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Organochlorine Pollutants in Remote Mountain Lake Waters

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ABSTRACT

Hexachlorocyclohexanes (HCHs; α - and γ -isomers), endosulfans (α - and β -isomers and the sulfate residue), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDTs), and polychlorobiphenyls (PCBs) were measured in waters from three European remote mountain lakes situated in the Alps, Pyrenees, and Caledonian mountains. Sampling encompassed both ice-free and ice-covered periods at different water column depths. High HCH concentrations were found in all lakes, those in the Alps and Pyrenees (990–2900 pg/L) being among the highest recorded in continental waters. Endosulfans and endosulfan sulfate (120–1150 pg/L) were the second major group of organochlorine contaminants, showing a remarkable stability upon atmospheric long-range transport. The concentrations of HCB, DDTs, and PCB (4–8, 0.6–16, and 26–110 pg/L, respectively) were low in comparison with other continental waters. Hexachlorocyclohexanes, endosulfans, and HCB were essentially found in the dissolved phase. Phase partitioning of the more hydrophobic compounds exhibited a dependence on temperature and water-suspended particles. Comparison between different sampling seasons and water depths indicated a remarkable concentration uniformity within lake, but major interlake differences. Normalization to turnover rates showed higher interlake similarity. Preferential accumulation of the less volatile compounds in the Alp lake and significant increase of baseline contributions of organochlorine compounds and residues in the Caledonian lake are also evidenced from these turnover rates.

A LARGE number of persistent organic pollutants (POPs) are organochlorine compounds (OCs) (United Nations Economic Commission for Europe, 2000). High mountain lakes are some of the remote areas under potential stress by POPs. These lakes can be defined as those situated above the timberline receiving their waters through atmospheric fallout. Their ecological and environmental value is high because they often support unique species of plant and animal communities. They are often the headwater catchments of water supplies and excellent sensors of environmental change for entire mountain environments.

Most OC studies in lacustrine waters have been developed in large lakes, such as the Great Lakes in the United States and Canada (Oliver and Niimi, 1988; Jeremiason et al., 1994; Pearson et al., 1996; Swackhamer et al., 1988), Lake Baikal in Russia (Kucklick et al., 1994; Iwata et al., 1995), and some lakes in the Arctic (Kidd et al., 1998). Very few studies have been concerned with high-altitude mountain lakes (e.g., USA [Datta et al., 1998] and India [Dua et al., 1998]). Not one of these studies has been conducted in Europe. The lakes in the mountain regions of Europe constitute the most remote and least disturbed inland environments and these lakes are especially sensitive to airborne pollutant deposition, because their catchments have only

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Abbreviations: DDT, dichlorodiphenyltrichloroethane; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane; OC, organochlorine compound; PCB, polychlorobiphenyls.

Table 1. General features of the lakes selected for study.

Lake	Mountain range	Latitude	Longitude	Altitude	Area	Volume	Catchment	Max. water depth	SPM†	Residence time	DOC‡	Ice-free period
				m asl§	ha	10 ⁶ m ³	km ²	m	mg/L	yr	mg/L	
Redó	Pyrenees	42°38'N	0°46'E	2240	24	7.7	1.55	73	0.23	4¶	1.5	May–Dec.
Gossenkölle	Alps	47°13'N	11°1'E	2417	1.7	0.078	0.20	9.9	0.46	0.5#	0.45	June–Nov.
Øvre Neådalsvatn	Caledonian	62°47'N	9°00'E	728	50	1.9	16	18	0.21	0.11††	0.73	June–Oct.

† Average suspended particulate matter.

‡ Dissolved organic carbon.

§ Meters above mean sea level.

¶ Catalan, 1988.

Nickus and Thies, personal communication, 2000.

†† Lien, personal communication, 2000.

thin soils and sparse vegetation cover, being therefore unable to prevent contamination from reaching surface waters.

The present study is devoted to the analysis of OC in the waters of these European lakes. For this purpose, three high-altitude lakes, one in each of the main mountain chains (Alps, Pyrenees, and Caledonian), were selected for study (Table 1). These lakes were situated

above the regional tree line and have no evidence of human disturbance in the lake or catchment area. These lakes are also oligotrophic, have a low content of suspended particulate matter (Fig. 1), and are seasonally ice covered for 5 to 8 mo, depending on location and year.

The study identified several OCs included in the persistent organic pollutants list (United Nations Economic Commission for Europe, 2000), pesticides such as hexa-

