Lead contamination of the Seine River, France: geochemical implications of a historical perspective.

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Abstract

Four sediment cores collected in the Seine River basin and dated between 1916 and 2003 were analysed for lead concentrations and isotopic composition. In all four cores, the measured Pb concentration (up to 460 mg.kg⁻¹) lies significantly above the natural background (27-40 mg.kg⁻¹), although a significant decrease (down to 75 mg.kg⁻¹) was observed during the second half of the 20th century which can be explained by the reduction of lead emissions. The ²⁰⁶Pb/²⁰⁷Pb ratio measured in these samples indicates that the main source of Pb used in the Paris conurbation is characterized by a “Rio Tinto” signature (defined as ²⁰⁶Pb/²⁰⁷Pb = 1.1634 ± 0.0001). A high contribution, up to 25%, from the leaded gasoline (characterized by ²⁰⁶Pb/²⁰⁷Pb = 1.08 ± 0.02) is revealed in the Seine River downstream Paris, indicating that lead from the leaded gasoline is preferentially released to the river.

The dominating Pb signature in the Paris conurbation that is currently sampled through incinerators fumes (²⁰⁶Pb/²⁰⁷Pb = 1.1550 ± 0.0005) and waste water treatment plant (²⁰⁶Pb/²⁰⁷Pb = 1.154 ± 0.002), represents a mixture of highly recycled lead from the Rio Tinto mine and lead from leaded gasoline (imprinted by the low ²⁰⁶Pb/²⁰⁷Pb of the Broken Hill mine). This signature is called “urban” rather than “industrial”, because it is clearly distinct from the Pb that is found in areas contaminated by heavy industry, i.e. the heavy industries located on the Oise River which used lead from European ores characterized by high ²⁰⁶Pb/²⁰⁷Pb ratios (~1.18-1.19) and possibly a minor amount of North American lead (²⁰⁶Pb/²⁰⁷Pb ratios > 1.20). The “urban” signature is also found in a rural area upstream of Paris in the 1970's. At the Seine River mouth in 2003, Pb with an urban signature represents 70% of the total Pb sediment content, with the 30% remaining corresponding to natural Pb.

Keywords: *Lead, isotope, pollution, Seine, industrial lead, urban lead, Paris, Broken Hill, Rio Tinto, gasoline.*

1. Introduction.

The Seine river basin (67,500 km²) drains one of the most urbanised areas in Europe. It covers 14% of the French territory but accounts for 25% of the agriculture production, 25 to 30% of the industrial activity and 23% of the French population. In the Paris conurbation (2,740 km², 9.5 million inhabitants), the Seine water and sediments are heavily contaminated by metals. Unfortunately, the sources and pathways of these contaminations are not well understood (Thévenot et al., 2007; Meybeck et al. 2007; Le Cloarec et al., 2009).

Lead (Pb) represents one of the major metallic contaminants of the Seine River. Dredged sediments are characterized by such high Pb contents that they are classified in the “moderated to highly contaminated sediment” category (Meybeck et al., 2007). Although the release of Pb into the environment has been strongly reduced, the lead contamination of the sediments on the downstream part of the Seine River is still three times higher than the geochemical background which is in the range of 27-40 mg kg⁻¹ (Thévenot et al., 2007).

The Pb concentration measured in the river sediments clearly reveals the high level of contamination of the river. However, it does not provide any information on the different sources of this contamination. The Pb isotopic composition represents a powerful tool to evaluate the different sources of Pb (natural, industrial, leaded gasoline) that are released into the environment (Monna et al., 2000; Shotyk et al., 1998). The overall balance of the lead cycle in the environment is not straightforward because some Pb stocks are strongly recycled and hence produce very small environmental leaks (e.g., Pb for car accumulators), whereas others are directly released into the environment (emission of tetraethyl Pb from leaded gasoline).

Gasoline lead additives were the main source of Pb to the road dust ($^{206}\text{Pb}/^{207}\text{Pb} = 1.101 \pm 0.001$), but were less important for indoor dust accumulated from 1971 to 1981 ($^{206}\text{Pb}/^{207}\text{Pb} = 1.120 \pm 0.001$) and even lower for the Seine River sediment ($^{206}\text{Pb}/^{207}\text{Pb} = 1.152 \pm 0.002$) sampled in 1979 (Elbaz-Poulichet et al., 1986). The contribution of gasoline lead additives to the Seine River decreased from 1979 to 2000 ($^{206}\text{Pb}/^{207}\text{Pb} = 1.169$; Millot et al., 2004). In 1997, the lead contained in the street dust of Paris ($^{206}\text{Pb}/^{207}\text{Pb} = 1.151$) came

mostly from gasoline lead additives, except nearby the Eiffel Tower ($^{206}\text{Pb}/^{207}\text{Pb} = 1.174$) where dust was contaminated by the lead contained in the paint used on the tower (Nageotte and Day, 1998). There are also differences in isotopic compositions of aerosols sampled in different sites in Paris, in 1989 and 1995 (Véron et al., 1999). From 1995 to 2002, the main lead source to Parisian aerosols shifted from gasoline to the so-called “industrial” end-member (Widory et al., 2004). As a whole, the previous data underline the spatial and temporal variability of the lead sources and their respective contribution to the pollution of the Paris conurbation, claiming for an integrative study.

Moreover, in order to evaluate the efficiency of past and ongoing environmental policies whose major goal is to reduce the heavy metal contamination, it is important to establish a historical record of the Seine River contamination and to detect its different contamination sources.

