

Temporal evolution of urban wet weather pollution: analysis of PCB and PAH in sediment cores from Lake Bourget, France

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ABSTRACT

In order to evaluate the historical impact of urban stormwater runoff on a lacustrine environment, eight sediment cores were collected in October 2006 in Lake Bourget (Savoie, France). Sediment samples were analysed for polycyclic aromatic hydrocarbons (PAH) and polychlorobiphenyls (PCB) in order to correlate the vertical profiles of contamination and the evolution of the urbanisation on the watershed for the last 100 years. Overall, we observe that vertical profiles of PCB and PAH concentrations in Lake Bourget are showing a downward trend, probably resulting from the pollution control measures. Concentrations of PCB and PAH measured in surface sediments are approximately 5–10 fold less than maximal concentrations found in the cores. Maximal PAH concentrations were found at the bottom of the cores (~40 cm) which approximately correspond to the beginning of the 20th century. Maximal PCB concentrations measured in cores L5 and L6 are respectively 850 and 790 $\mu\text{g/g}$ dw (dryweight). The peak of PCB corresponds to the maximum of PCB production and consumption in the 1970s. In surface sediments total PCB concentrations range between 47 and 79 $\mu\text{g/kg}$ dw. Those concentrations are particularly high compared to other values measured in lake sediments and highlight the problem of a local source of PCB contamination in the watershed. General trends were observed, yet the part of urban stormwater runoff in the total contamination could not be determined.

Key words | lake sediment records, persistent organic pollutants, urban contamination

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INTRODUCTION

In many countries urban stormwater runoff is of increasing concern considering diffuse pollution of water bodies (Gromaire-Mertz *et al.* 1999; Davis *et al.* 2001; Brown & Peake 2006). When other sources of pollution, especially punctual water discharges, are under control, they turn out to be the main source of pollution in urban areas.

Thanks to depth–time relationships, sediment cores taken in semi enclosed aquatic basins can provide an historical record of contamination and land use within the watershed (Arnaud & Revel-Rolland 2004; Couillard *et al.* 2004). Reconstruction of historical inputs of anthropogenic

chemicals is important for improving management strategies and evaluating the success of recent pollution control measures. Because of their persistency, toxicity and tendency to accumulate in living tissues polychlorobiphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) are part of the most damaging group of chemicals to which natural systems can be exposed. PAH can be derived from both natural and anthropogenic sources. Anthropogenic sources of PAH include combustion of fossil-fuel, vehicular emissions, abrasion of street asphalt and automobile tires, combustion processes of municipal waste incinerators,

domestic heating, etc. PCBs were first produced commercially in the 1930s and used in electrical transformers and capacitors. Their use was banned in 1987, yet 20 years later they are still present in many compartments of the environment. PCB and PAH show a high resistance to physical–chemical and biological degradation. In the absence of physical mixing of the sediment and bioturbation, both PCB and PAH are shown reliable for a time reconstruction of sediment contamination.

METHODS

Sampling

Lake Bourget, the largest lake in France, lies on the western edge of the pre-Alps. It is 18 km long, has a maximum width of 2.8 km and is 146 m deep in the northern basin (Figure 1). The lake is under the influence of a peri-urban catchment area and located near by an important urban agglomeration (Chambéry, Aix les Bains). Between 1972 and 1994, the surface of urban areas on its watershed has increased of 85% while the population increased by 30%. Nowadays the population is nearly reaching 200,000 inhabitants, and the actual tendency of urbanisation is still to increase.

Eight short sediment cores were collected in October 2006 in the Leysse Delta, downstream the city of Chambéry (Figure 1). The Leysse River is the main affluent of Lake

Bourget and it drains to most urbanised sector of the watershed. The catchment of Chambéry city is almost entirely equipped with separated drainage system and urban stormwaters are rejected into the lake via the Leysse River. Sediment cores were sampled along transects covering the plume of the Leysse River in order to evaluate the horizontal extent of the contamination. Two “reference cores” were collected, one in the Baie de Grésine (G1), a littoral area less submitted to urban influence and one in the southern basin (L6), corresponding to the plume of the Leysse River before the reshaping of its outlet in the 1950s.

