

## Research Article

# Persistent organic pollutants in remote freshwater ecosystems

Pilar Fernández\*, Guillem Carrera and Joan O. Grimalt

Department of Environmental Chemistry, (ICER-C.S.I.C.), Jordi Girona 18–26, E-08034 Barcelona, Catalonia, Spain

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**Abstract.** Persistent organic pollutants (POPs), including organochlorine compounds (OCs) and polycyclic aromatic hydrocarbons (PAHs) were measured in two European remote mountain lakes situated in the Pyrenees (Lake Redon) and the Tatra Mountains (Ladove). Both dissolved and particulate water phases were analyzed at different water column depths.

OCs already banned in most European countries showed similar concentrations in the two lakes, e.g. 6.7–8.5 pg L<sup>-1</sup> for HCB, 8.0–12 pg L<sup>-1</sup> for DDTs, and 60–64 pg L<sup>-1</sup> for PCBs (sum of seven individual congeners), being in general lower than those reported in other remote aquatic systems. On the contrary, compounds of present use or currently emitted to the atmosphere exhibited significant concentration differences between sites. Thus, the higher levels of HCHs (1000–2630 pg L<sup>-1</sup>) and endosulfans (780–1610 pg L<sup>-1</sup>) in Lake Redon than in Ladove are in agreement with an impact of

agricultural activities in the former. In contrast, the higher PAH concentrations in Ladove, 12 ± 1 ng L<sup>-1</sup> (mean ± standard deviation), than in Lake Redon, 0.77–1.6 ng L<sup>-1</sup> evidence higher deposition of combustion residues in the Tatra.

POP concentration decreases with depth were observed for the compounds present in the dissolved phase such as endosulfan, HCB, and the low molecular weight PCBs and PAH. The vertical differences were higher in Lake Redon, probably due to its deeper basin. These gradients are consistent with the incorporation of these compounds into the lakes by air-water exchange through the gas-dissolved phase.

In contrast, PCBs or PAH associated to the suspended particulate material (those of higher molecular weight) showed uniform concentrations throughout the water column, which may reflect high efficiency in the vertical transport of the compounds associated to this phase.

**Key words.** Polycyclic aromatic hydrocarbons; organochlorine compounds; lake water; remote lakes; dissolved-particle phase partitioning.

## Introduction

Persistent organic pollutants (POPs) have attracted a lot of attention in the recent years because of their toxicity, volatility, and chemical stability, which facilitates their world-wide distribution by long-range atmospheric transport (UNECE, 2000). There is therefore increasing inter-

est in determining the control processes that are responsible for their fate and transport on a global scale. This goal requires the study of environmental monitoring data in different media. Whilst extensive data have been reported on POPs levels in different compartments such as sediments (LaFlamme and Hites, 1978; Fernández et al., 1999; 2000), soils (Meijer et al., 2002; Grimalt et al., 2004a; 2004b; Meijer et al., 2003; Ribes et al., 2003), atmospheric deposition (Blais et al., 1998; Carrera et al., 2001; 2002; Agrell et al., 2002; Buehler and Hites, 2002; Fernández et al., 2003), and air (Halsall et al., 1997; 1998;

\* Corresponding author phone: +34-934006100;  
fax: +34-932045904; e-mail: pfrqam@iiqab.csic.es  
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Harner et al., 1998; Hung et al., 2001; Fernández et al., 2002; van Drooge et al., 2002; Jaward et al., 2004), little attention has been paid to their concentration in water (Tanabe et al., 1983; Mc Veety and Hites, 1988; Schindler et al., 1995; Datta et al., 1998; Gevao et al., 1998; Kidd et al., 1998; Vilanova et al., 2001a; 2001b). However, water constitutes a key environmental compartment for the overall understanding of the global distribution of these compounds in remote environments, including their interactions with food chains.

High mountain lakes constitute ideal ecosystems for the measurement of the effects of long-range atmospherically transported pollution in continental areas. These ecosystems constitute the least disturbed in-land aquatic environments. However, despite of their remoteness, they are under pollution stress by POPs as shown in previous studies on sediments (Fernández et al., 1999; Grimalt et al., 2001), water (Vilanova et al., 2001a; 2001b), and fish (Grimalt et al., 2001; Vives et al., 2004).

The present study is focused on POPs distributions in the waters of remote lakes located in two European mountain ranges, Pyrenees (Spain) and Tatra Mountains (Slovakia). Dissolved and suspended particulate matter (SPM) POP concentrations have been analyzed in fall 2000 and spring 2001 in order to provide information on their sources, transport and distribution between the dissolved and particulate phases in remote aquatic systems. Possible explanations for observed variations in concentration are presented. In addition, selective removal of particles larger than 200  $\mu\text{m}$ , basically zooplankton organisms, allowed assessing whether the observed pollutant levels found in SPM were affected by bioaccumulation processes.

## Materials and methods

### Sampling

Lake water samples (aprox. 100 L) were collected in two high mountain areas of Europe: Lake Redon (Pyrenees,

Spain) and Ladove Pleso (High Tatras, Slovakia). Samples were obtained at several depths, near surface (1 m depth), near bottom and at intermediate levels in September 2000 in Ladove, and November 2000 and May 2001 in Redon. Sampling and lake characteristics are summarized in Table 1.

The sampling device was a stand alone pump combined with in situ filtration and subsequent solid-phase extraction (Infiltrex II, Axys Environmental Systems Ltd, Sidney, Canada). The materials retained in the filters (GF/B, 1  $\mu\text{m}$  nominal cutoff, Whatman) and the resins (XAD-2, Supelco, Barcelona, Spain) were operationally defined as the particulate and the dissolved phases, respectively. In some cases, a nylon net (200  $\mu\text{m}$ ) was used to avoid zooplankton retention in the glass fiber filters. Filters were stored at  $-20^\circ\text{C}$ , whereas XAD-2 columns were kept refrigerated until analysis, no later than one week.