Sediment cores represent valuable archives of the anthropogenic river contamination (Alfonso et al., 2001; Chillrud et al., 2003; Arnaud et al., 2004; Soster et al., 2007; Le Cloarec et al., 2009), provided that they are sampled in undisturbed sites with continuous sedimentation. Unfortunately, navigation and channel dredging prevent continuous accumulation of sediments in the Seine River bed. The Seine River has no delta where marsh cores (Alfonso et al., 2001) can be sampled. Floodplains offer an alternative, but undisturbed floodplains are extremely rare along the Seine River. It was very difficult to find deposit sites allowing temporal reconstructions over the last 100 years (Le Cloarec et al., in press). Here, we report the Pb concentration and isotopic signature in four cores covering different periods determined with the ^{137}Cs - and ^{210}Pb method, and three sites. This allows to:

- 1) Assess whether the changes in Pb contamination in the Seine River are related to changes of the Pb source(s).
- 2) Constrain the actual Pb source(s) of the Seine River.
- 3) Evaluate the impact of leaded gasoline emissions on the past and present Seine River contamination.

2. Materials and methods.

2.1. Sampling sites and sediment core dating

Figure 1

The core TR01 was collected in an upstream Seine River site (Fig.1). This sampling site is located on an oxbow lake of the “Canal de la Haute Seine” that was built between 1806 and 1851 in order to connect Paris with agricultural and coal mining areas. This site drains an area of 3577 km², and the population density is low, 40 inhabitants km⁻². Agriculture and forestry are the major activities. The 80-cm long TR01 core was collected during March 2002. Bed soft sediments were cored using a hand pushed 10-cm diameter plastic tube, at a depth of 1 meter below the water surface.

Two cores, B2 and M1, were collected in the Seine River floodplain, about 100 km downstream of Paris and its main waste water treatment plant (WWTP Seine Aval at Achères, see Fig. 1). These two sampling sites drain 96% of the Seine River basin and are situated within the last major meander of the Seine River before it reaches its estuary. “Bouafles” is located just upstream of a dam, in ‘Les Andelys’ (Fig. 1), in an oxbow lake located on the right bank of the Seine River. It corresponds to a young accretion area as indicated by the recent burial of trees. This undisturbed sampling area has remained grassland for 30 years, and gradual sediment deposition has occurred. Inhabitants confirmed that this site has been flooded until 2004 at least once a year. Eleven cores collected in this area between 2003 and 2008 indicated a continuous sedimentation during the last 60 years (see Le Cloarec et al., in press).

The second site (Muids), where the M1 core was collected, (Fig.1) is located on the same bank 12 km further downstream in the same meander of the Seine River. It is composed of four islands which experienced regular flooding during wintertime.

All cores were sampled April 9th, 2003 using an Eijkelpamp device equipped with a percussion drill bit (with 10-cm diameter and 1-m length). The stainless steel soil corer could be opened laterally thus allowing an immediate transfer of the core into a PVC tube and avoiding any metal contamination.

The 1-meter long core S01 was collected in at Pontoise-les-Noyon, March 23rd, 2005, in a meander of the Oise River (Fig. 1). The site is located in an annually flooded pasture downstream the city of Chauny. The core was sampled with the same equipment as the samples from Bouafles and Muids. The sampling site drains an area of 4044 km² that was dominated by rural and low density urban areas. The Oise River basin has been industrialized since the beginning of the 1800’s. This led to an increase of local urbanization beginning shortly after the Second World War and continuing until 1975 (Le Cloarec et al., in press). Today many Oise industrial plants are no longer in activity. The Saint Gobain (glass industry) plant in Chauny (Fig 1), situated a few km above the sampling site, is particularly interesting

for this evaluation. This glass manufacture started its activity around 1665, employed large quantities of sulphuric acid and owned several lead chambers (7 in 1850, 22 in 1870).

In addition, treated wastewater issued from the Seine – Aval waste water treatment plant (WWTP) at Achères (Fig. 1) was sampled during December 2006 (Pernet-Coudrier et al, 2008). The Seine – Aval WWTP is connected to 80% of the Paris conurbation area combined sewers (9.5 million inhabitants).

2. 2. Core dating

Details on the dating of the cores, such as depth profiles and sedimentation rates, are given in Le Cloarec et al. (in press).

The sediment cores are dated through the measurement of two radionuclides, ^{137}Cs - and ^{210}Pb . Both are strongly adsorbed on the fine fraction of the sediment (Wang and Cornett, 1993; Gil-García et al., 2009). Artificial ^{137}Cs is used as an event-tracer, whereas natural ^{210}Pb provides the sediment age.

Both radionuclides are gamma emitters and can be analyzed in small quantities of sediments (ca. 50-100 g) without any previous chemical treatment. The sediments are dried at 115°C, sieved (< 2 mm), powdered and then placed into air-tight counting boxes. Counting was conducted during ca. 10^5 s using Germanium gamma-ray detectors (High purity germanium – GeHP, N-type, coaxial model) at the *Laboratoire des Sciences du Climat et de l'Environnement* (Gif-sur-Yvette, France). Efficiencies and background of the detectors are controlled with internal soil and sediment standards, pure KCl samples, and IAEA standards (i.e., Soil-6, -135 and -375). Activity decay was corrected taking the sediment collection period into account.

^{137}Cs , an artificial radionuclide ($t_{1/2} = 30$ years), was produced by the thermonuclear bomb testing conducted between the 1950's and the 1980's (the maximum input occurred in 1964) and the Chernobyl accident in 1986. Measurement of the ^{137}Cs activity in the sediment allows one to distinguish three events: fallout due to the first significant input in the atmosphere in 1954, maximum input in 1964 and fallout due to the Chernobyl accident in 1986. ^{137}Cs stock stored in soils decreases by radioactive decay and fine sediment transfer to the rivers. ^{137}Cs is easily identified in gamma spectrometry by a peak at 661 keV. The uncertainty on measurements corresponds to ca. 0.5%. The detection limit reaches 0.3 Bq.kg⁻¹.