Samples pre-treatment

After the sampling, cores were brought to the laboratory and opened through their length. Upon opening, cores are covered with polyethylene film to prevent water loss and to minimize color change due to oxidation. Half cores used for chemical analysis were sectioned at 1 cm intervals and stored in glass bottles. Those bottles followed a specific washing protocol: they were washed in TFD4 detergent for 24 h (to eliminate organic matter), rinsed with water and demineralised water, left for 24 h in an acidic bath (to eliminate trace metals) then rinsed again and grilled at 500°C for 24h. After sub-sampling, samples were quickly stored at –20°C then lyophilised. Half cores used for the sediment characterisation are kept in a cooler.

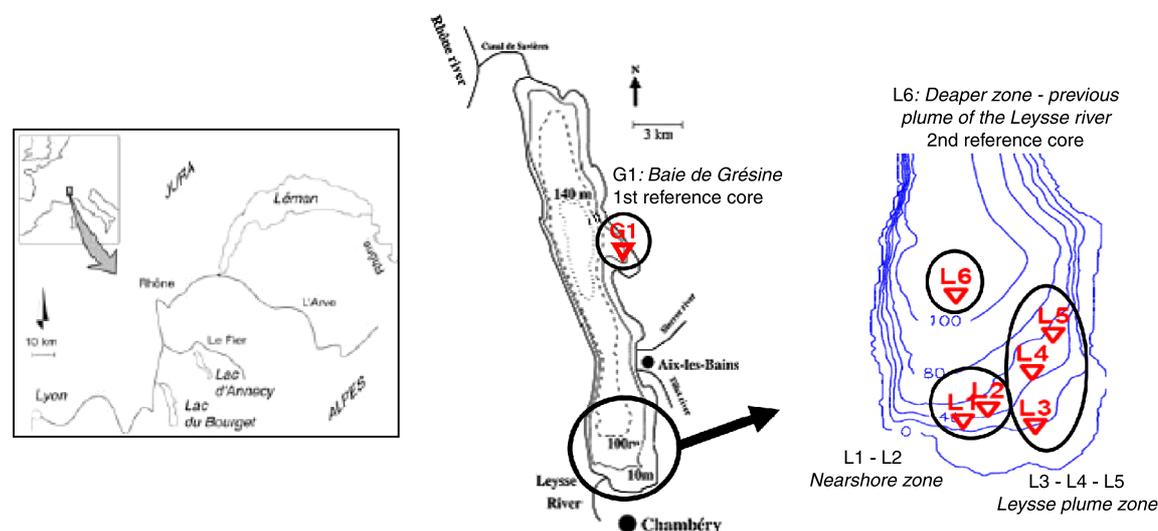


Figure 1 | Lake Bourget: localisation, bathymetry and sampling sites.

Chemical analysis: PCB and PAH

13 PAHs from the US Environmental Protection Agency's priority substances list are analysed. Our analytical method is not adapted for the analysis of naphthalene, acenaphthylene and acenaphthene which are too volatile. Deuterated internal standards are used for PAH quantification. 15 PCB congeners are analysed: PCB 18, 31, 28, 20, 52, 44, 101, 149, 118, 153, 105, 138, 180, 170, and 194. According to the French standard XP T 60-184, those congeners permit to calculate the PCB content as a function of Aroclor profiles (Aroclor 1242, 1254 and 1260). Internal standards used for PCB quantification are PCB 36, 112 and 209. All the organic pollutants analysed can be extracted simultaneously. Aliquots of 500 mg are extracted in a Soxhapp apparatus with dichloromethane/methanol (30:5 v/v) for 10 min. The solvent extract is then reduced to a volume of 500 μ l by means of a rotavapor and Turbo Vap evaporator. To avoid sulfur interferences in the PCB analysis, as illustrated in Figure 2, samples are desulfurized with activated copper. For the purification, samples are passed through a 2 g clean-up silica column. The first 15 ml of heptane/dichloromethane (98:2 v/v) eluent from this column recovers the PCB. PAH are recovered in the second fraction composed of 10 ml of heptane/dichloromethane (80:20 v/v) eluent. The analyses of those fractions are performed on a gas-chromatograph–mass spectrometer (GC-MS, Focus-DSQ, Thermo Electro Corporation, USA), operating in selected

ion monitoring mode. The GC is equipped with a RTX-5 SilMS (Restek) fused silica capillary column (60 m length, 0.25 mm ID and 0.25 μ m film thickness), the gas carrier is helium. The molecules are detected by a quadrupole mass analyser following ionisation by electronic impact. Each compound is corrected according to the recovery of the internal standards and the overall calibration is verified with a calibration check standard analysis every 12 samples.

