Article 5.

**PCBS IN PINUS UNCINATA, THE UPPERMOST GROWING TREE SPECIES OF
CENTRAL PYRENEAN HIGH MOUNTAINS (CATALONIA, SPAIN)**

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PCBs in *Pinus uncinata,* the uppermost growing tree species of Central Pyrenean high mountains (Catalonia, Spain)

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Abstract

The polychlorobiphenyl (PCB) composition of pine needles of *Pinus uncinata* from Pyrenean high mountains has been investigated. Samples from four altitudes (1750 m, 1950 m, 2150 m and 2250 m) were collected in March 2002 and June 2002 in a central area near the Lake Redon. Average atmospheric temperatures at these sampling sites were also determined. The observed concentrations were similar to those found in pine trees from rural areas in Europe. Highest PCB levels were generally found at higher altitude, e.g. the most remote sites. A correlation between log-transformed PCB concentrations and reciprocal of absolute average air temperature was observed for the less volatile congeners. Highest concentrations were found at lowest temperatures. Phase change enthalpies calculated from the slopes of the concentration-temperature dependences showed a good agreement with the enthalpies of vaporization.

The pine needle-atmosphere partition coefficients of the studied PCB congeners increased with higher degree of compound chlorination and with lower average air temperatures. They exhibit a good linear relationship with $\log(K_{oa})$ but the temperature dependence is stronger for $\log(K_{pa})$ than $\log(K_{oa})$.

Estimation of the PCB atmospheric concentrations at different mountain levels using $\log(K_{pa})$ and pine needle concentration data predicted lower values at higher altitude (lower air temperatures), in the order of 2.1 and 1.3 times, consistently with analytical measurements at similar levels performed in previous studies.
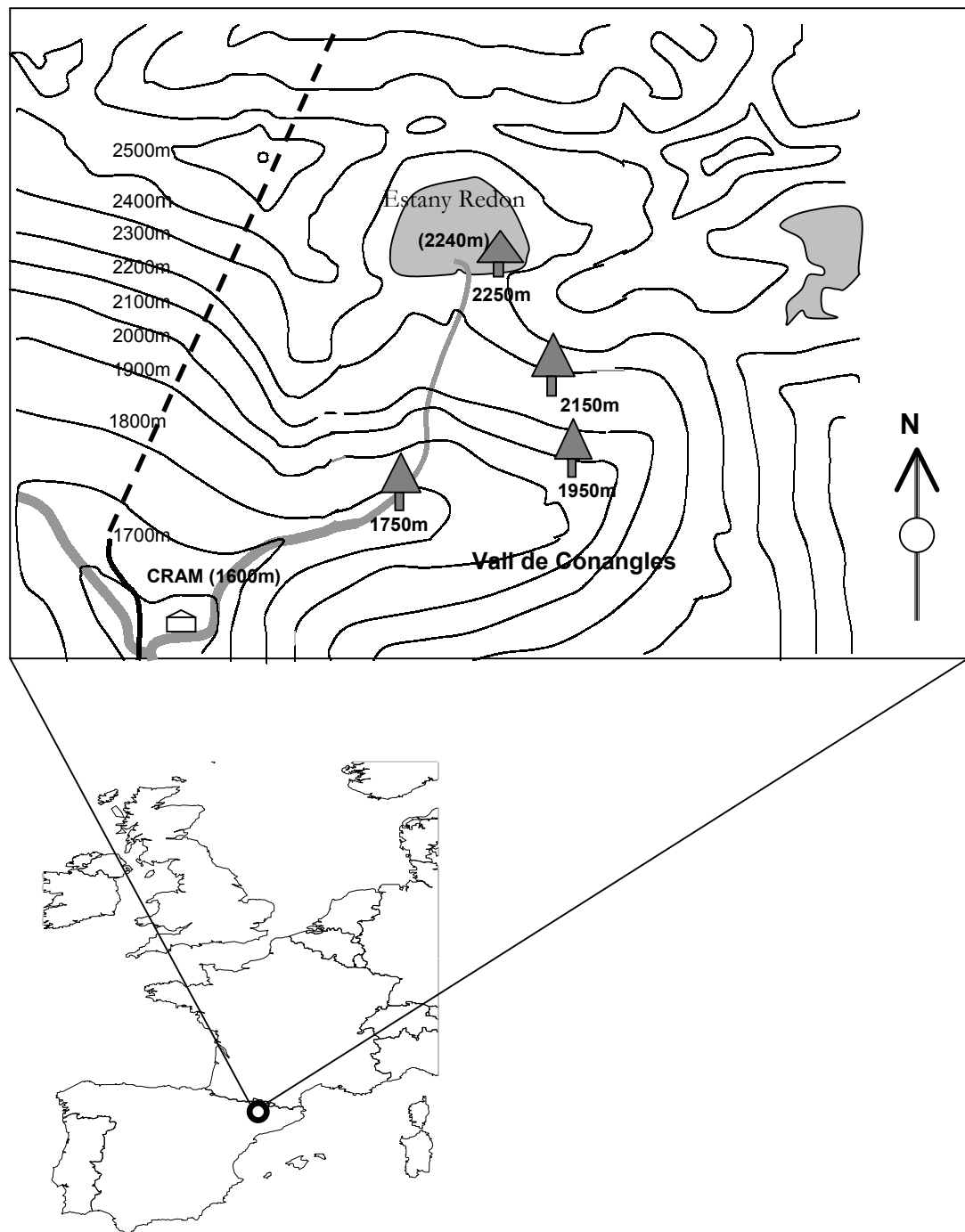
Figure 1. Sampling sites of *Pinus uncinata* needles in the Vall de Conangles and Lake Redon.

1. Introduction

In the recent years, semi-volatile organic compounds, like polychlorobiphenyls (PCBs), have been detected in the atmosphere and other environmental matrices of remote areas, including high-mountains (Calamari et al., 1991, Carrera et al., 2002, Vilanova et al., 2001, Grimalt et al., 2001, van Drooge et al., 2002). These areas are characterized by the absence of local contamination sources being impacted by long-range atmospheric transport of pollutants.

PCB have high octanol/water partitioning coefficients ($\log K_{ow} > 4$) and show affinity for organic materials such as pine tree needles (Gaggi and Bacci, 1985; Schonherr and Reiderer, 1989, Umlauf et al., 1994). In this respect, the pine species, *Pinus uncinata*, constitutes the dominant tree species at the timberline of the Central Pyrenees. This species can therefore be useful as sentinel organism for atmospheric pollution in these remote alpine-subalpine zones.

In present study, the potential of *Pinus uncinata* to monitor long-range transported pollution to high mountains such as the Central Pyrenees is investigated. This species has been measured in an altitude gradient between 1750 m and 2250 m (Figure 1). Samples in this gradient were collected in March and June 2002. The observed concentrations have been evaluated in terms of altitude and average air temperature dependence. They have also been compared with atmospheric PCB data measured at Lake Redon (42º38'34"N, 0º46'13"E, 2250 m) simultaneously to leave sampling. Phase change enthalpies between atmosphere and leave surfaces have therefore been calculated. The results have also been used to predict atmospheric PCB levels at other altitudes.

2. Materials and Methods

2.1. Materials

Residue analysis-grade *n*-hexane, dichloromethane, iso-octane, methanol and acetone were from Merck. Anhydrous sodium sulphate for analysis was also from Merck. Neutral aluminum oxide type 507C was from Fluka AG and silica gel was from Panreac. Cellulose extraction cartridges were from Whatman Ltd. Aluminum foil was rinsed with acetone and let dry at ambient temperature prior to use. The purity of the solvents was checked by gas chromatography-electron capture detection (GC-ECD). We detected no significant peaks for any of the reagents. Aluminum oxide, silica gel, sodium sulphate and cellulose cartridges were cleaned by Soxhlet extraction with hexane:dichloromethane (4:1, v/v) during 24 h before use. The purity of the cleaned reagents was checked by ultrasonic extraction with *n*-hexane:dichloromethane (4:1; 3 x 20 mL), concentration to 50 μL and analysis by GC-ECD. No interferences were detected. Aluminum oxide, silica gel and sodium sulphate were activated overnight at 400ºC, 120ºC and 110ºC, respectively. Aluminium oxide and silica gel were deactivated with 5% Milli-Q water.

2.2. Sample collection

Samples were collected with pre-cleaned tweezers, stored in glass tubes and transported to Barcelona at < 0°C. There, they where stored at –20°C until analysis.

2.3. Extraction and clean up

Whole pine needles (1-4 g fresh weight) of each sample were Soxhlet extracted for 24 h in 100 ml dichloromethane inside a pre-cleaned glassfiber cartridge containing 5 g Na_2SO_4. Internal standards of PCB#30 and PCB#209 were added to all samples and blanks before extraction. Then, the extract was evaporated until 0.5 ml by vacuum rotary evaporation and clean up with a two-layer column (diameter 1 cm) filled with slurry packing in hexane with 8 g of silica gel (bottom) and with 8 g neutral aluminium oxide (top). The column was topped with 0.5 g of Na_2SO_4. The column was then eluted with 20 ml of hexane and additionally with 20 ml hexane/dichloromethane (19:1 v/v) for PCB elution. The recovered fractions were vacuum evaporated to 0.5 ml, transferred to vials and then further concentrated under a gentle N_2-gas stream and redissolved in 50µl of isooctane.

2.4. Dry weight and lipid content

Dry weight (DW) and hexane-extractable lipids (HEL) were determined from sample aliquots (0.5-2 g). These aliquots were dried at 100°C for 24 hours in a hot air oven for DW. For HEL the dried needles were extracted two times with 20 ml of hexane in an ultrasonic bath for 15 minutes. The combined extracts were then vacuum evaporated to 0.5 ml and transferred to a pre-weighted vial where they were concentrated further under a gentle stream of N_2 until constant weight. HEL were calculated gravimetrically.

2.5. Instrumental analysis

Samples were injected in a TraceGC 2000 (Finnigan) series chromatograph coupled to a MS Agilent 5973 series. An HP-5 fused silica capillary column (30 m length, 0.25 mm i.d, 0.25 µm film thickness) coated with 5% phenyl 95% methylpolysiloxane was used for the analyses. The oven temperature program started at 100°C (holding time 1 min), increased to 120°C at 20°C·min^{-1}, to 240°C at 4°C·min^{-1} (holding time 12 min) and finally to 300°C at 4°C·min^{-1} (holding time 10 minutes). Injector, ion source, quadrupole and transfer line temperatures were 280°C, 200°C, 150°C and 310°C, respectively. Helium was used as carrier gas (0.9 ml s^{-1}). The MS was operating in selective ion monitoring (SIM) with electron impact (71 eV). Dwell time was 50 ms channel^{-1}. Quantification was performed by external standard method and corrected for surrogate recoveries. The PCB congeners analyzed in this study encompassed #28 (m/z=256, 186), #52 (m/z=292, 220), #101 (m/z=326, 254), #153 (m/z=360, 290), #138 (m/z=360, 290) and #180 (m/z=394, 324).