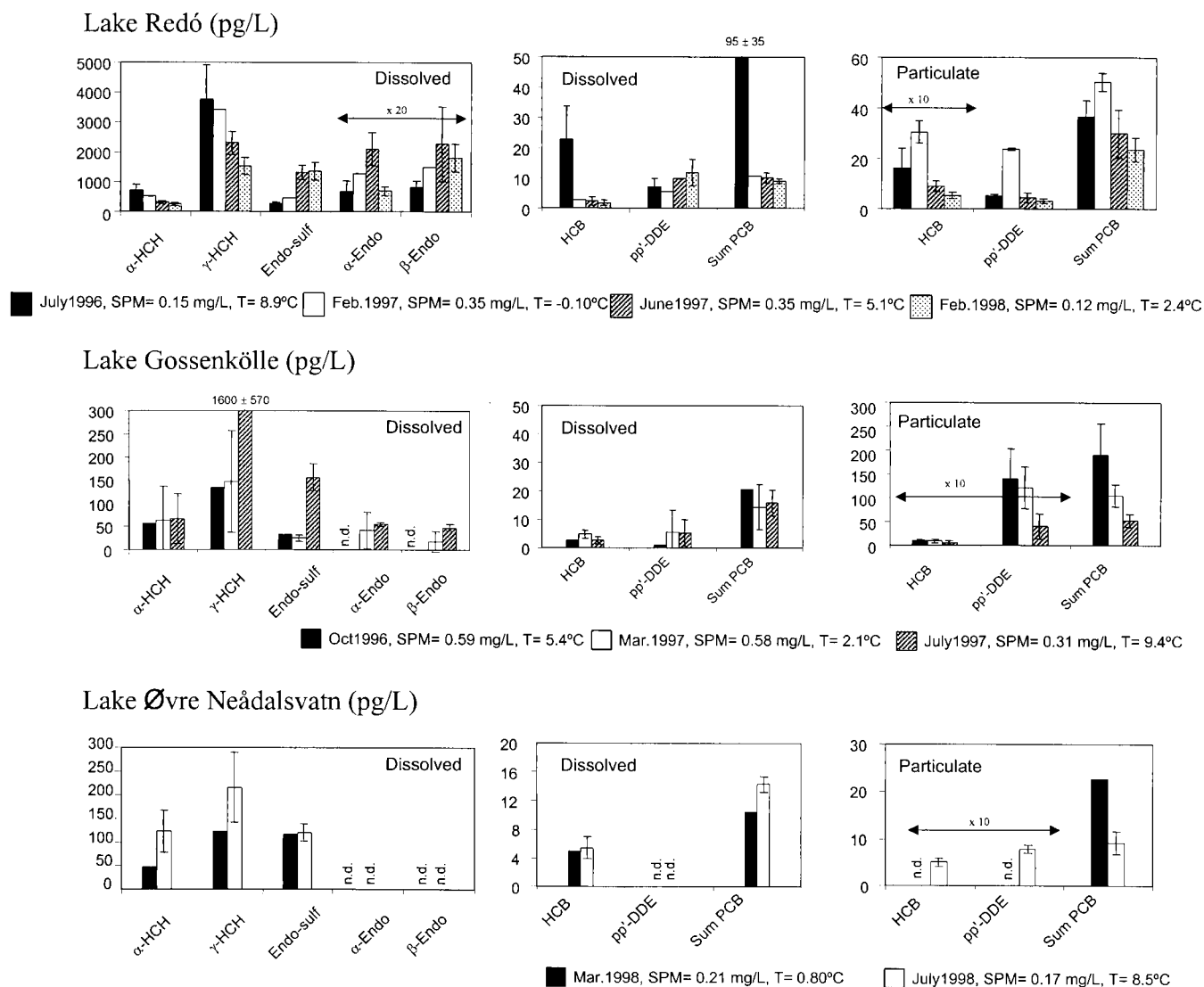


Fig. 1. Average concentrations of the main organochlorine compounds identified in the waters of Redó, Gossenkölle, and Øvre Neådalsvatn lakes between 1996 and 1998. Vertical bars: averaged values for all sampled depths. Interval: \pm standard deviation.

chlorocyclohexanes (HCHs), *p,p'*-DDT and its transformation product *p,p'*-DDE, and industrial chemicals like polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). However, other OCs not included in the United Nations Economic Commission for Europe persistent organic pollutants list, such as endosulfans, were found in high water concentrations. The present study is devoted to the description of these compounds in the particulate and dissolved phases as well as their water column distribution. The influence of season and location on concentration and phase partitioning is also evaluated. The observed concentration levels are compared with those reported in other aquatic environments. Budgets, inventories, and turnover are also considered.

MATERIALS AND METHODS

Sampling

Samples were taken in several seasons including periods of ice-free and ice-covered lake surface. In winter, a drilling device was used to access the water under the ice cover. Waters were collected at several depths: near the surface (1 m depth), near the bottom, and at intermediate levels.

The sampling device was a stand-alone pump (Infiltrax II; Axy Environmental Systems Ltd, Sidney, Canada) equipped with a GF/B glass fiber filter (1- μ m nominal cutoff, 14.2-cm diameter; Whatman, Maidstone, UK) and a PTFE column packed with 75 g of XAD-2 resin (Supelco, Barcelona, Spain) for collection of suspended particles and dissolved organic compounds, respectively. The resins were cleaned by successive Soxhlet extraction with *n*-hexane, dichloromethane, methanol, and dichloromethane (24 h each). The last dichloromethane extract was used for blank testing and the cleaned resin was stored in methanol. About 100 L of water were pumped through this filter and then through the PTFE column at a flow rate of 18 L/h. Filters were preweighed prior to use. Detailed adsorbent comparisons are reported elsewhere (Dachs and Bayona, 1997; Gómez-Belinchón et al., 1988a). Prior to the present study, this sampling system had been successfully used for trace organic pollutant analysis in seawaters (Dachs et al., 1997a,b). Examination of the hydrocarbons collected in the filtered water and the suspended particles retained in the filters shows a distinct composition of the two water phases allowing exclusion of interfering effects such as trapping of dissolved organic constituents onto filter-retained organic matter (De Lappe et al., 1983; Gómez-Belinchón et al., 1988b).

Filters were removed from the filter head, folded, and wrapped in pre-ashed aluminum foil. They were stored at -20°C until processing in the laboratory. The XAD-2 columns were stored sealed with endcapped fittings and kept refrigerated until analysis, no later than 1 wk.

Analytical Procedures

Filter samples were freeze-dried in an oil-free device and weighed for the determination of the suspended particulate matter. These samples were then cut in small pieces and extracted by sonication with (2:1) dichloromethane and methanol (3×30 mL, 20 min). The extract was spiked with PCB IUPAC No. 30 and 209 as surrogate recovery standards, vacuum-evaporated to 5 mL, and hydrolyzed overnight with 20 mL of 6% (w/w) KOH in methanol. The neutral fraction was recovered by extraction with *n*-hexane (3×10 mL), vacuum-evaporated until near-dryness, and transferred to a glass col-

umn (35 cm \times 0.9 cm i.d.) packed with 2 g of neutral alumina. The organochlorine compounds were collected by elution with 5 mL of *n*-hexane and dichloromethane (95:5), vacuum- and nitrogen-concentrated to near-dryness, and stored at -20°C until instrumental analysis.