Organic carbon analysis

Organic carbon analyses are performed using a Carbon Analyser (O.I. Analytical, College Station, TX, USA). Prior to the analysis, sediment samples are acidified in order to eliminate inorganic carbon. In the analyser, samples are calcinated at 1000°C and CO₂ is formed from the organic carbon present in the sediments. The CO₂ can then be measured by infrared spectroscopy.

Grain size analysis

Sediments from Lake Bourget can be described by two components: CaCO₃ (mostly biogenic calcite) and silicates (from detrital material). Like in most alpine lakes, a major part of the sediment consists of autochthonous calcite precipitated as a result of biological activity within the epilimnion. The autochthonous sediment is diluted by a mostly river-borne detrital fraction. This detrital material consists of a mixture of

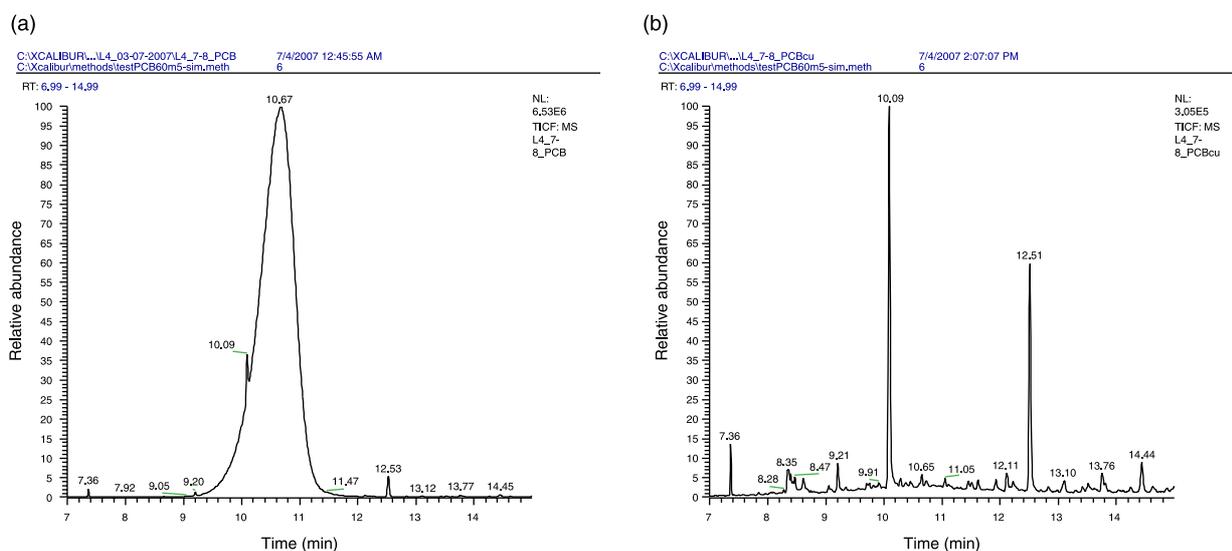


Figure 2 | (a) Chromatogram of the PCB fraction of a sediment sample from core L4 without desulfurization. (b) Chromatogram of the same sample treated with activated copper before the purification process.

carbonates, derived from sub-alpine sedimentary rocks, and silicates derived from inner alpine crystalline rocks. A one year sediment trap study, with traps placed at different depth in the lake showed that the main particules observed in the water column are: automorphous calcite in the shape of rhombohedral crystals (15 μm) and river-borne alumino-silicates (Si, Al, Mg, K, Ca, Fe) (20 μm) (Groleau 2000).

Grain size analyses are performed using a Malvern Mastersizer 2000 laser diffraction particle analyser.