²¹⁰Pb, a natural radionuclide ($t_{1/2} = 22.3$ years), is a decay product of ²³⁸U ($t_{1/2} = 4.5 \cdot 10^9$ years). ²³⁸U decays through a series of short-lived nuclides (e.g. ²²⁶Ra, ²²²Rn). ²²²Rn is a gas that partly remains *in situ*, forming “supported” ²¹⁰Pb, and that partly escapes to the atmosphere, forming “excess” ²¹⁰Pb. Excess ²¹⁰Pb is deposited on the soil surface via wet and dry fallout and strongly sticks to the soil particles. The ²¹⁰Pb activity in “excess” is calculated by subtracting the supported activity (determined using a ²³⁸U daughter, i.e. ²¹⁴Bi from the total activity of ²¹⁰Pb (Bonté et al., 2000). The uncertainty of the measurements (ca. 10%) is higher than that for ¹³⁷Cs.

2.3. Determination of lead concentration

Details of the determination of lead concentration in totally digested sediment samples are given in Le Cloarec et al. (2009). Samples of about 100 mg are dissolved by successive addition of 65% HNO₃ (3 mL) and 30% HCl (7 mL) mixture, 65% HNO₃ and 40% HF (5 mL each), and 65% HNO₃ and 69-72% HClO₄ (6 mL each) in Teflon vessels using a heating block (Digiprep, SCP Science). Ultra pure reagents were used (Normatom grade, VWR, France for HNO₃, and HCl, “for trace metal analyses”, Baker, SODIPRO, France, for HF, and HClO₄). The solutions were evaporated to dryness, retaken 3 times in 2 mL of HNO₃ and then diluted with 50 mL of MilliQ water. Three different analytical techniques were used to determine the lead content: atomic absorption spectrometry (AAS), inductively coupled plasma – atomic emission spectrometry (ICP-AES) and inductively coupled plasma – mass spectrometry (ICP-MS) (Table 1). The accuracy of the Pb concentration determination was evaluated through the analysis of the certified reference material SL-1 (lake sediment, AIEA, Vienna, Austria). The obtained value, $36.6 \pm 2.0 \text{ mg.kg}^{-1}$ (n=15), agreed with the certified concentration (37.7 mg.kg^{-1} , certification interval: 30.3 – 45.5 mg.kg^{-1}). For all these methods, the lead concentration determination uncertainty was up to 5%. The procedural “blank” contribution to the Pb concentration ranges from 0.06 % for sediments with high Pb concentration up to 0.4% for sediments with low Pb content.

Fifty millilitres of bulk water samples (containing 50 mg.L^{-1} of dry residue) from the Seine-Aval WWTP were evaporated, the residues were totally dissolved with a mixture of HNO₃, HCl, HF and HClO₄ (Normatom grade, VWR) in Teflon vessels using a heating block (Digiprep, SCP Science). The solutions were evaporated and 2 ml of HNO₃ were added afterwards (addition and evaporation sequence repeated three times) and then diluted with 50

mL of MilliQ water. Pb concentrations were determined by inductively coupled plasma – quadrupole mass spectrometry ICP-QMS (X Series, ThermoElectron, France). Determination of Pb in the reference river water NIST-1640a (National Institute for Standards and Technology, Gaithersburg, USA) falls within 3 % of the certified value (n=9).

2.4. Lead isotopic measurements.

Lead isotope ratios ($^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) were measured in the sediment solutions that were also used for lead concentration determinations and were made by ICP-QMS (X Series, ThermoElectron, France), following the conditions defined in Gallon et al. (2006). The experimental conditions were: three channels reading; dwell time of 30 ms; 100 sweeps; 5 replicates per sample. Mass bias and drift of the isotope ratios were corrected based on repeated measurements of the Pb reference material NIST SRM-981 that were analysed between every three samples. The 2σ -errors of isotopic ratios are 0.23% for the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the blank corresponds to 1.168 ± 0.003 (lying in the range of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the samples). SRM-981 was also analysed as a sample (n=25) to control the bracketing correction. Values $^{206}\text{Pb}/^{207}\text{Pb} = 1.0933 \pm 0.0015$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0084$ were obtained. Certified values for the SRM-981 are $^{206}\text{Pb}/^{207}\text{Pb} = 1.09333 \pm 0.00039$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0008$. The lead isotopic composition of three samples from core B2 were also determined by thermal ionisation mass spectrometry (TIMS, Finnigan Mat 261 in LSCE), following the method described in Doucelance and Manhès, 2001. Even though the data obtained using TIMS are more precise than the data obtained using ICP-QMS, the results obtained with both instruments are consistent (see Fig. 2). $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios were measured. The data are presented in the Supporting Information. Since both ratios are linearly correlated, only the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is used in the text.

Figure 2

3. Results.

Results are reported in Figure 3. Pb concentrations range from 76 mg.kg^{-1} up to 460 mg.kg^{-1} in B2 (Bouafles), 73 mg.kg^{-1} to 421 mg.kg^{-1} in M1 (Muids), from 36 mg.kg^{-1} to 342 mg.kg^{-1} in S01 (Oise) and from 41 mg.kg^{-1} to 90 mg.kg^{-1} in TR01 (Troyes). In all cores except that from Troyes (TR01) that starts in the 1970's, there is a peak of the Pb concentration

around 1960. The concentration then decreases significantly. In the Oise core, this decrease is preceded by a regular strong increase that occurs between 1916 and 1960.