The XAD-2 adsorbent column was eluted with 200 mL of methanol followed by 200 mL of dichloromethane delivered by a high performance liquid chromatography (HPLC) pump at 2 mL/min. The methanol fraction was vacuum-concentrated to half volume and extracted with 3×30 mL of *n*-hexane. The *n*-hexane extract was dried over anhydrous sodium sulfate, combined with the dichloromethane eluate, and spiked with the above-mentioned recovery standards. This combined extract was vacuum- and nitrogen-concentrated almost to dryness and stored at -20°C . The quantitative performance of this XAD-2 extraction procedure was previously evaluated (Dachs and Bayona, 1997).

Dissolved organic carbon was analyzed in samples filtered through GF/F fiberglass filters (Whatman) by using a Shimadzu (Kyoto, Japan) TOC-5000 analyzer (Camarero et al., 1999).

Prior to instrumental analysis, both filter and resin extracts were redissolved in iso-octane, and tetrachloronaphthalene (TCN) and octachloronaphthalene (OCN) were added as internal standards.

Instrumental Analysis

The organochlorine fraction was analyzed by gas chromatography (GC; Carlo Erba [Milan, Italy] GC8000 Series) coupled to mass spectrometry (MS) (Fisons MD800; Thermo-Quest, Manchester, UK). A 30-m HP-5MS column (0.25-mm i.d. \times 0.25- μ m film thickness; Hewlett-Packard, Palo Alto, CA) was used. The oven temperature program started at 90°C (held for 1 min) to 120°C at $10^{\circ}\text{C}/\text{min}$, and then to 310°C at $4^{\circ}\text{C}/\text{min}$ (final holding time 15 min). Injector, transfer line, and ion source temperatures were 280, 280, and 200°C , respectively. Helium was the carrier gas (1.1 mL/min) and the injector operated in the splitless mode (48 s). Data were acquired in the electron impact mode (EI; 70 eV ionization energy). Organochlorine compound analyses were performed in the selected ion recording mode (SIR) using the following diagnostic ions: *m/z* 181, 195, 219, 235, 241, 246, 256, 272, 284, 266, 292, 326, 360, 394, and 404 (dwell time 40 ms per single ion, ion windows according to standard retention time).

Identification and Quantitation

The identities of HCHs, endosulfans, HCB, and PCBs with more than four chlorine substituents were confirmed by gas chromatography-mass spectrometry in the chemical ionization mode and negative ion recording using ammonia as reagent gas (Chaler et al., 1998). In these instrumental conditions, the following PCB congeners coeluted: 28-31, 101-84, 138-163-160 (Larsen et al., 1992). Thus, notation for PCBs 28, 101, and 138 includes their coeluting congeners.

Quantitative data were obtained by the external standard method using multilevel calibration mixtures containing target, surrogate, and internal standard analytes. Recoveries for the analytical procedure based on surrogate data were typically: PCB 30, $58 \pm 17\%$ and PCB 209, $71 \pm 22\%$ for the filter analysis, and PCB 30, $44 \pm 14\%$ and PCB 209, $74 \pm 7\%$ for the resin analysis. The low recoveries observed for PCB congener No. 30 were due to volatilization losses. The instrumental detection and quantitation limits (LOD and LOQ, respectively) of the organochlorine compounds have been determined with calibration curves (five points each) closer to

the lowest detectable concentration range. These limits were defined by reference to the standard error of the slope and intercept of these curves as to the lowest value that can be detected with a 95% level of confidence. Typical values were in the order of 0.01 to 0.1 pg/L and 0.10 to 0.40 pg/L for LOD and LOQ, respectively. Method detection and quantitation limits (MDL and MQL, respectively) for both phases were defined as three and five times the noise measured near the compound peak in real samples that contained low quantities of the pollutant. The MDL and MQL for both phases were 0.3 and 0.5 pg/L, respectively. Only values above the MQL were reported. Reported data were corrected by surrogate recoveries.

RESULTS AND DISCUSSION

According to standard convention, PCBs denote the sum of PCB Congeners 28-31, 52, 101-84, 118, 138-163-160, 153, and 180 and DDTs the sum of *p,p'*-DDE and *p,p'*-DDT. In the particulate phase *p,p'*-DDT is quantified as *p,p'*-DDE because alkaline hydrolysis transformed *p,p'*-DDT into *p,p'*-DDE. Likewise, HCH and endosulfans were only determined in the dissolved phase because the alkaline hydrolysis prevented the determination of these compounds in the particulate fraction extracts. However, analysis of one water sample from Lake Redó without alkaline treatment of the particle extract showed that most (>99%) HCH and endosulfans were in the dissolved phase, which is in agreement with their relatively high water solubilities (2×10^{-2} to 8×10^{-4} mol/m³) in comparison with PCBs (in the range of 6×10^{-5} to 8×10^{-10} mol/m³ [Tomlin, 1995, p. 388-390; Ballschmitter and Wittlinger, 1991]).

HCH

As indicated above, these compounds are found in the dissolved fraction. They are the OCs found in the highest abundance in all lakes (Table 2, Fig. 1), the most abundant organochlorine pollutant being γ -HCH. This compound has an average concentration of 2500 pg/L in Lake Redó and 3 and 13 times lower than this value in Lakes Gossenkölle and Øvre Neådalsvatn, respectively (Table 2). The α -HCH isomer also has the highest value in Redó (410 pg/L) and six and four times lower than this maximum concentration in Gossenkölle and Øvre Neådalsvatn, respectively.

Total HCH concentrations show high HCH levels in Redó and Gossenkölle, 2900 and 990 pg/L, respectively. These values are similar or higher than those in lakes from urban and industrial areas, for example, Lake Baikal (Kucklick et al., 1994; Iwata et al., 1995) and the Great Lakes (McConnell et al., 1993; Oliver and Niimi, 1988) (Table 2). Thus, in Lake Redó the HCH concentrations are close to the highest concentrations described for lacustrine waters. These results are surprising for such remote sites that only receive atmospheric inputs. However, some Arctic Lakes in Canada, which receive pollution through atmospheric inputs, also have these high levels (Bidleman et al., 1995; Kidd et al., 1998).