Chronostratigraphy

The sediment cores are dated by gamma spectrometry of radionuclide ^{210}Pb and ^{137}Cs . Sedimentation rates are obtained using excess ^{210}Pb , whereas ^{137}Cs activity-depth distribution is used as a discrete time marker. In Europe, ^{137}Cs

originates from nuclear weapon testing and the accident of Chernobyl in May 1986 (Bonté et al. 2003). Analyses for the sediment dating are still under progress and all results are not available at the moment. Yet, preliminary analysis of excess ^{210}Pb on some samples from cores L6 and L5 permits to evaluate the sedimentation rates to 0.5 mm/year and 0.7 mm/year respectively on those two sites. Those sedimentation rate values were used to estimate the year corresponding to a core section as indicated in Table 1. Those values must be confirmed by the ^{137}Cs results.

RESULTS AND DISCUSSION

In this paper we will focus on the results obtained for cores L5 and L6.

Table 1 | Sediment characterization and PCB and PAH concentrations in cores L5 and L6 in Lake Bourget

	Core layer (cm)	Estimated year	Grain size mode (μm)	Silt (%)	Water content (%)	C_{org} (%)	ΣPAH^* (mg/kg dw)	ΣPCB^\dagger (mg/kg dw)
LDB06-L5	0–1	2005	37.24	70.3	–	–	0.555	0.079
	1–2	2004	24.61	81.3	–	–	0.523	0.083
	3–4	2001	21.43	83.7	63	1.54	0.328	0.112
	8–9	1994	21.43	85.2	59	1.32	0.830	0.111
	11–12	1990	24.61	83.3	–	–	0.959	0.364
	14–15	1985	24.61	84.7	58	1.35	0.883	0.242
	17–18	1981	24.61	75.7	58	1.46	0.887	0.191
	21–22	1975	24.61	81.5	–	–	1.423	0.726
	24–25	1971	18.67	84.1	59	1.17	1.771	0.850
	28–29	1965	18.67	85.7	59	0.76	1.849	0.475
	33–34	1958	–	–	61	1.42	3.243	0.598
	39–40	1950	–	–	58	–	3.656	0.027
LDB06-L6	0–1	2005	–	–	67	–	0.368	0.079 \pm 0.005
	3–4	1999	–	–	53	–	0.416	0.066
	6–7	1993	–	–	61	–	0.561	0.190
	11–12	1983	–	–	61	–	0.673 \pm 0.033	0.793 \pm 0.05
	14–15	1977	–	–	60	–	–	0.530
	15–16	1975	–	–	62	–	1.269	0.356
	19–20	1967	–	–	57	–	1.540	0.738 \pm 0.048
	24–25	1957	–	–	59	–	2.003	0.118
	33–34	1939	–	–	–	–	3.745	0.012
38–39	1929	–	–	–	–	1.532	0.018 \pm 0.003	

* ΣPAH or **Total PAH**: sum of 13 PAH (fluorene *Fl*, phenanthrene *Phe*, anthracene *Ant*, fluoranthene *Fluo*, pyrene *Pyr*, benzo(a)anthracene *BaA*, chrysene *Chr*, benzo(b)fluoranthene *BbF*, benzo(k)fluoranthene *BkF*, benzo(a)pyrene *BaP*, indeno(123)pyrene *IP*, dibenzo(ah)anthracene *DAnt*, benzo(ghi)perylene *BghiP*).

† ΣPCB or **Total PCB**: sum of 14 congeners from the 15 analysed. Concentrations of PCB 18 are not taken into account in our results.

Sediment characterization

Sediments from Lake Bourget are “sandy mud” sediments mainly composed of silt (~80%) with low levels of organic carbon (~1.5%) (Table 1). PAH and PCB are known to have a great affinity with fine sediments, especially silt, which present a great specific area and are enriched in aromatic structures.

In core L5 (Figure 3) the samples present a unimodal distribution with a mode value ranging between 37 μm in surface sediments to 19 μm downcore (Table 1). The coarsening of the particle size distribution in the upper part of the sediments from Lake Bourget has already been observed and explained in a study based on the analysis of carbonates and non carbonates particle size distribution (PSD) on a 9 metre long core (Arnaud 2005). For the carbonate fraction, the coarsening of the PSD is interpreted by an increase in the abundance of rhombohedral calcite crystals since the eutrophication of the lake around 1948.