Most of the Pb concentrations mentioned in the previous paragraph are above the natural background level. In the Seine River basin, Pb natural background is highly correlated to the clay content of the sediment, with a Pb/Al ratio of 0.61 mg/g (Thévenot et al., 2007). For the relatively Al-rich (fine grained) samples studied here, it corresponds to a Pb natural background of about 27-40 mg kg⁻¹.

The ²⁰⁶Pb/²⁰⁷Pb ratio varies similarly in the cores B2 and M1:

- the ²⁰⁶Pb/²⁰⁷Pb ratio is rather stable between 1920 to 1960, ranging from 1.163 ± 0.003 up to 1.166 ± 0.003
- between 1960 and 1986/1989, the ²⁰⁶Pb/²⁰⁷Pb ratio decreases to 1.144 ± 0.003
- starting from 1986/1989 up to the early 2000's, the ²⁰⁶Pb/²⁰⁷Pb ratio increases up to 1.163 ± 0.002 in 2000 and 1.166 ± 0.003 in 2003.

After 2000, the ²⁰⁶Pb/²⁰⁷Pb ratios in B2 and M1 are similar to that observed before 1960, the Pb concentration however is much lower. This is due to the above mentioned general decrease of the Pb concentration.

In TR01, the ²⁰⁶Pb/²⁰⁷Pb ratio increases from 1.1521 ± 0.0015 in the 1970's to 1.175 ± 0.001 in 2001.

In S01, the ²⁰⁶Pb/²⁰⁷Pb ratio decreases from 1.181 ± 0.002 in 1916 to 1.166 ± 0.001 in 1952 (with the highest variation occurring between 1916 and 1927). In 1960, the highest Pb concentration is accompanied at the same time by a trend towards a higher ²⁰⁶Pb/²⁰⁷Pb ratio (²⁰⁶Pb/²⁰⁷Pb = 1.173 ± 0.003). This higher ²⁰⁶Pb/²⁰⁷Pb ratio then decreases until 1981 (²⁰⁶Pb/²⁰⁷Pb = 1.1693 ± 0.0015) and increases again (²⁰⁶Pb/²⁰⁷Pb = 1.181 ± 0.003 in 2003) whereas the Pb concentration decreases. Today's lead concentration in the Oise sediment corresponds to 36 mg.kg⁻¹. This value lies close to the geochemical background (27-40 mg.kg⁻¹; Thévenot et al., 2007; Meybeck et al., 2007), while in 1960, concentration up to 342 mg.kg⁻¹ was recorded (see supporting information).

Figure 3.

Table 1

The Seine-Aval combined sewer system at Achères (SIAAP) collects 80% of the urban water originating from the Paris conurbation. The Pb concentration is $0.53 \pm 0.01 \mu\text{g.L}^{-1}$, this is in agreement with the detailed study of the Seine-Aval effluents composition by Buzier et al., (2006). The treated waste water, sampled during December 2006 (rainy period) is characterized by $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$ and may represent a mixture of lead originating from different sources (roof and road runoff, domestic and industrial wastewaters).

4. Discussion.

4.1. Anthropogenic lead sources in the Seine river basin.

Lead was widely used in Paris buildings long before leaded gasoline was introduced. Until now, the city of Paris has accumulated huge amounts of Pb. The accumulated lead stock in the Seine river basin corresponds to 594,000 t from 1940 to 2000 (Thévenot et al., 2007). The major part of the anthropogenic lead stock is distributed as follows: 100,000 t in natural soils, 200,000 t in landfills, 110,000 t in pipes, tubes and roofs, 30,000 t in rivers and estuaries. The remaining 154,000 t are divided between different anthropogenic items (cables, glasses, accumulators, etc). The ability of these materials to contaminate the sediment varies from one material to another. In addition, it may be difficult to attribute a specific Pb signature to each of these items, because different ores and recycled lead may have been used at different period.

During the second part of the 18th century, the majority of all Pb used in France was imported from Spain, French ores played only a minor role (Lestel, 2007). The major part of Pb imported by France from 1900-1914 came from Spain, Belgium-Luxemburg and United Kingdom, Pb extraction in French mines did not play an important role. Between World War 1 and World War 2, Spain, Mexico and Tunisia provided most of the Pb manufactured in France, the proportion of Pb furnished by French mines constantly decreased. After 1945, Pb was mainly imported from Morocco and Tunisia, more recently from the United State of America and the European Union. Today, all manufactured Pb in France originates from recycling.

Pb isotopic signatures in the environment are often interpreted as resulting from the mixing of three end-members: natural, industrial and gasoline Pb. The definition and the characterisation of the local natural and leaded gasoline end-members are rather

straightforward (Table 2). The local natural background signature ($^{206}\text{Pb}/^{207}\text{Pb} = 1.2007 \pm 0.0011$) was determined using a 8000 BP- ^{14}C dated sediment (Elbaz-Poulichet et al., 1986).

The signature of additives for leaded gasoline ($^{206}\text{Pb}/^{207}\text{Pb} = 1.08 \pm 0.02$) was determined based on information from Octel Ltd at Paimboeuf, the only provider of leaded additives for French gasoline (Véron et al., 1999).

