Reconstruction de l'historique des contaminations par les eaux pluviales urbaines dans les sédiments du Lac du Bourget

Historical assessment of urban stromwater contamination of Lake Bourget through sediment analysis

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RESUME

Les impacts des eaux pluviales urbaines sur les milieux récepteurs sont encore mal connus Cette recherche vise à évaluer l'impact des micropolluants des eaux pluviales urbaines sur un milieu aquatique via l'analyse de ses sédiments. Le principal site d'étude sera le lac du Bourget pour lequel l'analyse de carottes datées sera mise en relation avec l'évolution de l'urbanisation sur le bassin versant au cours des 100 dernières années.

ABSTRACT

The aim of our research is to evaluate the impacts of urban runoff on an aquatic environment through sediment analysis. The major part of the study will be conducted on Lake Bourget (Savoie, France). Dated sediment cores will be analysed for several urban pollutants in order to correlate the vertical profiles of contamination and the evolution of the urbanisation on the watershed for the last 100 years.

MOTS CLES

Heavy metals, lake sediment records, persistent organic pollutants, urban stormwater runoff.

INTRODUCTION

Urban stormwater runoff is of major concern considering anthropogenic pollution in water bodies. When other sources of pollution, especially waste water, are under control, they turn out to be the main source of pollution in urban areas. Several studies have shown that urban runoff can be significantly contaminated by mineral and organic micropollutants originating chiefly from roof and road runoff (Brown and Peake 2006, Davis et al. 2001, Gromaire-Mertz et al. 1999). Yet, the part of urban runoff on the contamination of receiving water bodies is still difficult to assess.

In urban runoff, solids are the main vector of pollution (Chebbo et al. 1995, Bibby and Webster-Brown 2006, Hwang and Foster 2005). More generally, because of their "particle-reactive" nature, many contaminants entering an aquatic system quickly adsorb to particulate solids and eventually settle out of the water column. Therefore sediments and particulate matter were chosen as the media of analysis in this study. They seem appropriate to monitor urban stormwater pollution in lake sediments. Numerous studies have documented that sediment cores taken in semi enclosed aquatic basins can provide an historical record of contamination and land use within the watershed (Arnaud et al. 2004, Couillard et al. 2004). Our research aims to apply this methodology to evaluate the impact of urban runoff on a lacustrine environment. Thus it is in line with the Water Framework Directive (2000/60 CE) which objectives are to reach the "good quality criteria" for surface waters by 2015.

The major part of the study will be conducted on Lake Bourget (Savoie, France). Dated sediment cores will be analysed for several urban pollutants in order to correlate the vertical profiles of contamination and the evolution of the urbanisation on the watershed for the last 100 years. Sediment traps will be placed at the outlet of the main affluent of the lake (the Leysse River) in order to characterise recent intakes to the Lake. Comparison between top core sediments and recent intakes to the lake (trap sediments) will permit to evaluate the loss in the signal due to early diagenesis and to differentiate wet and dry weather pollution. Organic and mineral pollutants, selected among priority pollutants' lists (Water Framework Directive, *CHIAT*[1] methodology), are analysed. The pollutants have been selected on two major criterions: their urban specificity and their persistency in sediments. The selected families of pollutants are: heavy metals, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE) and nonylphenols (NP). In the absence of physical mixing of the sediment and bioturbation, those elements are shown reliable for a time reconstruction of sediment contamination (Couillard et al. 2004, Eisenreich, 1989 Rawn et al. 2001, Lacey et al., 2001). Those conditions should be fulfilled on Lake Bourget, since previous studies have obtained a good chronostratigraphy on cores from the lake (Arnaud 2004, Chapron and Desmet, 2001). A large number of pollutants were chosen in order to discriminate between the different sources of urban contamination and identify what is due to urban runoff. Because of their persistency, toxicity and tendency to accumulate in living tissues PCBs and PAHs are part of the most damaging group of chemicals to which natural systems can be exposed. They both show a high resistance to physico-chemical and biological degradation. PAHs can be derived from both natural and anthropogenic sources. But if PAHs detected at the surface of agricultural soils were first assumed to be the result of natural process (Blumer, 1961 in Motelay-Massei, 2004) recent studies have concluded that anthropogenic PAHs predominate. Anthropogenic sources include combustion of fossil-fuel, vehicular emissions, abrasion of street asphalt and automobile tires, combustion processes of municipal