PAH temporal trends

Overall we observe a decrease in the PAH loadings to the lake since the 1940s (Figure 4). The highest ΣPAH concentration reached 3.66 mg/kg dw in core L5 at the bottom of the core (40 cm). For core L5, ΣPAH concentrations measured in surface sediments are approximately 7-fold less than maximum concentrations. In surface sediments ΣPAH concentrations are respectively 0.55 and 0.37 mg/kg dw in cores L5 and L6 (Table 1). Those values

are relatively low compared to other values from lakes and marine estuaries (Table 2) and to the French guideline values for dredged sediments (ΣPAH 22.8 mg/kg dw). The decrease in PAH concentrations is consistent with decreases reported in other European or American Lakes (Rose & Rippey 2002; Kannan *et al.* 2005). It might be the result of a shift to alternative energy sources and implementation of particulate emissions controls. The peak of PAH seems to correspond to the 1940s according to the results obtained on core L6 (Figure 4). On core L5, the end of the peak is not observed, the core being too short.

The proportions of individual PAH (expressed as percentages of the ΣPAH (total PAH) concentration) were calculated on each core samples for evaluation of temporal and spatial variations in PAH profiles. On average, fluoranthene is the predominant compound, accounting for 14% of total PAH concentrations. The PAH profile observed in Lake Bourget sediment cores and illustrated by Figure 5 for core L5 is characterized by high molecular weight PAH, resulting from high temperature combustion processes. Four and five ring PAH are the most abundant compounds, whereas three ring PAH are less abundant.

On average for cores L5 and L6, fluoranthene, chrysene, benzo(b)fluoranthene and benzo(ghi)perylene together account for 46% of the total PAH. Surprisingly, the PAH distribution along the cores does not vary (Figure 5). The contribution of individual PAH over the total PAH distribution is very similar in surface and bottom sediments whereas the sources of PAH should be very different. Nowadays, the main sources of PAH are road traffic and heating while in the 1940s we assume that coal combustion, wood burning and industries.

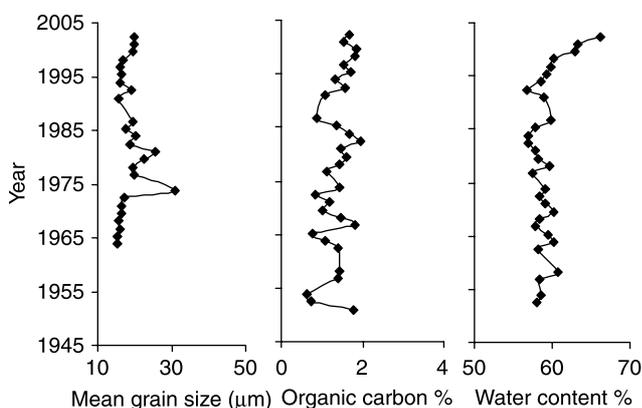


Figure 3 | Sediment characteristics of core L5.

PCB temporal trends

Maximum loadings of PCB occurred in the 20–30 cm core sections corresponding to the 1970s. This peak of PCB concentration, has already been observed in other lakes from industrialised countries (Sanders *et al.* 1992; Yamashita *et al.* 2000; Zennegg *et al.* 2007). It corresponds to the maximum of PCB production and consumption. In core L5 (Figure 5), ΣPCB concentration is 27 $\mu\text{g}/\text{kg}$ in the 40 cm core section, increasing to a maximum of 850 $\mu\text{g}/\text{kg}$ dw in the 25 cm core section. Inputs then decreased

