

Fig. 3. Downcore graphs of the main OC found in the soils (◆) and sediments (○) of Redon Lake. Concentrations in ng g^{-1} dry weight. The plots only compare the vertical structure of OC in soils and sediments, not involving temporal correspondences between the same depth levels.

3.3. Organochlorine compounds in sediments

The average PCB concentrations are higher in the sediment than in the soil cores in all cases (Table 1), 3–6 times higher in Redon and 10–20 times higher in Ladove. Average HCB concentration is also higher in the sediments than in the soils of Ladove Lake (about 5 times higher). However, in Redon Lake the average concentrations are four times higher in one soil core than in the sediment.

Average total DDT concentrations exhibit the lowest differences between soils and sediments. In both lakes, there is one soil core exhibiting similar concentrations than the sediment and the other soil core has lower values.

Radiometric measurements in soils and sediments show that there is little transport of fallout radionuclides from the catchment to Lake Redon and essentially none

in Lake Ladove. Average ^{210}Pb flux in soil and sediment cores of Lake Redon was 286 ($n = 5$) and 182 ($n = 7$) $\text{Bq m}^{-2} \text{y}^{-1}$, respectively, and in soils and sediments of Lake Ladove it was 154 ($n = 5$) and 106 ($n = 5$) $\text{Bq m}^{-2} \text{y}^{-1}$, respectively. Thus, the generally higher concentrations of OC in sediments than in soils cannot be explained by soil erosion into the lakes.

Leaching, i.e. OC extraction from soils by percolating water, is also another hypothetical pathway for the transfer of these compounds from catchment. However, the high octanol–water partitioning coefficients, K_{OW} , of these OC (generally $\log(K_{\text{OW}}) > 10^4$) point to the preferential retention of these compounds in soil organic matter than leached to the lake. On the other hand, the differences cannot be explained by higher affinity of OC to organic matter since soils exhibit larger TOC than sediments in most cases (Table 1).

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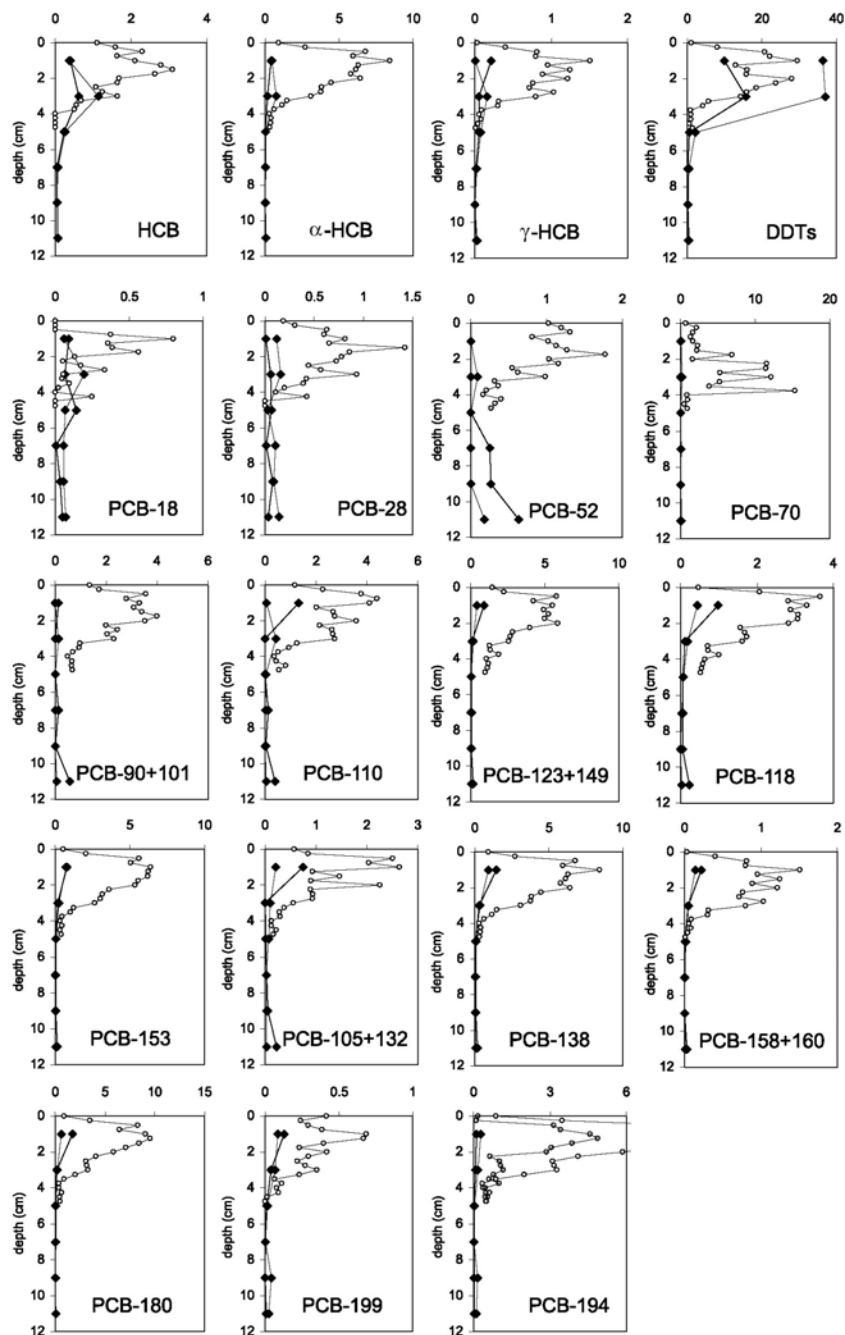
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Fig. 4. Downcore graphs of the main OC found in the soils (◆) and sediments (○) of Ladove Lake. Concentrations in ng g^{-1} dry weight. The plots compare vertical soil and sediment OC structures as indicated in Fig. 2.

Table 2
Dated sediment cores included in this study

Redo		Dugli Staw		Starolesnianske Pleso		Ladove			
Depth (cm)	Age (year)	Depth (cm)	Age (year)	Depth (cm)	Age (year)	Depth (cm)	Age (year)	Depth (cm)	Age (year)
0.15	1994	0.25	1992	0.25	1992	0.25	1999	2.50	1970
0.45	1984	0.75	1985	0.75	1990	0.50	1997	2.75	1966
0.75	1963	1.25	1977	1.25	1985	0.75	1995	3.00	1963
1.05	1943	1.75	1969	1.75	1979	1.00	1992	3.25	1960
1.35	1932	2.25	1961	2.25	1972	1.25	1988	3.75	1955
1.65	1916	2.75	1952	2.75	1963	1.50	1984	4.0	1954
2.85	1886	3.25	1940	3.75	1939	1.75	1980	4.5	1950
3.75	1842	3.75	1927	4.25	1925	2.00	1976	4.75	1949
		4.25	1914	4.75	1912	2.25	1973	5.00	1947

Having in mind the low catchment to lake transfer and that a priori both soils and sediments are under the same OC input, the OC concentration differences between the two reservoirs could be explained by higher retention efficiencies of the later than the former. Thus, the lake water column must essentially impede revolatilization to the atmosphere after deposition instead of obstructing air-to-sediment transfer. In this respect, lake bottom water temperatures are approximately constant at 4 °C in all seasons whereas soil temperatures have a strong seasonal variability reaching values higher than 10 °C in the warm periods (Catalan, 1992). The higher temperatures in the soils may enhance bioturbation in the warm periods and volatilization back to the atmosphere after deposition.

3.4. Vertical profiles in the lake sediments

Radiometric analysis showed that all lake sediment cores selected had rather uniform sedimentation (Fig. 2). No hiatus or periods of mixing were observed in the vertical structure of the recovered sediments. The average sedimentation rates of the sediment cores studied were 0.024, 0.054, 0.084 and 0.10 cm y⁻¹ for Redon, Dlugi Staw, Starolesnianske Pleso and Ladove. These rate differences and the core sectioning for analysis provide vertical OC profiles with different time resolutions at each site (Table 2).