### Analytical procedures

After freeze-drying, the filter samples were weighed for the determination of the total suspended particulate matter, extracted by sonication with (2:1) dichloromethane:methanol and spiked with a surrogate recovery standard mix (anthracene- $d_{10}$  (A- $d_{10}$ ), benz[*a*]anthracene- $d_{12}$  (B[*a*]A- $d_{12}$ ), benzo[*ghi*]perylene- $d_{12}$  (BPer- $d_{12}$ ) and the polychlorobiphenyl (PCB) congeners PCB 30 and PCB 209). Then, extracts were hydrolyzed overnight with 6% KOH in methanol, liquid-liquid extracted with n-hexane and column fractionated with 2 g of neutral alumina. Two fractions were collected: 5 ml of n-hexane:dichloromethane (95:5; OCs) and 10 ml of n-hexane:dichloromethane (1:2; PAH).

The XAD-2 adsorbent columns were eluted with 200 ml of methanol followed by 200 ml of dichloromethane. The former was extracted with n-hexane and dried over anhydrous sodium sulfate. The n-hexane was combined with the dichloromethane eluate and spiked with the above mentioned recovery standards.

**Table 1.** General features of the lakes selected for study and sampling data.

Lake	Lake Redon	Ladove
Mountain Range (Country)	Pyrenees (Spain)	High Tatras (Slovakia)
Altitude (m a.s.l.)	2240	2057
Area (ha)	24	1.7
Catchment area (km <sup>2</sup> )	1.55	0.13
Maximum water depth (m)	73	18
Ice free period	June–Dec.	June–Nov.
Sampling Date	Nov. 2000 and May 2001	Sept. 2000
Thermocline	No	Yes (6–7 m)
Water Temperature at sampled depth ( $^\circ\text{C}$ )	n.a.	6.8 (1 m), 5.5 (6.5 m), 4.1 (14 m)

n.a., not available.

All fractions were vacuum and nitrogen concentrated near to dryness and stored at  $-20^{\circ}\text{C}$ . Prior to instrumental analysis, both filter and resin extracts were redissolved with an internal standard mixture in iso-octane (naphthalene- $d_8$  (Naph- $d_8$ ), perylene- $d_{12}$  (Per- $d_{12}$ ), tetrachloronaphthalene (TCN), and octachloronaphthalene (OCN)).

### Instrumental analysis

The fractions of organochlorine compounds (OC) and polycyclic aromatic hydrocarbons (PAH) were analyzed by gas chromatography (GC) coupled to mass spectrometry (MS) equipped with a HP-5MS column. The oven temperature program started at  $90^{\circ}\text{C}$  (held for 1 min) to  $120^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$  and then to  $310^{\circ}\text{C}$  at  $4^{\circ}\text{C}/\text{min}$  (final holding time 15 min). Injector, transfer line and ion source temperatures were 280, 280 and  $200^{\circ}\text{C}$ , respectively. Data were acquired in electron impact and selected ion monitoring modes, except for endosulfans, which were analysed by negative ion chemical ionization using  $\text{NH}_3$  as reagent gas as described in Chaler et al. 1998. Molecular mass ions were used for identification and quantitation of individual PAH, except for retene quantified by the mass/charge fragment 219. In the case of OC, the following diagnostic ions were selected:  $m/z$  181, 195, 219, 235, 241, 246, 256, 272, 284, 266, 292, 326, 360, 394, and 404 in the electron impact mode, and 237, 372, 386, 406, and 422 in negative ion chemical ionization technique. Quantitative data were obtained by the internal standard method, and response factors were referred to the internal standard mixture.

### Quality control

Procedural blanks were added to each set of 8 samples. Recoveries for the analytical procedure based on surrogate data were: anthracene- $d_{10}$   $37 \pm 8\%$ , benz[*a*]anthracene- $d_{12}$   $64 \pm 13\%$ , benzo[*ghi*]perylene- $d_{12}$   $70 \pm 14\%$ , PCB 30 45  $\pm 14\%$ , and 67  $\pm 15\%$  for PCB 209. The values reported in this study were corrected for surrogate recoveries.

The method detection limits (MDL) were defined as three times the noise measured near the compound peak in real samples which contained low quantities of the pollutants. MDL were in the range of 1 to 10 pg, depending on the pollutant. For those compounds found in field blanks, MDL was defined as the averaged blank value plus three times the standard deviation of these values. This was the case of endosulfans with MDL of 0.18 pg/L ( $\alpha$ -endosulfan), 0.12 pg/L ( $\beta$ -endosulfan) and 0.04 pg/L (endosulfan sulfate) for a reference water volume of 100 L.

Additional details on analytical and instrumental analysis are reported elsewhere (Vilanova et al., 2001a; 2001b)

## Results and discussion

The POPs included in this study encompassed chemicals presently used, such as endosulfanes and  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH), compounds emitted to the atmosphere as consequence of current combustion processes, e.g. PAH, and compounds used in the past but banned at present in most European countries, e.g. DDTs, PCBs,  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH) and hexachlorobenzene (HCB). Nevertheless, ongoing atmospheric emissions of HCB are reported, mainly in relation to the chloro-alkali industry (Spigarelli et al., 1986; Grimalt et al., 1994). Both, dissolved and particulate phase concentrations, were determined. In addition, a SPM split was performed in some samples by inclusion of a nylon net of 200  $\mu\text{m}$  before glass fiber filtration for zooplankton removal, since the accumulation of pollutants into these organisms proceed through bioaccumulation instead of isothermal adsorption processes.

### Hexachlorocyclohexanes (HCHs)

HCHs are the OCs in highest concentration in Lake Redon. Their distributions are largely dominated by two isomers,  $\alpha$ -HCH and  $\gamma$ -HCH. They are present in the dissolved phase with levels varying between  $1326 \text{ pg L}^{-1}$  for total HCHs in November and  $2070 \pm 722 \text{ pg L}^{-1}$  (mean  $\pm$  standard deviation) in May. In Ladove HCHs concentration was  $207 \pm 110 \text{ pg L}^{-1}$ , being one order of magnitude lower than in the Pyrenees (Table 2, Fig. 1). HCHs are mostly used in southern Europe (EMEP, 2004) which is consistent with the differences between these two sites. The levels found in Ladove Lake for both isomers are similar to those reported in other remote aquatic systems, like Canadian Rocky Mountains lakes or the Arctic (Table 2), whereas the concentrations measured in Redon are clearly higher, which confirms the impact of these pollutants in this region.

