuse pollution in the European atmosphere originating from re-evaporation of past usages (16, 25–27).

$\gamma$ -HCH also exhibited rather uniform fluxes, with R:G:Ø ratios of 3.6:2.6:1. The flux differences between lakes were intermediate between those observed for  $\alpha$ -HCH and endosulfans. This compound is widely distributed in the environment (7, 28) and still used as a pesticide in agriculture. Geographical differences in its deposition fluxes may reflect an intermediate situation in which, in addition to a diffuse pollution over Europe, there is an influence of the agricultural activities from southern locations.

HCB deposition exhibited a different pattern, with R:G:Ø ratios of 0.10:0.10:1. The higher deposition levels of this compound in the northernmost lake may reflect the latitudinal distribution of volatile OC involving the transfer from southern to northern latitudes (6).

**Seasonal Differences.** Bulk atmospheric HCHs deposition is characterized by a constant baseline level in the range of 100–165  $\text{ng m}^{-2} \text{ month}^{-1}$  at all sampling sites. In addition, deposition increased in spring–summer at all lakes (Figure 3). Hence, peak levels have been found in deposition samples of Estany Redó between April and August of 1997, with a mean value of 900  $\text{ng m}^{-2} \text{ month}^{-1}$ . At Gossenköllesee the precipitation levels during this period amounted to 560  $\text{ng m}^{-2} \text{ month}^{-1}$ . A parallel difference between spring–summer and winter can also be observed in Øvre Neådalsvatn despite the lower number of samples available and the lower deposition HCHs fluxes detected in this lake.

These increases during warm seasons were also observed for endosulfans at all lakes (Figure 3). In some cases they involved differences of more than 1 order of magnitude, such as the fluxes between May and September 1997 and between October 1997 and May 1998 at Estany Redó and Gossenköllesee (Figure 3).

A seasonal trend in PCB deposition is also observed at all three lakes, showing again higher deposition in summer than in winter (Figure 3). In this case the differences were smaller, on the order of 2 at Estany Redó and Gossenköllesee or 1.2 at Øvre Neådalsvatn. Examination of the data with the *t*-test shows that these increases in the warm seasons are significant ( $p < 0.05$ ). Similar seasonality patterns have been observed

for wet deposition of PCBs in Chesapeake Bay (22) and a British rural lake (20).

Seasonal changes have also been observed for HCB, involving again higher fluxes in the warm periods, with differences on the order of 1.3–3 at Estany Redó and Gossenköllesee (Figure 3). These changes were not observed at Øvre Neådalsvatn which had higher depositions in October 1997–May 1998, 29  $\text{ng m}^{-2} \text{ month}^{-1}$ , than in May–October 1998, 13  $\text{ng m}^{-2} \text{ month}^{-1}$ .

For the OC in current use in agriculture, endosulfans and  $\gamma$ -HCH, the observed seasonal differences may be explained by the application regime of these pesticides. However, this is certainly not the case of the compounds that are not in use at present, e.g. PCBs,  $\alpha$ -HCH, and HCB. Their deposition fluxes are not correlated with precipitation, total suspended particles, or local lake air temperatures (Table 1, Figure 3). Consistent with the revolatilization mechanism of previously deposited residues indicated above (16, 25–27), enhancement of the transfer to the atmospheric pool likely occurs at the high temperatures of the warm seasons. Volatilization during the warm periods also increases for the OC in current agricultural use. Therefore, also in the case of these compounds, the observed higher deposition fluxes may reflect, at least in part, the seasonal temperature influence.

**Qualitative Changes.** Higher concentrations of  $\gamma$ -HCH than  $\alpha$ -HCH were found in all sites, with  $\alpha/\gamma$  ratios of 0.1–0.2 in most samples from Estany Redó and Gossenköllesee. At Øvre Neådalsvatn, the  $\alpha/\gamma$  ratio was higher, i.e., in the range of 0.4–0.8. The lower Henry constant of  $\gamma$ -HCH (0.024  $\text{Pa m}^3 \text{ mol}^{-1}$ ) in relation to the  $\alpha$ -isomer (0.68  $\text{Pa m}^3 \text{ mol}^{-1}$ ) (15) may selectively enhance the transport of the latter. Thus, Øvre Neådalsvatn, the lake more distant from sites of intensive agricultural use of these compounds, has a higher proportion of the more volatile compound. This difference may also reflect the present banning of technical HCHs mixtures containing significant amounts of compounds other than  $\gamma$ -HCH, since the composition of the mixtures arriving to the sites more distant from intensive agricultural use may depend on past usages.

$\alpha$ -Endosulfan levels were lower than  $\beta$ -endosulfan in almost all samples (mean  $\alpha/\beta$  ratio of 0.4 and 0.7 at Estany Redó and Gossenköllesee, respectively). These low ratios are not expected a priori since the technical mixtures applied have  $\alpha/\beta$  ratios of 2.3 (17). The Henry constants of the two isomers are high, 6.6 and 0.87  $\text{Pa m}^3 \text{ mol}^{-1}$  for the  $\alpha$ - and  $\beta$ -isomers, respectively (17). The high volatility of  $\alpha$ -endosulfan, which has a Henry constant 10 times higher than  $\alpha$ -HCH, may involve a very efficient diffusion into the atmosphere and a more effective transfer to distant sites than the  $\beta$ -isomer. Thus, Gossenköllesee has a higher proportion of the  $\alpha$ -isomer than Estany Redó. These differences may be related to longer range transport, assuming a higher application of endosulfan in the surroundings of the Pyrenean area, which is consistent with the higher total deposition fluxes at Estany Redó. The  $\alpha/\beta$  ratios detected in deposition samples are also reflected in the water concentrations of these lakes (5).