The best time resolved OC trend is the one for Ladove Lake where biannual resolution is achieved in most core sections. The time trend of the major PCBs found in this core, #101, 118, 153, 138 and 180 defines a period of highest concentration between 1976 and 1997 (Fig. 2). Thus, despite the restriction of these compounds in the eighties there is no decline in the input of these compounds to this lake until later than 1997. The time-profile also shows two additional periods of increase, one between 1949 and 1957 when levels increase from below limit of detection to some small concentrations (below 1 ng g⁻¹ per individual PCB congener) and a

second between 1963 and 1970 (about 3 ng g⁻¹ per individual PCB congener). These two periods probably reflect the historical use of PCBs in Europe which started to have significant exploitation after the Second World War.

Total DDTs in Ladove sediments exhibit a temporal pattern that is also showing concentration increases that started after the Second World War and arrive to maxima in 1976 (Fig. 2). This increase is also showing some steps but in general is more continuous and steep for the period between 1955 and 1976. After 1976 there is a significant drop in concentrations down to less than half the 1976 values between 1978 and 1990. However, there is a second maximum between 1992 and 1997 which likely reflects either a new period of use of DDTs in some parts of Europe or some remobilization of these compounds stored in some environmental compartment that produced a major second DDT pulse. As in the case of PCBs, after 1997 there is a strong decrease in the concentrations of these compounds in Ladove sediments.

The temporal concentration patterns of PCBs and DDTs in the other lakes of the Tatra mountains, Dlugi Staw and Starolesnianske Pleso, roughly agree with those in Ladove (Fig. 2). However, the temporal resolution is lower. Thus, less details are observable in the concentration changes.

The sediment core from Redo Lake is the one sampled at least time resolution (least sedimentation rate). In general it shows that the highest concentrations of both PCBs and DDTs correspond to the most recent section examined which, on average, is dated in 1994.

Overall, the cores show a concentration time dependence which is consistent with the known history of use of these compounds in Europe. Thus, they provide a reference material which can be used for comparison with the soils from the lake catchments. The depths corresponding to 1940 are 1.2, 3.2, 3.7 and 5.5 cm in Redon, Dlugi Staw, Starolesnianske Pleso and Ladove Lakes, respectively.

3.5. Vertical profiles in soils and sediments

In Figs. 3 and 4 the downcore profiles of the OC concentrations in the sediments and soils of Lakes Redon and Ladove are shown in the same graphs. The plots are only performed for comparison of the vertical structure of OC in soils and sediments. They do not involve temporal correspondences between the same depth levels.

The downcore OC profiles in the soils of both lakes generally exhibit higher abundances in the top sections (Figs. 3 and 4). This trend points to recent pollution episodes as the main factor for the occurrence of these compounds in these high mountains and is consistent with the observations in the sediments. However, both in Redon and Ladove the soil vertical profiles exhibit higher downcore spread than in the sediments (Figs. 3 and 4). This difference is observed in cases of both high and low OC soil pollution. Thus, DDTs, HCH and HCB in Redon Lake soils encompass the upper 4 cm whereas they only involve the upper 1 cm in the sediments. Similarly, at low OC concentration, e.g. PCB congeners #153, 138 and 180, there is a strong contrast between the concentration maxima found at the upper sections of the sediments and the maxima found at mid depths in the soil cores (Fig. 3). This difference suggests higher bioturbation in soils than sediments likely involving higher vertical OC spread in the former.

Further insight into the post-depositional changes in sediments and soil cores can be obtained by representation of the composition of the seven major PCB congeners, #28 + 31, 52, 90 + 101, 118, 153, 138 and 180, in both soil and sediment cores from all the lakes (Figs. 5 and 6). The upper sections are dominated by the heavier molecular weight congeners which are also the compounds found in higher concentration in the whole core. The incorporation of these compounds to both soil and lake sediments could be a consequence of their preferential condensation at the lake air temperatures (Grimalt et al., 2001; Simcik et al., 1999; Hippelein and McLachlan, 2000). The presence of these compounds in the air particulate phase may also enhance their preferential deposition although the condensation mechanism must dominate since these compounds are essentially found in the gas phase (van Drooge et al., 2002).

The concurrence of similar changes in downcore PCB congener predominance in both lake systems makes unlikely that these could reflect preferential deposition of congener mixtures dominated by the less chlorinated congeners in the past. In addition, there is not obvious reason for different deposition mechanisms in previous time periods. The dominance of the lower molecular weight PCB congeners at deeper sections is observed both in sediments and soils of both lakes being more significant in the later. Previous studies have already reported the occurrence of the less chlorinated PCB

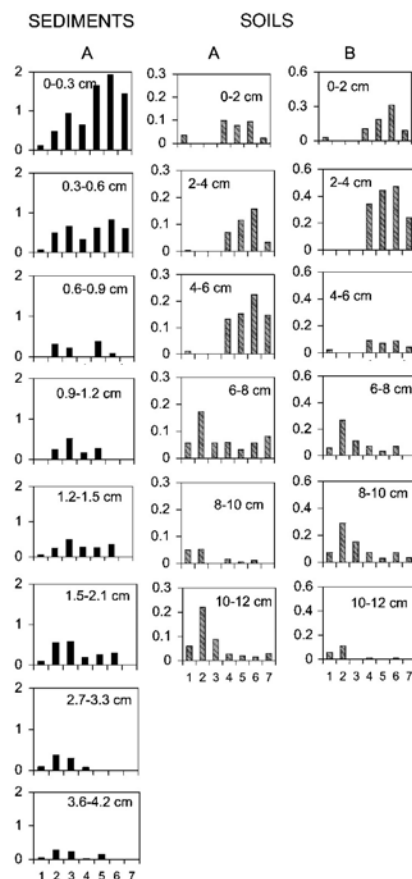


Fig. 5. Histograms showing the downcore composition of the major PCB congeners of the soils and sediment cores from Lake Redon. Foot captions as follows: (1) #28 + 31; (2) #52; (3) #90 + 101; (4) #118; (5) #153; (6) #138 and (7) #180. The plots compare vertical soil and sediment OC structures as indicated in Fig. 2.

congeners in deep soil sections corresponding to ages prior to commercial use (Sanders et al., 1995; Gevaio et al., 1998) being attributed to vertical transport associated to water table oscillations or other physico-chemical processes.

The increase in concentration with depth of the PCB congeners with lower degree of chlorination, e.g. #28 + 31 and 52 (Figs. 3 and 4), cannot be explained in terms of recent pollution inputs since the maxima are not close to the core tops. Two processes may explain the vertical distributions of these compounds. One concerns chemical diffusion, rainfall dissolution and water table oscillations (Rapaport and Eisenreich, 1988)

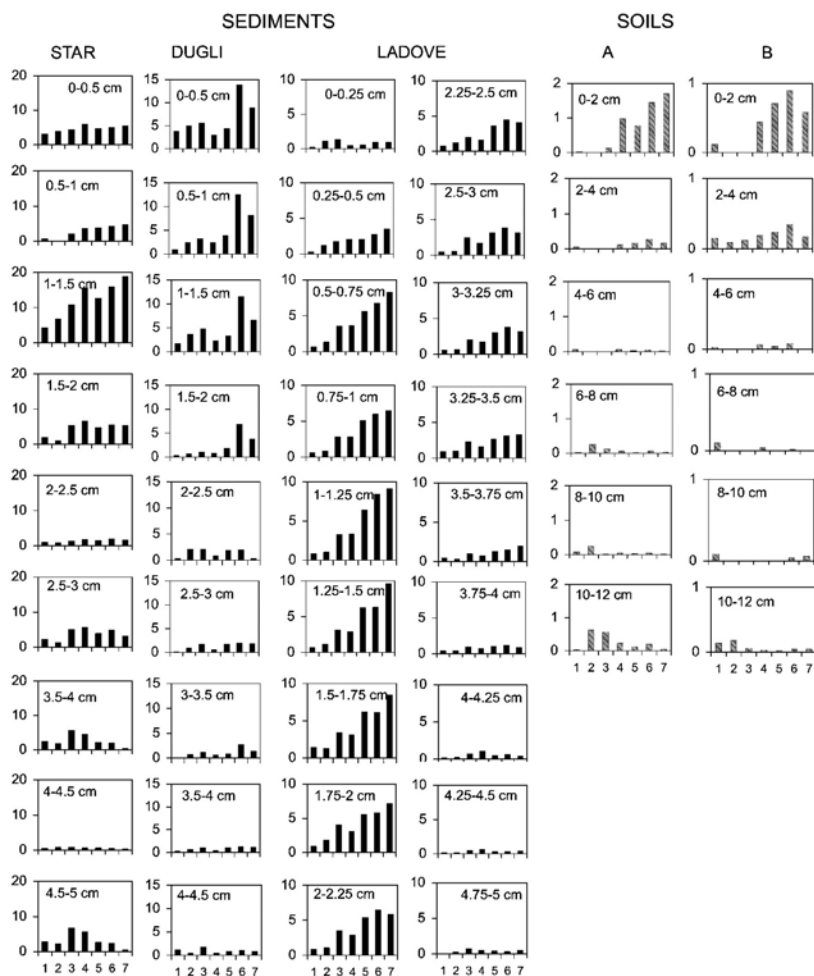


Fig. 6. Histograms showing the downcore composition of the major PCB congeners of the soils and sediment cores taken in the Tatra Lakes. Foot captions as in Fig. 5. The plots compare vertical soil and sediment OC structures as indicated in Fig. 2.