One important difference between HCH in the European Lakes and the previously studied aquatic systems

reported in Table 2 is the higher abundance of the γ isomer in the former whereas α -HCH is dominant in the latter. To this end, the α - to γ -HCH ratios for Lakes Redó and Gossenkölle, 0.16 ± 0.03 and 0.18 ± 0.19 , respectively, are low and suggest pure lindane (more than 90% of γ -HCH) as the likely source. The dominance of this isomer is in agreement with the accepted HCH product in the present European legislation. The higher content of α -HCH in Øvre Neådalsvatn (0.53 ± 0.10) could reflect the influence of HCH contributions accumulated in northern latitudes as consequence of the widespread use of technical mixtures in the past, which were characterized by high proportions of the α isomer (Jantunen and Bidleman, 1998; Bidleman et al., 1995; Breivik et al., 1999; Hargrave et al., 1997).

Endosulfans

This group of compounds also occurs in the dissolved phase and is the second major OC in the waters of the European remote mountain lakes considered for study (Table 2). This insecticide is of widespread use, being one of the few organochlorine insecticides still permitted in Canada, the United States, and Europe. Technical endosulfan is composed of α -endosulfan (64-67%) and β -endosulfan (29-32%) (Tomlin, 1995, p. 388-390) and one of their main residues is endosulfan sulfate (EPA 440/5-80-046; USEPA, 1980). Endosulfan is not considered an environmentally persistent compound because it does not readily bioaccumulate and it is not persistent in biological tissues (World Health Organization, 1984). However, it is toxic to aquatic organisms, particularly fish (EPA 440/5-80-046; USEPA, 1980) and is classified as a Class II component (moderately hazardous) by the World Health Organization (1984).

The α - and β -isomers of endosulfan were detected in all Lake Redó samples and in some from Gossenkölle, but not in Øvre Neådalsvatn (Table 2). Average values of α -endosulfan in Redó (60 ± 38 pg/L) are similar to Gossenkölle levels (44 ± 28 pg/L). However, average values of β -endosulfan in Redó (84 ± 46 pg/L) are three times higher than in Gossenkölle (28 ± 24 pg/L). Reports on endosulfan occurrence are scarce and no data was found for lakes. The concentrations of α - and β -isomers in Redó and Gossenkölle are higher than those found in the Arctic Ocean (2.0-7.2 and 0.35-5.3 pg/L for α - and β -endosulfan, respectively [Hargrave et al., 1997; Jantunen and Bidleman, 1998]), and one order of magnitude lower than the levels in Chesapeake Bay tributaries (400-800 and 500-1000 pg/L for α - and β -endosulfan, respectively [Lehotay et al., 1998]). Thus, endosulfan levels in these mountain lakes exhibit intermediate concentrations between high-latitude and polluted sites.

In terms of concentration, endosulfan sulfate is the second main OC pollutant in Redó and Øvre Neådalsvatn, 1000 ± 537 pg/L and 120 ± 16 pg/L, respectively (Table 2, Fig. 1). These concentrations are similar to those found in watercourses located near agricultural areas such as Chesapeake Bay tributaries (290-500 pg/L [Lehotay et al., 1998]). The sole presence of endosulfan

Table 2. Comparison of organochlorine concentrations in the waters of Lakes Redó, Gossenkölle, and Øvre Neådalsvatn with those reported in other studies.

Location and sampling date	PCBs	DDT	HCB	α-HCH	γ-HCH	HCH†	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	Reference
European mountain lakes										
Redó (Spain): July 1996, Feb. 1997, June 1997, Feb. 1998 (n = 12)	62 ± 44‡	16 ± 28§	8.4 ± 11	410 ± 220	2500 ± 1090	2900 ± 1300	60 ± 38	84 ± 46	1000 ± 537	this study
Gossenkölle (Austria): Oct. 1996, Mar. 1997, July 1997 (n = 9)	110 ± 64‡	14 ± 6.3§	4.0 ± 1.8	64 ± 53	930 ± 850	990 ± 860	44 ± 28	28 ± 24	92 ± 72	this study
Øvre Neådalsvatn (Norway): Mar. 1998, July 1998 (n = 5)	26 ± 5.4‡	0.59 ± 0.40§	6.2 ± 1.0	110 ± 52	200 ± 76	300 ± 130			120 ± 16	this study
Eastwaite Water Lake (UK) July 1996, June 1997	680 ± 190‡,¶									Gevao et al., 1998
Lake Baikal (Russia) May 1992, June 1992	18-590#	nd-15§	7.0-28	36-760	18-200	56-960				Iwata et al., 1995
June 1991	300-1500††	59 ± 23§	20 ± 3.7	1100 ± 81	240 ± 29	1300				Kucklick et al., 1994
Great Lakes (USA)										
Lakes Huron and Superior: before 1989		18-45§	18-70							Kucklick et al., 1994‡‡
Lake Ontario: Apr. 1984	380 ± 71‡	95 ± 21§	150 ± 50	2800 ± 400	300 ± 120	3100 ± 420				Oliver and Niimi, 1988
Lake Ontario: May-Oct. 1993			810-1000		360-400					Ridal et al., 1996
Lake Superior: Aug. 1986	180 ± 53¶,§§									Baker and Eisenreich, 1990
Lake Michigan: 1991	180 ± 20¶¶									Jeremiason et al., 1994
Lakes Huron, Michigan, Ontario: 1990	470##			980-1400	310-370					McConnell et al., 1993
Siskiwit Lake: Sept. 1983, Jan. 1984	580†††									Swackhamer et al., 1988
Sierra Nevada Mountains (USA) Lake Tahoe: 20-22 Dec. 1995	370¶,‡‡‡									Datta et al., 1998
Lake Manette: 18 Dec. 1995	670¶,‡‡‡									
Arctic Lakes (Canada) 1995, 1994, and before	18-470§§§	4-90		1300	280	490-1500				Kidd et al., 1998‡‡‡
Amituk Lake: Aug. 1992 (n = 1)						1600				Bidleman et al., 1995
Mediterranean Sea 1989-1990	24-30#	2.1		170-190	150-150	230				Iwata et al., 1993
June-July 1993	42¶¶¶	1.6###								Dachs et al., 1997‡‡‡
Arctic Ocean 1994, 1993, 1992, 1990		1.0 ± 0.30¶,††††	14-18	870-4700	180-700		2.0-7.2	0.35-5.3		Bidleman et al., 1995