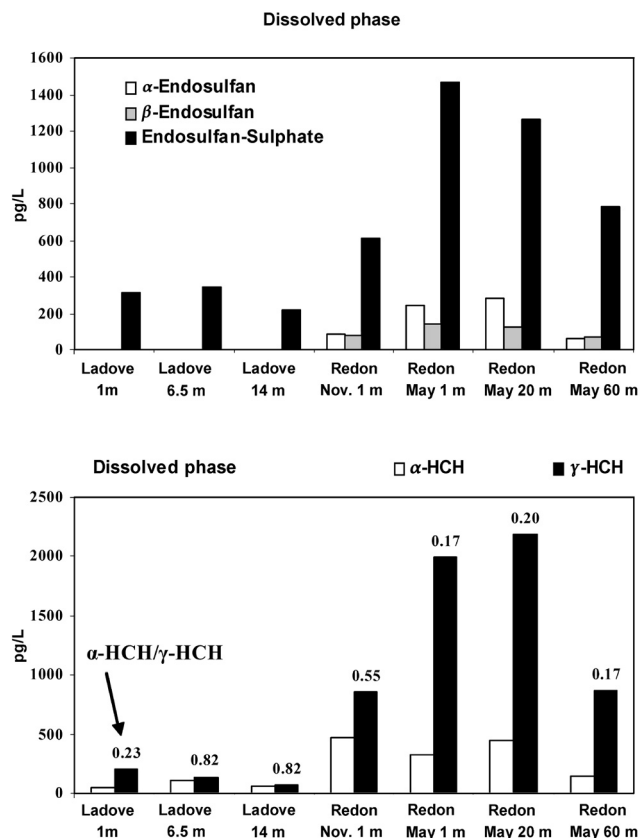
The dominance of  $\gamma$ -HCH in both lakes is in agreement with the present composition of this pesticide. In the past, a technical mixture dominated by the  $\alpha$ -isomer was used. The  $\alpha$ -HCH levels in the water column of Ladove are four times lower than in Lake Redon, whereas  $\gamma$ -HCH concentration ratios between the two lakes are up to thirteen (Table 2). On the other hand, similar concentrations of the  $\alpha$ -isomer in Lake Redon are found in November and May but the levels of  $\gamma$ -HCH are higher in May. The lower spatial and temporal concentration differences of the banned  $\alpha$ -isomer are consistent with diffuse pollution inputs whereas the stronger changes in  $\gamma$ -HCH reflect the present spatial and temporal patterns of use.

No clear trend with water depth has been observed for these compounds, although the lowest concentrations were found in the deepest samples of both lakes.

**Table 2.** Levels of OCs in the water column of the studied lakes ( $\text{pg L}^{-1} \pm$  standard deviation). Values from other remote aquatic ecosystems are included for comparison purposes.

Location	HCB	$\alpha$ -HCH	$\gamma$ -HCH	$\alpha$ -Endosulfan	$\beta$ -Endosulfan	Endosulfan-SO <sub>4</sub>
Ladove (1 m, n = 2)	5.2 $\pm$ 1.4	54 $\pm$ 39	204 $\pm$ 104	nd	nd	310 $\pm$ 42
Ladove (6.5 m, n = 1)	1	110	134	nd	nd	346
Ladove (14 m, n = 2)	10 $\pm$ 2	63 $\pm$ 20	77 $\pm$ 24	nd	nd	217 $\pm$ 43
<i>Ladove average (n = 5)</i>	<i>8.5 <math>\pm</math> 3.2</i>	<i>68 <math>\pm</math> 35</i>	<i>139 <math>\pm</math> 89</i>	<i>nd</i>	<i>nd</i>	<i>280 <math>\pm</math> 65</i>
Lake Redon Nov. 2000 1 m, n = 1	11	470	856	86	76	615
Lake Redon May 2000 1 m, n = 2	8.4 $\pm$ 0.5	331 $\pm$ 81	1994 $\pm$ 431	242 $\pm$ 41	140 $\pm$ 3	1470 $\pm$ 123
20 m, n = 1	3.9	442	2190	280	123	1260
60 m, n = 1	3.3	149	864	66	69	785
<i>Lake Redon average (n = 4)</i>	<i>6.0 <math>\pm</math> 2.4</i>	<i>313 <math>\pm</math> 120</i>	<i>1760 <math>\pm</math> 606</i>	<i>207 <math>\pm</math> 88</i>	<i>157 <math>\pm</math> 51</i>	<i>1246 <math>\pm</math> 293</i>
Lake Redon (1996–8) <sup>(a)</sup>	8.4 $\pm$ 11	410 $\pm$ 220	2500 $\pm$ 1090	60 $\pm$ 38	84 $\pm$ 46	1000 $\pm$ 540
Lake Gossenkölle (1996–7, Austria) <sup>(a)</sup>	4.0 $\pm$ 1.8	64 $\pm$ 53	930 $\pm$ 850	44 $\pm$ 28	28 $\pm$ 24	92 $\pm$ 72
Øvre Neådalsvatn (1998, Norway) <sup>(a)</sup>	6.2 $\pm$ 1.0	110 $\pm$ 52	200 $\pm$ 76	nd	nd	120 $\pm$ 16
Amituk Lake (1994, Arctic) <sup>(b)</sup>		630	169	28		
Sea water (Antarctica) <sup>(c)</sup>		3.4	0.7			
Arctic Ocean (1990, 1992–4) <sup>(d)</sup>	14–18	870–4700	180–700	2.0–7.2	0.35–5.3	
Lake Malawi (1996–8) <sup>(e)</sup>	4.4 $\pm$ 1.6	9.8 $\pm$ 6.2	14 $\pm$ 8.7	3.3 $\pm$ 6.2		
Bow Lake (2000, Canadian Rocky Mts) <sup>(f)</sup>	21	210	130	19	23	
Kananaskis (2000) <sup>(f)</sup>	15	160	140	15	17	

(a) (Vilanova et al., 2001a). (b) (Helm et al., 2002). (c) (Lakaschus et al., 2002). (d) (Bidleman et al., 1995; Hargrave et al., 1997; Jantunen and Bidleman, 1998). (e) (Karlsson et al., 2000). (f) (Wilkinson et al., 2005). nd, below detection limit (between 0.04 and 0.18  $\text{pg L}^{-1}$ ). n, number of analysed samples.

**Figure 1.** Average concentrations of current use pesticides in the water column of remote lakes. x-Axis labels indicate lake identification, sampling period and sampling depth.