enhancing the vertical transport of the more water soluble less chlorinated PCB. Alternatively, the higher abundance of the less chlorinated congeners may reflect downcore in situ production. The fact that these downcore concentration peaks are only observed for the less chlorinated PCB congeners points to dechlorination as a likely mechanism for their formation (Quensen et al., 1988). Simple examination of the composition of some of the major PCB congeners present in these soils and sediments, e.g. #101, 118, 138, 153 and 180, show that they could be transformed into congeners #52 and 28 upon dechlorination. This process usually requires anaerobic conditions which may be encountered in micro-

sites, in flooded or poorly drained soils (Haluska et al., 1995).

4. Conclusions

The concentrations of HCB, HCH, DDTs and PCBs in the soils and sediments from the lakes in the Pyrenees and the Tatra mountains exhibit parallel geographic distributions involving similar atmospheric mechanisms for the transport of these compounds to these two high-altitude sites. In general, DDTs were the most abundant OC, followed by total PCBs and HCB. In any case, the

concentrations of all OC are low suggesting absence of major pollution sources in these high mountain regions.

The vertical profiles of all OC from both soils and sediments exhibit higher abundances in the top sections, which indicate recent pollution episodes as the main reason for the occurrence of these compounds in the high mountain cores. However, both in Redon and Ladove Lakes the vertical profiles exhibit higher concentration gradients in the top sections of the sediments than in the soils which could reflect higher bioturbation in the later. In addition, the average OC concentrations are higher in sediments than soils in all cases. Both features point to higher retention efficiency of these compounds in the lake systems than in the catchment. In this respect, radiometric analysis shows that catchment to lake erosive transport of soil residues is minimal.

The higher sediment retention affinity does not reflect organic matter differences between soils and sediments since in most cases the former exhibit larger TOC than the latter. The constant low temperatures at the lake bottom (about 4 °C in all seasons) may be an important factor for the retention of these compounds. In contrast, soil temperatures have a strong seasonal variability reaching values higher than 10 °C in the warm periods. These higher temperatures may enhance soil bioturbation in the warm periods and increase volatilization back to the atmosphere after deposition.

The qualitative PCB distributions of soil cores are dominated by high molecular weight congeners in the top core sections and by the less chlorinated congeners at the bottom. Anaerobic microbial processes are currently invoked for the dechlorination of higher molecular weight congeners in soil/sedimentary environments. In the soils under study, these processes could occur in microsites, e.g. as observed in flooded or poorly drained soils. They also could be concurrent with bioturbation.

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Article 8.**POLYCYCLIC AROMATIC HYDROCARBON COMPOSITION IN SOILS AND
SEDIMENTS OF HIGH ALTITUDE LAKES**

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Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes

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Abstract

The polycyclic aromatic hydrocarbons (PAH) in lake sediments and nearby soils of two European high mountain regions, Pyrenees and Tatra, have been studied. Similar mixtures of parent PAH were predominant in all cases, indicating a predominance of airborne transported combustion products. PAH in superficial layers of soils exhibited a better parallelism with PAH in long-range transported aerosol mixtures than in sediments. This higher agreement is observed when comparing the composition of both photochemically refractory and labile compounds. The contrast between these two environmental compartments points to significant PAH degradation during lake water column transport.

Postdepositional transformation processes were different in soils than in sediments. In the former there is higher decomposition of more labile PAH such as benz[*a*]anthracene, benzo[*a*]pyrene and methylphenanthrenes in relation to chrysene+triphenylene, benzo[*e*]pyrene and phenanthrene, respectively, which involves better long-term post-depositional preservation conditions in lake sediments.

In addition, the deep lake sediments involve the in situ diagenetic formation of major amounts of perylene, which is not formed in soil cores. In contrast, soils exhibit downcore enrichments of phenanthrene maybe as consequence of the extensive aromatization of diterpenoids. Evaluation of the downcore profiles of retene in comparison to those of benzo[*b*]naphtho[2,1-*d*]thiophene, 1,7- and 2,6-dimethylphenanthrene also suggests a diagenetic origin for this diterpenoid in the lake sediments.

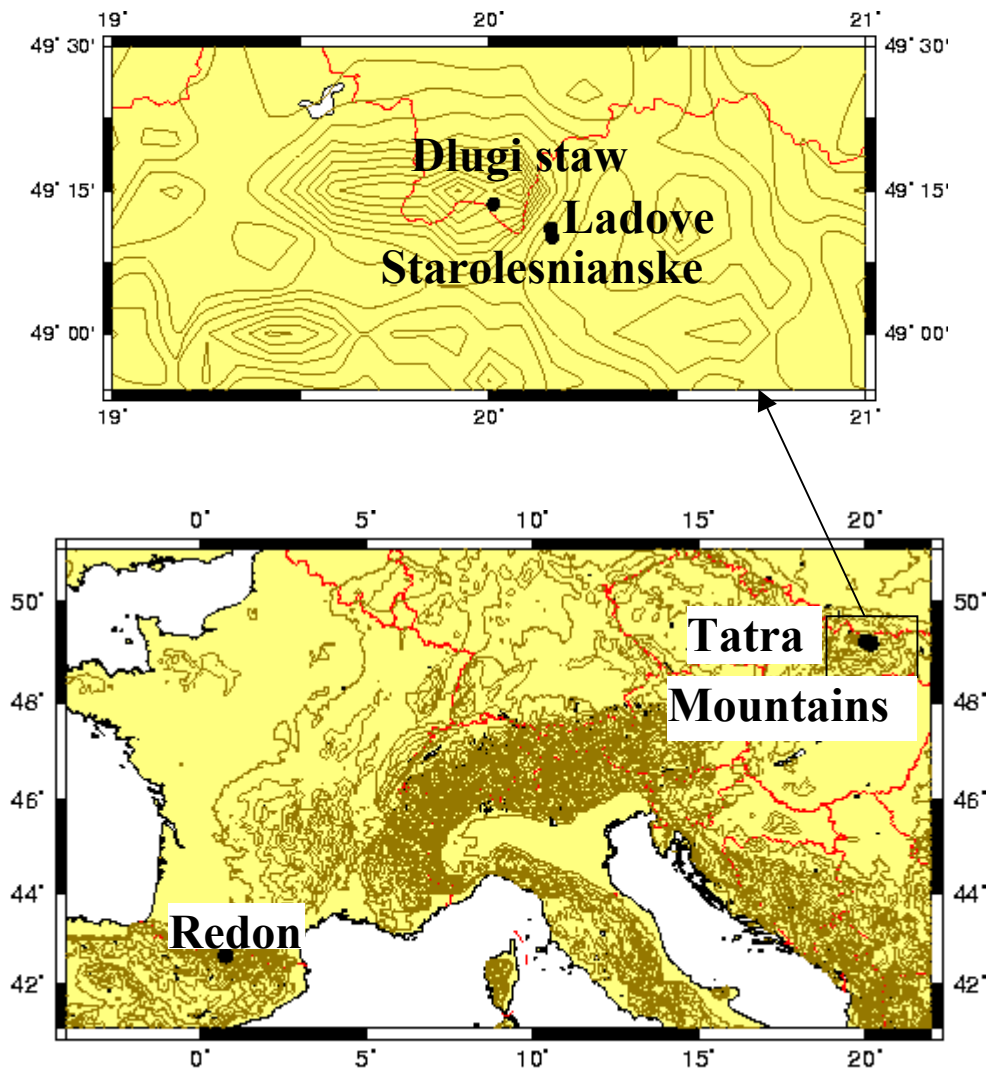


Fig. 1. Map showing the location of the soils and sediments sampled in high mountain European regions. Pyrenees, Redon (soils and sediments). Tatra, Ladove (soils and sediments), Długi staw and Starolesnianske pleso (sediments).