† Sum of α-HCH and γ-HCH.
 ‡ Sum of 28, 52, 101, 118, 138, 153, and 180.
 § Sum of p,p'-DDT and p,p'-DDE. Other references do not specify. nd, not detected. Redó, n = 9.
 ¶ Dissolved phase.
 # Sum of 40 PCBs.
 †† Sum of 61 PCBs.
 ‡‡ And the references therein.
 §§ Sum of 28, 101, 118, 108, 138, 153, and 180.
 ¶¶ Sum of 25 PCBs.
 ## Sum of 85 PCBs.
 ††† Sum of 52, 101, 118, 138, 153, and 180.
 ‡‡‡ Sum of 97 PCBs.
 §§§ Sum of 102 PCBs in Peter Lake.
 ¶¶¶ Sum of 12 PCBs (with 21 coeluting congeners).
 ### Sum of p,p'-DDT, o,p'-DDT, o,p'-DDE, and o,p'-DDE.
 †††† Resolute Bay (Bidleman et al., 1995).

sulfate in Øvre Neådalsvatn may reflect contributions from more distant sources than in Lakes Redó or Gossenkölle. Endosulfan sulfate has been reported to degrade at lower rates than the parent α - and β -endosulfans (Guerin and Kennedy, 1992).

Laboratory studies have shown that the half-life of endosulfan ranges between a few days to several months, depending on the experimental conditions (Guerin and Kennedy, 1992; Ferrando et al., 1992; Peñuela and Barceló, 1998). The identification of endosulfans during winter cover when no additional atmospheric inputs occur suggests that these compounds are quite stable in these lakes. Oxygen decreases in the waters during ice cover but the lakes never reach anoxia (Catalan, 1992; Ventura et al., 2001). In any case, the presence of endosulfans in these lakes confirms that this group of insecticide compounds is also transported over long distances and is chemically resistant to atmospheric photooxidation and in-lake degradation processes.

PCBs

PCB concentrations in Gossenkölle (110 ± 64 pg/L) are two times higher than in Redó (62 ± 44 pg/L) and four times higher than in Øvre Neådalsvatn (26 ± 5.4 pg/L) (Table 2). Comparison with data in the literature must be cautious because of differences in number of compounds quantified, the method of quantification, and the sampling year. Taking this into account, the values of these mountain lakes are generally lower than those reported in continental aquatic systems, including rural sites like Esthwaite Water Lake (Gevao et al., 1998) or the Siskiwit Lake (Swackhamer et al., 1988).

A predominant association of these compounds to the particulate phase (0.12–0.59 mg/L) is generally observed (Fig. 1). The suspended particulate matter is essentially composed of microbial plankton assemblages with a general phytoplankton to zooplankton ratio of 8:1 (Camarero et al., 1999; Felip et al., 1999; Thies et al., 1999). In Redó, the PCB proportion in the suspended particles was 72 to 82% ($n = 8$) of total water content except in July 1996 (27%, $n = 3$) when higher water temperatures were measured (8.9°C). In Gossenkölle, 77 to 90% of total aquatic PCB was in the particles ($n = 9$), with the waters collected in the warmer period (July 1997, 9.4°C) exhibiting higher PCB proportion in the dissolved phase (23%). In Øvre Neådalsvatn, the phase partitioning of PCB was also related to temperature, with particulate PCB representing 70 and 40% of total water content at 0.80 and 8.5°C, respectively.

The proportion of PCB in the particulate phase was also related to the amount of suspended particles. The higher proportion of dissolved than particulated PCB in Redó in July 1996 is consistent with the low content of water particles in this lake during this period (Fig. 1). In winter, the relative lower proportion of particulate PCB in Øvre Neådalsvatn (70%) than in the other lakes (80–92%) is also consistent with a lower water particle content.

The relative contribution of each PCB congener in the particulate and dissolved phase is shown in Fig. 2