2.6. Atmospheric PCB concentrations

The atmospheric concentrations used in this study for calculation of the distribution coefficients were obtained from samples collected at Lake Redon (2240 m) simultaneously to pine needle collection. The sampling method, analytical procedure and results are described elsewhere (van Drooge et al., submitted).

Table 1. Concentrations of PCB congeners (ng g^{-1} dry weight) in pine needles of *Pinus uncinata* from the Pyrenean high mountains.

March 2002									
Sample n°	altitude (m)	DW (%)	PCB 28	PCB52	PCB 101	PCB 153	PCB 138	PCB 180	∑PCB
1	2250	49	0.21	0.66	1.2	0.77	0.86	0.59	4.3
2	2150	49	0.25	0.80	1.2	0.85	1.0	0.69	4.8
3	1950	48	0.25	0.72	1.2	0.74	0.87	0.60	4.4
4	1750	49	0.20	0.64	1.1	0.65	0.77	0.52	3.9
June 2002									
Sample n°	altitude (m)	DW (%)	PCB 28	PCB52	PCB 101	PCB 153	PCB 138	PCB 180	∑PCB
1	2250	53	0.18	0.58	0.84	0.54	0.64	0.31	3.1
2	2150	60	0.23	0.57	0.89	0.56	0.65	0.37	3.3
3	1950	51	0.20	0.55	0.86	0.59	0.64	0.41	3.3
4	1750	52	0.22	0.57	0.79	0.50	0.60	0.29	3.0

3. Results and Discussion

3.1 Site of study

Needles from *Pinus uncinata* were collected in the Vall de Conangles and near the high mountain Lake Redon in the central Pyrenees at heights of 1750 m, 1950 m, 2150 m and 2250 m (Figure 1). The sites selected for study encompass sub-alpine to alpine environments. In this region, *Pinus uncinata* grows between 1700 m and 2400 m and is the last growing tree species at the local tree-line. Above 2000 m the appearance of this species becomes sparse and the size of the individuals is smaller. The highest site has an average annual ambient temperature of 3.7°C (data from 2002) and a snow cover between November and May. The lowest site has an average annual ambient temperature of 8.3°C (data from 2002). Samples were collected at heights of 1750 m, 1950 m, 2150 m and 2250 m in March and June 2002. Each sample is a composite of leaves older than one year from four different trees. Pine needles older than one year are assumed to have PCB concentrations not influenced by growth changes.

3.2. Temperature data

Average air temperatures (T$_a$) were obtained from the registers of the meteorological stations situated at Lake Redon (2240 m) and at the Centre of High Mountain Research (CRAM) (1600 m). Both stations are located in the same valley and near the sample sites.

At Lake Redon, T$_a$ were calculated from measurements taken every 30 min. They provided values of 1.4°C and 15.9°C for March and June 2002, respectively. At CRAM, T$_a$ were calculated

from the minimum and maximum daily temperatures which resulted into average values of 10.0ºC and 19.0ºC, respectively.

These T_a were used to calculate altitude lapse rates for the sampling sites at 1750 m, 1950 m and 2150 m. In March and June 2002 these rates were 1.3ºC/100 m and 0.5ºC/100 m, respectively. Thus, T_a for 1750 m, 1950 m and 2150 m were 8.0ºC, 5.4ºC and 2.7ºC in March 2002, respectively, and 18.3ºC, 17.3ºC and 16.4ºC in June 2002, respectively.

3.3. PCB concentrations in Pinus uncinata

The concentrations of individual PCB congeners ranged between 0.2 ng·g⁻¹ DW and 1.2 ng·g⁻¹ DW in March. In June the concentrations ranged between 0.2 ng·g⁻¹ and 0.9 ng·g⁻¹ (Table 1). These concentrations are similar to those found in pine needles from urban/rural areas (Jensen et al., 1992, Müller et al., 2001), and slightly higher than those from remote areas of Scandinavia (Brorström-Lundén and Löfgren, 1998).

The composition of PCBs is similar in both sample periods (Figure 2). PCB#101 predominated in all cases (27%), followed by #138 (20%), #153 (17%), #52 (17%), #180 (12%) and #28 (6%). This composition is similar to the one found in spruce needles of the Swedish west coast (Brorström-Lundén and Löfgren, 1998). At all sample sites the PCB levels are about 1.3 times higher in March than in June (Figure 2). Only the more volatile PCB#28 does not show significant differences (p>0.05).
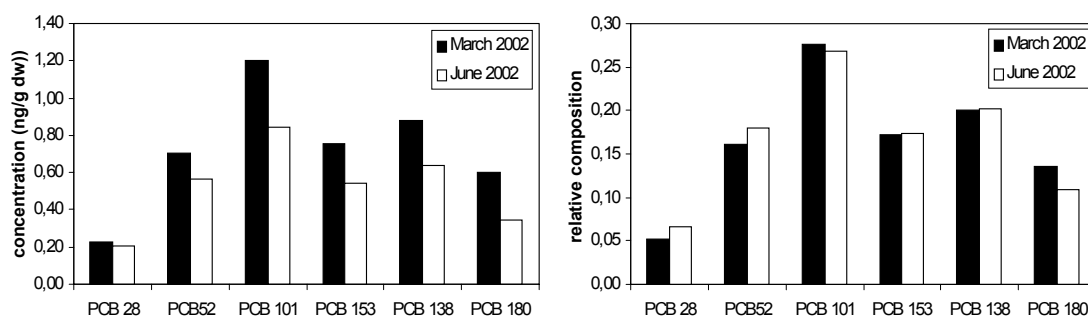

Figure 2. Average concentrations (top) and relative composition (bottom) of PCB in the *Pinus uncinata* needles collected in March and June 2002.

3.4. Concentration dependence with altitude and temperature

Representation of the March and June pine needle log-transformed concentrations vs. altitude shows a significant gradient in some PCB congeners, e.g. #101, 153, 138 and 180 in March and #138 in June (Table 2). This altitude gradient involves higher concentrations at the higher sites. Thus, the most remote sites (highest altitude) are those most polluted.

Table 2. Correlation coefficients (r^2) of the PCB concentrations in pine needle and altitude (data collected in March and June separately) and average air temperatures (all data).

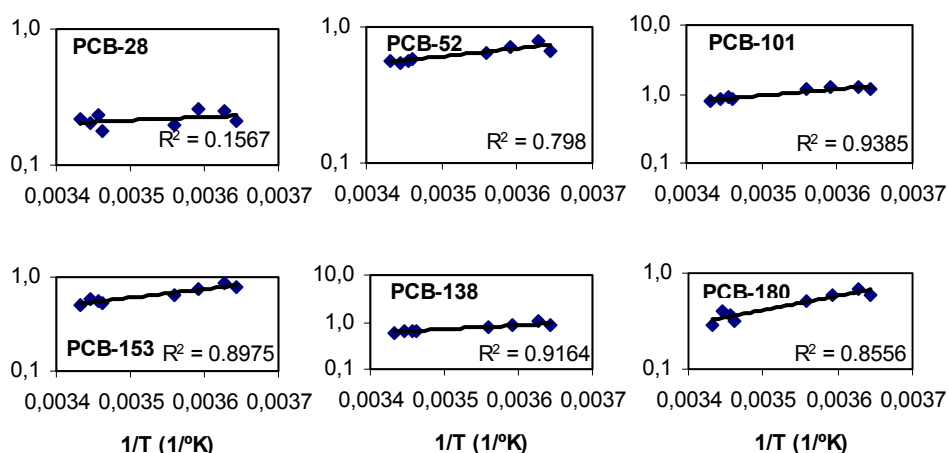| $\log(K_{pa})$	Altitude (March samples)	Altitude (June samples)	Temperature (All)
PCB 28	0.056	0.196	0.157
PCB 52	0.162	0.196	0.798
PCB 101	0.477	0.523	0.938
PCB 153	0.689	0.145	0.897
PCB 138	0.452	0.767	0.916
PCB 180	0.482	0.049	0.856

Figure 3. Correlation of the PCB composition in *Pinus uncinata* needles and average air temperatures

However, the underlying factor for the altitude gradient is temperature. Thus, joint representation of the log-transformed PCB concentrations in the samples collected in March and June vs. reciprocal of temperature (in K) shows very high correlation coefficients (r^2 between 0.798 and 0.938) for all PCB congeners except #28 (Table 2). These high correlation coefficients correspond to well defined linear fittings between log-transformed concentrations and $1/T$ (Figure 3), lower temperatures involving higher concentrations. This trend in consistent with previous observations on concentration of organochlorine compounds in fish muscle and sedimentary inventories obtained from a series of high mountain lakes distributed over Europe (Grimalt et al., 2001). In this study, a strong correlation of the concentrations of PCB congeners #101, 153, 138 and 180 with temperature and altitude was also observed. Again, lower temperatures involved higher PCB concentrations. Thus, the pine needle results provide new data supporting the selective accumulation of some PCB in high mountain areas which, in turn, is consistent with the predictions of the global distillation theory (Wania and Mackay, 1993).

The lack of correlation of PCB#28 with temperature in pine needles is also consistent with the previous data. Thus, in the fish and sediment study the temperature dependence was only observed for the less volatile PCB congeners, not for PCB #28 and #52 (Grimalt et al., 2001). In

the present case, the most volatile congener examined, PCB #28 does not show temperature correlation and PCB#52 exhibits a significant correlation coefficient but the lowest among those of the temperature dependent congeners. When the pine needle concentrations are normalized to lipid content the temperature dependence is only maintained for some PCB congeners, e.g. #180.

Contaminants in the gas phase diffuse into the interior of the needles via the stomata, the wax and the cuticle wall, so it may be that the whole pine needle provides an improved matrix for atmospheric contaminants over the surface wax only (Reischl et al., 1987, Jensen et al., 1992, Umlauf et al., 1994).

3.5. Pine needle/air partition distribution coefficients (K_{pa})

Air concentrations were measured at 2250 m (Lake Redon) in March and June during leave sampling. The obtained values can be used to calculate pine needle/air partition coefficients at this site during these two periods (cold and warm, respectively). Obviously, the calculation assumes that the exchange of PCBs between the atmosphere and pine needles has reached steady state conditions. Steady state is expected in view of the good temperature dependences described in the previous section.

The partitioning of PCB between atmosphere and tree leaves can be described by a pine needle/air-partitioning coefficient (K_{pa}) defined as:

$$K_{pa} = C_p/C_a \qquad\qquad (1)$$

where C_p is the pine needle concentration (pg kg^{-1} dry weight) and C_a is the atmospheric concentration (pg L^{-1}).

Table 3. Pine needle/air partition coefficients log(K_{pa}) and phase change enthalpies for PCBs in *Pinus uncinata* at 2250m.

logK_{pa}	March	June	Slope (x10^3)	ΔH_{pa}	ΔH_{vap}*
PCB 28	8.4	7.7	3.92	75	78
PCB52	8.5	8.0	2.84	54	81
PCB 101	8.8	8.1	3.99	76	85
PCB 153	9.2	8.2	5.16	99	91
PCB 138	9.1	8.3	4.47	86	92
PCB 180	9.3	8.4	5.29	101	97

* Obtained from Kömp and McLachlan, 1997a.