1. Introduction

PAH in the environment are deserving increasing attention for their widespread occurrence and mutagenic, carcinogenic and teratogenic effects (Freitag et al., 1985). They may be generated from organic matter diagenesis and anthropogenic processes (Simoneit, 1977; LaFlamme and Hites, 1978; Wakeham et al., 1980a and b). However, the anthropogenic contribution usually outweighs the inputs from other sources and is responsible for their general increase over the last 100 yr (Hites et al., 1977, Fernández et al., 2000).

Depending on their physico-chemical properties, atmospheric PAH are distributed between the gas and particulate phases, mainly in association with small particles (< 1 µm) (Aceves and Grimalt, 1993; Masclet et al., 1988; Allen et al., 1996; Ribes et al., 2003). They are transported through the atmosphere to remote sites giving rise to a general background level in soils (Hartmann, 1996; Wilcke and Zech, 1997; Wild and Jones, 1995; Vogt et al., 1987; Berteigne et al., 1988; Jones et al., 1989a and b; Guggenberg et al., 1996; Wilcke et al., 1996) and lake sediments (LaFlamme and Hites, 1978; Gschwend and Hites, 1981; Atlas et al., 1981; Simcik et al., 1996; Fernández et al., 1996; 1999; 2000) where they accumulate due to their high stability and small mobility as consequence of their low water solubility. Soils and lake sediments are therefore good environmental compartments to record the historical environmental burden of these compounds as consequence of human activities.

In this respect, European high mountain lakes have been observed to accumulate significant loads of atmospherically transported PAH despite of their remoteness (Fernández et al., 1996; 1999; 2000; Carrera et al., 2001; Vilanova et al., 2001). These lakes are defined as those situated above the local tree-line, far from any pollution source and lacking major water inputs from the catchment. They constitute unique environments for the assessment of the atmospheric pollution load over continental areas. Geographical and historical patterns of this pollution load in Western Europe have been described recently based on the study of sediments from these lakes (Fernández et al., 1999; 2000). However, PAH not only accumulate in lake sediments but also in other environmental compartments such as soils. A global understanding of their overall burden in these high mountain areas also requires the study of this compartment.

High mountain areas are therefore ideal environments for comparison of PAH accumulation in soils and lake sediments since both compartments are under the same atmospheric precipitation fluxes. Accordingly, the Pyrenees and the Tatra mountains have been selected for the study of PAH in lake sediments and nearby soils.

The Pyrenees are a mountain range where moderate pollution levels by PAH have been recorded (Fernández et al. 1999; 2000). 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. Two lake sediment cores and two soil cores collected nearby

the lake are considered in the present study. The sediment cores, A and B, were retrieved from the deeper parts of the two basins, 73 and 32 m water column depth, respectively.

The Tatra mountains are situated in central Europe and constitute one of the most polluted mountain range for these compounds (Fernández et al. 1999; 2000). Two soil and one sediment cores from Ladove Lake (49°11'03"N, 20°09'46"E; 2057 m) were collected. The sediment core is compared to others collected in lakes from the same mountain range such as Starolesnianske Pleso (49°10'48"N, 20°10'4"E; 2000 m) and Dlugi Staw (49°13'36"N, 20°0'39"E; 1783 m) (Fig. 1). Lakes Ladove and Starolesnianske Pleso are situated less than 2 km apart.

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

2. Materials and Methods

2.1. Materials

Residue analysis *n*-hexane, dichloromethane, iso-octane, methanol and acetone were from Merck (Darmstadt, Germany). Anhydrous sodium sulfate for analysis was also from Merck. Neutral aluminum oxide type 507C was from Fluka AG (Buchs, Switzerland). Cellulose extraction cartridges were from Whatman Ltd (Maidstone, England). 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-mass spectrometry (GC-MS). No significant peaks should be detected for acceptance. 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 x 20 mL), concentration to 50 μ L and analysis by GC-MS. No interferences were detected. Sodium sulfate and aluminum oxide were activated overnight at 400°C and 120°C, respectively.

2.2. Sampling

Sediment samples were taken in the deepest points of the lakes using a gravity coring system (Glew, 7.5 cm diameter, 30 cm long). A 7 cm (diameter) x 20 cm (long) stainless steel cylinder was used for soil core collection. All soils were taken within the lake catchment areas. The sediment samples except those from Ladove Lake were collected between 1993 and 1994 whereas the soil cores and the sediments from Ladove Lake were sampled in 2001. Immediately after sampling soil and sediment cores were 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 aluminium foil at -20°C until analysis.

2.3. Analysis

The following PAHs were determined in both soils and sediments: acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, dibenzothiophene, methylphenanthrenes (3-MPhe, 2-MPhe, 9+4-MPhe, 1-MPhe), methyl dibenzothiophenes (4-MDBT, 3+2-MDBT, 1-MDBT), fluoranthene, pyrene, dimethylphenanthrenes (3,6-DMPhe, 2,6-DMPhe, 2,7-DMPhe, 1,3+2,10+3,9+3,10-DMPhe, 1,6+2,9-DMPhe, 1,7-DMPhe, 2,3-DMPhe, 1,9+4,9-DMPhe, 1,8-DMPhe), retene, benzo(*b*)naphtho[2,1-*d*]thiophene, benz[*a*]anthracene, chrysene+triphenylene (they coeluted upon GC-MS analysis so they were considered together), benzo[*b+j*]fluoranthenes, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, dibenz[*a,b*]anthracene and coronene.

2.4. Sample extraction

Soils (25-50 g) were weighed into a Whatman Soxhlet cellulose thimble. About 1:1 w/w sodium sulfate were mixed with the soil in order to improve Soxhlet extraction by water removal. Samples were extracted with hexane:dichloromethane (4:1) for 18 h. Standards of d₁₀-anthracene, d₁₀-pyrene, d₁₂-benz[*a*]anthracene and d₁₂-benzo[*ghi*]perylene were added to the extracts that were first concentrated by rotary vacuum evaporation to 3-5 mL and subsequently eluted through a drying column filled with 1 g of anhydrous sodium sulfate.

After rotary vacuum evaporation to ~0.5 mL, the extracts were fractionated on a neutral aluminum oxide column (2 g). A first non-polar fraction was obtained by elution with 8 mL of hexane:dichloromethane (9:1). The second, obtained by elution with 10 mL of hexane:dichloromethane (1:2), corresponded to the fraction of PAHs and other aliphatic esters. This PAH fraction was then hydrolyzed overnight with KOH in methanol for removal of the aliphatic esters. Neutral compounds were recovered with *n*-hexane and fractionated again by adsorption chromatography with aluminum oxide (2 g). After elution with hexane:dichloromethane (1:2), the PAH fraction was concentrated to 50 μL in isooctane by rotary vacuum evaporation followed by a gentle stream of purified N₂.

For sediments, about 0.1-1 g of wet sediment was extracted by sonication with methanol (1 x 20 mL; 20 min) in order to separate most of the interstitial water from the sediment. The subsequent extractions were performed with (2:1, v/v) dichloromethane-methanol (3x20 mL; 20 min). All extracts were combined and spiked with deuterated PAH internal standards (d₁₀-anthracene, d₁₀-pyrene, d₁₂-benz[*a*]anthracene and d₁₂-benzo[*ghi*]perylene). Then, they were vacuum evaporated to almost 10 mL and hydrolyzed overnight with 20 mL of 6% (w/w) KOH in methanol. The neutral fractions were recovered with *n*-hexane (3 x 10 mL), vacuum evaporated to almost dryness, and fractionated with a column containing 2 g of alumina. The aromatic fractions (10 mL of dichloromethane: *n*-hexane, 2:1) were vacuum and nitrogen concentrated almost to dryness and redissolved in isooctane prior to GC-MS analysis.