### Endosulfans

This pesticide mixture composed by  $\alpha$ -endosulfan (67%) and  $\beta$ -endosulfan (30%) is one of the few organochlorine insecticides still used in Canada, USA and Europe. Endosulfan sulphate is one of its main environmental transformation products. Although endosulfans are not properly considered as POP, they are toxic to aquatic organisms, particularly fish (Tomlin, 1995) and are classified as a Class II substance by WHO (1984) or Class Ib pesticide by EPA. Recently, endosulfans have been included in the persistent toxic substances list (PTS, <http://www.chem.unep.ch>).

The two active  $\alpha$ - and  $\beta$ -isomers and endosulfan sulfate mainly occur in the dissolved phase which is consistent with their relatively high water solubility. In Lake Redon these compounds constitute the second main OC group (Fig. 1, Table 2). The  $\alpha$ - and  $\beta$ -isomers occur at levels between 66 and 280  $\text{pg L}^{-1}$  but the major concentrations correspond to endosulfan sulphate (785–1470  $\text{pg L}^{-1}$ ). These endosulfan concentrations are similar to those found in other aquatic systems located near agricultural areas, and higher than those reported for other remote lakes (Table 2). Endosulfan sulfate is the only compound found in Ladove Lake (280–346  $\text{pg L}^{-1}$ ) which may reflect contributions from more distant areas since the use of endosulfans is characteristic from southern Europe. The concentrations of endosulfans in Lake Redon are higher in May than in November. In previous studies in this and other high altitude Euro-

pean lakes, a relatively high concentration of pesticide residues were found in water (Vilanova et al., 2001a), snow (Carrera et al., 2001) and atmospheric deposition (Carrera et al., 2002), with the highest deposition fluxes being observed in spring-summer (Carrera et al., 2002). The large predominance of endosulfan sulfate over the  $\alpha$ - and  $\beta$ -isomers is indicative of strong influence of past inputs, since the lake was still ice-covered in May.

Endosulfans are found in higher concentrations in the superficial than in the deep waters. Endosulfan sulfate is the compound showing most pronounced decrease with depth. This trend is not observed in Lake Ladove, probably due to its shallow water column.

### Hexachlorobenzene (HCB)

The concentrations of HCB are similar in the two lakes and do not exhibit major differences between sampling periods (Table 2). The levels of this compound in Lake Redon varied between  $6.0 \pm 2.4$  pg L<sup>-1</sup> in May and  $11$  pg L<sup>-1</sup> in November, the highest concentrations being found in the superficial waters. The average concentration of HCB in the water column of Lake Ladove was  $8.5 \pm 3.2$  pg L<sup>-1</sup> with the lowest levels found in the samples taken at 1 m.

This OC is found in both the particulate and the dissolved phases. An average proportion of  $25 \pm 11\%$  in Ladove Lake was associated to SPM. In Lake Redon this percentage varied between 0% in May and 40% in

November following the changes in SPM of this lake (Table 5).

The concentrations of HCB in both lakes are similar to those found in other European and Canadian remote lakes and in previous measurements of Lake Redon waters (Table 2). They are in the low range of HCB water levels reported in the literature. (Vilanova et al., 2001a, and references herein)

### DDTs

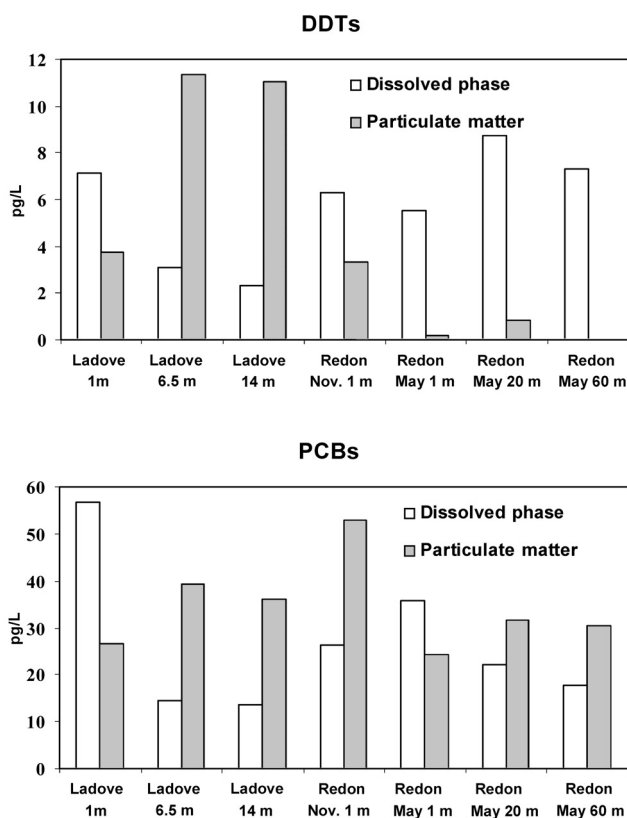
The total DDT concentrations (representing the sum of 4,4'-DDE and 4,4'-DDT) in the water column of Lakes Redon and Ladove are similar (Table 3, Fig. 2). In the former, they vary between 5.7 and 9.6 pg L<sup>-1</sup> with an average value of  $7.1 \pm 2.9$  pg L<sup>-1</sup>. In the latter they range between 11 and 14 pg L<sup>-1</sup> (average concentration of  $12 \pm 3$  pg L<sup>-1</sup>). No significant differences in DDT concentrations have been observed between seasons or along the water column (Mann-Whitney non-parametric test,  $p < 0.05$ ). These levels are similar to those previously recorded in high mountain lakes in Europe. They are however lower than previous water column determinations in Lake Redon for the 1996–98 period (Vilanova et al., 2001a).

The distribution of these compounds between both water phases is variable. In Ladove Lake they are predominantly found in association to the particulate phase except in the superficial waters where they predominate in the dissolved phase (Fig. 2). This distribution could

**Table 3.** Levels of PCBs and DDTs in the water column of the studied lakes (pg L<sup>-1</sup>  $\pm$  standard deviation). Values from other remote aquatic ecosystems are shown for comparison proposes.