Log(K_{pa}) in March and June increase at higher degree of PCB chlorination (Table 3). They are also higher at lower ambient temperature. That is, the March samples (Table 3). In general it is assumed that gas-solid surface coefficients such as log(K_{pa}) are proportional to the octanol/air partition coefficients log(K_{oa}) (Paterson et al., 1991; Bacci et al., 1990; Gobas et al., 1991). This relationship is effectively observed when comparing the pine needle and the atmospheric

concentrations of both March and June samples from the present study (Figure 4). The $\log(K_{oa})$ values were obtained from the equation

$$K_{oa} = K_{ow} RT / H \tag{2}$$

where K_{ow} is the octanol/water partition coefficient (Mackay et al., 1992), R is the gas constant $(8.314 \ J \cdot {}^\circ K^{-1} \cdot mol^{-1})$, T is ambient temperature and H is the Henry constant (Dunnivant et al., 1992). H was corrected for ambient temperature using the phase change enthalpies of octanol/water from Kömp and McLachlan (1997a).

The regression lines for March (1.4°C) and June (15.9°C) are significantly different (p<0.001). The March plot shows both higher $\log(K_{pa})$ and $\log(K_{oa})$ values. The slopes of the regression lines are 0.56 and 0.37 for March and June, respectively. The increase of the slope at lower temperature shows that K_{pa} has stronger temperature dependence than K_{oa}. This difference has also been observed in previous studies with other plant species (Kömp and McLachlan, 1997b). In the case of *Pinus uncinata* the low slopes shown in Figure 4 indicate that K_{pa} and K_{oa} do not behave similarly upon temperature change.
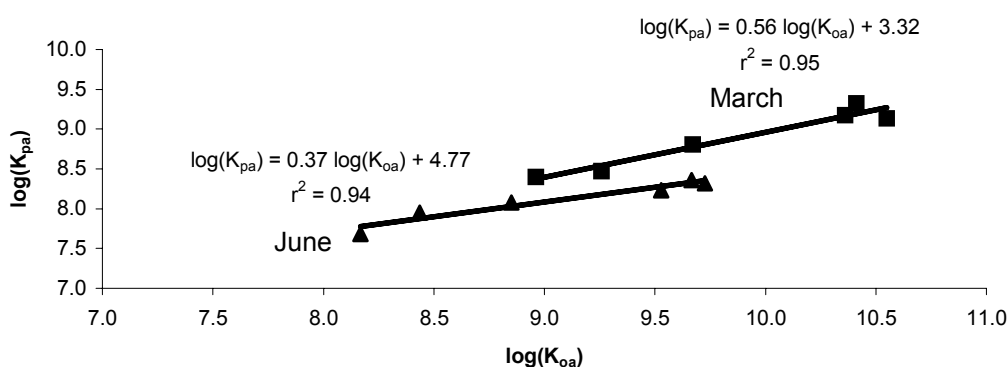

Figure 4. $\log(K_{pa})$ vs $\log(K_{oa})$ of the concentrations of PCB congeners #28, #52, #101, #153, #138 and #180 in *Pinus uncinata* collected in March and June.

3.6. Temperature dependence of K_{pa}

Representation of K_{pa} vs. T_a provides slopes in the 2.84-5.29 range (Table 3). These values are similar to those found in other species (Kömp and McLachlan, 1997b) and increase with higher chlorination of the PCBs (Table 3). The slopes can be used to calculate phase change enthalpies from pine needle to air using the following expression

$$\Delta H_{pa} = 2.303 \ RS \tag{3}$$

where S is the slope, 2.303 is the factor of correction for common to natural logarithm (ln(10)) and R is the gas constant (8.314 $J \cdot °K^{-1} \cdot mol^{-1}$).

The calculated ΔH_{pa} range between 54 and 101 $kJ \cdot mol^{-1}$ (Table 3). As expected from the above discussed slope values, the atmosphere-pine needle phase change enthalpies increase at increasing degree of chlorination of the PCB congeners. Comparison of these values with the theoretical enthalpies for vaporization of the subcooled liquid, ΔH_{vap}, shows a very good agreement indicating that transfer between these two environmental compartments is driven by vaporization/condensation processes.
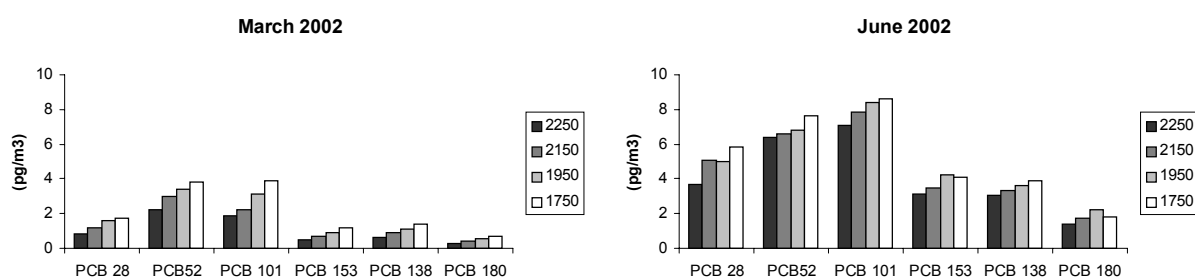

Figure 5. Estimated atmospheric PCB levels at different altitudes based on the K_{pa} coefficients and the pine needle concentrations.

3.7. Estimation of atmospheric concentrations from Pinus uncinata data

The observed dependence between K_{pa} and temperature (Table 3) allows the estimation of K_{pa} at different altitudes. Then, the estimated constants can be used to predict atmospheric concentrations if the pine needle concentrations at these altitudes are known (equation 1). The results of this approach for the altitude gradients considered in the present study are shown in Figure 5. Decreasing atmospheric PCB levels at increasing altitude is predicted. Between 2250 m and 1750 m these decreases involve ratios of 2.1±0.3 times and 1.3±0.1 times in March and June, respectively. Again, the underlying reason of change is temperature, the differences being higher at lower values. These decreases are consistent with values of 1.8 times obtained from measurements of the differences in atmospheric PCB concentrations between Redon Lake (2250 m) and CRAM (1600 m) in January 2003 using a HiVol-sampler.

4. Conclusions

The PCB concentrations in the pine needles of *Pinus uncinata* from Central Pyrenean high mountains are similar to those found in pine trees from rural areas in Europe. Highest PCB levels were generally found at higher altitude, e.g. the most remote sites, as consequence of the lower temperatures at higher altitudes. A strong correlation between log-transformed PCB concentrations and reciprocal of absolute average air temperature has therefore been observed. Highest

concentrations were found at lowest temperatures. The correlation is observed for all PCB congeners considered in the study except #28 which is in agreement with previous data on fish concentrations and sediment inventories showing that the less volatile PCB congeners accumulate selectively with temperature dependence. Phase change enthalpies calculated from the slopes of the concentration-temperature dependences show a good agreement with the enthalpies of vaporization. Overall, the concentrations exhibit good steady state conditions being in equilibrium with the environmental. This pine species is therefore useful as sentinel organism for monitoring the levels of atmospheric PCB pollution in high mountain areas.

Log(K_{pa}) range between 8.4-9.3 and 7.7–8.4 in March and June, respectively. These partition coefficients increase with higher degree of congener chlorination and with lower average air temperatures. They exhibit a good linear relationship with log(K_{oa}) but the slopes of the correlations are lower than one, 0.37-0.56, indicating stronger temperature dependence of Log(K_{pa}) than log(K_{oa}). Estimation of the PCB atmospheric concentrations at different mountain levels using Log(K_{pa}) and pine needle concentration data predicts lower values at higher altitude (lower air temperatures), in the order of 2.1 and 1.3 times, which is consistent with analytical measurements at levels of 1600 m and 2240 m (1.8 times).

Acknowledgements

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Article 6.

PASSIVE SAMPLING OF ATMOSPHERIC ORGANOCHLORINE COMPOUNDS BY SPMDS IN A HIGH-MOUNTAIN AREA (CENTRAL PYRENEES)

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Passive sampling of atmospheric organochlorine compounds by SPMDs in a remote high-mountain area

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Abstract

Since the ban of most the organochlorine compounds their atmospheric concentrations in remote areas have only decrease little, if any, and therefor it is of interest to study the evolution of the atmospheric SOC levels on a long time range. Passive air samplers, such as Semipermeable Membrane Devices (SPMDs) allow time-integrated sampling of the atmosphere without the need f energy supply, which makes them ideal for deployment in remote areas over long periods. Triolein containing SPMDs were exposed for 1.5 years to the atmosphere in the Central Pyrenees (Catalonia, Spain), and were analyzed for HCB and PCBs. The performance reference compound (PRC) method was applied to calibrate the sampling rates of the SPMDs in situ. The purpose of the present study was to assess atmospheric concentrations of HCB and PCBs along a height gradient (1600-2600 m) and to validate sampling by SPMDs against sampling by HiVols. Sampling rates between 0.55 and 1.3 m^3 d^{-1} were observed for the performance reference compound PCB155. Although errors in the application of physico-chemical properties in the model calculations may cause considerable uncertainties in the obtained sampling rates, the observed atmospheric concentrations obtained by the SPMD were in good agreement with the observed atmospheric concentrations obtained by HiVols. These findings suggest that SPMDs can be applied as monitoring systems of the atmospheric concentrations of organochlorine compounds in these remote high mountain areas.
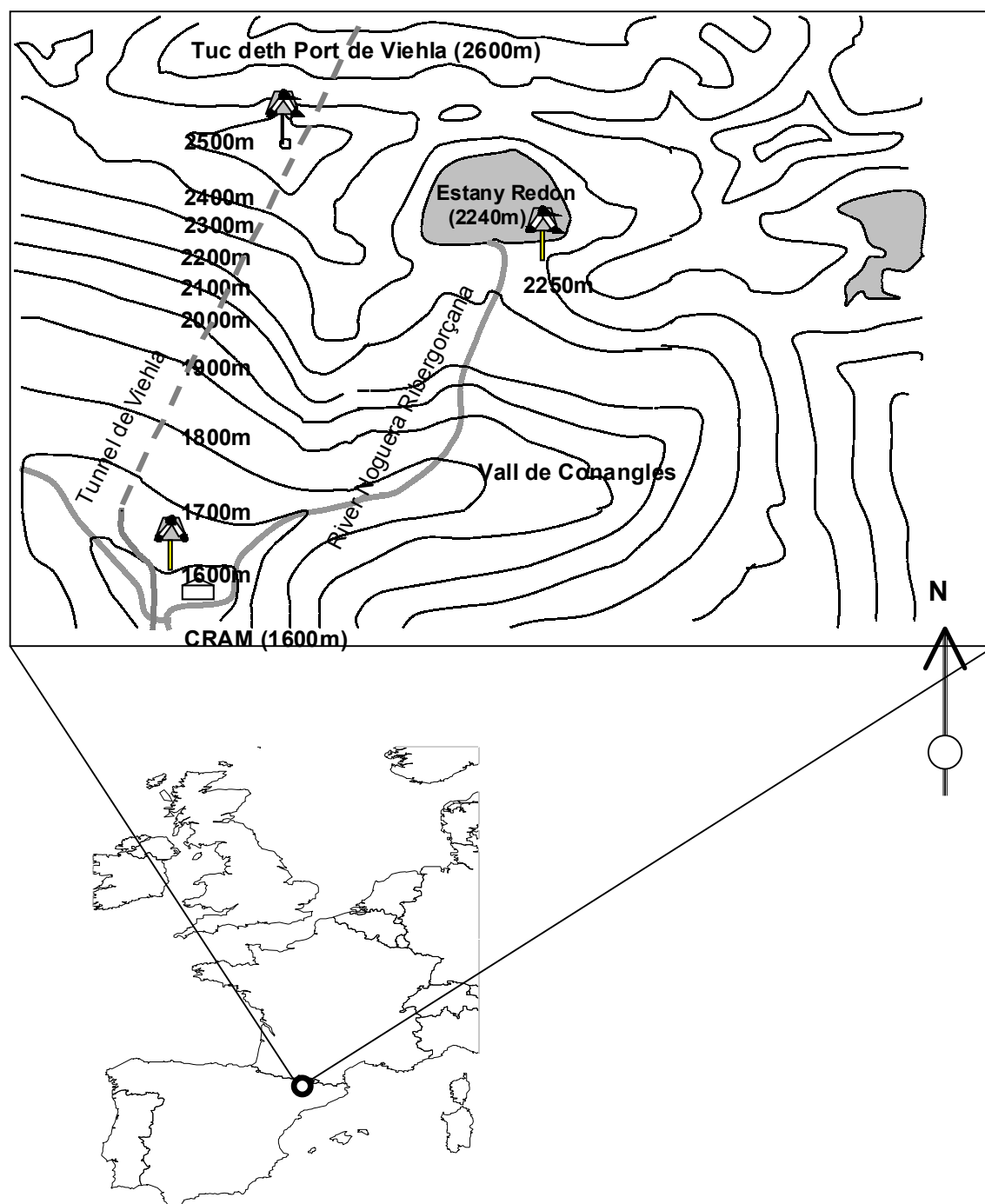
Figure 1. Location of the SPMD sampling sites near Estany Redon (central Pyrenees, Catalonia, Spain)