[1] CHIAT (Chemical Hazard Identification and Assessment Tool): tool developed for the european program Daywater

waste incinerators, domestic heating, … PCBs may arise by volatilisation from buildings, motor car traffic, industrial waste, combustion processes of municipal waste incinerators… The atmospheric compartment plays a major part in the transport and fate of organochlorinated pollutants in the environment. Yet, PCB deposition levels were reported to be related to precipitation (Teil et al., 2004). The main factors that rule the fate of PCBs are the ambient temperature, the rainfall pattern and the wind direction. Polybrominated diphenylethers (PBDEs) are widely used as flame retardants in electronic equipement, plastics, textiles, building materials, carpets, and in vehicles and aircraft. They are highly resistant towards acids, bases, heat, light and reducing and oxidising compounds and, as a result, are extremely persistent when released in the environment (Allchin et al., 1998). Alkylphenols (APs) in the environment are mainly originated from the degradation of alkylphenol polyethoxylates (APEOs). APEOs have been widely used in domestic detergents, pesticide formulations and industrial products, such as textiles, coatings, paints, lube oil, fuels, plastics, paper…Nonylphenol ethoxylates (NPEOs) is the most common surfactant in the marketplace, it accounts for about 80% of APEOs. In the environment, NPEOs are rapidly degradated to nonylphenols (NPs) by biodegradation and photodegradation mechanism (Li et al., 2004). NPs are considered to be endocrine disruptors. Therefore, the UE have banned the usage of nonylphenol ethoxylates surfactants since 2005 (directive 2003/53/CE).

1 STUDY AREA

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 covers an area of 42 km². The lake's 146 m-deep northern basin is separated from the 112 m-deep southern basin by a 110 m-deep sill, formed by the Sierroz river fan. The rivers Leysse and Sierroz are permanent tributaries of Lake Bourget (figure 1). Under normal hydrological conditions, the lake flows into the Rhone River, but during major floods water from the Rhone flows into the lake.

Lake Bourget was chosen for this research for multiple reasons. (1) For the last 20 years, several studies have been conducted on the lake therefore a large database is accessible.

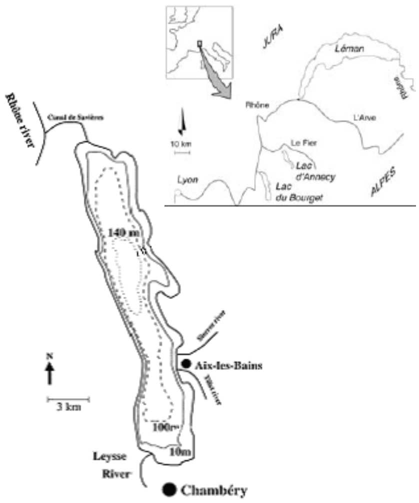

Figure 1: Lake Bourget, localisation and bathymetry

Moreover, (2) the only source of urban contamination to the lake should theoretically be atmospheric deposition and urban runoff after transfer through the lake tributaries. Since the 1980, neither wastewaters nor wastewater treatment plant effluents arrive to the lake. And finally (3) Lake Bourget is the largest natural lake in France located near by an important urban agglomeration (Chambery, Aix les Bains). During the last 30 years the population on its watershed has increased of nearly 60% reaching nowadays 175 750 inhabitants. And the actual tendency of urbanisation is still to increase. The quality of the landscape and the strategic location of the lake, at the merge of European communication routes (connection Lyon-Turin), explain this urban development. But human and urban activities endanger the environmental quality of the site.

2 METHODS

2.1 Field sampling

The sampling is concentrated on the Leysse Delta, downstream the city of Chambery (Fig. 1). The Leysse River is the main affluent of Lake Bourget and it drains to most urbanised sector of the watershed. Analysis are conducted both on bottom sediments (from sediment cores) and on trap sediments. Eight short sediment cores were sampled on the 24th of October 2006 (fig. 2).

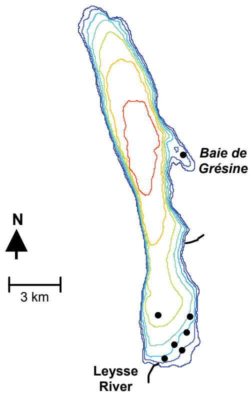

Figure 2: Sampling sites

Five cores were sampled in the actual plume of the Leysse River (Bournet 1996) in order to evaluate the horizontal extent of the contamination. One core was sampled in the southern basin, corresponding to the plume of the Leysse river before the reshaping of its outlet in the 1950s. And two cores were sampled in the Baie de Grésine, a litoral area with no direct urban runoff contamination. Three sediment traps will be placed at the outlet of the affluent, along the actual plume. On our first field campaign traps were placed at 10 m depth.

