Remanence of lead pollution in an urban river system : a multi-scale temporal and spatial study in the Seine River basin, France

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S. Ayrault[1,*], P. Le Pape[1,2,$], O. Evrard[1], C. R. Priadi[1,3], C. Quantin[2] and P. Bonté[1,] M. Roy-Barman[1]

[1] Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), UMR 8212 (CEA/CNRS/UVSQ), Domaine du CNRS, Avenue de la Terrasse, bat 12, 91198 Gif-sur-Yvette, France

[2] Interactions et Dynamique des environnements de Surface (IDES), UMR 8148 (UPS - CNRS), Bâtiment 504, Campus universitaire d'Orsay, 91405 Orsay Cedex, France

[3] Civil Engineering Department, Engineering Faculty, Universitas Indonesia, UI Depok Campus, Depok 16424, Indonesia

$ Present address: Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC), UMR 7360 CNRS, Université de Lorraine, Pôle de l'eau, Avenue du charmois, 54500 Vandoeuvre les Nancy, France

*Corresponding author: Dr Sophie Ayrault (Tel. +33 1 69 82 43 54, Fax +33 1 69 82 35 68, E-mail address: sophie.ayrault@lsce.ipsl.fr).

Abstract

Total lead (Pb) concentration and Pb isotopic ratio ($^{206}Pb/^{20}7Pb$) were determined in 140 samples from the Seine River basin (France), covering a period time from 1945 to 2011 and including bed sediments (bulk and size fractionated samples), suspended particulate matter (SPM), sediment cores, and combined sewer overflow (CSO) particulate matter to constrain the spatial and temporal variability of the lead sources at the scale of the contaminated Seine River basin. A focus on the Orge River sub-catchment, which exhibits a contrasted land-use pattern, allows documenting the relation between hydrodynamics, urbanization and contamination sources. The study reveals that the Pb contamination due to leaded gasoline that peaked in the 1980s has a very limited impact in the river nowadays. In the upstream Seine River, the isotopic ratio analysis suggests a pervasive contamination which origin (coal combustion and/or gasoline lead) should be clarified. The current SPM contamination trend follows the urbanization/industrialization spatial trend. Downstream of Paris, the lead from historical use originating from the Rio Tinto mine, Spain ($^{206}Pb/^{207}Pb = 1.1634 \pm 0.0001$) is the major Pb source. The analysis of the bed sediments (BS) (bulk and grain size fractionated) highlights the diversity of the anthropogenic lead sources in relation with the diversity of the human activities that occurred in this basin over the years. The "urban" source, defined by waste waters including the CSO samples ($^{206}Pb/^{207}Pb = 1.157 \pm 0.003$), results of a thorough mixing of leaded gasoline with "historical" lead over the years. Finally, a contamination mixing scheme related to hydrodynamics is proposed.

Keywords: suspended particulate matter, lead isotopes, sewer overflow, urban lead, sediment cores

1. Introduction

Lead (Pb) is a problematic metallic contaminant in numerous river systems across the world (Kachur et al., 2003; Sun et al., 2011; Grosbois et al., 2012). Reconstructing the history of Pb contamination and quantifying the dynamics of Pb transport in river systems is important to design appropriate remediation policies and evaluate their environmental impact. The historical record of Pb contamination in river sediments may be accessed by dating and analyzing sediment cores collected within floodplains (Alfonso et al., 2001; Ayrault et al, 2012). In addition, the comparison of lead concentrations and lead isotopic ratios along the entire sediment sequence may provide powerful constrains on the evolution of natural and anthropogenic sources that supplied Pb to the river throughout time (Monna et al., 2000; Shotyk et al., 1998). However, extrapolation of floodplain data to the whole river system is not straightforward because of several problems detailed hereafter. Fine particles that deposit in floodplains may differ in Pb concentration and isotopic composition from coarse bed sediment particles that may represent a large fraction of the river particulate flux (Horowitz and Elrick, 1987; Stone and Droppo, 1996). Moreover, fine particles collected in floodplains during a short time period (i.e., during high water stages) may not be representative of the average fine particles transported by the river.

Therefore, the relevance and/or the impact of those potential biases must be evaluated to strengthen the understanding of Pb behavior in river systems. In the present study, we focus on the Seine River system (64,700 km²) which is highly impacted by Pb contamination (Meybeck et al., 2007, Ayrault et al., 2012). The Seine catchment is affected by very high anthropogenic pressures and is characterized by a very limited dilution of metallic contaminants due to the low suspended matter concentrations prevailing in the Seine River waters. As a consequence, the Seine Basin is structurally fragile and its river course, downstream of Paris megacity, has been and is still ranked among the world's most contaminated rivers (Meybeck et al., 2007). Indeed, cores collected within a floodplain located downstream of Paris revealed high levels of contamination (Pb up to 400 mg/kg) between 1920s and 1960s followed by a decrease in Pb