Location	PCBs (pg L <sup>-1</sup> )				DDTs (pg L <sup>-1</sup> )
	Total	Particulate	Dissolved	% in SPM	Total
Ladove (1 m, n = 2)	83 $\pm$ 40	27 $\pm$ 4	57 $\pm$ 35	39 $\pm$ 14	11 $\pm$ 4
Ladove (6.5 m, n = 1)	53	39	14	74	14
Ladove (14 m, n = 2)	50 $\pm$ 6	36 $\pm$ 7	14 $\pm$ 1	72 $\pm$ 6	12 $\pm$ 0.5
Ladove average (n = 5)	64 $\pm$ 30	33 $\pm$ 8	31 $\pm$ 31	59 $\pm$ 19	12 $\pm$ 3
Lake Redon Nov. 2000 1 m, n = 1	79	53	26	67	9.6
Lake Redon May 2000					
1 m, n = 2	60 $\pm$ 13	24 $\pm$ 11	36 $\pm$ 3	38	5.7 $\pm$ 3.5
20 m, n = 1	54	32	22	59	9.6
60 m, n = 1	48	30	18	63	7.3
Lake Redon average (n = 4)	56 $\pm$ 11	28 $\pm$ 8	29 $\pm$ 8		7.1 $\pm$ 2.9
Lake Redon (1996–8) <sup>(a)</sup>	62 $\pm$ 44				16 $\pm$ 28
Lake Gossenkölle (1996–7, Austria) <sup>(a)</sup>	110 $\pm$ 64				14 $\pm$ 6.3
Øvre Neådalsvatn (1998, Norway) <sup>(a)</sup>	26 $\pm$ 5.4				0.59 $\pm$ 0.40
Amituk Lake (1994, Arctic) <sup>(b)</sup>	372				27
Arctic Ocean (1990, 1992–4) <sup>(c)</sup>					1.0 $\pm$ 0.30*
Eastwaite Water Lake (1996–7, UK) <sup>(d)</sup>	680 $\pm$ 190**				
Lakes in Southern Sweden (1997) <sup>(e)</sup>	8–144***				

<sup>(a)</sup> (Vilanova et al., 2001a). <sup>(b)</sup> (Helm et al., 2002). <sup>(c)</sup> (Bidleman et al., 1995). <sup>(d)</sup> (Gevao et al., 1998). <sup>(e)</sup> (Berlung et al., 2001). \* Only dissolved phase. \*\* Sum of 61 PCBs. \*\*\* Sum of 49 PCBs. n, number of samples analysed.



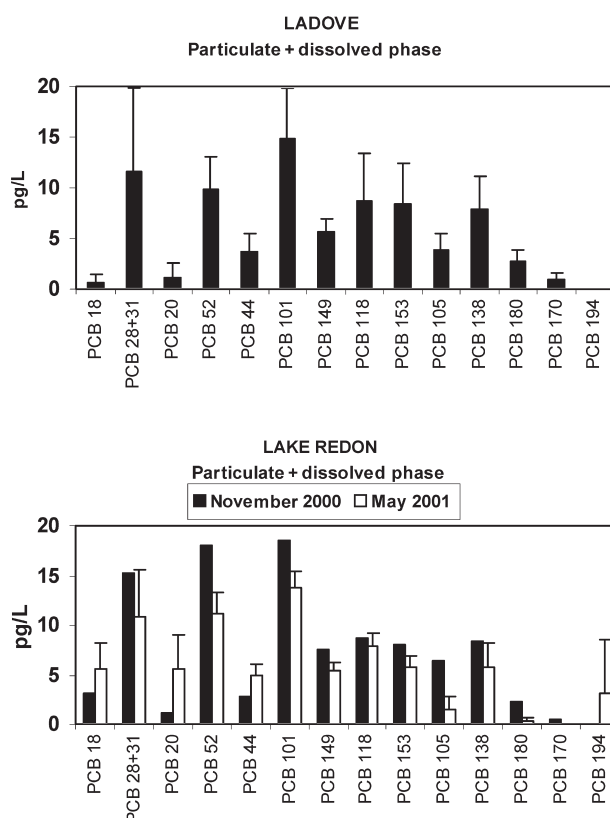
**Figure 2.** Average concentrations of DDTs (sum of pp'-DDE and pp'-DDT) and PCBs (sum of PCB 28+31, 52, 101, 118, 153, 138, and 180) in the particulate and dissolved phases of the water samples. Sample identification as in Figure 1.

reflect the stratified conditions of the water column during sampling in which the thermocline was situated between 6 and 7 m depth (Table 1). On the other hand, in Lake Redon dissolved DDTs were predominant in all samples, mainly in May (Fig. 2). These differences are probably related to the SPM amounts, as it will be discussed below (Table 5).

### Polychlorinated biphenyls (PCBs)

Fourteen PCBs individual congeners have been analyzed in the waters of the two studied lakes (Fig. 3). Their distribution is dominated by the less chlorinated compounds, PCB 101 being the most abundant congener in both lakes. No significant qualitative differences in PCB composition were observed between seasons and water column depth (Mann-Whitney non-parametric test,  $p < 0.05$ ), except for a slightly higher contribution of the more chlorinated compounds in the deepest samples of Lake Redon.

For comparison purposes, we defined total PCB content as the sum of congeners 28+31, 52, 101, 118, 153, 138, and 180. These summed values average  $64 \pm 30$  pg L<sup>-1</sup> in Ladove Lake and between  $56 \pm 11$  pg L<sup>-1</sup> in May and  $79$



**Figure 3.** PCB congener composition in the water column of the studied lakes. Error bars correspond to standard deviation.

pg L<sup>-1</sup> in November in Lake Redon (Table 3). These concentrations are lower than those reported in other remote aquatic ecosystems from Europe and Canada, but similar to those previously measured in Lake Redon (Table 3).

PCBs phase partitioning parallels water stratification. Thus, as shown in Ladove (Sept. 2000) and Redon (May 2001), PCBs exhibit highest association to the dissolved phase in the top water column. In turn, dissolved PCBs are those exhibiting highest vertical differences with maxima in the upper layers. Conversely, particulate PCB concentrations are rather constant throughout the water column (Table 3). The higher abundance of dissolved phase PCB in the top waters is the factor determining vertical differences of PCB concentrations in both lakes. These vertical gradients suggest a predominant incorporation of these compounds by air-water exchange to the dissolved phase and a secondary transfer to suspended particles that could have a predominant role in their transfer through the water column.