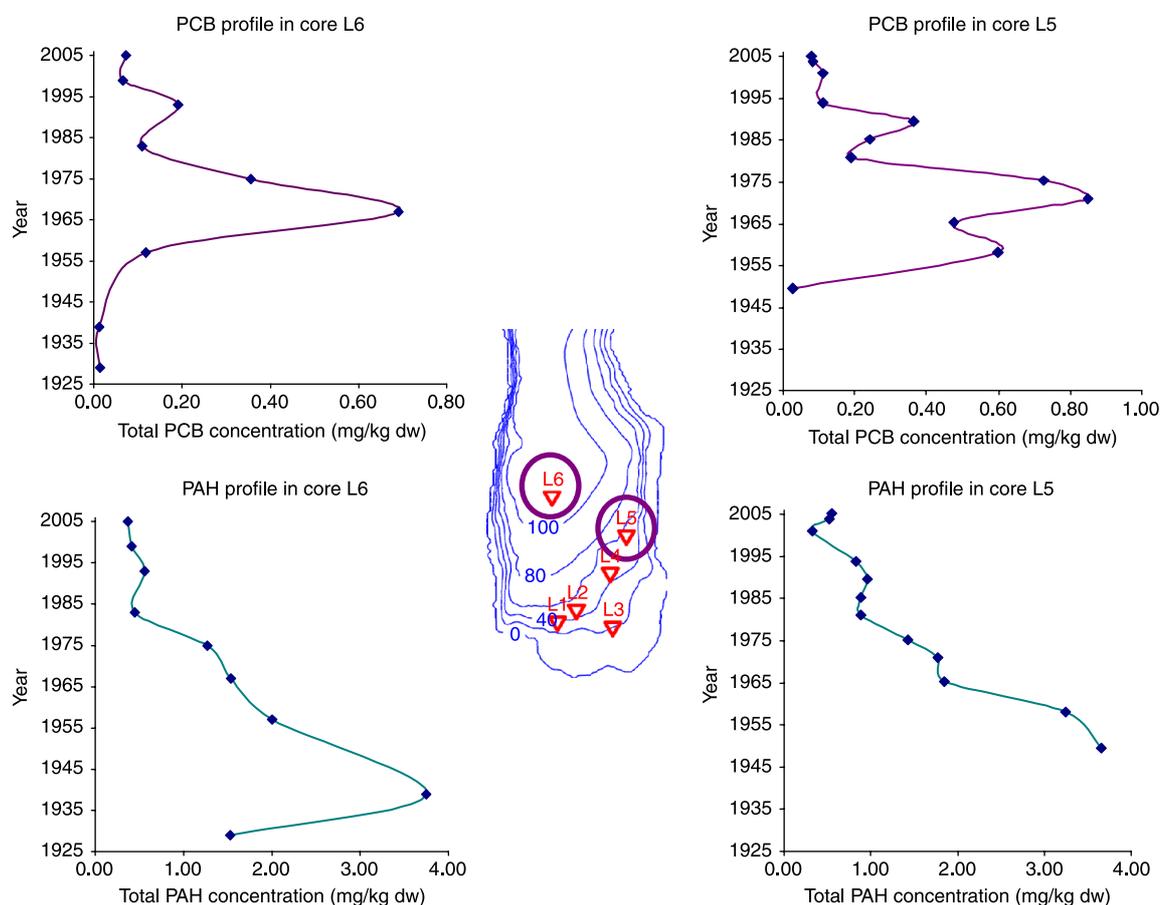


Figure 4 | Vertical profiles of Σ PAH and Σ PCB in cores L5 and L6, Lake Bourget.

Table 2 | Total PCB and PAH concentrations data from various other regions

References	Site	Depth (cm)	Total PAH ($\mu\text{g/g}$)	Total PCB ($\mu\text{g/kg}$)	
Zennegg <i>et al.</i> (2007)	Greifensee	1–2	–	8.7	
		13–14	–	158.4	
		25–26	–	0.7	
Ollivon <i>et al.</i> (2002)	Marne River	St Maurice	0.5	33.13	6.1
	Seine River	Port à l'anglais (upstream)	1	16.18	56.9
		Saint Cloud (downstream)	2	3.25	27.4
			25.5	–	109.7
Yamashita <i>et al.</i> (2000)	Tokyo Bay	0–2	0.36	43.8	
		12–14	2.01	151.0	
		85–90	–	3.4	
Kannan <i>et al.</i> (2005)	Michigan Inland Lakes	Cadillac		6.58	–
		Higgins	0–2	2.39	–
This study	Bourget Lake	core L5	0.5	0.56	79.0
			24.5	1.77	850.0
			39.5	3.66	27.0