Table 2

The determination of the nature and isotopic signature of the “industrial” end-member is more difficult. Industrial lead is characterized by an isotopic composition that is intermediate between the end-members of natural and leaded gasoline ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.146 - 1.162$; Monna et al., 2000; Véron et al., 1999; Widory et al., 2004) but at the same time it is characterized by significantly higher Pb concentrations. Carignan et al. (2005) suggest to use $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.003$ as the best estimate for the average French industrial atmospheric signature emission. Paradoxically, several heavy industries use Pb with isotopic signatures that are quite distinct from the “industrial” Pb signature (Carignan et al., 2005; Nageotte and Day, 1998; Véron et al., 1999). In this section, we discuss the possible sources and characteristics of the so-called “industrial” lead of the Seine basin and we compare it to values from previous studies. While Pb ores with different origins have been used throughout history, some prevailing ore isotopic signatures are relevant (Table 3):

European ores: the isotopic signature of most European ores (including French ores) falls in the range $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.16 - 1.19$. Tunisian ores also lie in this range.

Rio Tinto: The isotopic signature of the Spanish ore ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.1634 \pm 0.0001$; Marcoux, 1998) distinctively falls on the low end of the European signature. Ores from Morocco are characterized by a similar signature.

Broken Hill: this Australian ore (together with other ores) is specifically used for the production of the leaded gasoline additives. Its low isotopic signature ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.040 \pm 0.001$) is due to the old age of the crust from which the ore was formed.

Most ores from North American (Mississippi valley, Mexico) have distinctively higher Pb signatures ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.20 \pm 0.02$; Rabinowitz et al., 2005).

Table 3

B2 and M1 cores

The similarity between the temporal evolution of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of B2 and M1 (Fig.3) indicates that both profiles represent a global signal that characterizes the Pb isotopic signature after Paris and that they are not affected by local effects or sample heterogeneity. The minor difference in the concentration observed in the both profiles can be explained by different clay content (Ayrault et al., 2010).

It is possible to discriminate distinct Pb sources in a diagram where the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is plotted as a function of $1/[\text{Pb}]$ ratio, where $[\text{Pb}]$ is the lead concentration (mg.kg^{-1}). In this diagram, all samples representing a mixing of 2 end-members fall on a straight line (Fig. 4).

Figure 4

Between 1927 and 1968, the lead isotopic signature of B2 and M1 plots in a narrow range that resembles Rio Tinto (and possibly Moroccan) ores, suggesting that these ores represent the most important Pb sources reaching the river. Significant contribution of other European or North American ores would raise the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio above the observed values unless it is exactly compensated by addition of Pb from Broken Hill (see Table 3 for ores isotopic lead signatures). This hypothesis is unlikely because the oldest samples from Muids (1927) preceded the introduction of leaded gasoline (1931) and corresponded to a time when road traffic was marginal. Contamination of the 1930 sediments by younger sediments that come from the leaded gasoline period is unlikely, since:

- the similarity between the ^{137}Cs profile and the ^{137}Cs fallout history precludes mixing of the sediments (both ^{137}Cs and Pb are particle reactive);
- the Pb content is 3-4 times higher in ancient sediments than in the sediments from 1980;
- the *in situ* lead mobility is negligible (Alfonso et al., 2001; Kober et al., 1999).

Therefore the Rio Tinto signature probably represents the main lead contribution to the Seine River basin. This Rio Tinto ore signature may be the best source estimation for Pb that accumulated over centuries in the Seine River basin and may be called “historical” Parisian lead. Around 1850, English companies took the control of the major Spanish mines including Rio Tinto. Spain began to produce large quantities of lead, sold below the price of lead from British mines, the former biggest provider to Europe. From 1878, with the declining ore reserves in Britain, Spain became the major lead producer in Europe (Fletcher, 1991).

Surprisingly, the contribution of Pb from “heavy industries” characterized by a high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio cannot be resolved in the average Seine River basin lead, although it can be

detected locally (i.e., near the Eiffel Tower; Nageotte and Day (1998)). From 1968 to 1986/1989, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreases from 1.165 (Rio Tinto ~ historical Parisian Pb) to 1.145 ± 0.001 (line 1 on Fig. 4). This decrease is clearly coupled with the raise of the leaded gasoline emission in combination with the new environmental regulations which lead to a reduction of other than gasoline anthropogenic lead sources. In 1963, a directive on industrial effluents quality controls was published. Between 1960 and 1980 domestic wastewater treatment plants (WWTP) were gradually implemented. One important WWTP, the Seine-Aval combined sewer system at Achères, was operational at the end of the 70's. In addition to the reduction of industrial effluents, leaded gasoline reduction started in 1986 and leaded gasoline was completely banned after 2000. This mixing of historical Parisian lead with lead from leaded gasoline produces an “urban” lead signature (previously called “industrial”) will be discussed in more details hereafter.

After 1989, the Seine River sediment signature evolves from the urban to the natural end-members (line 2, Fig. 4). Between 2000 and 2003, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the sediment is identical to the 1945-1968 sediments but the low Pb concentration in the 2000-2003 sediments produces a clear trend towards the natural end-member: lead in the Seine River sediment today represents a mixture of “urban” lead and natural background lead produced by soil erosion. The concentrations and isotopic signature observed for the most recent deposits at Bouafles and Muids are in agreement with the data observed at the Seine River mouth for the same period (Milot et al., 2004).

Previous studies have pointed out the decrease of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the time interval between 1900 and 1930 in the Lake Constance sediments (Germany) (Kober et al., 1999), in the French Alps lake sediments (Arnaud et al., 2004) and in the Mont Blanc ice record (Rosman et al., 2000). As in the case of the early signatures in the Seine sediments (M1), this early trend towards low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios cannot be explained by leaded gasoline because leaded gasoline was only introduced on 1931 in France, Italy and Germany. In contrast the increase of industrial Pb uses, combined with the predominant use of Rio Tinto Pb, results in a source of Pb that is characterized by a low $^{206}\text{Pb}/^{207}\text{Pb}$ ratio at the European scale.

