High resolution lead-isotope record in Lake Geneva sediments (Switzerland–France)

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Stable Pb isotope geochemistry in environmental studies provides powerful information about the origin of contamination. Basically, this method is based upon the discrepancies of isotopic abundance which exist between different groups of material (e.g. rocks, gasoline additive, industrial emissions...). We have investigated the origin and the history of Pb input into lake Geneva (France–Switzerland) by analysing sediment cores. Two different sites were choosen: (1) Bay of Vidy (BV), in front of the city of Lausanne and very close to a major waste water input which began in 1964, and (2) in the centre of the Lake (PC), as far as possible from point sources (fig.1). Additionally, the fluxes of other heavy metals, such as Tl, Zn, Cd and Cu, were also calculated.

Location and sampling

The cores were recovered using PVC-tubes corers (50 cm in length), handled from the submersible FA Forel. Such a method allows precise selection of the coring site in respect with the appearance of the sediment–water interface (by avoiding the most disturbed area), and to keep the tube vertically during coring [1]. For each site, five to eight cores were taken, and the best two selected for further analysis. They were immediately extruded and sliced. For PC cores the interval of subsampling was 0.5 cm for the first 20 cm and then 1 cm, whereas constant interval of 1 cm was used for the BV's cores. Such a sub-sampling allows to reach almost a yearly resolution.

Methods

Heavy metal concentrations (Pb, Zn, Cd, Cu, Tl), as well as major elements (Ca, Fe), were measured using a POEMS equipment from Thermo Jarell Ash Co. This later shrewdly combines the ICP-MS and the ICP-OES facilities in a same equipment, and allows a simultaneous measurement of trace and major elements from ppt to percent. Reliable dating was obtained by ^{210}Pb and ^{137}Cs methods. Pb isotopic compositions were analysed by ICP-MS. Briefly, the variations of ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios were found significant above approximately 2.10^{-3} and 5.10^{-3} level respectively. Volumic magnetic susceptibility (VMS) was also measured and gives chronological information based upon the introduction of $FeCl_3$ for the waste water treatment at Vidy (core BV).

Isotopic signatures of potential sources

The major source of anthropogenic Pb in the last three decades was indisputably Pb added as anti-knock agent in the gasoline. In Switzerland as in the majority of West European countries, Pb has been progressively eliminated from gasoline since 1985. Unfortunately, only very few data are available about the isotopic signature of this source. In the early 70's Chow and Earl measured ^{206}Pb/^{207}Pb 1.14 directly in gasoline used at Bern [2]. It is assumed that the Pb compounds used since the 80's are mostly imported from Canada and Australia (Precambrian ores) with ^{206}Pb/^{207}Pb ratios between 1.04 and 1.10. These data are in good agreement with the direct measurements

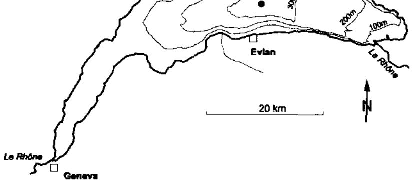

FIG. 1. Sampling location and simplified bathymetry of lake Geneva.

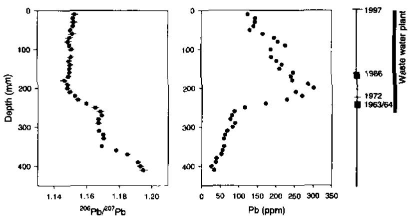

FIG. 2. $^{206}Pb/^{207}Pb$ ratios and Pb content profiles at Bay of Vidy (BV).

recently made in gasoline used at Geneva (Chiarada M. pers. communication). Even though in Switzerland, analysis are not available for 'industrial' end-member, we can strongly suspect its existence by analogy to the neighbour countries [3-4]. This latter is characterised by $^{206}Pb/^{207}Pb$ ratios between 1.14 and 1.16, but a complete investigation of this source in Switzerland is currently in progress. Finally, the last generic group is the natural Pb coming from local soils and rocks. It can be easily assessed by the isotopic compositions of pre-industrial sediments. In lake Geneva, the unpolluted sediment layers are characterised by $^{206}Pb/^{207}Pb$ ratios at about 1.20-1.21. These values are quite similar to those generally considered for natural Pb in Western Europe [4-5].

Profiles of Pb in the cores

Pb isotopic compositions and Pb contents of the core sampled close to Lausanne (BV) are reported on fig. 2. The chronology is indicated on the right side of the diagram by taking into account the ^{137}Cs and ^{210}Pb dating. The '1972' mark is obtained from the VMS profile, because from this date $FeCl_3$ was added during the water treatment processes (unpublished data). The history of Pb input in this area can be divided into three main periods. 1) the Pb concentrations slowly and regularly increase from 25 to 90 ppm between the bottom (*c.* 1900–1920) to the mid 60's whereas simultaneously, the $^{206}Pb/^{207}Pb$ ratios decrease from 1.195 to 1.165 and then stabilise. That can be explained by an increasing influence of a contamination source characterised by a signature of about 1.14–1.15. Despite of the lack of data concerning the signatures of the potential sources already evoked above, one can reasonably assume that this Pb was mainly coming from gasoline, at least during the 1950-1960 period, with a small proportion of 'industrial' Pb. 2) a dramatic and sudden increase of Pb content induced by the opening of the waste water treatment plant. A peak of contamination is recorded in the sedimentary column in the late 70's (300 ppm). This abrupt change in the feeding conditions of the bay, under the influence of a larger amount of organic material coming from Lausanne, is undoubtedly illustrated by a concomitant change of the $^{206}Pb/^{207}Pb$ ratios (shifted to about 1.15), and by an increase of the sedimentation rate. 3) during the last twenty years the Pb input has regularly declined because of the environmental policies [6]. Nevertheless, the concentration still remains high near the sediment surface (125 ppm). Almost since the opening of the waste water treatment plant, the isotopic signature of the sediments is the same: $^{206}Pb/^{207}Pb$ 1.15. However, the deconvolution of the Pb signals (isotopic and concentration) into three contributions corresponding to each end-member – gasoline, industrial, and natural –, necessitates a precise knowledge of the isotopic evolution of the two first sources through time. Indeed, the sources of importation have frequently changed, as well as their isotopic compositions, following the economical consideration [4]. The establishment of such a database is currently in progress.

It can be also noticed that similar concentration trends are observed for Cd, Cu and Zn with a peak appearing in the 70's horizon at 5.5, 340 and 1000 ppm respectively.

The second core, which was obtained in the central part of the lake, exhibits different and more scattered Pb content profile (not shown here). The Pb concentrations slowly raise from 20 ppm to a maximum of 60 ppm in the 70's, and then diminishes to 35 ppm at the top. The $^{206}Pb/^{207}Pb$ ratios have inverse trend, ranging between 1.165 and 1.205. It is interesting to remark that the few turbidites, which disturb the regular layers are characterised by low Pb concentrations, while isotopic compositions are shifted toward more radiogenic values, which reflects a sudden increase of detritic material delivery. In the layers corresponding to the early 80's, the isotopic composition of the anthropogenic end-member alone seems to be less radiogenic than the one observed in the BV core for the same period. That would suggest the relative contribution of gasoline is likely more important at the PC site.

References

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