### Polycyclic aromatic hydrocarbons (PAH)

Twenty-three individual parent PAH and the methyl- and dimethylphenanthrenes have been analyzed in the lake

waters considered in this study. The average PAH distributions in the particulate and dissolved fractions are shown in Figure 4.

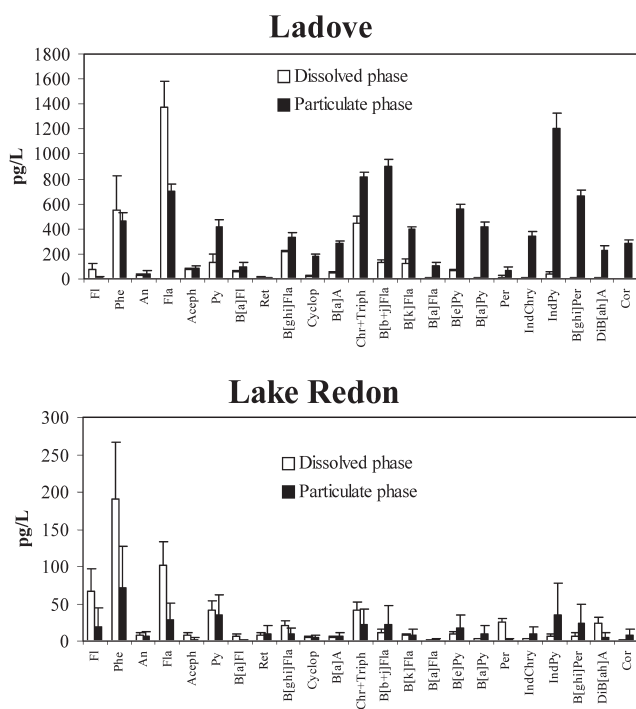
The qualitative PAH distributions in Ladove Lake are rather uniform along the water column in both water phases (Table 4) and this is reflected by the low standard deviation in Figure 4. Higher variability is found in Lake Redon where significant differences can be detected in the PAH composition between samples, mainly related to particle associated compounds. The qualitative PAH composition differs considerably between lakes. In Lake Redon, phenanthrene (Phe) was the most abundant compound either in the dissolved phase (ca. 30% of the total PAH) or in the SPM (ca. 10–20%). Other abundant PAH in both water phases were fluorene (Fl), fluoranthene (Fla), pyrene (Py) and chrysene+triphenylene (Chr+Triph). In addition, a significant contribution of the high molecular weight compounds (HMW), encompassing from benzo[ghi]fluoranthene (B(ghi)Fla) to coronene (Cor) ( $\log K_{ow} > 5$ ), was also found in the SPM. This qualitative distri-

bution is similar to that observed in other remote lake waters in Europe and USA (Baker and Eisenreich, 1990; Gevaio et al., 1998; Vilanova et al., 2001b).

In contrast, the dissolved phase PAH composition in Lake Ladove was dominated by Fla (ca. 40%), being Phe (16%) and Chry+Tri (13%) major secondary compounds. The SPM showed a high contribution of HMW compounds, dominated by indeno[1,2,3-*cd*]pyrene (IndPy), benzo[fluoranthenes (BFlas), and Chr+Triph. This profile is remarkably similar to the PAH composition found in the atmospheric aerosols and sediments from these remote lakes (Fernández et al., 1999; 2002). This similarity points to significant contributions of SPM PAH to the mixtures accumulated in the sediments of this lake, and/or to a preferential loss of LMW PAH (from Fl to Pyr,  $\log K_{ow} < 5$ ) during water transport either by degradation or by solubilization/volatilization processes.

Evidence of this preferential loss of LMW PAH can be obtained by comparison of the relative fluoranthene concentrations between different environmental compartments from these lakes. As mentioned above, high levels of this compound have been detected in the dissolved phase of Ladove, which constitutes a distinctive feature of this site. Its occurrence is consistent with high relative proportions of Fla in aerosol samples from the Tatra Mountains. Thus, 15% of Fla was found in atmospheric particulate matter of this lake (van Drooge, 2004) and only 9% in Lake Redon (Fernández et al., 2002). Snow exhibits the same differences between the two lakes (15% Fla in Ladove and 10% in Lake Redon) (Carrera et al., 2001). However these differences are not observed when comparing the PAH distributions in soils or sediments of these two lakes (Grimalt et al., 2004a).

In terms of concentrations, total PAH (sum of all parent compounds of Fig. 4) exhibit remarkably higher levels in Ladove than in Lake Redon. The average PAH concentration in Ladove is  $12 \pm 1 \text{ ng L}^{-1}$  ( $n = 5$ ), whereas in Lake Redon it varied between  $0.77 \pm 0.20$  ( $n = 4$ ) and  $1.6 \text{ ng L}^{-1}$  ( $n = 1$ ) in May and November, respectively (Table 4). The differences are mainly due to the HMW PAH in the particulate phase (Fig. 5). Comparison of these levels with others found in freshwater and marine systems shows that the concentrations in Lake Redon are similar to those reported in remote areas, whereas those found in Ladove Lake are one order of magnitude higher and similar to waters near urban centers or polluted areas (Table 4). These present results are consistent with previous studies showing the occurrence of high PAH concentrations in different environmental compartments from the Tatra mountains, namely snow (Carrera et al., 2001), fish (Vives et al., 2004), soils (Grimalt et al., 2004a) and sediments (Fernández et al., 1999; Grimalt et al., 2004a). The overall evidence points to a significant impact of atmospheric transport of PAH to these high mountain lakes despite their geographical remoteness.



**Figure 4.** Mean PAH distributions and standard deviations in the dissolved phase and suspended particulate matter of remote mountain lake waters. Compound abbreviations: Fluorene (Fl), Phenanthrene (Phe), Anthracene (An), Fluoranthene (Fla), Acephenanthrylene (Aceph), Pyrene (Py), Benzo[*a*]fluorene (BaFl), Retene (Ret), Benzo[*ghi*]fluoranthene (B(ghi)Fla), Cyclopenta[*cd*]pyrene (Cyclop), Benz[*a*]anthracene (BaA), Chrysene+Triphenylene (Chr+Triph), sum of Benzo[*b+j*]fluoranthene (B(*b+j*)Fla), Benzo[*k*]fluoranthene (B(*k*)Fla), Benzo[*a*]fluoranthene (B(*a*)Fla), Benzo[*e*]pyrene (BePy), Benzo[*a*]pyrene (BaPy), Perylene (Per), Indeno[7,1,2,3-*cdef*]chrysene (IndChry), Indeno[1,2,3-*cd*]pyrene (IndPy), Benzo[*ghi*]perylene (B(ghi)Per), Dibenz[*ah*]anthracene (DiB(*ah*)A), and Coronene (Cor).