Introduction

In recent years semi-volatile organic compounds, such as hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB), have been detected in remote high-mountain sites (1-4). Due to their relatively high vapor pressure (10^{-1} – 10^{-4} Pa) and resistance against degradation during atmospheric transport, these compounds are widely spread into high mountain areas, where they were never produced or used (3, 5). Although, their production and use are prohibited or restricted now for many years, there has only been a clear decline in concentrations in areas of production and application (6). At remote sites the decrease of atmospheric concentrations is little, if any, and HCB and PCBs are still detected at trace levels (7). This is of concern since these compounds may cause toxic effects (8-9). It is therefore of interest to study the evolution of the atmospheric SOC levels at remote sites, like mountain areas, on a long time range.

Atmospheric contaminant levels are typically assessed using conventional high-volume (HiVol) samplers. These samplers suffer from a number of methodological difficulties, such as adsorption of gaseous analytes to the glass fibre filter, desorption of particle-bound compounds, and the snap-shot image these devices produce of the possibly highly variable atmospheric concentrations (10). In addition, the operation of HiVol samplers in remote areas requires the use of generators, adding to logistical difficulties.

Semi-permeable membrane devices (SPMDs) have been used since 1993 for sampling of atmospheric organic contaminants, both in remote and in densely populated areas (10-15). These samplers allow for time-integrative sampling of the contaminants, and do not require a power supply, which makes them ideal for deployments in remote areas.

Standard-design SPMDs consist of a low-density polyethylene lay-flat tubing (wall thickness of 75-95 μm) filled with 20% (w/w) triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol), with a surface area of about 460 cm² per mL triolein (16). Concentrations in air (C_a) can be calculated from the absorbed amounts (N_s) by (14, 15, 17).

$$N_s = C_a \, K_{sa} \, V_s \, [1-\exp(-k_e \, t)] \tag{1}$$

where K_{sa} is the SPMD-air partition coefficient, V_s is the SPMD volume, and t is the exposure time. The (first order) exchange rate coefficient (k_e) is defined by (17-18)

$$k_e = k_o \, A \, / \, K_{sa} \, V_s \tag{2}$$

where A is the SPMD surface are, and k_o is the overall mass transfer coefficient. For short exposure times (kinetic sampling), equation 1 reduces to

$$N_s = C_a \, k_o \, A \, t \tag{3}$$

$$= C_a \, R_s \, t \tag{4}$$

From analyses of SPMD with different exposure times Ockenden et al. (13) observed a linear uptake of PCBs. The air sampling rates (R_s) were calculated by dividing the atmospheric concentrations (C_a) obtained with HiVols by the uptake rates. A drawback of this method is that the R_s can only be calculated if atmospheric concentrations are available, or if it is assumed that R_s will not differ among locations. Moreover, this calculation is only possible at short exposure times, when the uptake is linear. If equilibrium sampling has been reached, after long exposure time, an underestimation of atmospheric concentrations will be a result of this method.

Combining equations 2 - 4, the air sampling rate (R_s) can be written as

$$R_s = k_o A = k_e K_{sa} V_s \qquad (5)$$

For long exposure times (equilibrium sampling), equation 1 reduces to

$$N_s = C_a K_{sa} V_s \qquad (6)$$

which shows that C_a can be calculated using the SPMD-air partition coefficient. The advantage of using equation 1 is that it covers both the kinetic sampling and the equilibrium sampling phase, as well as the intermediate phase (19) Good estimates of k_e and K_{sa} should be available, however. To our knowledge, no published K_{sa} values exist, but reasonable estimates can be obtained from SPMD-water partition coefficients (K_{sw}) and Henry's law constants (H)

$$K_{sa} = K_{sw} R T / H \qquad (7)$$

where R is the gas law constant , and T is the absolute temperature. The group H/RT represents the air-water partition coefficient in volume concentration units. SPMD-water partition coefficients of HCB and PCBs have been shown to be independent of temperature (18, 20). A strong temperature dependence can be expected for K_{sa}, because Henry's law constants increase strongly with increasing temperature (21, 22). Exchange rate constants can be obtained from the dissipation of performance reference compounds (PRCs) that are spiked into the SPMDs prior to exposure (20). When PRCs are chosen that do not occur in significant levels in the environment, such as PCB29 and PCB155, the k_e values for these compounds can be obtained from

$$k_e = - \ln (N / N_0) / t \qquad (8)$$

where N is the PRC amount remaining after the deployment, and N_0 is the amount that was initially present in the SPMD at $t = 0$ (20). Typically, only PRCs with a narrow volatility range can be used to calculate k_e. Compounds with smaller K_{sa} values will have dissipated to below their detection limit, and PRCs with higher K_{sa} values will often show a decrease that is too small to quantify. When the exchange kinetics between air and SPMDs are controlled by the air boundary layer, some basic models can be applied to calculate k_e values for all compounds, using the measured k_e of a

single PRC. For boundary layer controlled uptake the overall mass transfer coefficient is equal to the mass transfer coefficient for the boundary layer ($k_o \approx k_a$)

$$k_e = k_a \, A \, / \, K_{sa} \, V_s \tag{9}$$

Therefore, PRC-based exchange rate coefficients ($k_{e,PRC}$) can be used to calculate the coefficients for other compounds (k_e) using

$$k_e = k_{e,PRC} \, (K_{sa,PRC} \, / \, K_{sa}) \, (k_a \, / \, k_{a,PRC}) \tag{10}$$

Mass transfer coefficients for fluid boundary layers are typically proportional to the 2/3 power of the molecular diffusion coefficient (23-25). Hence,

$$k_e = k_{e,PRC} \, (K_{sa,PRC} \, / \, K_{sa}) \, (D_a \, / \, D_{a,PRC})^{2/3} \tag{11}$$

The dominant factor in equation 11 is the ratio of SPMD-air partitioning coefficients, which differ between compound by order of magnitudes. The ratio of diffusion coefficients is typically quite small. For example, the ratio of diffusion coefficients of HCB and PCB180 as calculated from the Fuller, Schettler & Gillings equation (26) is only a factor of 1.2.

Little is known about whether the uptake from air is indeed controlled by the boundary layer or instead by the membrane. For water-SPMD exchange, membrane controlled uptake results in a log R_s versus log K_{ow} slope that is close to (but somewhat smaller than) unity, whereas boundary-layer controlled uptake results in log R_s - log K_{ow} slopes that are slightly negative (18). For uptake by SPMDs from air, a similar reasoning may be applied. Ockenden et al. (13) report that sampling rates for tri- to heptachloro biphenyls increase with log K_{oa}. For tri- and tetrachlorobiphenyls (log K_{oa} <8.2), the log R_s versus log K_{oa} slope ranges between 0.4 (winter data) and 0.7 (summer data), indicating predominantly membrane controlled uptake. For penta- to heptachlorobiphenyls (log K_{oa} >8.8) the log R_s - log K_{oa} slopes are 0.0 (summer) and 0.1 (winter), which is indicative of boundary-layer controlled uptake. Lohman et al. (10) report that the sampling rates of PAHs with 5 to 6 aromatic rings (log $K_{oa} \approx 11$) decrease with molecular size, and that the ratio of sampling rates of tetra- and pentachloro dibenzo-p-dioxins (log K_{oa} range 10.0 to 11.4) at three sampling sites attained values of 0.5, 0.9, and 2.0 for three sampling sites. These observations suggest that the air-SPMD boundary layer is rate limiting for the uptake of compounds with a log $K_{oa} > 8.5$. The uptake of compounds that are more volatile than the PRC could be partially or completely membrane controlled. The application of equation 11 for these compounds would likely result in the overestimation of their k_e values. This would not result in appreciable errors in the estimate of C_a, because the PRC usually has attained a significant degree of equilibrium, and the more volatile

compounds will have attained a larger degree of equilibrium. This means that the group $1-\exp(-k_e t)$ in equation 1 is close to one for these compounds anyway, and that the calculated C_a values are quite insensitive to uncertainties in k_e, and never exceed the estimates from the equilibrium model.

The purpose of the present study was to assess atmospheric concentrations of HCB and a number of PCBs along a height gradient (1600-2600 m) in the Pyrenees over a 1.5 year period, and to validate atmospheric sampling by SPMDs against sampling by HiVols.

Table 1. Sampling days and average temperatures (°C) of the three sites and the average amounts in the SPMDs, the dissipation rate constants of PRC 155, sampling rates of PRC 155 and PRC 29, and the state of equilibrium of the studied compounds in the SPMDs.