TR01 core

The samples (covering the 1970-2002 period) fall on the mixing line between urban lead and natural lead, very similar to the samples B2 and M1 after 1990. They lie closer to the natural end-member than the B2 and M1 samples because Pb contamination was less

significant in this weakly urbanized and industrialized area. Nevertheless, the anthropogenic end-member in Troyes seems to consist of “urban” lead that is also present in B2 and M1.

S01 core

The Oise River had already been strongly polluted in 1916 by heavy industries as indicated by Pb concentrations above the natural background. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio rapidly increases several times and this may be caused by changes of the lead ores used by the industry and/or changes in the industrial activity or recycling. Samples from 1916 to 1952 fall on a mixing line between the natural and the Rio Tinto signature ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1634 \pm 0.0001$). Between 1952 and 1960, there is a clear shift towards higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (~ 1.17) in agreement with the use of European, Tunisian or north American ores together with recycled ores. This isotopic shift is associated with the highest Pb concentration in the core. Subsequently the concentrations decrease. And after 1976, the samples tend to be aligned onto the urban/natural mixing line, similar to the other sites for the last 35 years, suggesting that the industrial source characterized by high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has efficiently been removed.

The implementation of environmental regulations on industrial waste discharge to the river in the 1970's and the decrease of the industrial activity on the Chauny site, associated to the fact that an industrial discharge is a point source that is easier to mitigate than diffuse urban sources, have contributed to improve the quality of the Oise River environment. The Oise River represents a successful example of river resilience towards water pollution.

4.2. Industrial lead signature revisited.

We showed in the previous section that systematic variations of the Pb isotopic signature occurred over the last 75 years in a large urbanised river basin. Until now, these changes were not observed because suitable archives were lacking. Our investigation sheds new light on the “industrial” lead signature. Until now the industrial lead signature in France was estimated based on untreated and treated urban wastewater from South France (Monna et al. 2000) and urban incinerators (Cloquet et al., 2006; Widory et al., 2004) that were collected between 1992 and 2001. The observed signatures in this study range from $^{206}\text{Pb}/^{207}\text{Pb} = 1.146$ up to $^{206}\text{Pb}/^{207}\text{Pb} = 1.162$. Over this short time span and for these very different sites, the scattering of the data was so high that no significant temporal evolution could be resolved. The significantly lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for indoor Parisian dust (1971-1981) and roadside

atmospheric particles (1974): 1.120 ± 0.001 and 1.101 ± 0.001 , respectively, registered by Elbaz-Poulichet et al. (1986) are probably due to sample contamination by leaded gasoline.

Considering that Pb rejected by the waste water treatment plant (WWTP) directly enters the river and that the waste waters combine most contaminant sources of lead for the river (roofs, pipes, accumulators, and oxide-containing glasses), the signature of the waste waters constitutes the urban lead signature for the river sediments. Indeed the urban lead signature defined by the isotopic signature of the WWTP Seine –Aval at Achères sewage ($^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$) is not significantly different from the signature of the three major Parisian municipal solid waste incinerators (1.1550 ± 0.0005 ; Widory, 2004), the leaded paint chips and the tap water contaminated by lead pipes (Table 2).

The urban signature measured nowadays after the complete stop of leaded gasoline in 2000 ($^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$) is significantly different from the measured signature in the Seine sediments before 1960 ($^{206}\text{Pb}/^{207}\text{Pb} = 1.167 \pm 0.002$). This suggests that leaded gasoline created an “in-depth” contamination of the environment. As argued in the previous sections, the lead accumulated in the Parisian conurbation is largely dominated by the Rio Tinto ores signature. This domination is enforced by recycling. The contribution of recycled lead in manufacture is significant in France: 50% in 1950 increasing to 70% in 2000 (Lestel, 2007). Today all manufactured Pb that is used in France comes from recycling. The large amount of lead accumulated in the urban structures tends to buffer the isotopic signature in the river which is marginally shifted by the leaded gasoline in depth imprint.

The “industrial lead” denomination is ambiguous because several heavy industries in the Seine basin and in France show Pb isotopic signatures that are distinct from the “industrial Pb” (see section “TR01 core”). The lead signature of the Oise river sediment, directly issued from industrial activities, is quite distinct ($^{206}\text{Pb}/^{207}\text{Pb} = 1.174 \pm 0.003$). Therefore the denomination “industrial” attributed to all the signatures but gasoline additives may be abusive. In order to prevent any confusion, we use the term “urban” ($^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$) for the most common Parisian Pb signatures and “heavy industries” for the relevant industries.

4.3. Impact of leaded gasoline of the Seine sediment contamination.

The leaded gasoline represents a small part of the total Pb used in France (5% in the early 1970’s: 14,000 t for leaded additives over 271,000 t in total in 1974) (Meybeck et al,

2007). At the same time leaded gasoline represents almost 90% of the anthropogenic atmospheric lead emission (Ferrand et al., 1999), thus raising the possibility that the Seine river catchment suffers from a wide contamination by road traffic. The present data can be used to evaluate the contribution of the leaded gasoline to the Seine contamination.

The maximum impact of the leaded gasoline in the Seine sediment contamination was reached in 1986/1989 (Fig. 3), when the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was at its lowest value (1.146 ± 0.002). Considering that the lead was a mixture of leaded gasoline ($^{206}\text{Pb}/^{207}\text{Pb} = 1.08 \pm 0.02$) and historical lead whose signature is defined by the oldest sedimentary deposits ($^{206}\text{Pb}/^{207}\text{Pb} = 1.165 \pm 0.002$ in 1943 (B2)), as shown by the mixing line 1 on Fig. 4, the fraction of lead issued from the gasoline (f_{gasoline}) in the Seine River sediments is given by Equation 1:

$$f_{\text{gasoline}} = \frac{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{sample}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{historical}}}{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{gasoline}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{historical}}} \quad (\text{Eq. 1})$$

From Eq. 1, we calculate that the fraction of lead issued from the gasoline in the Seine River sediments is $23 \pm 6 \%$ when the impact of the leaded gasoline is on the climax. The choice of the value for the “urban” signature strongly affects the calculated Pb fraction originating from gasoline. If we had assumed as in previous studies, that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the urban/industrial end-member is 1.155, the calculated contribution of leaded gasoline would have been only $13 \pm 4 \%$.