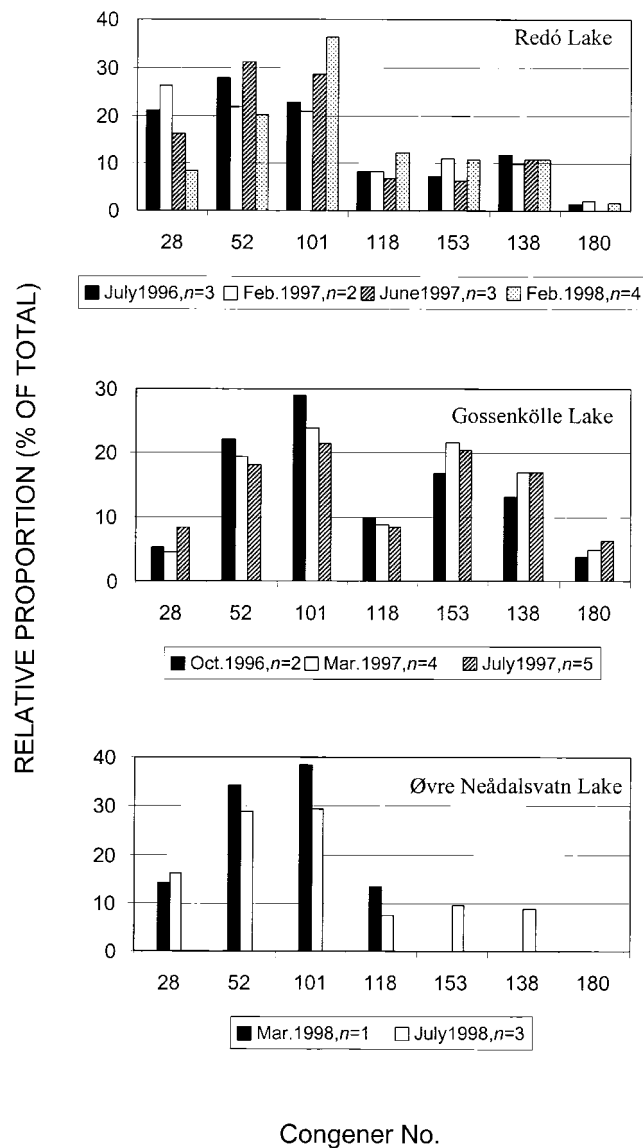


Fig. 2. Relative congener distribution of the PCB mixtures in the suspended matter of the water samples analyzed in Lakes Redó, Gossenkölle, and Øvre Neådalsvatn.

and 3, respectively. All lakes show a rather uniform PCB distribution in the latter, which is characterized by the lack of predominance between the group of lower and higher chlorinated congeners, No. 28, 52, and 101 vs. No. 153 and 138, respectively. The particulate PCB distribution in Gossenkölle is very similar to this general dissolved-phase pattern. In contrast, the particulate PCB in Redó and Øvre Neådalsvatn lakes are dominated by the lower-chlorinated congeners (PCBs 28, 52, and 101), representing 70% of the total sum.

DDTs

The total concentrations of DDTs (filtered + filtrate matter) are similar in Redó and Gossenkölle (16 ± 28 and 14 ± 6.3 pg/L, respectively), which are similar to those found in some of the Great Lakes (Table 2). The waters from Øvre Neådalsvatn (0.59 ± 0.40 pg/L) have

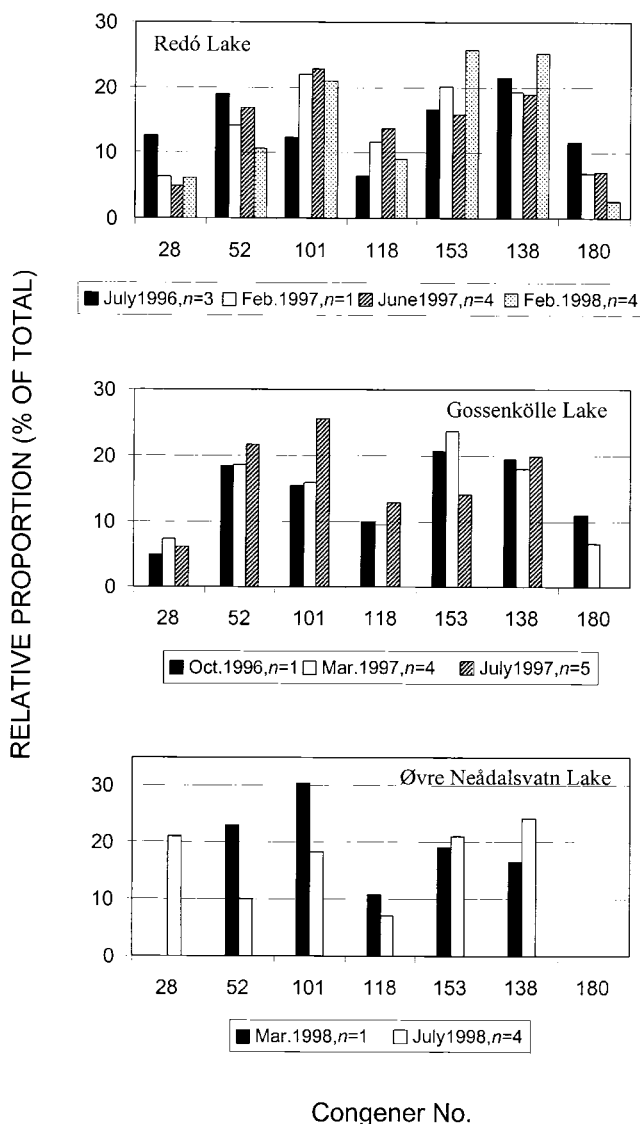


Fig. 3. Relative congener distribution of the PCB mixtures in the dissolved fraction of the water samples analyzed in Lakes Redó, Gossenkölle, and Øvre Neådalsvatn.

about 30 times less DDTs than Redó and Gossenkölle. The levels in this lake range among the lowest found in the literature, being even lower than those reported in the Arctic Ocean and in Canadian arctic lakes (Kidd et al., 1998).

The phase partitioning of these compounds does not show such well-defined trends as does PCB. In this case, the percent of particulate DDTs range between 21 and 95% (Fig. 1). In general, lower water column suspended particles gives rise to lower proportions of these compounds in the particulate phase and lower temperatures correspond to higher association to suspended particles.

HCB

Levels of HCB are similar in all three lakes, although two times higher in Lake Redó (8.4 ± 11 pg/L) than in Gossenkölle (Table 2). In any case, they are in the low range of those reported in the literature and are even

lower than those found in the Arctic Ocean (Hargrave et al., 1997).

HCB was found mainly in the dissolved phase, at 70 to 100% of its overall (dissolved + particulate phase) water concentration ($n = 22$). In two winter samples from Redó Lake, the proportion of HCB in the dissolved phase was 45 to 54% of overall water concentration. These samples correspond to those of lowest water column temperature (-0.1°C), which enhanced association to the particulate phase.

Water Column Distribution

Further insight into the occurrence of these compounds in remote mountain lakes may be obtained from their water column concentration gradients. To this end, particular attention has been devoted to Redó lake, the one with the deepest water column (73 m, Table 1). The other two (10 and 18 m) show the same trends, but with lower vertical differences.