Period Days		Sampling I 25/3/2-18/6/2 85	Sampling II 18/6/2-15/1/3 211	Sampling III 15/1/3-25/6/3 161
Average Ta (°C)	Tuc (2600m)	-0,9	3,9	1,2
	Estany Redon (2250m)	2,6	5,8	4,0
	CRAM (1600m)	8,8	9,3	9,0
N_s (pg SPMD^{-1})	HCB	1120 (171)	3865 (461)	461 (114)
	PCB18	55 (30)	67 (20)	156 (10)
	PCB28	117 (18)	158 (43)	304 (243)
	PCB52	112 (26)	215 (38)	551 (314)
	PCB101	280 (84)	435 (107)	459 (149)
	PCB110	170 (65)	180 (35)	378 (72)
	PCB153	298 (148)	355(21)	293 (42)
	PCB138	147 (113)	276 (14)	287 (61)
	PCB180	89 (59)	76 (29)	107 (40)
$k_{e,CB155}$ (d^{-1})	Tuc (2600m)	0.0069 (23%)	0.0038 (16%)	0.0032 (12%)
	Estany Redon (2250m)	0.0077 (-)	0.0049 (13%)	0.0046 (2%)
	CRAM (1600m)	0.0084 (2%)	0.0048 (17%)	0.0064 (16%)
$R_{s, CB155}$ (m^3 d^{-1})	Tuc (2600m)	1,3	0,61	0,55
	Estany Redon (2250m)	1,3	0,75	0,72
	CRAM (1600m)	1,1	0,64	0,82
$R_{s, CB29}$ (m^3 d^{-1})	Tuc (2600m)	2,9	-	-
	Estany Redon (2250m)	2,5	-	-
	CRAM (1600m)	1,6	-	-
Equilibrium %	HCB	92	98	94
	PCB18	81	92	84
	PCB28	67	81	72
	PCB52	68	80	72
	PCB101	39	51	43
	PCB110	37	49	41
	PCB153	3,2	5,4	4,1
	PCB138	2,2	3,6	2,8
	PCB180	0,3	0,6	0,4

Materials and methods

SPMD-sampling. SPMDs were exposed in duplicate during 3 sampling periods of 85, 161 and 210 days, between March 2002 and June 2003 (Table 1) near the high mountain lake Estany Redon (42°38′33.5′′N; 0°46′12.7′′E; 2240m), in the central Pyrenees (Catalonia, Spain). They were analyzed for HCB and eight individual PCB congeners. Additional exposures were performed made simultaneously in the valley and on the mountaintop, close to the Centre of High Mountain Research (CRAM) at 1600m and near Tuc deth Port de Vielha at 2600m, in the vicinity of Estany Redon (Figure 1). All sites are characterized by their sub-alpine to alpine environments, with an average annual ambient temperature in 2002 of 3.7ºC and snow cover from November until May at Estany Redon and an average annual ambient temperature of 8.3ºC at 1600m.

The SPMDs (30 x 2.5 cm, wall thickness 70µm) were filled with 270 mg spiked triolein (Sigma, 95%). The triolein content was 21% (w/w) and the surface area to triolein volume ratio was 510 cm2/mL, which is slightly higher than for standard design SPMDs (20%, and 460 cm2/ml, respectively). The triolein was spiked with 40, 7, 7 ng of PCB4, PCB29 and PCB155, respectively. None of these PCBs were detected in the high-volume air samples (see below). To protect the SPMDs against direct sunlight and wind they were mounted inside a sampler, which consisted of an untreated wood pole with an upside-down zinc bucket that was closed off with a steel wire screen (maze width 8 mm). A similar sampler was used successfully in other studies (15). For each sampling period, two non-exposed SPMDs filled with spiked triolein where analyzed as blanks. The limit of quantification (LOQ) was calculated from the average blank value plus 3 x the standard deviation. Blank values of detected compounds were about 0.03-0.2ng per SPMD. LOQs were about 0.1-0.5ng per SPMD. Blank correction was applied to all samples.

The SPMDs were stored in closed glass bottles at –20ºC. During transport to and from the sampling sites, the bottles were stored at 0ºC for a couple of hours. Handling of SPMDs was done with pre-cleaned tweezers. After exposure, the exteriors of the SPMDs were wiped off with a paper tissue to remove eventually attached particles. After cutting off the triolein-free mounting loops, the SPMDs were extracted twice for 24h by soaking in 100 ml hexane:dichloromethane (DCM) (4:1 v/v) (Merck, Darmstadt, Germany). Internal standards, PCB30 and PCB209, were added at the beginning of the first extraction period. The analytical recovery was studied twice using SPMDs that contained PCB spiked triolein. Recoveries of 93±13% were observed for all compounds. The recoveries of the internal standards, PCB30 and PCB209 in the samples were 87±21% and 87±17%, respectively. For each series, 2 SPMDs were used as a control, to determine the initial concentrations of the PRCs. These SPMDs were processed together with the exposed SPMDs. PRC recoveries from the control SPMDs were 40±27% for PCB4 and 93±10% for PCB29 and PCB155, relative to the calculated spike levels.

All extracts were concentrated to 0.5 mL. Clean-up of the extracts was done using a column that was filled with 8 g silica (Pancreac, Spain) (5% H_2O), 8 g aluminum oxide (Fluka Type 507C,

Fluka AG, Switzerland) (5% H_2O), and 1 g Na_2SO_4 . The samples were eluted with 20 mL hexane, followed by elution with 20 mL hexane:DCM (19/1 v/v). The collect fraction was evaporated to 0.5 mL using vacuum rotary evaporation and further concentrated until 50 μL in iso-octane (Merck, Darmstadt, Germany) under a gentle nitrogen stream. Before injection, 25 μL of tetrachloronaphthalene was added to correct for variations in instrument sensitivity and sample volume. The samples were injected on a Hewlett-Packard 5890 Series II gas chromatograph equipped with an electron capture detector for the analysis of HCB and PCB congeners #18, #28, #52, #101, #110, #153, #138, #180. The GC was equipped with a fused silica capillary column DB5 (50 m x 0.25 mm i.d. x 0.25 μm film thickness; J&W Scientific, Folsom, CA). Nitrogen and helium were used as make up gas (60 mL min^{-1}) and carrier gas (0.33 mL min^{-1}), respectively. The oven temperatures were programmed from 100°C (1 min) to 150°C at 15°C min^{-1}, following a heating of 4°C min^{-1} until 240°C (holding time 12 min.), and then to 300°C at 4°C min^{-1} with a final holding time of 10 min. Samples were injected in split/splitless mode at 280°C. The detector temperature was 310°C.

HiVol-sampling. The method of atmospheric sampling with the HiVol-sampler is fully described in Van Drooge et al. (4, 27). Briefly, samples and blanks were collected between November 2000 and June 2003 at Estany Redon using a high volume pump (HiVol) (MCV, S.A., Collbato, Catalonia, Spain) equipped with two plugs of polyurethane foam (PUF) and a glass fiber filter (GFF). Collected air volumes were between 120 m[3] and 280 m[3]. After sampling, PUFs and GFFs were stored at 0°C during transport to the laboratory. PUFs and GFFs were Soxhlet extracted for 24h in hexane and hexane:DCM (4:1 v/v), respectively. The extracts were concentrated to 1 mL by vacuum rotary evaporation and cleaned-up by column adsorption chromatography on 2 g of aluminum-oxide and elution with 8 mL hexane:DCM (1:2 v/v). The extracts were then concentrated in iso-octane to 50 μL under a gentle stream of nitrogen. Prior to injection, tetrachloronaphthalene was added to the vials as an injection standard. The same instrumental analysis procedure was used as for the SPMD extracts.

Table 2. Physico-chemical properties of analysed organochlorine compounds (at 25°C).

		#4	#29	#155	HCB	#18	#28	#52	#101	#110	#153	#138	#180
logKow	(28)	4,9	5,6	7,0	5,5	5,6	5,8	6,1	6,4	6,3	6,9	7,0	6,9
logKsw	(19)	4,8	5,3	6,3	5,2	5,3	5,4	5,7	5,9	5,8	6,2	6,3	6,2
H (Pa/m³ mol) (21,29)		33,3	30,0	85,2	53,0	32,4	28,9	32,3	24,9	19,9	16,7	13,2	10,9
DHaw (kJ/mol) (21,22)		42,0	41,0	27,0	49,0	42,0	41,0	27,0	29,0	29,0	79,0	79,0	149,0
LogKsa	*)	6,7	7,2	7,8	6,9	7,2	7,4	7,5	7,9	7,9	8,4	8,6	8,6
D_a (10^{-6} m²/s) (26)		5,1	4,9	4,3	5,1	4,9	4,9	4,7	4,5	4,5	4,3	4,3	4,2

*) calculated from Ksw and H

Physico-chemical properties. The required physico-chemical properties of the studied compounds are summarized in Table 2. The log K_{ow} values were obtained from Mackay et al. (28). Because no values or CB138 and CB180 are listed in this reference, the average value of hexaCB and heptaCB were chosen, respectively. The log K_{sw} values were calculated from the equation given by Booij et al. (18). Henry´s Law constants (H) for PCB and HCB were obtained from Dunnivant et al. (29) and from Ten Hulscher et al. (21), respectively. Water-air transfer enthalpies (ΔH_{aw}) were taken from Ten Hulscher et al (21) for HCB, and from Bamford et al. (22), adopting the average value for PCBs with the same number of chlorine atoms and the same number of ortho-chlorines. Diffusion coefficients (D_a) were calculated using the Fuller, Schettler & Gillings equation (26).

Ambient Temperature. Ambient temperatures (T_a) were obtained from the meteorological stations situated at Estany Redon (2250m) and at the Centre of High Mountain Research (CRAM) (1600m). Both stations are located in the same valley, near the sampling sites. At Estany Redon, the average T_a was calculated from measurements taken every 30 min. At CRAM, T_a was calculated from the daily minimum and maximum temperatures. Values of T_a of these sites were used to calculate the temperature lapse rates, this in order to estimate the T_a for the sampling sites at 2600m. For the three sampling periods the lapse rates were 1.0, 0.5 and 0.8 ºC per 100 m, respectively. The average T_a values are summarized in Table 1.

Results and discussion

Performance reference compounds. The amounts of CB4 were below the detection limit for all exposed SPMDs. CB29 was only detected in the SPMDs exposed during the first sampling period (85 days). In the other sampling periods CB29 was below the detection limit. The average retention of CB155 was 45% in exposed SPMDs, with a standard deviation of 10%. Dissipation rate constants (k_e) could therefore only be estimated for CB155 for all exposure period and for CB29 for the first exposure period. The k_e of CB155 for one of the SPMDs from the first sampling period at Estany Redon was exceptionally high (0.016 d^{-1}) compared to the estimated for other altitudes and exposure periods. This value was therefore excluded from the further calculations. No significant differences (p>0.05) in k_e estimates were observed among the different sampling heights for all three sampling periods. CB155 dissipation rate constants for the second and third sampling period were virtually the same at all sites, while the average k_e for the first sampling period is significantly higher ($p<0.0001$) compared to periods 2 and 3 (Table 2). The coefficients of variation among the duplicates ranged between 2 and 23%. The dissipation rate values of CB155 were used to calculate the sampling rate (R_s) of compounds with the same physico-chemical properties as CB155, using equation 5. The $R_{s,CB155}$ for the first sampling period were higher than in the other two samplings by a factor of 1.8 (Table 2). The higher sampling rates during the first period are not likely to be temperature-related, because temperature differences were larger among sampling sites

(~ 10 °C) than among sampling periods (~ 3 °C), but no differences in R_s among sites were observed.