concentrations since 1960. In 2003, Pb concentrations (Pb ≈ 50 mg/kg) were still significantly above the estimated geochemical background (Pb ≈ 20 mg/kg, Thévenot et al., 2007). The contribution of three main sources that may be used as « end-members » in mixing models (Ayrault et al., 2012) has been previously identified based on the use of stable Pb isotopes (a full literature review can be found in Komarek et al., 2008). (1) The local natural background signature ($^{206}Pb/^{207}Pb = 1.2007 \pm 0.0011$) was determined using a 8000 BP-^{14}C dated sediment (Elbaz-Poulichet et al., 1986). A very similar value ($^{206}Pb/^{207}Pb = 1.2035$) was obtained in an undisturbed C soil horizon developed in loess deposits collected next to the Chateau de Versailles gardens (Semlali et al., 2004). Those soils are widely found in the Seine River watershed, particularly in its downstream part. (2) The lead from historical (hereafter called "historical" Pb) originating from the Rio Tinto mine in Spain ($^{206}Pb/^{207}Pb \approx 1.1634 \pm 0.0001$; Marcoux, 1998) that has accumulated in the Seine basin since the 19th century at least (Ayrault et al., 2012). (3) Pb used in additives to gasoline ($^{206}Pb/^{207}Pb = 1.08 \pm 0.02$), that contain high proportions of Australian lead from the Broken Hill mine ($^{206}Pb/^{207}Pb \approx 1.040 \pm 0.001$) ; this latter signature was determined based on information from Octel Ltd at Paimboeuf, which was the single provider of leaded additives for French gasoline (Véron et al., 1999). A fourth source of lead to Parisian soils, coal combustion, has been evidenced by Semlali et al. (2004) ($^{206}Pb/^{207}Pb \sim 1.183$) but was not detected by Ayrault et al. (2012) in the downstream core sediments.

Over the years, mixing between "historical" and "gasoline" Pb have yielded a composite "urban" Pb signature ($^{206}Pb/^{207}Pb = 1.154 \pm 0.002$), as determined by analyzing waste water treatment plant (WWTP) effluents collected in 2006 (Ayrault et al., 2012). Owing to this mixing, the "urban" end-member is supposed to vary in both space and time, in particular because of the prohibition of gasoline leaded additives in 2000. However, despite their sampling during different campaigns and the different nature of the analyzed urban wastes (liquid/solid), the WWTP signature did not significantly differ from the signature of the three major Parisian municipal solid waste incinerators in 2001 (1.1550 ± 0.0005; Widory, 2004). It appeared therefore necessary to constrain the evolution of the "urban" Pb signature at different scales

within the Seine River basin.

Previous work showed a significant decrease in the gasoline-originated lead contribution to the Seine River sediment contamination from 1986 to 2003 due to the implementation of regulations on the use of leaded gasoline additives and their subsequent ban in 2000 (Ayrault et al., 2012). In this context, Pb found in the Seine River is dominated by a mixing between urban lead (coinciding with high lead concentration) and natural lead (coinciding with low lead concentration). Similar trends were observed in the very urbanized Orge River subcatchment (1300 km²) (Le Pape et al., 2013).

Atmospheric Pb deposition across the Seine River basin was estimated to vary between 2000 (1994-2003; Thévenot et al., 2007) and 2900 $t.y^{-1}$ (1955-2004; Saby et al., 2006), whereas the Pb emissions were estimated to 2700 $t.y^{-1}$ (1955 to 2004, considering that the Seine River basin contributes to 30% of the total French emissions; Pacyna and Pacyna, 2000). In addition to the Pb accumulation in soils, a large urban stock of Pb exists in the region. Thévenot et al. (2007) constructed the Pb budget at the scale of the Seine River basin. They concluded that a huge amount (594,000 t) of Pb has accumulated since centuries in Paris megacity because of its use in roof covers, pipes, cables shielding, oxide containing glasses, etc. These stocks show different environmental behaviors and lifetimes.

Pb-bearing soil particles may be delivered to the rivers during erosion events. The Seine River basin is affected by low to moderate soil erosion rates, which is reflected by mean exports estimated to 10 $t.km^{-2}.y^{-1}$ (Meybeck et al., 1998). The residence times of particles in soils are long (5000–40,000 yrs depending on their location within the catchment). In contrast, the residence time of the particles within the river is much shorter (180–500 days) Altogether, those findings led us to investigate whether gasoline-originated lead could have been completely washed out from the Seine River basin since their ban in 2000. The complete flush of the gasoline-lead bearing particles would then provide an original and alternative method to evaluate the sediment turnover of the river.