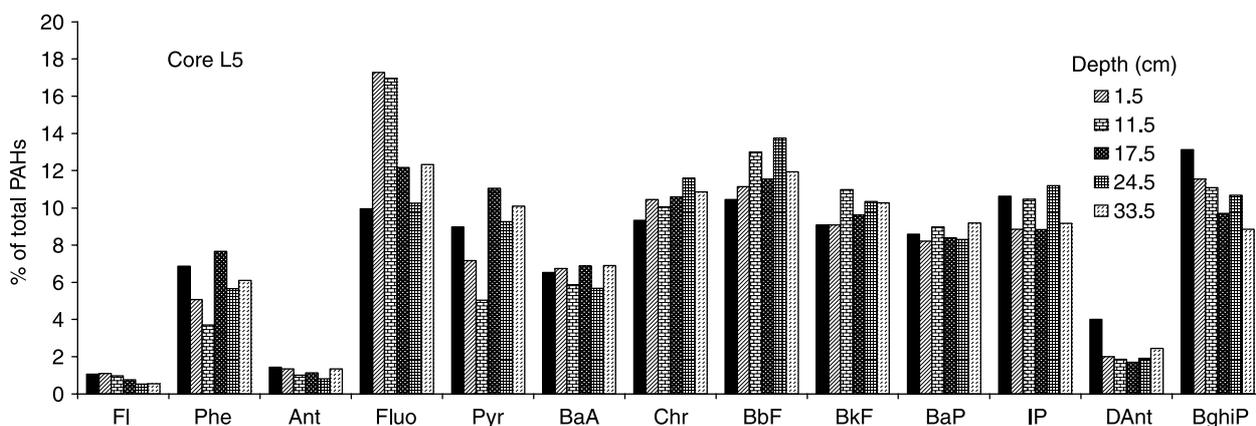


Figure 5 | Temporal variations in PAH distribution in sediment core L5 from Lake Bourget.

gradually and concentrations measured in surface sediments are approximately 11-fold less than maximum concentrations. This decrease is consistent with the ban on PCB production which occurred in France in 1987. In surface sediments Σ PCB concentrations are $79 \mu\text{g}/\text{kg dw}$ in cores L5 and L6 (Table 2). Those concentrations are particularly high compared to other values measured in lake sediments. Surface sediments values in Lake Bourget are up to 9-fold higher than those measured in Lake Greifensee in Switzerland (Zennegg *et al.* 2007). The PCB inputs in Lake Greifensee are mostly atmospheric and can therefore give an idea of the atmospheric contribution of the contamination in the area. Surface concentrations are even higher than those from Tokyo Bay sediments (Yamashita *et al.* 2000), whereas it is a much more industrialized and

urbanized area. Those results highlight the problem of a local source of PCB contamination in the watershed.

In the most contaminated layers of the cores, the PCB profile is dominated by heavily chlorinated PCB congeners (Figure 6). 6-Cl PCB congeners account for approximately 20% of the total PCB in the contaminated section, whereas in surface and bottom sediments, which are less contaminated, 3-Cl PCB congeners are predominant. The PCB contamination seems to correspond to a Arochlor 1260 profile.

CONCLUSIONS

The methodology applied for this study aimed to evaluate the impact of urban stormwater runoff on an aquatic environment. Our first results on PAH and PCB concentrations in sediment cores from Lake Bourget do not permit to distinguish between different sources of contamination. Yet a general downward trend is observed whereas the trend for urbanization is to increase. *Total PAH* concentrations in surface sediments are under the American reference guidelines values and are relatively low compared to values from other lake. The ban on PCB production in 1987 resulted in an important decrease in the environmental loading of PCB as observed in the cores from Lake Bourget. Nevertheless, *total PCB* concentrations measured in surface sediments are quite alarming, indicating a local source of contamination.

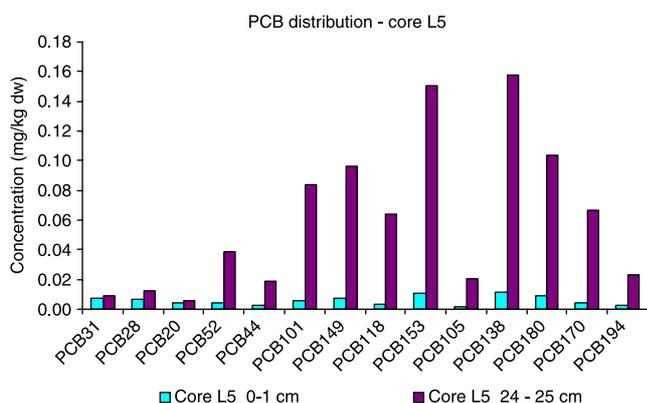


Figure 6 | PCB distribution in core L5 in surface sediments and in the most contaminated section.

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