**Table 4.** PAH concentrations in the particulate and dissolved phases of the waters from Lakes Redon and Ladove ( $\text{ng L}^{-1} \pm$  standard deviation). Values from other freshwater and marine systems are also given for comparison.

Location	PAH part.	PAH dissol.	PAH tot	LMW part.	LMW dissol.	HMW part.	HMW dissol.
Ladove (1 m, n = 2)	9.0 ± 3.9	3.5 ± 0.1	12.5 ± 0.5	1.9 ± 0.1	2.4 ± 0.2	6.9 ± 0.3	1.1 ± 0.1
Ladove (6.5 m, n = 1)	8.6	4.1	12.7	1.6	2.6	6.8	1.4
Ladove (14 m, n = 2)	8.0 ± 0.7	3.0 ± 0.04	11.0 ± 0.7	1.4 ± 0.2	1.91 ± 0.02	6.6 ± 0.5	1.0 ± 0.01
<i>Ladove average (n = 5)</i>	<i>8.5 ± 0.7</i>	<i>3.4 ± 0.4</i>	<i>12 ± 1.0</i>	<i>1.6 ± 0.3</i>	<i>2.2 ± 0.3</i>	<i>6.8 ± 0.4</i>	<i>1.1 ± 0.2</i>
Lake Redon Nov. 2000							
1 m, n = 1	1.0	0.55	1.6	0.43	0.43	0.57	0.11
20 m, n = 2*	0.88 ± 0.10	–	–	0.30 ± 0.01	–	0.56 ± 0.00	–
60 m, n = 2*	1.2 ± 0.4	–	–	0.29 ± 0.09	–	0.84 ± 0.30	–
<i>Lake Redon average (n = 5)</i>	<i>1.0 ± 0.3</i>	–	–	<i>0.34 ± 0.10</i>	–	<i>0.66 ± 0.22</i>	–
Lake Redon May 2001							
1 m, n = 2	0.17 ± 0.01	0.77 ± 0.05	0.94 ± 0.06	0.08 ± 0.01	0.55 ± 0.05	0.08 ± 0.02	0.21 ± 0.00
20 m, n = 1	0.23	0.50	0.73	0.13	0.36	0.10	0.13
60 m, n = 1	0.17	0.30	0.47	0.09	0.20	0.08	0.09
<i>Lake Redon average (n = 4)</i>	<i>0.18 ± 0.03</i>	<i>0.58 ± 0.2</i>	<i>0.77 ± 0.20</i>	<i>0.09 ± 0.02</i>	<i>0.41 ± 0.15</i>	<i>0.09 ± 0.02</i>	<i>0.17 ± 0.05</i>
Lake Redon (1996–8) <sup>(a)</sup>	0.41 ± 0.13	0.27 ± 0.19	0.70 ± 0.21				
Lake Gossenkölle (1996–7, Austria) <sup>(a)</sup>	0.57 ± 0.34	0.35 ± 0.19	0.86 ± 0.44				
Øvre Neådalsvatn (1998, Norway) <sup>(a)</sup>	0.50 ± 0.08	0.56 ± 0.06	1.1 ± 0.1				
Esthwaite Water Lake (UK) <sup>(b)</sup>		92 ± 32					
Raritan Bay (New Jersey, USA) <sup>(c)</sup>	7.0 – 7.1	3.2 – 7.4	10 – 15				
Hamilton Harbour (Lake Ontario; USA) <sup>(d)</sup>			45 ± 4				
Niagara River <sup>(d)</sup>			17 ± 5				
Danube Estuary <sup>(e)</sup>	0.13 – 1.25	0.18 – 0.21					
Northern Chesapeake Bay <sup>(f)</sup>			8.7 – 14				
Southern Chesapeake B. <sup>(g)</sup>							
Hampton (urban)	2.9	3.2					
York River (semiurban)	5.2	5.2					
Elizabeth River (industrial)	23	43					
Baltic Sea <sup>(h)</sup>			0.32 – 7.5				
Baltic Sea (remote) <sup>(i)</sup>	0.07 – 0.33	0.57 – 0.74	0.64 – 1.08				

<sup>(a)</sup>(Vilanova et al., 2001b). <sup>(b)</sup>(Gevao et al., 1998). <sup>(c)</sup>(Gigliotti et al., 2002). <sup>(d)</sup>(Michor et al., 1996). <sup>(e)</sup>(Maldonado et al., 1999). <sup>(f)</sup>(Ko and Baker, 1995). <sup>(g)</sup>(Gustafson and Dickhut, 1997). <sup>(h)</sup>(Witt, 1995). <sup>(i)</sup>(Broman et al., 1991). \* Only SPM.

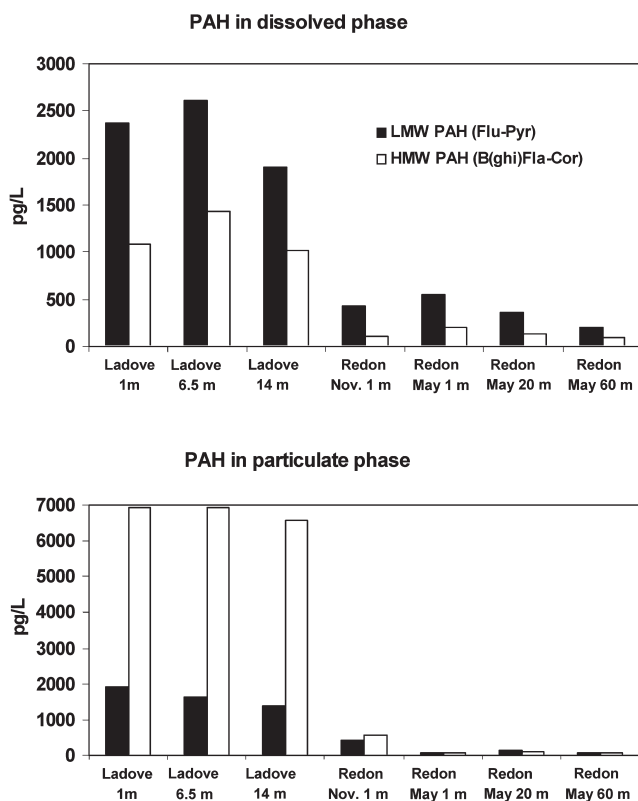
The concentrations in the particulate phase are, in general, higher than in the dissolved phase. The average values for total particulate PAH are  $8.5 \pm 0.7 \text{ ng L}^{-1}$  in Ladove and between  $0.18 \pm 0.03 \text{ ng L}^{-1}$  and  $1.0 \pm 0.3 \text{ ng L}^{-1}$  in Lake Redon, whereas average PAH levels in the dissolved phase are  $3.4 \pm 0.4$ , and  $0.58 \pm 0.20 \text{ ng L}^{-1}$  in Ladove and Lake Redon, respectively. This phase decoupling obviously depends on PAH water solubility. Thus, the HMW PAH concentrations are always higher in the particulate phase, whereas the more soluble LMW PAH are preferentially found in the dissolved phase (Table 4).