We propose to compile Pb elemental and isotopic data collected on different material types (i.e. suspended particulate matter, riverbed sediment, overflow plain sediment) along a network of

nested stations to document the processes occurring at different temporal scales (flood, seasonal, annual, decadal) and at two catchment scales: Seine (64,700 km²) vs. Orge (1300 km²). However, owing to evident logistical and analytical constrains, it was not possible to conduct such a detailed study compiling Pb data measured in all sediment types (suspended particulate matter (SPM), bed sediment (BS)) and taking into account the different hydrological stages throughout the year at the scale of the entire Seine River basin. We therefore focused a significant part of the sampling effort on the Orge River basin (1300 km²), which drains into the Seine River just upstream of Paris, because its land uses are characterized by a gradient of increasing anthropogenic influence along its course, from headwaters dominated by forests and cropland to its junction with the Seine River where its flows across densely inhabited areas (Le Pape et al., 2012). Detailed investigation of the processes occurring in this catchment will provide important insights on the role of river hydrodynamics and provide a way to better constrain the relative contribution of pollution sources in space and time (Le Pape et al., 2013). We will finally attempt to extrapolate the conclusions drawn from the Orge River study to the entire Seine River basin.

2. Materials and Methods

2.1. Study sites

All sampling sites were located in the Seine River basin (Fig. 1), a sedimentary basin situated in the north of France, and flowing across the Greater Paris Region. This river drains an area of 64,700 km^2 characterized by a mean population density of 215 inh./km^2, and constitutes therefore an ideal example of highly urbanized basin as it accounts for 25% of French agriculture, 30% of the country's industry and 23% of its population. The Orge River subcatchment is located in the upper part of the Seine River basin, and drains an area of 1300 km^2 with a population density ranging between 200 inh./km^2 in upper parts to 8000 inh./km^2 close to the junction with the Seine River.

Figure 1

2.2. Sampling

All the sample locations and collection periods are detailed in Table 1.

Table 1

2.2.1. Suspended sediment from the entire Seine River basin

At the scale of the whole Seine River basin, the sampling scheme aimed to distinguish the impacts of two anthropogenic sources on the Seine River (Priadi et al., 2011a). The first source is diffuse and coincides with the area of Greater Paris itself, including the most densely urbanized area with more than 3700 inh./km^2. Treated municipal wastewater from small treatment units and urban runoff are the major sources identified as supplying metal to the river in this area (Thévenot et al., 2007). The second source is point-based, and coincides with the Seine-Aval wastewater treatment plant (WWTP) treating around 1.7 million m^3 per day and located 30 km downstream of Paris. Therefore, the first sampling site was located at Marnay-sur-Seine, in upper parts of the Seine River catchment (Priadi et al. 2011b, and Fig.1). It was chosen as being representative of a site unaffected by the Greater Paris region where the population density is only 15-30 inhabitants/km^2. The second site is located at Bougival, 40 km downstream of Paris city (Strahler order 7). It was chosen to study the impact of Greater Paris just upstream of the Seine-Aval WWTP effluent outflow. A third site, located 40 km further downstream, at Triel-sur-Seine, was selected to take the additional inputs of this WWTP into account. The Triel station is situated downstream of the junction between the Seine River and one of its major tributaries, the Oise River. SPM sampling was performed in sediment traps collected monthly from October 2008 to October 2009.

2.2.2. Riverbed sediment (BS) from the entire Seine River basin

Riverbed sediments were collected in the framework of the National River Network (sampling operated by the Service Navigation de la Seine (SNS)) in 2007-2009, at a succession of sites within Paris as well as along the 10-km river section located just downstream of Paris.

2.2.3. Combined sewer overflow (CSO) sampling.

Details on the CSO sampling are given in Passerat et al. (2011). The CSO occurred in August 2008, during a summer storm that affected Paris. It lasted for 6 h (from 5:50 a.m. to 11:50 a.m.) and resulted in the discharge of ca. 600,000 m^3 of untreated urban waste water into the Seine River. Twelve successive samples were collected automatically in the CSO, each sample being a time-proportional composite of the waters discharged during a 30-min period. The analyses of each sample allowed to apportion the volume of domestic waste water and the runoff over the CSO duration. In parallel, the plume impacted by the CSO was sampled four times during its flow from the release point to a distance of 20 km.

2.2.4. Sediment sampling in the Orge subcatchment

Sampling campaigns were performed in 2001 and in 2010/2011 along the Orge River, including two of its tributaries, to exhibit spatio-temporal trends of urban contamination at the scale of this small but densely populated catchment (Le Pape et al., 2012). Sampling sites were selected to document the urbanization and land use gradients: upstream sites in forests and agricultural areas "D" (for Dourdan) and "C" (for Saint Chéron), the sites "R" (for Rémarde) and "E" (for Egly) considered to be under a slight urban influence, and the most urbanized downstream sites "L" (for Longpont-sur-Orge), "Y" (for Yvette) and "V" (for Viry-Chatillon). The bed sediments sampled in the Orge River (10 uppermost cm) during the 2010/2011 campaigns were frozen and quickly freeze-dried. For the third campaign (April 2011), 10 to 15 g of each bed sediment sample were sieved using deionized water and separated into three grain size fractions: > 200 µm, 200 µm > X > 63 µm, and < 63 µm. Each recovered fraction composed of water and sediment was then dried at 40°C in an oven. After drying, the mass of each fraction was measured and compared to the initial mass of sediment sieved to calculate the contribution (% mass) of each grain size in the samples.