2.5. Instrumental analysis

The internal standard d_{12} -perylene (L.D. Ehrenstorfer) was added to the vials prior to injection. Samples were injected into GC-MS (Fisons 8000 Series, Mass Selective Detector 800 Series). A fused silica capillary column, HP-5 of 50 m and 0.25 mm i.d (0.25 μm film thickness) was used. The oven temperature program started at 90°C (1 minute hold), followed by a 4°/min ramp up to 300°C (15 minutes hold). Injector, transfer line and ion source temperatures were 280°C, 300°C and 200°C, respectively. Helium was used as carrier gas (1.1 mL/min). PAH were determined in the electron impact and selected ion recording modes. The following mass fragments were used for identification and quantification: m/z 166, 178, 184, 192, 202, 206, 219, 226, 228, 234, 252, 276, 278, and 300 (dwell time 40 ms per single ion, ion window according to retention times of standards). Diagnostic ions of the corresponding perdeuterated standards m/z : 188, 212, 240, 264, and 288 were also used.

2.6. Quantification

Quantification was performed by combination of the external standard (EPA, Mix 9 Dr Ehrenstorfer) and retention index methods. Calibration curves (detector response *vs* amount injected) were performed for each compound. The range of linearity of the detector was evaluated from the curves generated by representation of detector signal/amount injected *vs* amount injected. All measurements were performed in the ranges of linearity found for each compound. The quantitative data were corrected for surrogate recoveries.

2.7. Quality control

Procedural blanks were performed with each set of 9 samples to check for the presence of interfering peaks. Recoveries of d_{10} -anthracene, d_{10} -pyrene, d_{12} -benz[*a*]anthracene and d_{12} -benzo[*ghi*]perylene averaged 60, 70, 76 and 82%, respectively. Replicate analysis of soil samples gave an error $<\pm 15\%$. The method detection limits based on signal to noise ratio of 3 in real samples ranged from 100 (compound) to 400 pg (compound). Both soil and sediment analytical procedures were successfully calibrated with a standard reference material with certified PAH values (marine sediment HS-4, Institute for Marine Biosciences, Canadian National Research Council).

2.8. Total Organic Carbon

Soil and sediment samples were treated 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 analysed 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 keV 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 keV 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 $^{137}\text{Cs}/^{241}\text{Am}$ stratigraphic records.

Table 1. Average PAH concentrations, PAH ratios and TOC in the soil and sediment cores from Lake Redon.

	0-2 cm	2-4 cm	4-6cm	6-8 cm	8-10 cm	10-12 cm
SOILS						
Parent PAH ^a	770	670	190	34	39	47
Fla/(Pyr+Fla)	0.61	0.58	0.54	0.54	0.57	0.56
BaA/(BaA+C+T)	0.21	0.24	0.24	0.17	0.11	0.19
BaP/(BaP+BeP)	0.32	0.35	0.39	0.37	0.34	0.43
Ind/(Ind+Bghi)	0.55	0.57	0.56	0.56	0.55	0.56
SUM MPhe/(SUM MPhe+Phe)	0.45	0.56	0.59	0.28	0.46	0.48
Ret/(Ret+BNT)	0.32	0.01	0.45	0.89	0.58	0.35
1,7-/(1,7- + 2,6-)DMPhe	0.70	0.67	0.62	0.77	0.67	0.62
TOC (g/g dw)	0.33	0.30	0.23	0.18	0.16	0.21
SEDIMENTS ^b						
Parent PAH ^a	760	550	100	130	87	
Fla/(Pyr+Fla)	0.65	0.68	0.59	0.57	0.67	
BaA/(BaA+C+T)	0.16	0.13	0.12	0.12	0.12	
BaP/(BaP+BeP)	0.20	0.20	0.25	- ^c	-	
Ind/(Ind+Bghi)	0.62	0.63	0.64	0.78	0.69	
SUM MPhe/(SUM MPhe+Phe)	0.33	0.58	0.47	0.44	0.20	
Ret/(Ret+BNT)	0.21	0.28	0.85	-	0.74	
1,7-/(1,7- + 2,6-)DMPhe	0.56	0.62	0.63	0.49	0.67	
TOC (g/g dw)	0.04	0.04	0.05	0.04	0.04	

^aUnits in ng/g dry weight. These values correspond to the sum of all compounds indicated in the caption of Figure 2 except perylene. ^bCore B. ^cNot determined because of interferences from the huge amount of perylene.

Table 2. Average PAH concentrations, PAH ratios and TOC in the soil and sediment cores from Ladove lake.

Core Sections:	0-2 cm	2-4 cm	4-6cm	6-8 cm	8-10 cm	10-12 cm
SOILS						
Parent PAH ^a	1900	3400	430	75	63	90
Fla/(Pyr+Fla)	0.71	0.54	0.57	0.61	0.52	0.50
BaA/(BaA+C+T)	0.32	0.23	0.14	0.13	0.11	0.13
BaP/(BaP+BeP)	0.42	0.39	0.27	0.18	0.31	0.26
Ind/(Ind+Bghi)	0.53	0.47	0.39	0.30	0.47	0.46
SUM MPhe/(SUM MPhe+Phe)	0.34	0.37	0.78	0.48	0.18	0.25
Ret/(Ret+BNT)	0.29	0.02	0.02	0.05	0.14	0.04
1,7-/(1,7- + 2,6-)DMPhe	0.79	0.63	0.77	0.79	0.56	0.59
TOC (g/g dw)	0.23	0.16	0.12	0.07	0.07	0.07
SEDIMENTS						
Parent PAH ^a	12000	11000	3000	3000		
Fla/(Pyr+Fla)	0.62	0.61	0.60	0.59		
BaA/(BaA+C+T)	0.18	0.18	0.17	0.19		
BaP/(BaP+BeP)	0.30	0.28	0.29	0.30		
Ind/(Ind+Bghi)	0.56	0.56	0.54	0.53		
SUM MPhe/(SUM MPhe+Phe)	0.26	0.25	0.27	0.25		
Ret/(Ret+BNT)	0.03	0.06	0.14	0.22		
1,7-/(1,7- + 2,6-)DMPhe	0.61	0.62	0.68	0.79		
TOC (g/g dw)	0.08	0.07	0.07	0.07		

^aUnits in ng/g dry weight. These values correspond to the sum of all compounds indicated in the caption of Figure 2 except perylene.

3. Results and Discussion

3.1. Lake features

The lakes considered in this study are situated above the local tree line, they are oligotrophic (median total phosphorous 4.1 µg/L) and remain ice-covered for long periods. Three dominant types of land cover are found in the lake catchments, 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). Pollution inputs are related to atmospheric transport since the lakes are free from local anthropogenic sources. Nevertheless, significant differences in pollution load are observed in both lake groups since much higher PAH levels are encountered in Tatra mountains (Fernández et al. 1999; 2000).

TOC exhibits much higher values in the soils than in the sediments of Lake Redon, 16-33% and 4-5%, respectively (Table 1). In Ladove lake, higher TOC values are also found in soils than sediments in the upper 6 cm, 12-23% and 7-8.3%, respectively (Table 2). However, between 6-8 cm the difference between the two environmental compartments vanishes, 7% in both cases (Table 2). A strong depth-dependent TOC decrease is therefore observed in Ladove soils whereas sedimentary TOC remains nearly constant. In Lake Redon, soil TOC values also decrease significantly with depth, from 33% to 16-21%, whereas the sediment values are nearly constant (Table 1).