With boundary-layer controlled uptake, increasing wind speed may cause an increase in sampling rates. Wind speeds normally increases with altitude (30), but no increase of $R_{s,CB155}$ with altitude was observed. It is there for not clear what the reason may be for the difference in sampling rates between the first sampling period and the other two.

The range of $R_{s,CB155}$ values found in this study are smaller than the wintertime values of penta- and hexachlorobiphenyls observed by Ockenden et al. (14). After applying a correction for the differences in surface area (152 cm² versus 460 cm²), the present sampling rates are a factor 3.2 smaller than those observed by Ockenden et al. (14). Differences in wind speed may be responsible for these differences in sampling rates. Another explanation is related to uncertainties in the K_{sa} values used to calculate the sampling rates in the present study. Errors in the K_{sa} values may arise from uncertainties in the log Kow values used to calculate the SPMD-water partition coefficient. A 0.2 log unit increase in log Kow would cause the sampling rate estimates to increase by a factor of 1.4. Uncertainties in the Henry's Law constants for CB155 are a similar source of error. For the first sampling period, additional sampling rate estimates could be made using the dissipation of CB29. R_s values based on the dissipation of CB29 were higher than CB155-based sampling rates by a factor of 1.9. This difference is most likely caused by the lack of reliable experimental K_{sa} values for these PRCs.

Equilibrium of OCs in SPMDs. The dissipation of CB4 (log K_{sa} = 6.7) was complete, and CB29 (log Koa = 7.2) had dissipated more than 93% in the first exposure period (85 d). This implies that equilibrium was complete (equilibrium sampling mode) for all compounds with log K_{sa} values smaller than ~ 7.2 (HCB, PCB18). The dissipation of CB155 (log K_{sa} = 7.8) was 55%, indicating that compounds with similar log K_{sa} values (PCB101, PCB110) were neither in the equilibrium sampling mode, nor in the kinetic sampling mode, but in the intermediate mode instead. The use of equation 1 for calculating the atmospheric concentrations accounts for the partial attainment of equilibrium for these compounds. The log K_{sa} values of PCB28 (~7.4) and PCB52 (~ 7.5) are larger than the log K_{sa} of CB29, and smaller than the log K_{sa} of CB155, which means that the extent of equilibrium attainment is somewhere between 55 and 100%. Assuming that the degree of equilibrium can be estimated by interpolation over this narrow log K_{sa} range, the equilibrium attainment of CB28 and CB52 would be ~ 80% and ~ 74%, respectively. The calculation method proposed in the introduction (application of equation 1 and k_e estimation using equation 11), yields equilibrium estimates between 67 and 81% for CB28 and 68 to 80% for CB52 (Table 1). These values are clearly consistent with the equilibrium percentages obtained by the interpolation method. This indicates that the proposed model may be applied for compounds with log K_{sa} values smaller than that of the PRC. We would like to stress that we do not imply that the uncertainties in the method is in the range of a few percent for the low K_{sa} range. Instead, the errors involved are of the

same order as the errors in the K_{sa} values, which may attain values of up to 0.3 log units, depending on the accuracy of the parameters log Kow and H.

Atmospheric concentrations. SPMD-based atmospheric concentrations are shown in Figure 2 for all altitudes and sampling periods. The concentrations of the PCB congeners are very similar for all three sampling periods. There is a slight decrease of the atmospheric levels with increasing altitude in sampling I, but in general the concentrations of the analyzed compounds are in the same range for the three sampling sites.
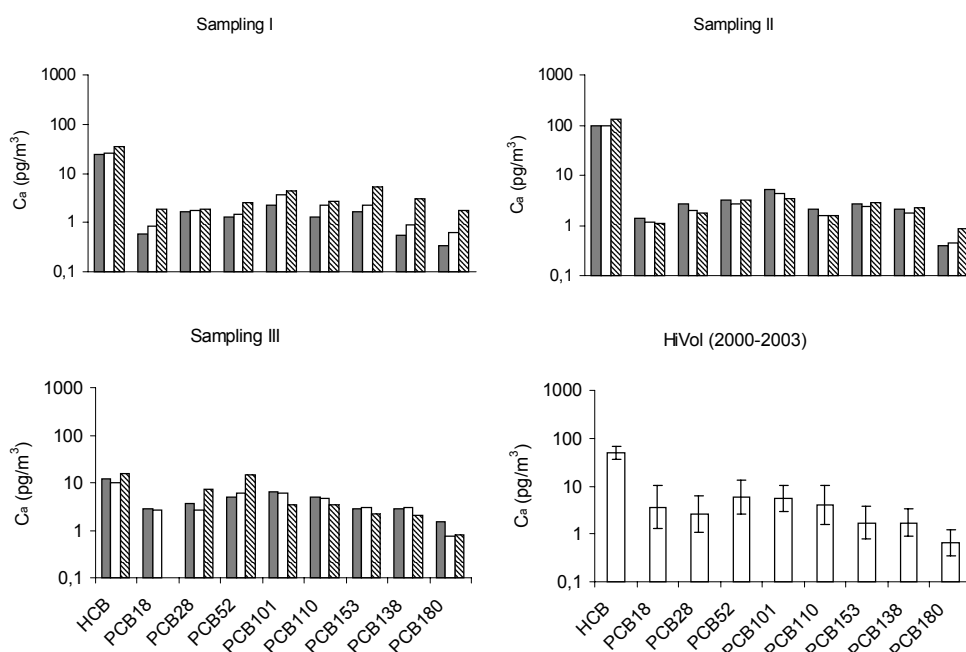

Figure 2. SPMD-derived concentrations for sampling periods I (top), II (middle), and III (bottom) measured at 2600m (filled bars), 2240 m (open bars) and 1600m (hatched bars) as well as the average HiVol-derived atmospheric OC concentrations between 2000 and 2003 (N=20).
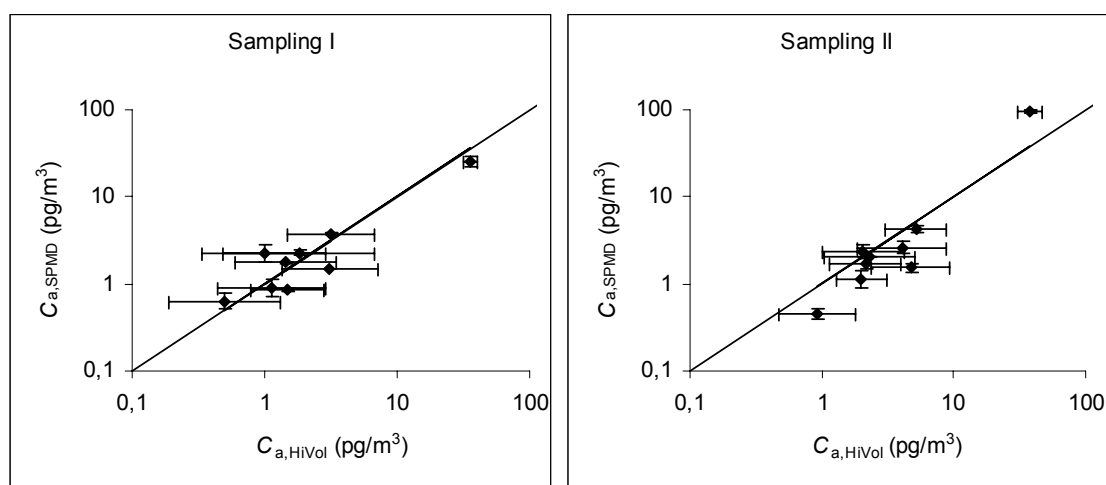

Figure 3. Comparison of average atmospheric log concentrations (pg m^{-3}) obtained from the SPMD and HiVol-sampling at Estany Redon (2250m)

Comparison with HiVol data. HiVol samples were taken at the beginning an at the end of exposure periods I and II near Estany Redon. The SPMD-based atmospheric concentrations ($C_{a, SPMD}$) are plotted versus the mean HiVol-derived concentrations ($C_{a,HiVol}$) in Figure 3. The ratio $C_{a,SPMD}$ / $C_{a,HiVol}$ attained values between 0.4 and 3.1, with a geometric mean of 1.2. The error bars on the HiVol-based concentrations reflect the high time-variability associated with this technique (factor of ~ 2.1). The variability among $C_{a,SPMD}$ duplicates was a factor of ~ 1.1. The good correspondence between the two techniques is better than one would expect, considering the uncertainties in the log K_{sa} values that are needed to obtain $C_{a,SPMD}$ estimates. The similarity in C_a values obtained by both methods also indicates that reliable estimates of atmospheric concentrations of PCBs and HCB can be obtained by SPMD deployments in remote areas using the PRC method.

Acknowledgements.

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Article 7.

PERSISTENT ORGANOCHLORINE COMPOUNDS IN SOILS AND SEDIMENTS OF EUROPEAN HIGH ALTITUDE MOUNTAIN LAKES

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Persistent organochlorine compounds in soils and sediments of European high altitude mountain lakes

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Abstract

The composition of persistent organochlorine compounds (OC) in soils and sediments from two high altitude European mountain lakes, Redon in the Pyrenees and Ladove in the Tatra mountains, has been studied. Sediment cores from two additional lakes in the Tatra mountains, Starolesnianske Pleso and Dlugi Staw, have also been examined. DDTs (1.7–13 ng g^{-1}) were the most abundant OC in soils followed by total polychlorobiphenyls (PCBs; 0.41–1.5 ng g^{-1}) and hexachlorobenzene (HCB; 0.15–0.91 ng g^{-1}). In sediments, the dominant OC were also DDTs (3.3–28 ng g^{-1}) and PCBs (2.3–15 ng g^{-1}). These concentrations are low, involving absence of major pollution sources in these high mountain regions.

The downcore OC profiles in soils and sediments were similar but higher concentrations and steeper vertical gradients were observed in the latter. Radiometric determinations showed absence of significant OC transport from catchment to lake. The sediment–soil difference points therefore to a better retention of the OC load in sediments than soils which may be related to the low temperatures that are currently encountered at the bottom of the lake water column and the depletion of sediment bioturbation in these cold environments.

Significant qualitative changes in the soil PCB distributions are observed downcore. These involve a dominance of the high molecular weight congeners in the top core sections and those of lower weight (i.e. less chlorinated) in the bottom. Anaerobic dechlorination of higher molecular weight congeners occurring in microsites, e.g. as observed in flooded or poorly drained soils, could be responsible for these changes. This process could be concurrent to bioturbation.