Chemical and lead isotopes analyses were finally carried out on one crushed gram of each grain size fraction, following the methods described in sections 2.3 and 2.4.

2.3. Elemental determination

The Seine River and Orge River SPM and BS samples were totally digested according to the procedures described in Priadi et al. (2011b) and Le Pape et al. (2012). In brief, the total digestion step was conducted in PTFE closed flasks, on a digestion block (Digiprep, SCP Science) by successive additions of concentrated ultra-pure acids (HCl, HNO_3, HF, and $HClO_4$).

The solutions were evaporated to dryness, retaken 3 times in 2 mL of HNO_3 and then diluted with 50 mL of MilliQ water. The elemental content was analyzed by inductively coupled plasma – mass spectrometry ICP-MS (XII CCT series, Thermo Electron), according to the procedures referred to above. The Seine River cores samples analyses were described in Ayrault et al. (2012). The data quality of the elemental concentration determination was controlled with the reference material IAEA-SL-1 (lake sediment), provided by the International Atomic Energy Agency, Vienna. The values obtained with this procedure were in good agreement with the certified values. The uncertainties of the determination of Pb and Al concentrations discussed in the present paper were 5% and 14%, respectively.

2.4. Lead isotopes ratio determination.

Lead isotope ratios ($^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$) were measured in the same solutions as for elemental concentration determinations, after appropriate dilution, using a ICP-QMS (X Series, ThermoElectron, France), following the procedure detailed in Ayrault et al. (2012). 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 was analyzed every three samples. SRM-981 was also repeatedly analyzed as a sample to control the bracketing correction. Certified values for the SRM-981 are $^{206}Pb/^{207}Pb = 1.09333 \pm 0.00039$. The figure of merits for the Seine River core samples and the Orge River SPM are in Ayrault et al. (2012) and Le Pape et al. (2013), respectively. For the Orge River bulk and sieved BS analyses, the ratio was $^{206}Pb/^{207}Pb = 1.0933 \pm 0.0025$ (n=14). For the Seine River BS and trapped SPM analyses, the measured ratio were $^{206}Pb/^{207}Pb = 1.0933 \pm 0.0018$ (n=4) and $^{206}Pb/^{207}Pb = 1.0929 \pm 0.0027$ (n=19), respectively.

2.5. Enrichment factor

The lead concentrations in the SPM are expressed as an enrichment factor (EF) calculated in reference to the local geochemical background and normalized by the SPM aluminum (Al) contents with the following background concentrations: Pb = 20 mg/kg (Meybeck et al., 2004;

Thévenot et al., 2007) and background Al = 36 g/kg (Thévenot et al., 2007), (Eq. 1). The 20 mg/kg value may be overestimated, due to the anthropogenic disturbance of the watershed and the difficulty to sample pristine sediment. The systematic analysis of the various lithologies found in the Seine River would be necessary to confirm the relevance of this value, as proposed by Reimann and de Caritat (2005). Similar limitations could be drawn on Al background concentration that may be underestimated in the upstream part of the catchment and particularly in the crystalline Yonne River subcatchment, whereas it may be overestimated in the downstream part of the catchment after the confluence with the Marne River draining carbonate-rich substrates/rocks. The EF of the Bouafles sediment core were calculated using scandium (Sc) instead of Al, considering the background value of Sc = 11 mg/kg (Ayrault et al., 2010).

$$EF\ (Pb) = \frac{\frac{[measured\ Pb]}{[measured\ Al]}}{\frac{[background\ Pb]}{[background\ Al]}} \quad \text{(Eq. 1)}$$

3. Results

3.1. Pb concentration

In the Seine River, Pb concentration ranged from 75 to 282 mg/kg in the bed sediments (BS) (Table 2) and from 18 to 245 mg/kg in the SPM (Table 3). These concentrations remained generally consistent with those measured in the TR01 upstream core (40-90 mg/kg; Ayrault et al., 2012). The downstream cores B2 and M1 exhibited much higher concentrations in the SPM deposited prior to 1970 (up to 460 mg/kg). Overall, there is a Pb concentration gradient increasing from the upstream areas, i.e. with low urbanization/industrialisation and low Pb content, to the downstream areas, i.e. with high urbanization/industrialisation and high Pb concentration. Extremely high Pb concentrations are obtained in the CSO samples (Pb= 244-948 mg/kg) and in the CSO plume generated in the Seine River (Pb= 175-407 mg/kg) (Table 4). The EF ranged from 1 in the less urbanized/industrialized area (Marnay) to 3-11 in most urbanized/industrialized area and to 4-22 in the “dirty water plume”. It even peaked up to 54-105 in the CSO samples.

Tables 2, 3 and 4

The Pb content in the Orge River BS ranged from 15 to 83 mg/kg in the bulk bed sediments and remained much lower than in the SPM collected at the same locations (Table 5). There was no increase in the BS Pb concentration along the urbanization gradient. For SPM, the correlation is only valid during high water periods. In the case of the size fractionated bed sediments of the Orge River, the range of Pb concentration was somewhat larger (10 – 110 mg/kg), but remained in the same order of magnitude.