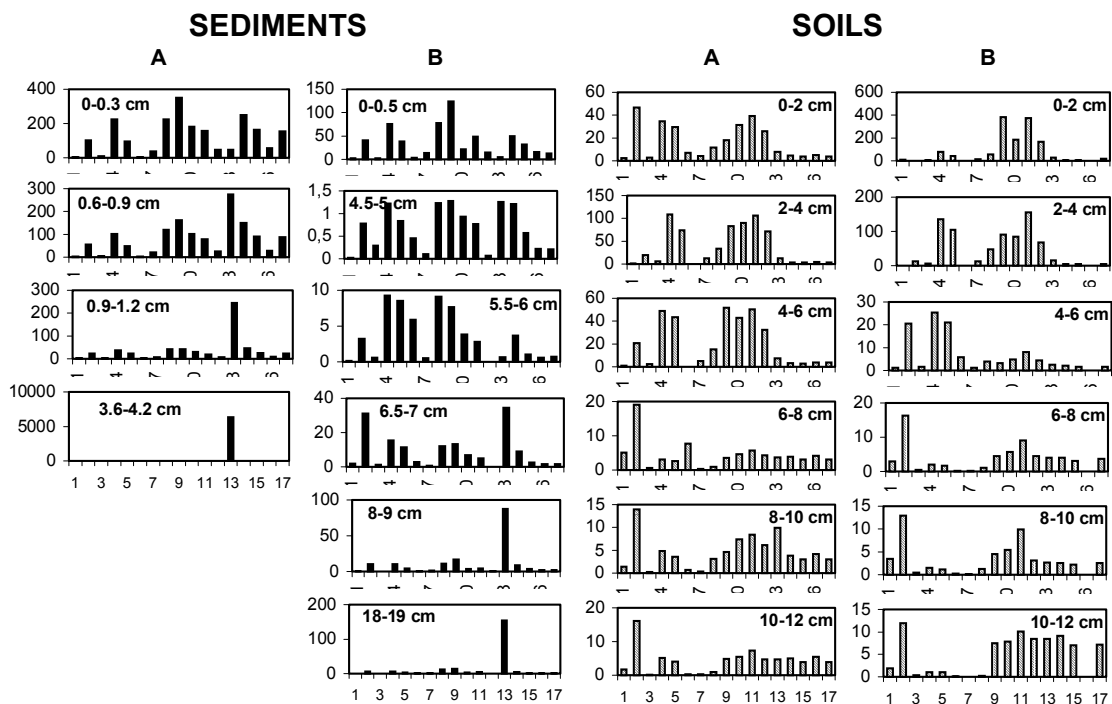


Fig. 2. PAH in the soils and sediments from Lake Redon. A and B refer to different cores analysed in the lake surroundings. 1, fluorene; 2, phenanthrene; 3, anthracene; 4, fluoranthene; 5, pyrene; 6, retene; 7, benz[*a*]anthracene; 8, chrysene+triphenylene; 9, benzo[*b*+*j*]fluoranthenes; 10, benzo[*k*]fluoranthene; 11, benzo[*e*]pyrene; 12, benzo[*a*]pyrene; 13, perylene; 14, indeno[1,2,3-*cd*]pyrene; 15, benzo[*ghi*]perylene; 16, dibenz[*a,b*]anthracene, 17, coronene. PAH units in ng/g.

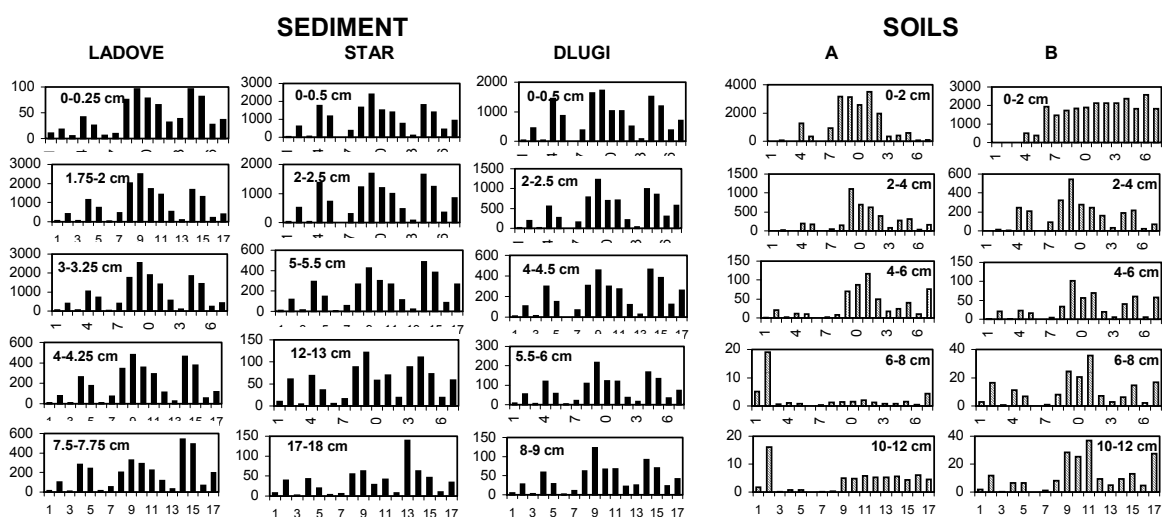


Fig. 3. PAH in the soils and sediments from Ladove lake. Numbers in abscissas as in Fig. 2. PAH units in ng/g.

3.2. PAH distributions

The PAH distributions found in the sediments and soils of the Pyrenees and Tatra lakes are shown in Figs. 2 and 3. The distributions are always dominated by parent PAH, from phenanthrene to coronene, with a predominance of high molecular weight compounds of catacondensed structures in the upper sections. Total methylated + dimethylated PAH were in low amounts (0.2-10% of total PAH).

The PAH distributions in the sediments from Pyrenees and Tatra mountains are remarkably similar despite the variability of PAH sources to the atmosphere. This similarity is also observed independently of the high differences in PAH load between the Pyrenees and Tatra which, in terms of sedimentary concentration, involve top sediment concentrations of 980 and 12000 ng/g total PAH, respectively (Tables 1 and 2). This uniform sedimentary PAH profile exhibits a high parallelism with the PAH composition in the atmospheric aerosols collected at these high altitude sites (Fernández et al., 2002). This PAH distribution is quite ubiquitous and has been reported in sediments from remote/rural areas (Sanders et al., 1993; Tolosa et al., 1996; Fernández et al., 1999; 2000) and corresponds to the airborne combustion mixtures refractory to photooxidation and chemical degradation (Simcik et al., 1996; Simó et al., 1997).

The soil PAH mixtures also exhibit a predominance of parent PAH in which the heavier molecular weight compounds are present in higher relative proportion (Figs. 2 and 3). However, the qualitative and quantitative differences between soil cores from the same area are higher. Thus, the top distributions in the Tatra lakes exhibit high relative concentrations of chrysene+triphenylene, benzo[*b+j*]fluoranthenes, benzo[*k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene in both cores. Nevertheless, one of them, B (Fig. 3), also has benz[*a*]anthracene, perylene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, dibenz[*ab*]anthracene and coronene in high relative proportion. These compounds are not so significant in core A (Fig. 3). The PAH top soil distributions of Lake Redon are also dominated by benzo[*b+j*]fluoranthenes, benzo[*k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene but in one case, A (Fig. 2), phenanthrene, fluoranthene and pyrene are also present in significant relative concentration.

3.3. Regular differences in soil and sediment PAH composition

The PAH ratios of some soil and sediment sections from Redon and Ladove lakes are compared in Tables 1 and 2. The ratios are grouped in core sections only for comparison of the vertical PAH structure. The grouping does not involve temporal correspondences between the same soil and sediment depth levels.

The benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene) ratios from the upper core sections exhibit higher values in the soils than in the sediments. Thus, in Lake Redon (0-8 cm) the differences range between 0.17-0.24 in the former case and between 0.12-0.15 in the second (Table 1). In Ladove lake (0-4 cm) the values span between 0.23-0.32 in soils and exhibit a constant ratio of 0.18 in the sediments (Table 2). However, in the deeper sections the ratios of the

soil values are lower, e.g. 0.11 and 0.12 for soils and sediments of Lake Redon (8-10 cm), respectively (Table 1), and 0.13-0.14 and 0.17-0.19 for the soils and sediments of Ladove lake (4-8 cm), respectively (Table 2).

Benz[*a*]anthracene is more labile to photo-oxidation than chrysene+triphenylene (Kamens et al., 1986; 1988). Accordingly, the benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene) ratio in atmospheric aerosols collected over high mountain lakes has average values of 0.12 in summer and 0.35 in winter (Fernández et al., 2002). Having in mind that PAH are present in higher concentration in the winter samples (Fernández et al., 2002), the soil ratios in the top sections of the soil cores are likely more representative of the PAH atmospheric fallout. Benz[*a*]anthracene is also less stable than chrysene+triphenylene upon diagenesis since the highest relative content in the former is generally encountered in the top core layers. The difference between soils and sediments suggests that the original atmospherically-transported PAH composition is initially better preserved in the soils (upper core sections) but at deeper core sections the benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene) ratio deviates further from the original mixtures in soils than sediments.

Benzo[*a*]pyrene is photochemically less stable than benzo[*e*]pyrene (Nielsen 1988). In the top cores (0-4 cm) the benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) ratios show higher values in the soils than in the sediments. Thus, in Lake Redon they range between 0.32-0.35 and 0.22-0.23, respectively (Table 1), and in the Tatra lakes between 0.39-0.42 and 0.28-0.30, respectively (Table 2).

The benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) ratios in aerosols collected in high mountain regions average 0.27 in summer and 0.41 in winter (Fernández et al., 2002). Again, considering the higher PAH load in winter than in summer the soil values are more likely to reflect better the original PAH atmospheric composition. At deeper core sections no significant change is observed in the sediments, e.g. 0.25 and 0.29-0.30 in Redon and Ladove, respectively. Similarly, the deeper soil sections of Lake Redon exhibit ratios between 0.34 and 0.43 (Table 1). However, in Ladove soils the deep section ratios show larger scatter and lower values (0.18-0.31; Table 2). In some deeper soil sections the benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) ratios are even lower than those of sediments showing that benzo[*a*]pyrene is less preserved in the former than the latter.

The ratio between phenanthrene and its methyl derivatives is also labile to photooxidation, the transformation involving a loss of methylated compounds upon long-range transport (Simó et al., 1997). Comparison of the methylphenanthrenes/(methylphenanthrenes + phenanthrene) ratio in soils and sediments shows ranges between 0.28-0.59 and 0.20-0.47, respectively, in Lake Redon (Table 1), and between 0.18-0.78 and 0.25-0.30, respectively, in Ladove lake (Table 2). In all cases except one section of Lake Redon (6-8 cm) the ratio is higher in the soil than in the sediments showing a better preservation of the more labile compounds in the former.

The indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene) ratio is a priori more stable to photooxidation than the ratios discussed above. In Redon it ranges between 0.55-0.57 and 0.62-0.78 in soils and sediments, respectively (Table 1), and in Ladove lake between 0.30-0.53 and 0.53-0.56 in soils and sediments, respectively (Table 2). The measured range in high mountain aerosols is 0.55 in both winter and summer (Fernández et al., 2002). These values are again closer to the soil than to the sediment values in Lake Redon. In contrast, in Ladove lake there is a higher difference between the atmospheric ratio and those in soils than in sediments. There is no obvious explanation for this deviation although it must be indicated that the aerosol values taken as reference (Fernández et al., 2002) correspond to a series of data including atmospheric samples from Lake Redon but not from the Tatra mountains.

The fluoranthene/(fluoranthene + pyrene) ratios in soils range between 0.54-0.61 and 0.50-0.71 in Lakes Redon and Ladove. In the sediments they range between 0.59-0.66 and 0.59-0.62 at these two sites, respectively (Tables 1 and 2). The average values of this ratio in the high mountain aerosols are 0.44 in summer and 0.59 in winter (Fernández et al., 2002). The winter values are closer to those in the soils than in the sediments from Lake Redon but in Ladove lake the sediment values are the closest to this mountain aerosol winter ratio. In any case the differences between soils and sediments are small in the case of fluoranthene/(fluoranthene + pyrene) ratios.

3.4. Downcore sedimentary PAH

Radiometric analysis shows that all lake sediment cores selected for study have rather uniform sedimentation. No hiatus or periods of mixing were observed in the vertical structure of the recovered sediments. The average sedimentation rates of the sediment cores studied were 0.024, 0.054, 0.084 and 0.10 cm/y for Redon, Długi Staw, Starolesnianske Pleso and Ladove. These rate differences and the core sectioning for analysis provide vertical PAH profiles with different time resolutions at each site.

The best time resolved PAH trend is the one for Ladove Lake where biannual resolution is achieved in most core sections between 1924 and 2001 (Figure 4). Total pyrolytic PAH were maxima between 1980 and 1988. Another period of maximum PAH input was observed between 1963-1966. Before this time, 1924-1954, much lower PAH concentrations are observed. On the other hand, after the 1988 PAH maximum, a strong decrease in PAH concentrations is found which extends up to 2001 (the most recent recorded date in the sediment collected). This PAH decrease is consistent with the improvement of the combustion techniques in central Europe.

The pyrolytic PAH in the other lakes from the Tatra mountains exhibit similar profiles but with smaller temporal resolution. As these cores were taken in 1993, the most recent PAH decrease is not observed. Pyrolytic PAH in the sediment core of Lake Redon also exhibit a similar temporal trend. Like in the sediments from Długi Staw and Starolesnianske Pleso, the temporal resolution is lower than in Ladove lake and the most recent date recorded is 1994.

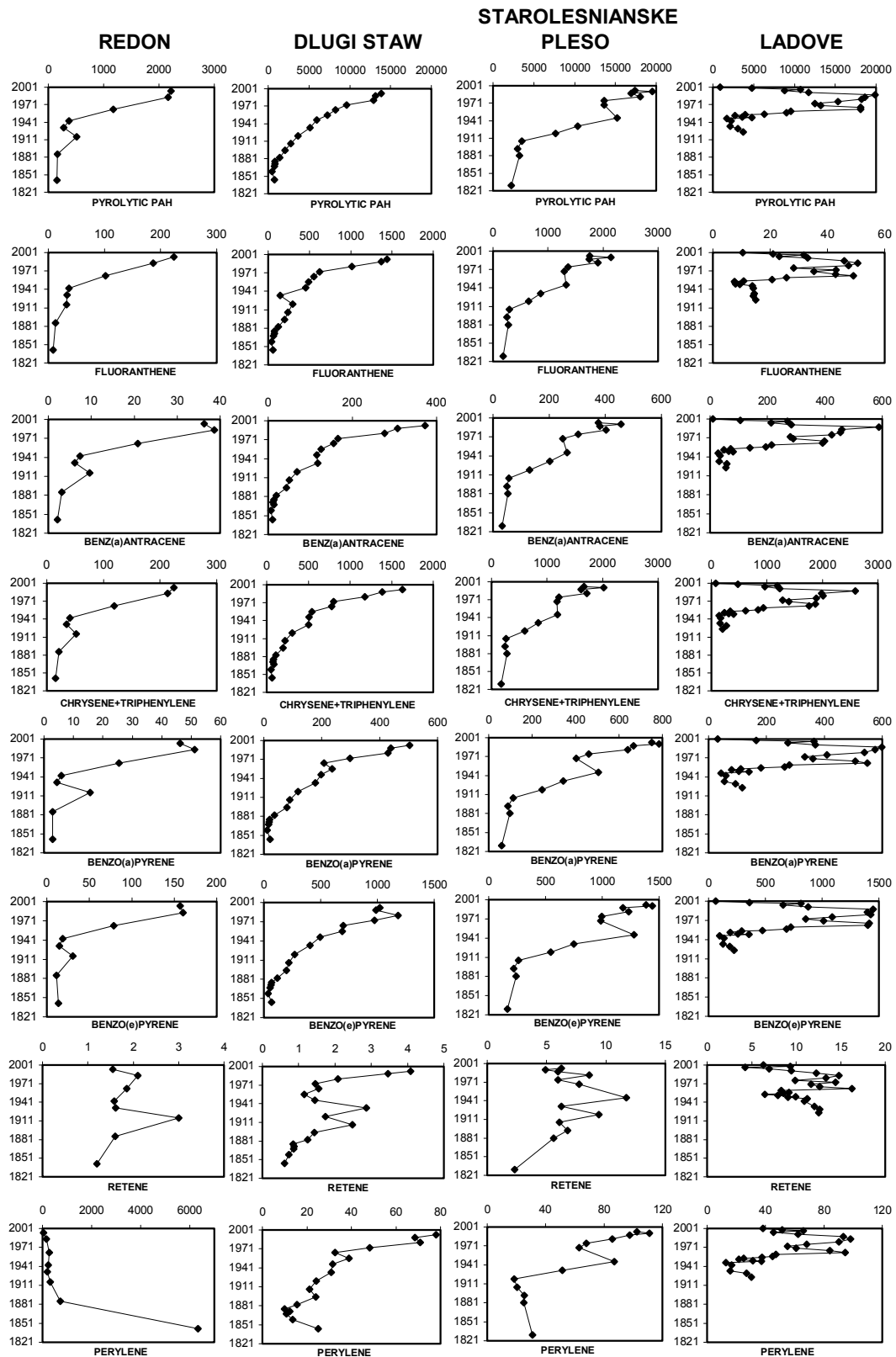


Fig. 4. Time scales of the concentrations of total pyrolytic PAH and selected parent PAH determined from the sediment cores analyzed in the Pyrenees and the Tatra mountains. PAH units in ng/g.