Particulate matter should be recovered after 15 days approximately. Long exposition periods might leed to artifacts. (Lee et al., 1997 in (Groleau 2000) have shown that traps left for more than 15 days in the euphotic zone[2] were exposed to zooplankton grazing and bacterial consumption. Depending on the pluviometric context and lack of rain events the exposition will be reiterated.

2.2 Analytical methods and preliminary results

Analyses are under progress and results should be available by June 2007.

2.2.1 General methodology

Stratigraphic analysis of cores from Lake Bourget sites include (1) organic contaminant concentrations (HAPs, PCBs, PBDEs, NPs) (2) trace metal concentrations (Cu, Pb, Zn, Cd) (3) particulate organic carbon (4) grain size distribution (5) spectrophotometer analysis (6) chronostratigraphy using radiometric dating. One half of the cores will be used for the sediment characterisation and datation and the other half will be used for chemical analysis (Fig. 3).

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[2] The euphotic zone is the depth of the water that is exposed to sufficient sunlight for the photosynthesis to occur.

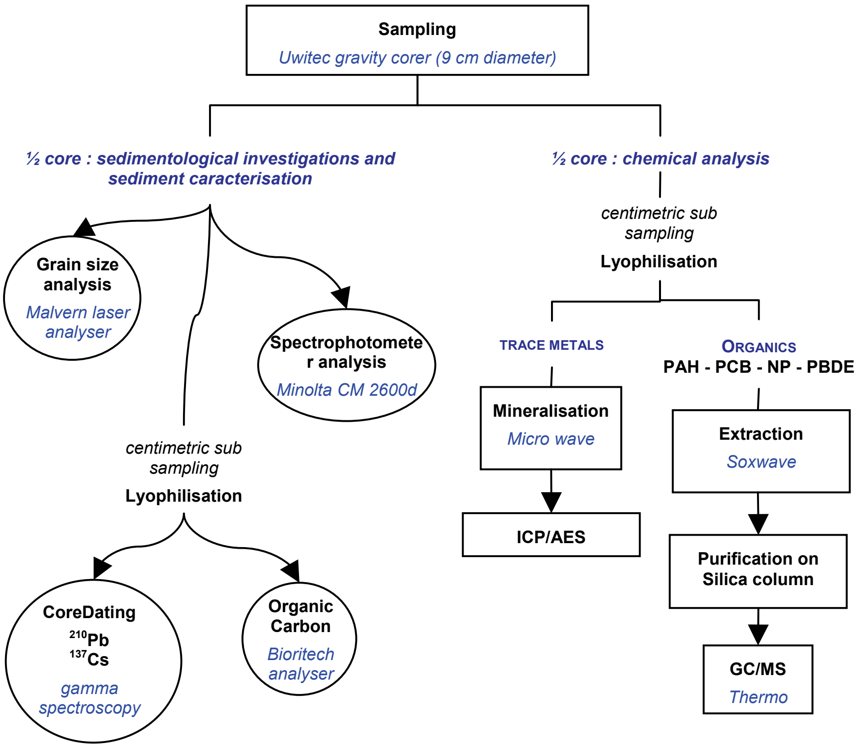

Figure 3: General methodology for the cores' analysis

2.2.2 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 24h (to eliminate organic matter), rinsed with water and demineralised water, left for 24h 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.

2.2.3 Geochemistry

- Organic contaminants

The polycyclic aromatic hydrocarbons analysed are the 16 PAHs from the EPA's priority substances list (*naphtalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene*). Deuterated internal standards are used for PAHs quantification (*Naphtalène D8* for naphtalene and acenaphtalene, *Acenaphtene D10* for acenaphtene and fluorene, *Phenanthrene D10* for phenanthrene, anthracene, fluoranthene, pyrene and benzo(a)anthracene, *Chryzene D12* for chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and *Perylene D12* for indéno(123)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene. Internal standards must have the same physico chemical properties as the components, must be absent from the natural sample and should not create co-elution. The polychlorobiphenyls analysed are the 11 congeners analysed in the french standard *XP T 60-184*: PCBs 31, 28, 20, 52, 101, 149, 118, 153,105,138,180. The analysis of those 11 PCBs permits to calculate the PCB content as a function of Aroclor profiles (Aroclor 1242, 1254 and 1260). Internal standards used for PCBs quantification are PCBs 76, 112 and 209. All the organic pollutants analysed can be extracted simultaneously. Aliquots of 500 mg are extracted in a Soxewave apparatus with dichloromethane/methanol (30:5 v/v) for 10 mn. The solvent extract is then reduced to a volume of 500ml by means of a rotavapor and Turbo Vap evaporator and passed through a 2 g clean-up silica column. The first 15 ml of heptane eluent from this column recovers the PCBs. PAHs are recovered in the second fraction composed of 10 ml of heptane/dichloromethane (80:20 v/v) eluent. Those fractions are then reduced to 50 µl for analysis by gas chromatography-mass spectrometry (GC-MS).