Table 5

3.2. $^{206}Pb/^{207}Pb$ ratio

The $^{206}Pb/^{207}Pb$ ratio measured in most of the Seine River (SPM and bed sediments) and Orge River basins (bed sediments) ranged from 1.15 to 1.18. Only one sample of bed sediment collected in the Seine River had a $^{206}Pb/^{207}Pb$ ratio as low as 1.138 ± 0.002. In the Seine River, there is a rough correlation between the degree of urbanization/industrialization of the area sampled and the $^{206}Pb/^{207}Pb$ ratio measured in the SPM and the bed sediments. Hence, the study of Seine River SPM collected each month in sediment traps (2008-2009) showed an upstream-downstream trend with a signature decreasing from 1.175± 0.003 for the most upstream site to $^{206}Pb/^{207}Pb$ = 1.1627 ± 0.0025 (n=9 site T)in the most downstream section of the Seine River. The signature of this site sampled over one hydrological year fits well with the signature determined in the upper section of the cores, corresponding to sediment deposited in 2003. We can therefore conclude that the signature derived from the dated floodplain cores is representative of the average annual signature of the SPM.

Figure 2.

In contrast, the study of the Seine River bed sediment showed variable signatures (from $^{206}Pb/^{207}Pb$ = 1.138 ± 0.003 to 1.165 ± 0.002) coupled to very variable lead contents. Among the 7 samples studied here, two sites have been sampled twice (yearly sampling during low waterflow), exhibiting significant variation between samples (e.g., at site Sar, $^{206}Pb/^{207}Pb$ = 1.163 ± 0.002 and 1.158 ± 0.003, in 2008 and 2009, respectively; Table 2). Above all, the bed sediment collected at Colombes in August 2009 combines the highest lead content being and the highest gasoline lead contribution to the isotopic ratio. After removing this point from further analysis, the bed sediments collected between 2007 and 2009 at locations close to the Bougival

site had an average isotopic signature of $^{206}Pb/^{207}Pb = 1.163 \pm 0.003$ (n=6), close to the trapped SPM at site B ($^{206}Pb/^{207}Pb = 1.161 \pm 0.002$, n=8). This indicates that both SPM and bed sediment are associated with similar sources, but that bed sediment composition may be punctually affected by local releases or river hydrodynamic changes. SPM and riverbed sediment may be submitted to differential transport processes (Chon et al., 2012).

In the Orge River, the lead signature of the BS remained close to that of the SPM. Surprisingly, BS collected during high waterflow exhibited a Pb signature close to the one of urban lead at all sites including the less urbanized one, whereas those collected during low waterflow were characterized by a dominance of the natural source signature (Fig. 3). The lead isotopic signature ($^{206}Pb/^{207}Pb$) measured in SPM collected in 2010/2011 was significantly higher than the one measured in material sampled in 2001, and was closer to the natural lead signature. On the contrary, there was no significant difference in the isotopic signature of SPM collected under low and high waterflows (Fig. 3).

Figure 3

4. Discussion

4.1. Temporal variability of lead sources in the Seine River

During most of the 20th century, Pb found in the Seine sediments originated from the huge amount of this metal that has accumulated in Paris since the 19th century (in painting, roof single elements, …) and coming ultimately from the Rio Tinto mine. At the end of the 20th century, the isotopic composition of the downstream sediment core showed that "gasoline" Pb supplied up to 20% of the Pb contained in the Seine River sediment, with a peak around 1986 (Ayrault et al., 2012). "Gasoline" Pb was over-represented in the Seine River sediments compared to other possible sources/stocks, most likely because it was emitted directly to the atmosphere and often deposited in urban areas where it was rapidly washed out towards the Seine River. Natural Pb in the Seine River basin has a distinct isotopic signature ($^{206}Pb/^{207}Pb$=1.2007). We can therefore use Pb isotopes to determine the nature and contribution of the different Pb sources to the environment.

Mixing between Pb of different sources can be studied with diagrams representing the isotopic

ratio as a function of the inverse of the concentration, as a binary mixing produces a linear correlation (Ayrault et al., 2012).

We considered a sediment (s) constituted of 3 components: a natural component (n), an anthropogenic component (a) and a Pb-free component (d) that dilutes the two others. The sample mass, Pb concentration, Al concentration and Pb isotopic ratio are noted *m*, *Pb*, *Al* and *R*, respectively. Mixing equations are:

$m_s = m_n + m_a + m_d$ (Eq. 2)

$Al_s = \frac{(m_n Al_n + m_a Al_a + m_d Al_d)}{m_s}$ (Eq. 3)

$Pb_s = \frac{(m_n Pb_n + m_a Pb_a + m_d Pb_d)}{(m_s)}$ (Eq. 4)

$R_s = \frac{(m_n Pb_n R_n + m_a Pb_a R_a + m_d Pb_d R_d)}{C_s}$ (Eq. 5)