A decrease of PAH levels in the particulate phase with depth can be observed in Ladove lake. The vertical differ-

ences can likely be attributed to losses by solubilization during particle transport to the sediments. This vertical decrease is also observed in the November samples from Lake Redon, but only for the more soluble LMW compounds. In this lake, a vertical decrease in the concentration of PAH in the dissolved phase is also observed in May.

The main difference in PAH composition between the samplings performed in Lake Redon concern the concentrations in the particulate phase that are much higher in the November samples (Table 4). The difference is probably related to total SPM in both periods. In May (Table 5) the lake has the maximum thickness of ice-cover. This period is characterized by low productivity, unmixed water





**Figure 5.** Average concentrations of LMW PAH (sum from Fl to Pyr) and HMW PAH (sum from B(ghi)Fla to Cor) in the water column of the studied lakes. x-Axis labels as in Figure 1.

column, and low amount of suspended particulate matter, which has been deposited to the sediment during the whole winter. On the contrary, in November the water column is efficiently mixed, giving rise to a peak of production and therefore, an increase of SPM in the water (Catalan et al., 2002).

#### Pollutant distribution within the coarse and fine size suspended particulate matter

The evidence that a significant fraction of the total suspended particles collected in these high mountain lakes is

often constituted by zooplankton prompted us to perform several comparative measurements of SPM POPs collected with and without prefiltration through nets of 200  $\mu\text{m}$ . Only filter retained particles were analyzed for both types of samples (with and without net).

The results for the fine-grain fractions collected in both cases are summarized in Table 5. High differences in SPM content were observed in the samples collected in May. In terms of SPM pollutant concentrations, the higher differences between levels with and without 200  $\mu\text{m}$  net are also observed in May but not all compounds showed the same behaviour. No significant differences can be observed in the concentration of PCBs and PAH, either LMW or HMW compounds, although samples taken without net show, in general, higher variability as reflected in the higher standard deviations. Only DDTs show clear higher concentrations in the coarse-size particulate phase. The increase of these compounds in the samples encompassing higher size particles suggests that zooplankton bioaccumulation is partially responsible for the SPM concentrations of these pollutants.

Finally, HCB concentrations are similar in both sample types in November, but not in May. However the low levels of SPM measured in this sampling period could increase the uncertainty of the determination of this compound, which preferentially occurs in the dissolved phase.

#### Conclusions

Significant concentrations of OC of current use, namely HCHs and endosulfans, have been found in the waters of Lake Redon, in the Pyrenees. The concentrations are similar to those already determined in previous studies from 1996–8 (Vilanova et al., 2001a), indicating continuous inputs of pollution derived from agricultural activities in this site. In contrast, the concentrations of these OC groups in Ladove Lake from the Tatra Mountains are much lower and qualitatively different. It reflects inputs of these compounds by mixtures released in the past.

The OCs already banned like HCB, DDTs or PCBs, exhibit rather uniform concentrations between the two mountain areas. The measured levels range among the

**Table 5.** Comparison of pollutant levels in the water particulate matter of Lake Redon with and without net.

	Particles ( $\mu\text{g L}^{-1}$ )	PAH ( $\text{ng L}^{-1}$ )	LMW PAH ( $\text{ng L}^{-1}$ )	HMW PAH ( $\text{ng L}^{-1}$ )	PCBs ( $\text{pg L}^{-1}$ )	HCB ( $\text{pg L}^{-1}$ )	DDTs ( $\text{pg L}^{-1}$ )
<i>Lake Redon Nov. 2000</i>							
With net (n = 3)	280 $\pm$ 28	1.00 $\pm$ 0.02	0.41 $\pm$ 0.01	0.56 $\pm$ 0.01	29 $\pm$ 7	3.0 $\pm$ 1.7	1.9 $\pm$ 2.0
Without net (n = 3)	310 $\pm$ 16	0.86 $\pm$ 0.13	0.28 $\pm$ 0.11	0.56 $\pm$ 0.01	23 $\pm$ 21	2.4 $\pm$ 2.6	3.1 $\pm$ 0.58
<i>Lake Redon May 2001</i>							
With net (n = 4)	27 $\pm$ 11	0.18 $\pm$ 0.03	0.09 $\pm$ 0.02	0.08 $\pm$ 0.01	28 $\pm$ 8	n.d.	0.31 $\pm$ 0.35
Without net (n = 6)	101 $\pm$ 31	0.19 $\pm$ 0.03	0.07 $\pm$ 0.02	0.11 $\pm$ 0.02	22 $\pm$ 3	0.15 $\pm$ 0.08	4.1 $\pm$ 2.2

nd, below detection limit (0.03  $\text{pg L}^{-1}$  for HCB).

lower values of those determined in continental waters from remote sites.

In contrast, high concentrations of PAH have been found in the waters of Lake Ladove in levels similar to those reported for continental waters near urban or industrial areas. These results are consistent with previous studies in other environmental compartments from this lake, and point to a specific case of pollution by combustion sources in this area.

The overall results show that different pollution sources have influenced the high mountain lakes included in this study. That is, industrial/urban inputs in Tatra Mountains and agricultural activities in the Pyrenees. In both cases, the pollutants have been incorporated into the lake waters by long range transport.

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