Representation of the temporal changes of the major parent PAH such as fluoranthene, benz[*a*]anthracene, chrysene+triphenylene, benzo[*a*]pyrene, benzo[*e*]pyrene and many others shows the same trends as for total pyrolytic PAH. Perylene is also showing the same temporal trend as the major pyrolytic PAH in the lakes from the Tatra mountains. However, in Lake Redon the highest values are observed at deep core sections. Thus, the downcore changes in PAH may reflect the atmospheric inputs of these compounds arriving to the high mountain areas through time or in situ diagenetic processes involving the formation of some PAH such as perylene in Lake Redon.

Retene is the compound exhibiting a more distinct behavior with time. Their downcore profiles do not show a steeper decrease since the concentrations in the ancient core sections are not too different from those in which highest total pyrolytic inputs are found.

3.5. Diagenetic formation of PAH

In Lake Redon, PAH qualitative distribution in the deeper sections show a high predominance of perylene, sections 0.9-4.2 cm in core A and 8-19 cm in core B (Fig. 2). This predominance also involves a net perylene concentration increase in both cores revealing in situ formation of this PAH, e.g. in the deeper sections of core A it reaches more than 6000 ng/g which is higher than all other PAH in all the other core sections (Fig. 2). In the Tatra mountains this trend is not observed (Figs. 3 and 4). Only in the deeper sections of Starolesniaske Pleso core a predominance of perylene is observed but without absolute concentration increase (Fig. 4).

The predominance of perylene in ancient sediment layers of freshwater (Wakeham et al., 1980a; Tan and Heit, 1981) and marine systems (Aizenshtat, 1973; Wakeham et al., 1979; Venkatesan, 1988) has been reported in the literature but its precursor/s still remain unknown. The downcore profiles observed in Lake Redon are consistent with an in situ production from sedimentary precursor/s which, considering the high dominance of terrigenous markers among the distributions of hydrocarbons and alcohols/sterols (data not reported here), are likely to be related to higher plant residues.

In contrast, no diagenetic formation of perylene is observed in the downcore soil PAH mixtures (Figs 2 and 3) where this hydrocarbon is always a minor component. Since most terrigenous inputs probably originate from the local grassland vegetation the difference from the sediment composition is probably related to the lack of anoxic conditions in the soils.

An enrichment in the relative concentration of phenanthrene is observed when considering the PAH downcore distributions in the soils (Figs. 2 and 3). However, this enrichment is only relative to the concentration of the other PAH. The increase in absolute concentration is small. A net production of phenanthrene after sedimentation is therefore unclear. This hydrocarbon is the end member product in the transformation of many diterpenoids following aromatization pathways (Simoneit, 1986; Simoneit et al., 1986).

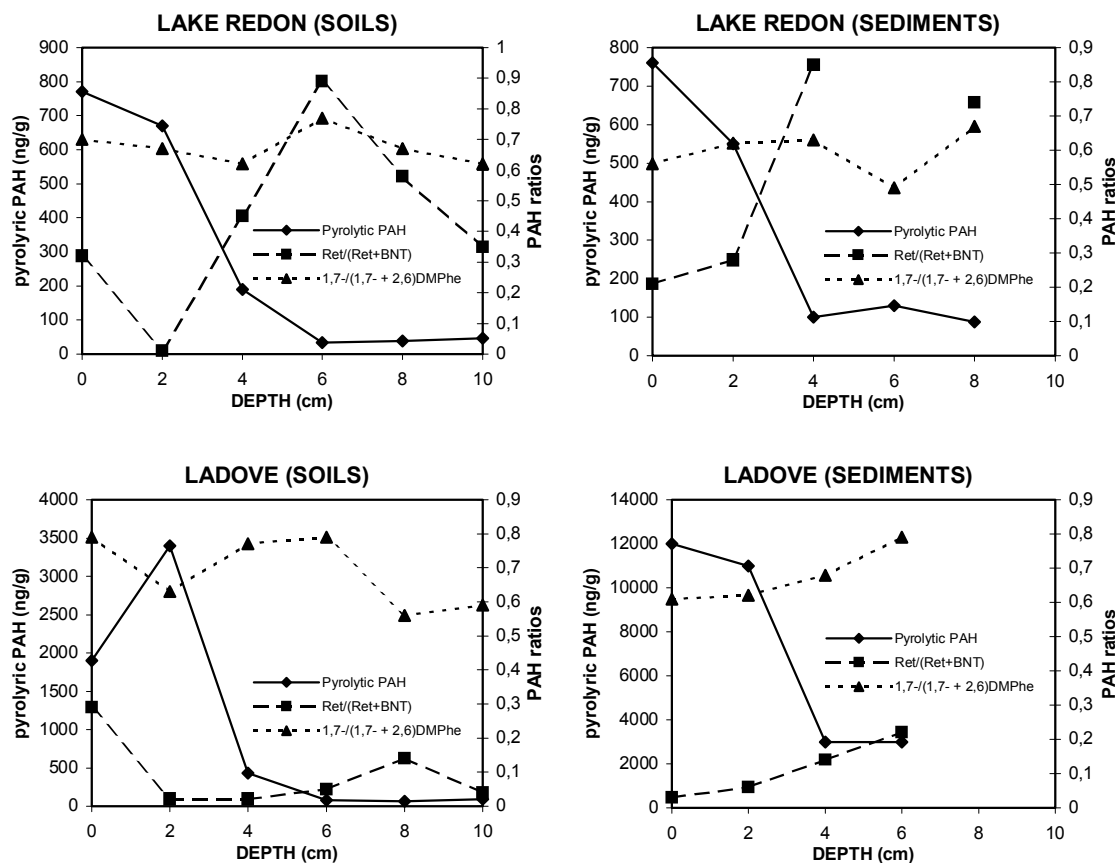


Fig. 5. Downcore distributions of pyrolytic PAH and the indices retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) and 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene) in the soils and sediments from Redon and Ladove lakes.

Retene may be produced during wood combustion (Ramdahl, 1983) or diagenesis (Simoneit, 1977; LaFlamme and Hites, 1978; Wakeham et al., 1980b). In contrast, benzo(*b*)naphtho[2,1-*d*]thiophene is a specific marker of coal combustion (Fernández et al., 1996). Compilation of the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) ratio affords therefore a standardized index for comparison of the downcore variation of retene vs the major pyrolytic inputs (Fig. 5). This index may be compared to the changes in 1,7-dimethylphenanthrene vs 2,6-dimethylphenanthrene which has also been proposed as a marker of wood to fossil fuel combustion (Benner et al., 1995) as shown in studies on lake Mystic and Boston harbor (Gustaffson et al., 1997). This index has been calculated for the soils and sediments of the high mountain lakes considered for study and compared to the retene index and total PAH (Fig. 5).

The 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene) exhibits similar values and a rather constant downcore profile in both Redon and Tatra sediments and soils. In contrast, the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) index increases downcore

in the sediments of both lakes (Fig. 5). This increase is also observed in Redon soils but not in the Tatra soils. The sedimentary downcore increase of the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) index and the nearly constant ratio of the 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene) sediment suggest that the presence of retene in the deeper sediments is due to diagenetic processes. Thus, in these high mountain environments it cannot be taken as a wood combustion marker.

CONCLUSIONS

In high mountain areas there is a better parallelism between the PAH composition in long-range transported aerosol mixtures and top soil sections than in top lake sediment layers. This higher agreement is observed when comparing diagnostic ratios such as indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene) but also ratios involving photochemically labile compounds such as benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene), benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) and methylphenanthrenes/ (methylphenanthrenes + phenanthrene). In all cases, labile PAH are found in higher relative concentration in soils and the corresponding ratios are closer to those found in the aerosols than in the lake sediments. The contrast between these two environmental compartments points to significant degradation of labile PAH during water column transport from atmosphere to underlying sediments in high mountain lakes.

In contrast, at deeper core sections, higher relative proportion is found of the more labile PAH in sediments than soils. This is observed for the relative content of benz[*a*]anthracene to chrysene + triphenylene, benzo[*a*]pyrene to benzo[*e*]pyrene) and methylphenanthrenes to phenanthrene. Thus, after sedimentation, preservation of the labile PAH is better in the lake sediments than in soils from the catchment.

The diagenetic processes in soils and sediments are also different, involving the formation of major amounts of perylene in the later but not in the former. In soils downcore enrichment of phenanthrene is observed maybe as consequence of the extensive aromatization of diterpenoid compounds. In this respect, examination of the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) and the 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene) ratios in sediments and soils indicates a diagenetic origin for this diterpenoid.

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