Vertical concentration profiles for HCH, endosulfans, HCB, DDTs, and PCB were measured in Lake Redó in July 1996, June 1997, and February 1998 (Fig. 4). In February 1997 the meteorological conditions were too difficult for a complete water column sampling. In all cases, the vertical distribution of concentrations is rather uniform. The samples collected in July 1996 exhibit some differences in the top 10 m. These samples are those showing higher average concentrations of these compounds. They were collected under the strongest stratification conditions (a gradient of 7°C in the upper 10 m).

The uniform vertical distribution points to efficient vertical mixing processes for the pollutants contributed by atmospheric deposition. Uniformity is also observed during ice cover. In this period there is a 1.8°C rise from 0 m to the 2 to 3 m depth (from 0°C to 1.8°C) and then a slow temperature rise to 2.5 or 3°C at deeper levels.

Derivatives such as endosulfan sulfate also show the same uniform vertical distribution. Thus, the ratio between (α -endosulfan + β -endosulfan) and endosulfan sulfate is rather uniform with depth and the differences at some levels do not show a consistent vertical gradient. Likewise, the ratio between α -HCH and γ -HCH is also uniform throughout the water column. In this case there seems to be a slight increase in the α isomer in the deeper levels. However, the difference is small.

Turnover

The above-mentioned uniform concentrations of organochlorine pollutants suggest that calculations of global lake parameters such as budget, inventory, and turnover can be done. Transformation into budget (concentration \times water volume) or inventories (budget and lake surface) shows that large amounts of organochlorine compounds have been accumulated in Redó Lake (Table 3). However, this aspect essentially reflects the large water volume of this lake in comparison with the others (Table 1).

Turnover (inventory/residence time) provides a more comparable magnitude since it takes into consideration

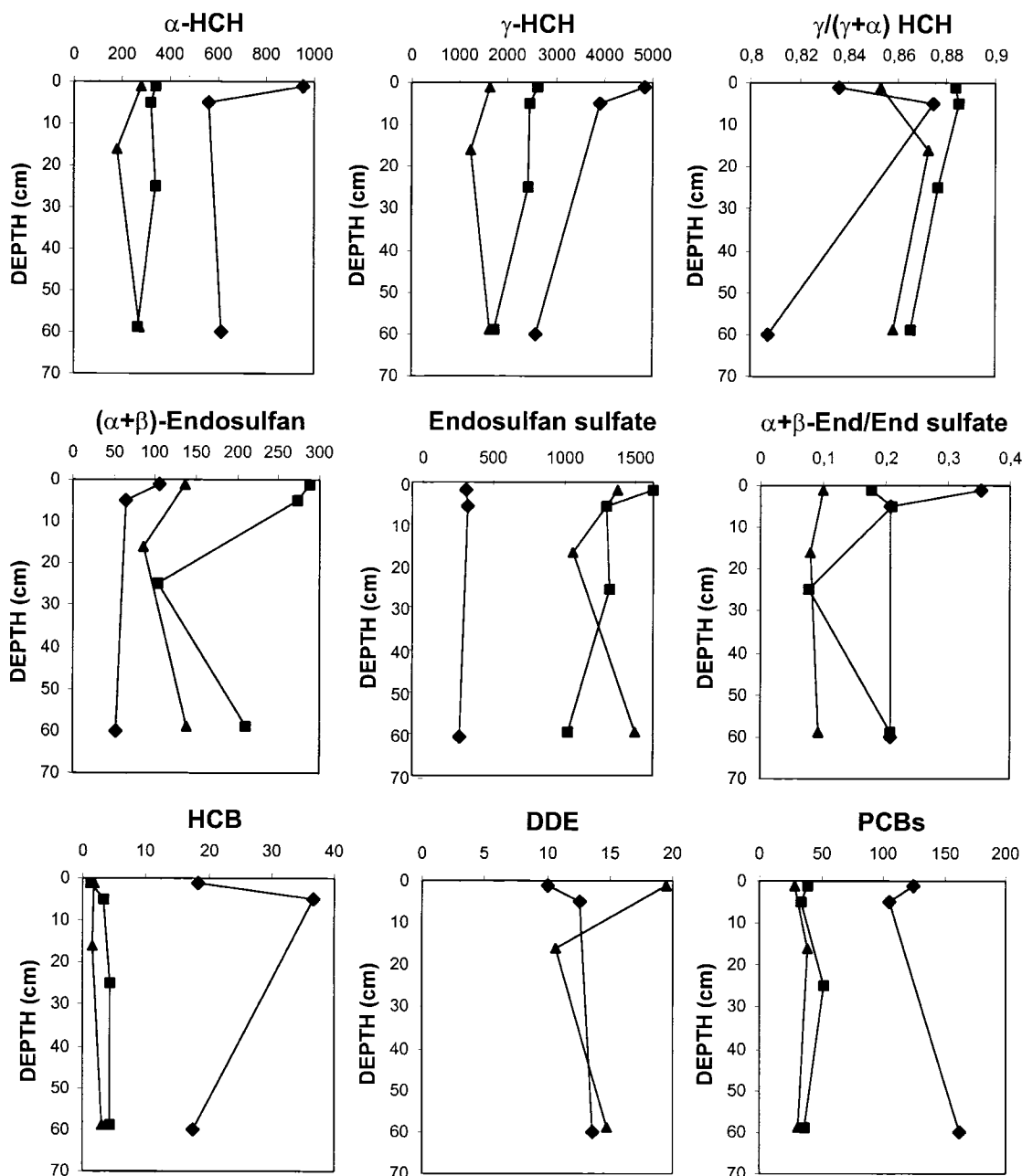


Fig. 4. Vertical concentrations (pg/L) of the main organochlorine compounds identified in Redó Lake. ♦ July 1996, ■ June 1997, ▲ February 1998.

water residence time. This ratio provides an estimate of the net input fluxes (precipitation – evaporation) needed to maintain the water concentrations through time. Total input fluxes are in fact higher than turnover because they also have to compensate for losses to sedimentation. However, these are small, representing between 5% and 10% of the turnover rate for the low and high molecular weight compounds, respectively (Martínez-Vélez, 1999).