2.2.4 Organic Carbon analysis

Organic carbon analyses are performed using a Bioritec analyser. Prior to the analysis, sediment samples are acidified in order to eliminate inorganic carbon. In the analyser, samples are calcinated at 1000°C and CO_2 is formed from the organic carbon present in the sediments. The CO_2 can then be measured by infrared spectroscopy.

2.2.5 Grain size analysis

Grain size analyses are performed using a Malvern Mastersizer 2000 laser diffraction particle analyser. Particles size distributions obtained by this analysis are then plotted as a function of depth in order to characterize the sedimentation processes (fig.4).

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 autochtonous sediment is diluted by a mostly river-born detrital fraction. This detrital material consists of a mixture of 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 rhomboedral crystals (15 µm), river born alumino-silicates (Si, Al, Mg, K, Ca, Fe) (20 µm) (Groleau, 2000).

A study based on the analysis of carbonates and non carbonates particle size distribution (PSD) on a 9 meter long core from lake Bourget, showed a coarsening in the upper part of the core. This trend was observed in both fractions. For the carbonate fraction, it is interpreted by an increase in the abundance of rhomboedral calcite crystals since the eutrophication of the lake around 1948. The coarsening of the non carbonate fraction might be due to an increase in the abundance of diatoms relative to river born silicates. Diatoms are virtually absent from lower levels of the core; their abundance in upper sediments layers is also thought to be due to an increase in trophic level (Arnaud, 2005).

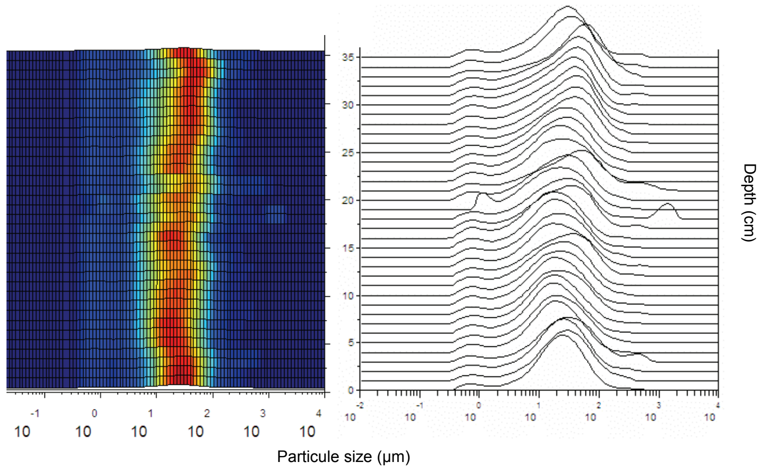

Figure 4: Particle Size Distribution of core *LDB06-L2 (taken near the outlet of the Leysse River)*

2.2.6 Spectrophotometer analysis

Spectrophotometry data can be used as a high resolution tool to identify variations in sediment components since colour variations are often related to major changes in sediment composition. Reflectance spectrophotometry allows rapid data acquisition without damaging the core. Sediment colour analysis are carried out at the LSE laboratory using a Minolta CM 2600d, which provides reflectance intensity measurements for visible wavelengths, between 400 and 700 nm with a 20 nm increminent. The down core measurement interval is 5 mm. Spectral analysis are taken directly on the core surface through the polyethylene film.

2.2.7 Chronostratigraphy

The sediment cores will be 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.

3 CONCLUSION

At the time of the paper redaction, the work is still in progress. Preliminary results on the physical properties of the cores are presented and results from the geochemistry analyses are expected by May 2007.

Analysis performed on Lake Bourget sediments should permit to correlate the vertical profiles of contamination and the evolution of the urbanisation on the watershed. Yet, signals generated by lacustrine environments are complex to interpret for they combine several parameters: Moreover, on the vast watershed of Lake Bourget, sources of contamination are multiple: industries, agriculture, transport …Thus, in order to discriminate the different sources of contamination, we will work on detention basin, with smaller catchment and a specific type of land use. It is also envisaged to work on a stormwater detention basin in Brazil, in an area with different pluviometric conditions and urbanistic characteristics.

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