By definition, $Pb_d = 0$. In addition, we assume that $Al_d = 0$ and $Al_a = 0$

$Al_s = \frac{m_n Al_n}{m_s}$ (Eq. 6)

$Pb_s = \frac{(m_n Pb_n + m_a Pb_a)}{m_s}$ (Eq. 7)

$R_s = \frac{(m_n Pb_n R_n + m_a Pb_a R_a)}{C_s}$ (Eq. 8)

The EF calculation equation (Eq. 1) may then be written as:

$EF = \frac{(Pb_s/Al_s)}{(Pb_n/Al_n)} = \frac{(m_n Pb_n + m_a Pb_a)/m_n Al_n}{(Pb_n/Al_n)} = 1 + \frac{m_a Pb_a}{m_n Pb_n}$ (Eq. 9)

Dividing the numerator and denominator of Eq. 8 by $m_n Pb_n$, we obtain:

$$R_s = \frac{\left(R_n + \frac{m_a Pb_a}{m_n Pb_n} R_a\right)}{1 + \frac{m_a Pb_a}{m_n Pb_n}}$$

$$= \frac{R_n + (EF-1)R_a}{EF}$$

$$= R_a + (R_a - R_n)\frac{1}{EF}$$ (Eq. 10)

Therefore, the mixing of the two Pb-bearing phases “natural” + “anthropogenic” diluted by

Pb-free materiel (e.g., quartz sand) produces a linear relationship between the $^{206}Pb/^{207}Pb$ ratio and 1/EF. Suspended particles collected in 2008/2009 at sites M, B and T form a broad linear array in a $^{206}Pb/^{207}Pb$ vs 1/EF diagram with the EF factor increasing (1/EF decreasing) from weakly to highly urbanized and industrialized area (Fig. 2). It suggests a mixing between an anthropogenic and a natural end-member.

The isotopic signature of the "natural" end member should be defined by the $^{206}Pb/^{207}Pb$ ratio at EF = 1. It corresponds to the Marnay sediments, in which $^{206}Pb/^{207}Pb$ ratio is significantly below the $^{206}Pb/^{207}Pb$ ratio (= 1.20) of the natural end-member determined in the literature. This difference might be due to locally different bedrocks or to pervasive contamination by gasoline Pb or both. Only 20% of gasoline lead would be sufficient to shift the $^{206}Pb/^{207}Pb$ ratio of the Marnay sediment from 1.20 to 1.18. Such a small EF variation might not be significantly resolvable considering the uncertainties on the natural background Pb level discussed above.

The anthropogenic end-member is best represented by the collected waters overflowing in the Seine River during heavy rain events (noted CSO hereafter, for combined sewer overflow). This material is made up of 27% of organic matter carried by urban waste waters, mixed with rain waters. The high Pb EF of the CSO samples is consistent with the affinity of Pb for organic matter (Balabane and van Oort, 2002, Pernet-Coudrier et al., 2011). Urban runoffs have been shown to contain high Pb concentration, together with Zn and Cu (Gromaire-Mertz et al., 2001). The $^{206}Pb/^{207}Pb$ ratio of the CSO ($^{206}Pb/^{207}Pb = 1.1573 \pm 0.0025$) corresponds to the urban signature determined by analyzing the WWTP effluent collected in 2006 ($^{206}Pb/^{207}Pb = 1.154 \pm 0.002$, Ayrault et al., 2012). It represents a mixing between the historical Pb accumulated since the 19th century and "gasoline" Pb. We note that the range of $^{206}Pb/^{207}Pb$ ratio covered by CSO is narrower than the range found in the Bouafles sediments throughout the 20th century (Fig. 2). This suggests that Pb transported nowadays by the Seine River is produced by a thorough mixing between historical and gasoline lead, mixing that displayed a steady signature over the last decade. This implies that 20 years after the complete ban of leaded gasoline in France, gasoline Pb still contributes to the Pb contamination in the Seine River.

There is a significant scattering of the CSO samples and of the different types of SPM data

below the urban-natural mixing line. This scattering is likely due to the involvement of punctual sources in Paris *intra muros* that have not been completely homogenized. Nevertheless, the observed scattering is generally smaller than the change in isotopic ratio observed in the Seine River sediment during the 20th century and recorded in the B1 core.

The isotopic signature of suspended particles collected in the river nearby the core sampling site can be compared to top-core sediments. The upstream Seine River core TR01 samples (covering the 1970–2002 period) are plotted on a mixing line between urban lead and natural lead (Ayrault et al., 2012). The recent TR01 sample signature (1.175 ± 0.003 in 2001) is consistent with the signature found in Marnay SPM. Unfortunately, Al or Sc was not measured on core TR01 samples, preventing calculation of the EF. For the 1994-2003 period, the downstream Seine River core B1 samples are plotted on a mixing line between urban lead and natural lead (Fig. 2). For the 1994-2003 period, the downstream Seine River core B1 samples are plotted on a mixing line between urban lead and natural lead (Fig. 2) with a 206Pb/207Pb ratio of 1.166 ± 0.004 in 2003, a signature on the high boundary (but not significantly different) of the downstream Seine River sites Bougival and Triel (with comparable EF).