In any case, the contribution of leaded gasoline to the Seine basin is significantly more important than its contribution to the lead used in France in 1986 (<5% in Lestel, 2007). This implies that Pb from leaded gasoline has a larger environmental mobility than other Pb sources. This is consistent with sequential extraction experiments on soils and soakaway sediments (Kumar et al., 2009). This is not surprising because Pb from combustion of leaded gasoline is directly emitted in the atmosphere whereas the other sources of lead tend to be stored or recycled rather than being directly dispersed into the environment.

Although Pb from leaded gasoline is preferentially transported by the Seine River compared to other sources, it does not represent the majority of the lead present in the sediments. As discussed in more detail in section 4.2., important stocks of Pb have been

accumulated in the Paris conurbation (soils, buildings, pipes) and their slow release in the environment produces most of the Pb contamination. Leaks also occur in rural areas. The residence time of particles on soil reaches up to 30,000 years at Andrésy, a site located between the Seine-Aval WWTP and Bouafles (Le Cloarec et al., 2007). The strong affinity of Pb for organic matter is responsible for atmospheric lead immobilisation on the uppermost soil layer (Kabata-Pendias and Pendias 1992). Much shorter residence time is found for particles on non-permeable soils, because of runoff washing out.

The stock of anthropogenic lead in the soils of Paris area is estimated to lie close to 143,000 t (Saby et al., 2006). This stock includes the fallouts issued from the leaded gasoline combustion. Therefore, most Pb issued for the leaded gasoline combustion did not (yet) reach the river. The lead issued from gasoline that is seen in the Seine sediment around 1986 was probably brought to the river by road and roof runoff. The direct contamination of Pb from leaded gasoline in the atmosphere compared to the other sources of Pb also explains that the fraction of Pb from leaded gasoline is lower in the urban lead characterised in the hydrosystem ($^{206}\text{Pb}/^{207}\text{Pb} = 1.146 \pm 0.002$) than in Parisian aerosols samples approximately at the same period ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1187 - 1.1260$ in 1989; Véron et al., 1999).

4.4. Lead sources today.

Since runoff has probably washed out the labile lead source (i.e., the lead-contaminated particles on non-permeable surfaces) and since the direct inputs of lead from the heavy industries are very low, the lead concentration today in the Seine river sediments represents a mixture of natural and urban lead (line 2 in Fig. 4). Considering the respective signature of the natural lead ($^{206}\text{Pb}/^{207}\text{Pb} = 1.2007 \pm 0.0011$) and the signature of urban lead ($^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$) (line 2 in Fig. 4), we calculate that the lead today ($^{206}\text{Pb}/^{207}\text{Pb} = 1.166 \pm 0.004$) is constituted of 30% of natural lead and 70% of urban lead. This result is compatible with the concentration data, as the natural background concentration is 27-40 mg kg⁻¹ and the total lead sediment concentration is 77 mg kg⁻¹. If the Pb concentration in the urban end-member is much higher than in the natural one, it corresponds to 34% of natural lead and 66% of urban lead. Moreover, these findings are also consistent with the study by Thévenot et al. (2007). These authors evaluate the sources and pathways budget for seven metals including lead in the Seine River basin for the period, 1994 – 2003. The total lead inputs to the river reached 65 t y⁻¹, 14 t y⁻¹ come from erosion (22%). The anthropogenic

sources of lead to the river (51 t y^{-1}) are mainly located in urban areas (48 t y^{-1}). Thévenot et al. (2007) estimated urban sources to contribute to 74% of the lead input to the river, the urban contribution corresponds to 70% as deduced from the isotopic data.

5. Conclusion.

Most studies on the Pb isotopic signature in the Paris area or in France have focussed until today on aerosols, incinerator fumes and waste water treatment plants sewage collected between 1970 and 2005. The present study provides the first continuous record of the Pb isotopic signature for the Paris conurbation between 1930 and 2003. These are the first records that monitor the temporal evolution of riverine Pb contamination in a large urbanised area. In particular, this study allows us to characterize the average isotopic signature of Pb accumulated in the Paris conurbation until 1960 during the “pre-leaded gasoline” period, hence defining the reference value that is used to determine the contribution of leaded gasoline after 1960. This average pre-gasoline signature corresponds to the Rio Tinto ore that has been highly exploited since the middle of the 19th century. As a result, we show that during the 1980’s, the contribution of leaded gasoline to the Seine River contamination (around 24%) exceeds by far the contribution of the leaded gasoline additives use to the global flux of Pb entering the Seine basin (5% or less). Therefore, the information brought by the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio will contribute to reevaluate and improve the Pb fluxes in the Seine River basin.

The impact of this study goes far beyond the Seine River basin. As the Rio Tinto ore has a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio that is lower than most lead ores used in Europe earlier than 1800, increasing use of the Rio Tinto ore during the 19th century could account for the general decrease of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio during the 19th and early 20th century that is observed in various European archives (ice core, lake sediments, peat bog) which remained unexplained until now because it occurred before the “leaded gasoline era”.

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571 In Supporting Information are reported the lead concentration and lead isotope composition
572 for the four cores.