The observed changes also reflect the degradation of endosulfans upon long-range atmospheric transport. Accordingly, endosulfan sulfate, which is more resistant to degradation than the  $\alpha$ - and  $\beta$ -isomers (29), is found in higher proportion at Gossenköllesee than at Estany Redó (Figure 2). Furthermore, all endosulfan found at Øvre Neådalsvatn is in the form of the sulfate derivative. The differences in endosulfan sulfate deposition between the three lakes are also consistent with the differences in lake water composition. Thus, only endosulfan sulfate is found in Øvre Neådalsvatn waters (5).

The selective transfer of the more volatile species to these remote lake sites is also evidenced when the PCB distributions

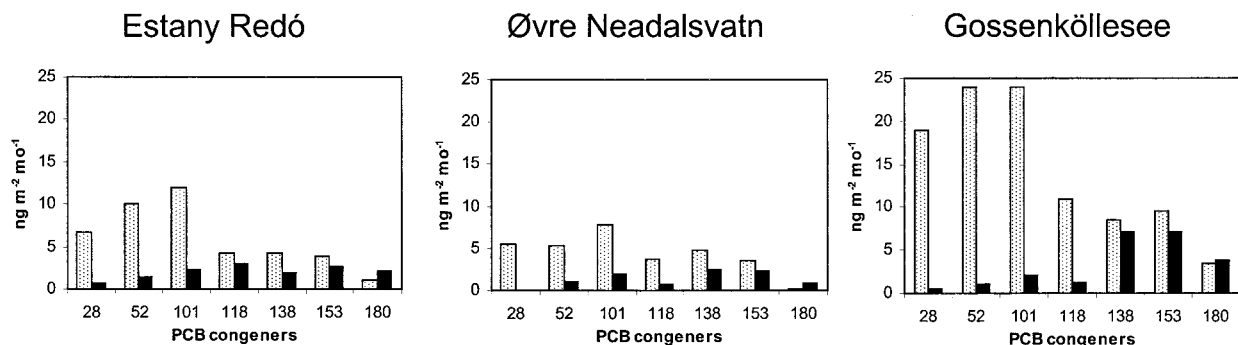


FIGURE 5. Comparison of the atmospheric deposition (dotted bars) and sedimentation fluxes (solid bars) of PCB congeners in high mountain lakes.

are compared. Thus, the deposition samples collected at the three sites have PCB mixtures dominated by the more volatile congeners, e.g., sites 28, 5, and 101 (volatility > 0.0032 Pa; Figure 4). The distributions are rather uniform irrespective of location. In this respect, the latitudinal difference between Estany Redó and Øvre Neådalsvatn is 20° and the linear distance between these two lakes is 2300 km.

These uniform PCB distributions are in agreement with the above-mentioned geographical and seasonal similarities in atmospheric input fluxes. Accordingly, the overall mixing of revolatilized OC used in the past results in rather uniform atmospheric PCB mixtures at present. Therefore, the OC deposition load to remote high mountain sites is rather uniform and independent of local conditions, at least at the European scale.

In contrast, local conditions determine the ultimate accumulation of the deposited pollutants. Whereas the atmospheric PCB input is similar in all three lakes, large differences between lakes are observed in water composition and a major contrast is observed in the sediments (Figure 4). These two last environmental compartments, and particularly sediments, are enriched in lower volatility congeners with respect to the deposition, e.g., PCBs 138, 153, and 180.

These differences in composition are in agreement with the differences in average air temperature among the three lakes. The lake in which the less volatile compounds have been accumulated to a higher extent, Gossenköllesee, has the lowest average annual air temperature, 0.5 °C (Table 1; Figure 4). This preferential accumulation of less volatile compounds at lower temperature is also in agreement with the previously reported selective trapping of organochlorine compounds in mountain lakes of temperate areas (3) and highlights that the mechanism for the ultimate accumulation of OC in these high mountain lakes is related to local temperature, which discriminates among the rather uniform input of atmospheric pollution load arriving to the lakes.

**Implications for the Global Distillation Model.** The global distillation model of OC proposes not only an efficient dispersion mechanism related to the volatility and persistence of these compounds but also a concentration process associated with the condensation of these contaminants in cold environments (7). Overall, the mechanism involves an efficient transfer of OC from warm to cold ecosystems, not a simple dilution effect to the atmosphere or seawater. Within this context, the condensation effects related to cold trapping are one of the aspects less understood.

The qualitative differences related to the PCB distributions described above (Figure 4) provide further insight into this question. Straightforward comparison of the atmospheric deposition fluxes of the initial PCB congeners determined in the present study together with the sedimentation rate of these compounds (3) shows that both fluxes are very distinct for the more volatile compounds, namely, compounds 28, 52, and 101, and rather close for the congeners of lower

volatility, namely, compounds 138, 153, and 180 (Figure 5). These results evidence that the high mountain areas, at least those situated in temperate zones, retain efficiently the less volatile PCBs but not those of higher vapor pressure.

In addition, the lake exhibiting highest similarity between atmospheric deposition and sedimentation fluxes for the less volatile PCBs is Gossenkölle, having the lowest average air temperature (Table 1). Most likely, the more volatile PCB congeners will condense and be retained at sites colder than these high mountain lakes, like those found at higher latitudes.

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