4.2. Temporal variability of lead sources in the Orge River

For the Orge River catchment, lead concentrations were found to be 2 to 6 times higher in SPM than the natural local background (20 mg/kg) and to be a function of the urbanization density (Le Pape et al., 2013) (Table 4, Fig. 3). The trends indicated a change in the lead contamination origin during the last decade. Indeed, the lead fingerprints evolved from a three-end member system (natural + urban + gasoline) to a two-end member one (natural + urban) (Fig. 3), corresponding to the end of lead gasoline supply to the river (Le Pape et al., 2013). These results highlighted the consequences of gasoline-lead ban in France (2000), as already observed in the Seine River basin (Ayrault et al., 2012). The lack of $^{206}Pb/^{207}Pb$ ratio lower than the urban signature in the SPM of the Orge River, a small and partly channelized urban catchment, could be explained by a faster turnover of sediments compared to one in the Seine River watershed that presents depositional areas allowing transitory to long term storage of particles. In a $^{206}Pb/^{207}Pb$ vs $1/EF$ diagram, the 2010/2011 Orge SPM samples correspond to the same mixing trend as the one observed at the Seine basin scale, with most samples falling slightly below the urban-natural mixing line (Le Pape et al., 2013). The Orge SPM displays a larger scattering

below the urban-natural mixing line. During the high waterflow, the 2010/2011 SPM samples contamination displayed a clear upstream ($^{206}Pb/^{207}Pb$ =1.177±0.002) to downstream ($^{206}Pb/^{207}Pb$ =1.158±0.002) trend matching the urbanization trend, suggesting a shift from a diffuse source of lead to an urban contamination. During low waterflow, no clear pattern appears in the upstream to downstream signature trend. This may be attributed to local urban runoff releases occurring during low waterflow periods, as shown in Le Pape et al. (2013).

The behavior of the Orge River bed sediment is clearly different from that of the SPM. Whatever the hydrodynamics of the river, the upstream to downstream signature trend did not follow the urbanization gradient, with the most upstream, less urbanized, site "D" signature varying from $^{206}Pb/^{207}Pb$ =1.165±0.002; 40.5 mg/kg to $^{206}Pb/^{207}Pb$ =1.150±0.002; 70.9 mg/kg; lying between the "historical" and the "urban" end-members.

In the Orge River, the ratio $^{206}Pb/^{207}Pb$ is never higher than 1.179±0.002 (Pb=54.8±2.7 mg/kg, site D) at the most upstream, less urbanized, site. These $^{206}Pb/^{207}Pb$ ratios remain significantly below the natural $^{206}Pb/^{207}Pb$ ratio and similar to the recent TR01 upstream core sample signature (1.175 ± 0.003 in 2001). Their signature is also close to the one of material collected in upstream Seine River sections even though they contain a higher Pb concentration. It might suggest the implication of a pervasive contamination by an anthropogenic Pb source that is more radiogenic than the gasoline additives, at the scale of the Orge River watershed. Studying A horizons collected each year at Versailles (15 km from Paris, 20 km from the Orge River watershed) from 1929 to 2000, Semlali et al. (2004) demonstrated that more than half of the anthropogenic Pb present nowadays in the topsoil was deposited before 1928. It has an isotopic signature $^{206}Pb/^{207}Pb$~1.18 (the ratio in the 1929 soil is $^{206}Pb/^{207}Pb$=1.183±0.001) and it could be related to coal combustion, coal used in Europe having a $^{206}Pb/^{207}Pb$ ratio very close to 1.18 (Komarek et al., 2008; Chiarada et al., 2000; MacKinnon et al., 2011; Semlali et al., 2004). This is in agreement with other European studies that attributed the value of 1.18 to a "pre-gasoline" anthropogenic signature (Farmer et al., 2000; MacKinnon et al, 2011; Catinon et al., 2013). In a study dedicated to agricultural soils in the UK, MacKinnon et al. (2011) observed that despite the proximity to motorway and roads, non- gazoline Pb from historical, industrial and coal-burning emissions was the dominant component except for very limited areas located in the immediate vicinity of roads.

Although Pb isotopic signature in soils seems to be significantly affected by coal combustion and industrial fallout during the 19th century, the Seine River SPM collected at downstream floodplain sites during most of the 20th century are largely dominated by the Rio Tinto signature (Ayrault et al., 2012) with no significant contribution of a "coal" signature. To document this apparent contradiction, a detailed study of the Pb concentration, isotopic signature and lability is

currently performed in the Orge River catchment, with a special attention paid to the different soil types and horizons. This scheme will be further extended to the entire Seine River basin.