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Keywords: Organochlorine compounds; High mountains; Soils; Lacustrine sediments; Trace chemical pollution in remote environments

1. Introduction

An important increase of organochlorine compounds (OC) such as polychlorobiphenyls (PCBs), DDTs, hexachlorocyclohexanes (HCH) and hexachlorobenzene (HCB) in the global environment has been observed over the last century as a consequence of their extensive use since the Industrial Revolution (Keith and Telliard,

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1979; Eisenreich et al., 1989; Alcock et al., 1993; Sanders et al., 1994). In the seventies, concern over their potential toxicity and high persistence, led to the implementation of many regulations for their restricted use or banishment. Over the last decade, scientific interest has been focused on the study of historic inputs in soil/sediments for the evaluation of the success of these international environmental policies (Rapaport and Eisenreich, 1988; Oliver et al., 1989; Sanders et al., 1995; Wong et al., 1995; Muir et al., 1996; Krauss et al., 2000). However, evaluation of long-term changes in remote sites has been barely considered.

Environmental contamination with persistent OC may be related to point sources (industrial discharges and waste plant effluents) or, more frequently, to diffuse sources (atmospheric transport and deposition) which are the major pathway for the transfer of these persistent organic pollutants to remote sites.

In principle, the accumulation of OC in soils and sediments of remote sites should provide similar downcore records. However, soils and sediments possess different microenvironmental conditions affecting air and water exchange and post-depositional processes. Comparison of the accumulation patterns of OC in these two environmental compartments is therefore a pre-condition for an integrated understanding of the pollution load of these compounds in remote sites. High mountain areas are ideal environments for this purpose since both compartments are under the same atmospheric precipitation fluxes.

In this respect, it should be mentioned that a priori soils contribute to lake sediments but not the reverse. Thus, the terrestrial pathway is different between the two reservoirs. In the present study, radiometric measurements have been performed in order to ascertain the specific links between them.

The Pyrenees are a mountain range where moderate OC pollution concentrations have been recorded (Grimalt et al., 2001). Lake Redon (42°38′34″N, 0°46′13″E; 2240 m above sea level; Fig. 1) is the largest high mountain lake in this area (24 ha) and has been used as reference lake for many environmental studies (Catalan, 1988, 1992). One lake sediment core and two soil cores collected near the lake are considered in the present study.

The Tatra mountains are situated in central Europe. Sediment cores from Ladove Lake (49°11′03″N, 20°09′46″E; 2057 m), Starolesnianske Pleso (49°10′N,
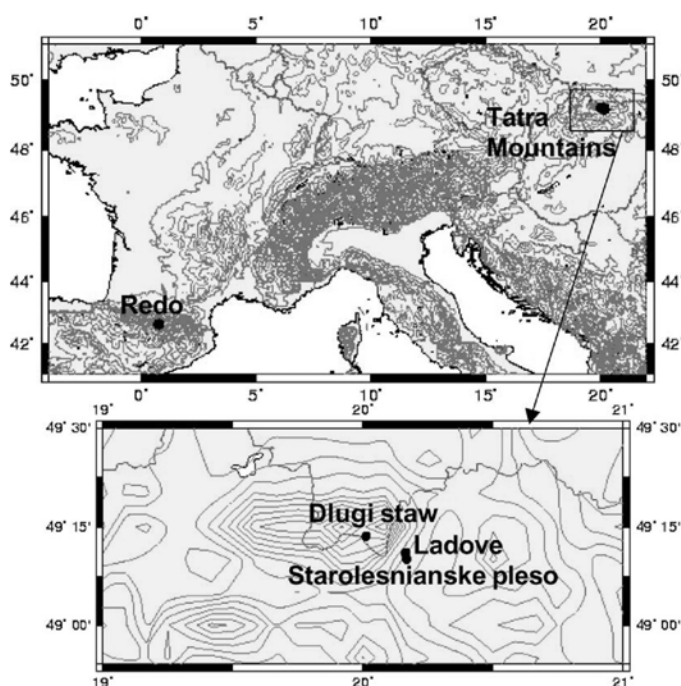

Fig. 1. Maps showing the location of the lakes considered for study.

20°10′E; 2000 m) and Dlugi Staw (49°13′36″N, 20°0′39″E; 1783 m) are considered for study (Fig. 1). The two former lakes are situated at less than 2 km of distance. Two soil cores were analyzed near Ladove Lake.

To the best of our knowledge, this is the first study comparing downcore distributions of OC in soils and lake sediments, particularly in high mountain areas.

2. Materials and methods

2.1. Materials

Residue analysis-grade *n*-hexane, dichloromethane, isooctane, methanol and acetone were from Merck. Anhydrous sodium sulfate for analysis was also from Merck. Neutral aluminum oxide type 507C was from Fluka AG. Cellulose extraction cartridges were from Whatman Ltd. Aluminum foil was rinsed with acetone and let dry at ambient temperature prior to use. The purity of the solvents was checked by gas chromatography-electron capture detection (GC-ECD). We detected no significant peaks for any of the reagents. Aluminum oxide, sodium sulfate and cellulose cartridges were cleaned by Soxhlet extraction with hexane:dichloromethane (4:1, v/v) during 24 h before use. The purity of the cleaned reagents was checked by ultrasonic extraction with *n*-hexane:dichloromethane (4:1; 3×20 ml), concentration to 50 µl and analysis by GC-ECD. No interferences were detected. Sodium sulfate and aluminum oxide were activated overnight at 400 and 120 °C, respectively.

2.2. Sampling

Sediment samples were taken in the deepest points of the lake using a gravity coring system (Glew, 7.5 cm diameter, 30 cm long). A 7 cm (diameter) × 20 cm (long) stainless steel cylinder was used for soil core collection. All soils were taken in the lake catchment areas. Soil and sediment cores were immediately divided in sections of 2 and 0.5 cm, respectively (0.3 and 0.25 cm in the case of Redon and Ladove sediments, respectively), and stored in pre-cleaned aluminum foil at −20 °C until analysis.

2.3. Analysis

The following OC were determined in the soil cores: HCB, α-HCH, β-HCH, γ-HCH, δ-HCH, DDTs and PCB congeners #18, 28, 52, 70, 90, 101, 105, 110, 118, 123, 132, 138, 149, 153, 158, 160, 180, 194 and 199. In sediments, HCB, DDTs and the polychlorobiphenyl congeners #28, 52, 90, 101, 118, 123, 138, 149, 153, 160 and 180 were determined. In addition, PCB congeners 70, 105, 110, 132, 158, 194 and 199 were also analyzed in the sediment core of Lake Ladove.

2.4. Sample extraction

Soils were weighed into a Whatman Soxhlet cellulose thimble. About 1:1 w/w sodium sulfate were mixed with the soil samples in order to improve Soxhlet extraction by water removal. Prior to extraction, samples were spiked with PCB congeners #30 and 209 which were used as surrogate standards. Samples were extracted with hexane:dichloromethane (4:1) for 18 h. All extracts were first concentrated by rotary vacuum evaporation to 3–5 ml and subsequently eluted through an anhydrous sodium sulfate column. After rotary vacuum evaporation to ∼0.5 ml, the extracts were fractionated on a neutral aluminum oxide column (2 g). The OC were eluted with 8 ml of hexane:dichloromethane (9:1).

For sediments, about 0.1–1 g of wet sediment was extracted by sonication with methanol (1×20 ml; 20 min) in order to separate most of the interstitial water. The subsequent extractions were performed with (2:1, v/v) dichloromethane–methanol (3×20 ml; 20 min). All extracts were combined and spiked with PCB congeners #30 and 209. Then, they were vacuum evaporated to 10 ml and hydrolyzed overnight with 20 ml of 6% (w/w) KOH in methanol. The neutral fractions were recovered with *n*-hexane (3×10 ml), vacuum evaporated until dryness, and fractionated by adsorption column chromatography as described for the soil samples.

Activated copper (∼1 g) was added to soil and sediment organochlorine fractions for removal of sulfur-containing compounds. This copper powder was removed by filtration though glass wool and rinsed with *n*-hexane. Elution solvent and rinses were concentrated to 50 µl in isooctane after rotary vacuum and nitrogen stream evaporation.

2.5. Instrumental analysis

The extracts were injected into a Hewlett Packard 5890 Series II GC-ECD. An HP-5 fused silica capillary column (30 m length, 0.25 mm i.d., 0.25 µm film thickness) coated with 5% phenyl 95% methylpolysiloxane was used for the analyses. The oven temperature program started at 100 °C (holding time 1 min), increased to 120 °C at 20 °Cmin⁻¹, to 240 °C at 4 °Cmin⁻¹ (holding time 12 min) and finally to 300 °C at 4 °Cmin⁻¹ (holding time 10 min). Injector and detector temperatures were 280 and 310 °C, respectively. Helium and nitrogen were used as carrier (0.33 mlmin⁻¹) and make-up (60 mlmin⁻¹) gases, respectively. Compound identification was confirmed by GC coupled to mass spectrometry in the chemical ionisation mode and

negative ion recording (Fisons 8000 Series, Mass Selective Detector 800 Series).

2.6. Quantification

Solutions of tetrachloronaphthalene and octachloronaphthalene were added to the vials prior to injection. Calibration curves (detector response vs amount injected) were performed for each compound to be quantified. The range of linearity of the detector was evaluated from the curves generated by plotting detector signal/amount injected vs amount injected. All measurements were performed in the ranges of linearity found for each compound. In some cases, the samples were rediluted and reinjected for fitting within the linear range of the instrument. The quantitative data were corrected for surrogate recoveries.

2.7. Total organic carbon

Soil and sediment samples were extracted with HCl 3N to remove inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH (7 ± 0.2) and dried at 60 °C. The determination of TOC was performed by flash combustion at 1025 °C followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. The limit of detection was 0.1%.

2.8. Radiometric dating

Sediment and soil samples were analyzed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al., 1986). ^{210}Pb was determined via its gamma emissions at 46.5 keV and ^{226}Ra by the 295 and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662 and 59.5 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy γ-rays within the sample (Appleby et al., 1992). Supported ^{210}Pb activity was assumed to be equal to the measured ^{226}Ra activity. Unsupported ^{210}Pb activity was calculated by subtracting supported ^{210}Pb from the measured total ^{210}Pb activity. ^{210}Pb radiometric dates were calculated using the CRS and CIC dating models (Appleby and Oldfield, 1978) where appropriate and validated where possible against the 1986 and 1963 depths determined from the ^{137}Cs/^{241}Am stratigraphic records.

3. Results and discussion

The lakes considered for study are situated above the local tree line, they are oligotrophic (median total phosphorous <4.1 µg l^{-1}) and remain ice-covered for long periods during the year. Three dominant types of land cover are found in the lake catchment, dry alpine meadows, moraines and solid rock. Among these, the former were selected for study. Soils in the dry alpine meadows are mostly undeveloped (e.g. leptosol, podsol and histosol) with average mineral horizons of about 33 cm thickness and shallow organic matter horizons (5–17 cm, average 4 cm). These soils are covered by grass in summer and under snow during the cold months (Catalan, 1988). All pollution is presumably derived from atmospheric transport since the lakes are free from local anthropogenic sources.