Turnover generally provides more interlake uniform values than water concentrations (Fig. 5). The highest concentrations for all compounds, except PCBs, are observed in Redó Lake, but the differences between lakes are not so large when the values are transformed into turnover. In any case, the longer water residence time

of this lake involves a higher accumulation capacity of atmospherically transported organochlorine pollutants.

Øvre Neådalsvatn exhibits the highest turnover for α -HCH and HCB. The high value for α -HCH supports the previous assumption of significant baseline contributions in this lake, which are characterized by high proportions of this isomer (Jantunen and Bidleman, 1998; Bidleman et al., 1995; Hargrave et al., 1997). The presence of this compound is also consistent with the large turnover of endosulfan sulfate, the degradation product of α - and β -endosulfans. The high value shows that the contribution of this residue is not minor even in sites situated at remote distances from production or use. On the other hand, the high input flux of HCB may reflect the latitudinal distribution of this compound as

Table 3. Budget, inventory, and turnover of the organochlorine compounds found in the remote mountain lakes selected for study.

Compound	Budget			Inventory			Turnover		
	Redó	Gossenkölle	Øvre Neådalsvatn	Redó	Gossenkölle	Øvre Neådalsvatn	Redó	Gossenkölle	Øvre Neådalsvatn
	mg			mg/hm ²			mg/hm ² /yr		
α-HCH	3 200	5	210	130	3	4.2	33	5.9	38
γ-HCH	19 500	72	380	810	42	7.7	200	85	70
α-Endosulfan	470	3.4	0	19	2	0	4.9	4	0
β-Endosulfan	660	2.2	0	27	1.3	0	6.8	2.6	0
Endosulfan sulfate	7 800	7.2	230	320	4.2	4.6	80	8.5	42
HCB (particulate)	9.9	0.06	0.58	0.41	0.03	0.01	0.1	0.066	0.07
HCB (dissolved)	56	0.26	12	2.4	0.15	0.23	0.59	0.3	2.7
DDTs (particulate)	38	0.28	1.1	1.0	0.17	0.02	0.26	0.33	0.21
DDTs (dissolved)	82	0.7	0	4.0	0.41	0	1.0	0.95	0
PCBs (particulate)	250	7.5	24	10	4.4	0.49	2.6	8.8	4.3
PCBs (dissolved)	240	1.2	25	10	0.73	0.51	2.5	1.5	4.7

a consequence of the global distillation effect (Simonich and Hites, 1995).

Gossenkölle Lake has a lower turnover than Redó for most compounds except DDTs and PCBs, which are two groups of organochlorine compounds with lower volatility. If this difference is representative for the lakes in the Alps, it means that this mountain lake receives a higher input of the lower volatility compounds than the Pyrenees and the Caledonian mountains.

CONCLUSIONS

High concentrations of HCH have been found in all remote mountain lakes considered for study, those in the Alps and Pyrenees (990–2900 pg/L) being among the highest recorded in continental waters. Endosulfans and endosulfan sulfate (120–1150 pg/L) were the second major group of organochlorine contaminants, exhibiting a remarkable stability upon atmospheric long-range transport. In contrast, the concentrations of HCB, DDTs,

and PCB (4–8, 0.6–16, and 26–110 pg/L, respectively) were lower in comparison with values from other continental waters reported in the literature.

HCHs, endosulfans, and HCB were essentially found in the dissolved phase. The phase partitioning of the more hydrophobic compounds depends on temperature and amount of water-suspended particles.

The concentration differences between lakes are very significant and contrast with the concentration uniformity observed within a lake, either in terms of seasonal changes or water depth. However, normalization to turnover rates shows a higher interlake similarity, indicating that the atmospheric load of these compounds at high altitudes is more similar than a priori observations from direct examination of water concentrations. In any case, significant differences are also observed for the calculated turnover rates, such as the preferential accumulation of the less volatile compounds in the Alp lake. To this end, the high input flux of HCB in Øvre Neådalsvatn may reflect the latitudinal distribution of this compound as a consequence of the global distillation effect.

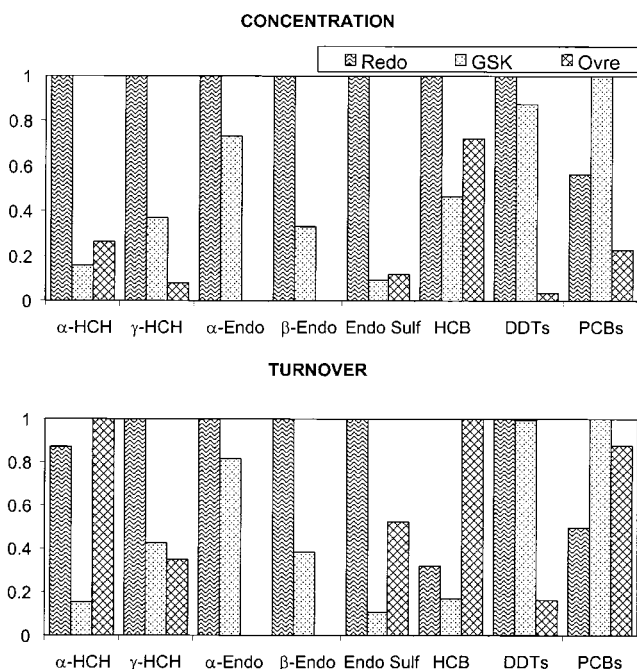


Fig. 5. Comparison of the relative differences in organochlorine compound concentrations and turnover between Lakes Redó, Gossenkölle, and Øvre Neådalsvatn.

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