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Tables

Table 1. Details on the four analysed cores sampled in the Seine River basin.

Table 2. $^{206}\text{Pb}/^{207}\text{Pb}$ signature of samples issued from the Seine River basin.

Table 3. $^{206}\text{Pb}/^{207}\text{Pb}$ signature of lead in ores potentially imported by France from 1900 to today.

Figures

Figure 1. Core sampling sites (black circles) in the Seine River basin. The major waste water treatment plant (WWTP) Seine Aval at Achères, downstream Paris, is indicated with a black square. The lined area represents the Paris conurbation that concentrates 80% of the Seine River basin population (14 million inhabitants).

Figure 2. Lead isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$) by thermal ionisation mass spectrometry (TIMS) and inductively coupled plasma – mass spectrometry (ICP-QMS) in three sediment samples (2 σ error bars).

Figure 3. Lead concentration and isotope ratio in the dated depth profiles in four cores in the Seine River basin.

Figure 4. Evolution of the lead isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$) in the Seine River basin sediment: influence of geochemical background, leaded gasoline and heavy industries.

Figure

Figure

Figure 2. Lead isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$) by thermal ionisation mass spectrometry (TIMS) and inductively coupled plasma – mass spectrometry (ICP-QMS) in three sediment samples (2σ error bars).

Figure

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Figure

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Table 1. Details on the four analysed cores sampled in the Seine River basin.

	Upstream Seine	Oise river	Downstream Seine	
Core reference	TR01	S01	B2	M1
More recent strata	2002	2005	2003	2003
More ancient strata	1970	1915	1948	1934
Sedimentation rate (cm yr ⁻¹)	2.6 ^a	1.1 ^b	1.1 ^b	1.8 ^b
Lead concentration peak(s) date(s)	1976; 1990	1960	1963; 1994	1938; 1960
Lead concentration determination techniques	AAS	ICP-AES	AAS & ICP-MS	
Population (1940)	130,000	240,000	9,000,000	
Population (2000)	180,000	260,000	14,000,000	

^a ²¹⁰Pb-based chronology; ^b ¹³⁷Cs-based chronology. AAS: atomic absorption spectrometry; ICP-AES: inductively coupled plasma – atomic emission spectrometry; ICP-MS: inductively coupled plasma – mass spectrometry

Table 2. ²⁰⁶Pb/²⁰⁷Pb signature of samples issued from the Seine River basin.

Sample	Sampling date / sample age	²⁰⁶ Pb/ ²⁰⁷ Pb	Reference
Geochemical background	8000 BP	1.2007 ± 0.0011	Elbaz-Poulichet et al. (1986)
Road dust (suburbs)	1978	1.101 ± 0.001	id
Indoor dust (Paris)	1971 – 1981	1.120 ± 0.001	id
Street dust (Paris)	1997	1.151	Nageotte and Day (1998)
Eiffel tower paints	1997	1.174	id
Municipal solid waste incinerators	2001	1.1550 ± 0.0005 ^a	Widory (2004)
Urban heating plants (Paris)	2003		
burning oil		1.11	id
burning gas		1.14 – 1.20	id
Leaded gasoline	1980 - 1987	1.10 ± 0.04	Véron et al. (1999)
	1987-1992	1.08 ± 0.03	id
	1993	1.09 ± 0.02	id
	1994-1995	1.06 ± 0.02	id
Unleaded paints ^b	>> 1940	1.1534 ± 0.0066	Laurenst (2001)
Leaded paints ^b	< 1940	1.1596 ± 0.0023	id
Tap water (presence of lead pipes, [Pb] = 25 µg/L)	1996 – 1998	1.1561 ± 0.0031	id
Urban waste waters (combined sewer)	2006	1.154 ± 0.002	This work

^a Average of 3 Parisian incinerators (Issy, Ivry-sur-Seine, Saint Ouen).

^b Professional use of leaded paint in France was banned in 1926. In-house uses of leaded paints were banned in 1993, while ceruse was progressively replaced with titanium oxides since 1940. A lead diagnostic is mandatory to sell or rent any inhabitation built before 1949.

Table 3. ²⁰⁶Pb /²⁰⁷Pb signature of lead in ores potentially imported by France from 1900 to today.

	²⁰⁶ Pb/ ²⁰⁷ Pb	Reference
Belgium	1.16 -1.18	De Vleeschouwer et al., 2007 Dejonghe et al., 1989
Germany		
(Harz Mountains)	1.178 ± 0.004	Alfonso et al., 2001
(Rammelsberg)	1.164 – 1.169	"
(Rheinisches Schiefergebirge)	1.159 – 1.185	Krahn and Baumann, 1996
(North Eifel and North Sauerland)	~1.17	Large et al., 1983
Spain		
(Mazarrón, Cartagena)	1.191 – 1.195	Arribas and Tosdal, 1994
(Rio Tinto)	1.1633 – 1.1635	Marcoux., 1998
France		
(L'Argentière)	1.1701	Arribas and Tosdal, 1994
(La Maligne)	1.1742	Arribas and Tosdal, 1994
United Kingdom		
(Mendips)	1.176 – 1.189	Alfonso et al., 2001
(Debyshire)	1.171 – 1.188	"
Mexico	1.200 ± 0.006 (n=48)	Cuming et al., 1979
Tunisia	1.1971 ± 0.0045 (n=11)	Sahnoun et al., 2009
Morocco	1.1638 ± 0.0071 (n=30)	"
USA (Mississippi valley-type deposits)	> 1.2	Deloule et al., 1986 ; Kesler et al., 1994
Australia (Broken Hill)	1.0412 ± 0.0011	Townsend et al. 1998