3.1. Total organic carbon

TOC is generally higher in the soil than in the sediment cores. In Redon Lake it ranges between 16% and 34% (average values 19% and 28% in the two cores) in the soils and between 2% and 5% in the sediments (average 3.6%) (Table 1). The core sections of soils and sediments in the Tatra mountains show smaller differences. Thus, TOC range between 6% and 35% (average values 8.6% and 15% in the two cores) in Ladove soils and between 9% and 14% (average values 9.2% and 12.5%) in the sediments from the lakes in the Tatra mountains (Table 1).

In contrast to other studies (Ribes et al., 2002) no significant correlation ($P > 0.05$) was found between the concentrations of TOC and OC in the soils of these two lakes (Table 1). Therefore, soil concentrations have not been TOC normalized.

3.2. Organochlorine compounds in soils

Total average PCB levels range between 0.41–0.68 and 0.87–1.5 ng g^{-1} in Redon and Ladove soils, respectively (Table 1). All concentrations refer to dry weight unless otherwise stated. The concentrations of these soils from high mountain lacustrine catchments are similar to those found in woodland regions of Germany (0.2–4.8 ng g^{-1}; Krauss et al., 2000) and Austria (0.2–7.5 ng g^{-1}; Weiss et al., 1998) and rural areas of Thailand (1.1–6.2 ng g^{-1}; Thao et al., 1993). In contrast, Redon and Ladove soil concentrations are low in comparison to those reported in industrial areas of Austria (6.4–95 ng g^{-1}; Weiss et al., 1994) and Poland (4.6–3400 ng g^{-1}; Falandysz et al., 2001), rural sites of UK and Norway (1.2–2000 ng g^{-1}; Creaser et al., 1989; Alcock et al., 1993; Sanders et al., 1995; Lead et al., 1997), Germany (8.4–60 ng g^{-1}; Wilcke and Zech, 1998) and Brazil (27–49 ng g^{-1}; Wilcke et al., 1999) or even in woodland re-

Table 1
Total organic carbon (TOC, %) and concentrations of the main organochlorine compound groups (ng g^{-1} dw) in the sediment and soil cores of the high altitude lakes considered in this study

	Redó			Ladove			Starolesnianske Pleso	Dugli Staw
	Sediment	Soil (A)	Soil (B)	Sediment	Soil (A)	Soil (B)	Sediment	Sediment
TOC	3.6[a]	28	19	9.2	15	8.6	12.5	9.2
'	(5.1[b]–1.7[c])	(34–24)	(33–18)	(14–9.1)	(35–5.8)	(11–8.8)	(14–13)	(10.5–8.9)
HCB	0.18	0.15	0.91	1.3	0.23	0.33	4.2	1.6
	(1.1–0)	(0.29–0.004)	(3.4–0.013)	(1.1–0)	(0.40–0.06)	(0.37–0.08)	(11–0.81)	(4.5–0)
HCH	–	0.08	0.19	–	0.28	0.49	–	–
		(0.29–0.007)	(0.44–0.016)		(0.80–0.13)	(0.46–0.80)		
DDT[d]	3.3	1.7	3.4	12	4.5	13	28	25
	(15–0.27)	(2.9–0.07)	(6.9–0.03)	(1.0–1.4)	(10–0.42)	(37–0.26)	(54–1.3)	(43–2.7)
PCB[e]	2.3	0.41	0.68	15	1.5	0.87	15	10
	(7.2–0.74)	(0.33–0.46)	(0.72–0.20)	(5.4–2.7)	(5.1–1.8)	(2.8–0.5)	(32–3.1)	(44–0.45)

[a] Average concentration value of the whole core.
[b] Concentration of the upper section.
[c] Concentration of the bottom section.
[d] Sum of DDT and DDE.
[e] Sum of congeners #28–31, 52, 90–101, 118, 153, 138 and 180.

gions of Norway (5.3–30 ng g^{-1}; Lead et al., 1997) and USA (7.5–250 ng g^{-1}; Smith et al., 1993).

Average total DDTs (4,4′-DDE + 4,4′-DDT) are 1.7–3.4 ng g^{-1} and 4.5–13 in Redon and Ladove soils, respectively (Table 1) which is lower than concentrations reported in industrial/urban areas from Germany (500–400 000 ng g^{-1}; Wilken et al., 1994) and Poland (8.6–2400 ng g^{-1}; Falandysz et al., 2001) or woodland regions of USA (2.1–270 ng g^{-1}; Smith et al., 1993) but in the same order of woodland regions from Austria (<22 ng g^{-1}; Weiss et al., 1998).

Total HCH, average values of 0.08–0.19 and 0.28–0.49 ng g^{-1} in Redon and Ladove soils, respectively, (Table 1) are also low, e.g. concentrations reported in urban/industrial areas of Poland range between 0.36 and 110 ng g^{-1} (Falandysz et al., 2001) and in woodland regions of Austria between 0.6 and 6.6 ng g^{-1} (Weiss et al., 1998). γ-HCH dominates over α-HCH in the soils of Redon Lake whereas the α-isomer is dominant in the soils of Ladove Lake (Figs. 3 and 4). The difference between the two lakes probably reflects the historic use of this pesticide in the pure form or as technical mixtures containing high proportions of the α-isomer, respectively. At present, only pure lindane (γ-HCH) is approved for use (Harner et al., 1999).

Total HCB exhibit average values of 0.15–0.91 and 0.23–0.33 ng g^{-1} in Redon and Ladove soils, respectively, (Table 1). These concentrations are again lower than soil values reported in urban/industrial areas of Germany (100–1300 ng g^{-1} ; Wilken et al., 1994) and Poland (0.19–30 ng g^{-1}; Falandysz et al., 2001) but in the same order than in woodland regions of Austria (<1.9 ng g^{-1} ; Weiss et al., 1998).

These low concentrations suggest the absence of major pollution sources in these high mountain regions. They are also much lower than those reported for total PCBs and DDTs in mountain soils located near to industrial sites such as the Giant Mountains (Czech–Polish border) where concentration ranges of 5–140 and 20–5100 ng g^{-1}, respectively, have been found (Holoubek et al., 1994, 1998). In contrast, the concentrations of HCB in the soils of these high mountain lakes and the Giant Mountains, 0.47–48 ng g^{-1}, are more similar than for PCBs and DDTs (Holoubek et al., 1994, 1998).

In all cases except one, HCB in Redon soil B (Table 1), the concentrations of OC are higher in the soils from the lakes in the Tatra mountains than in Redon. This likely reflects the influence of higher use and production of these compounds near the Tatra region. Thus, high levels of HCH (0.36–110 ng g^{-1}), DDTs (8.6–2400 ng g^{-1}) and PCBs (4.6–870 ng g^{-1}) have been reported in cities from southern of Poland due to industrial activity (Falandysz et al., 2001). Furthermore, total PCB soil concentrations ranging between 1.5 ng g^{-1} (agriculture fields) and 53 mg g^{-1} (asphalt/gravel mixing plants) have been observed in north Slovakia as a consequence of 25 years in the manufacture of PCBs (Kocan et al., 2001).

Despite no direct sources of these OC are found nearby the lakes, it seems clear that air masses travelling up to the Tatra mountains carry higher amounts of these pollutants than those arriving to the Pyrenees. At these latitudes westerlies are generally dominant which involves that air arriving to the Tatras will pass over central continental areas whereas that reaching the Pyrenees may often come directly from the Atlantic ocean.
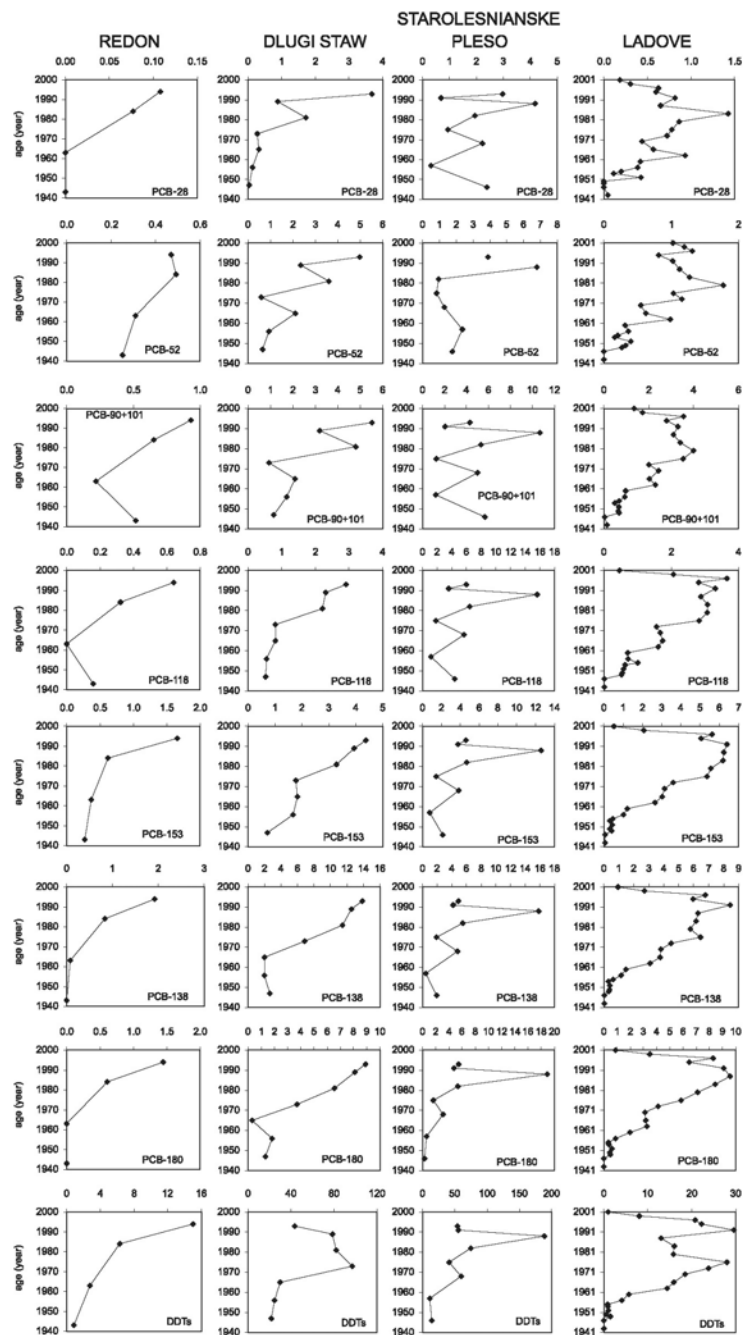
Fig. 2. Time scales of the concentrations of the major PCBs and DDTs (4,4′-DDE + 4,4′-DDT) determined from the sediment cores analyzed in Redon, Dlugli Staw, Starolesnianske Pleso and Ladove Lakes.