4.3. Lead-bearing particles in the river

The possible relationship between the grain size and the Pb isotopic signature was investigated using the Orge River sampling campaign Jan 2011 (high waterflow) bed sediment. For this campaign, the SPM signature exhibits a clear upstream to downstream trend. We assumed that SPM originate from the BS finest fractions through resuspension of the bed sediment as it represents the major contamination pathway of the water column (Chon et al., 2012). Except at the most urbanized site where BS can be sampled (Y) (where the three fractions display similar signatures), the analyses of the sieved fractions showed that the signature of the different grain size fractions varied randomly from one site to the next (Table 5, Fig. 4). The finest fraction (<63 µm) is the most contaminated one (up to 110 mg/kg at the most urbanized site Y). However, because the coarser fractions (> 63 µm and > 200 µm) provide the bulk of the total mass of the BS samples, these coarse fractions bear a significant part of the Pb content (up to 72% of Pb is recovered in the >200 µm fraction at site Y).

Table 5, Figure 4

The comparison of the signature of SPM versus BS as a function of river hydrodynamics is given in Fig. 5. It tends to show that during low waterflow, SPM signature tends to be closer to the "natural" end-member than the BS signature, whereas during high waterflow, the SPM signature is on average closer to the urban end-member than the BS one. This clearly supports the hypothesis of a BS resuspension during high waterflow conditions.

Figure 5

Lead $^{206}Pb/^{207}Pb$ ratio was also measured in "road deposit sediments" (RDS), corresponding to sediments sampled in a road gutter at a strongly urbanized site (8000 inh/km^2). The result ($^{206}Pb/^{207}Pb = 1.144 \pm 0.003$, Table 4) revealed the remanence of leaded gasoline in this sample that is mainly composed of coarse grains (Le Pape et al., 2013). In the UK, RDS exhibited signatures ranging from 1.13 to 1.145 (2001 samples) and 1.14 to 1.17 (2010 samples) (Mac Kinnon et al., 2012). The persistent leaded gasoline pollution at places where urban dust accumulated over decades was progressively leached by runoff over long periods of time

contributing to the contamination of the bed sediment. Moreover, our results show that there is no direct contamination of the SPM from the RDS. This is consistent with the results of Catinon et al. (2013) showing that dust coarse fraction (200-2000 µm) trapped in an outdoor urban building for 40 years have similarly conserved the memory of the gasoline lead contamination ($^{206}Pb/^{207}Pb == 1.146 \pm 0.002$).

SEM analysis of the lead-bearing particles in the Seine River bed sediment showed the presence of coarse particles (> 50 µm, up to 200 µm) bearing Pb and evidencing an anthropogenic origin (alloys, quartz particles covered with a thin layer of Pb; Priadi, unpublished results). The results on the Orge River sediments analyses are similar (Le Pape et al., 2013), showing Pb-containing paint chips (# 20 µm) whereas the finest particles (Pb-phosphates; # 5 µm) are provided by soil erosion. Unfortunately, SEM analyses only do not permit to conclude on lead isotopic signature in those particles.

The lead contamination on coarse particles observed by SEM , and the isotopic signature measured on the RDS, which mainly contained coarse particles outline a difference compared to results of previous studies exhibiting that exogenous Pb is linked to very fine particles, such as the clay fraction (Semlali et al., 2001; Sutherland et al., 2003). However, those studies were investigating diffuse atmospheric contamination due to gasoline emissions, whereas urban rivers receive water-transported anthropogenic Pb from different origins (gasoline, paints, alloys…). Sediment sieving to 50 µm or 63 µm conventionally performed in river contamination studies may then lead to the loss of this coarse fraction, which seems to play an important role in both the urban Orge River Pb transport and contamination. Further studies would be necessary to evaluate if this observation is applicable to other urban with varying geological characteristics.

4.4. Towards a river contamination mixing scheme.

Leaded gasoline additives have been significantly used from the 1950s, with a maximum of emissions in 1971 (Ferrand et al., 1999). From 1970 to 1990, successive regulations reduced lead concentration in gasoline. The leaded gasoline was progressively replaced with unleaded gasoline from 1990 to 2000. Lead from gasoline was intensively emitted for 30 years, from 1960 to 1990 at a rate of 5000 to 12000 t per year (roughly 1500 to 3500 t per year for the Seine River basin).

Here, we compare the flux of “gasoline” Pb transported by the river to the flux of “gasoline” Pb emitted over the Seine Basin in 1986, when the gasoline contribution was the highest in the

Seine River sediment. The flux of "gasoline" Pb transported by the Seine is given by: $F_{gazolinePb\text{-}river} = f^{*}Pb^{*}F_{particles}$ = 26 ± 7 ton/y, where f is the fraction of Pb in the sediment derived from gasoline (≈ 23 ± 6%), Pb is the total concentration of Pb in the sediment (≈153 ± 18 mg/kg) in 1986 downstream Paris and the Seine-Aval WWTP at the Muids and Bouafle sites (Ayrault et al., 2012). $F_{particles}$ is the annual flux of particles (≈750 ton/y, Meybeck et al., 1998).

Assuming that the Seine River basin receives 25% (Saby et al., 2006) of the 7500 tons of gasoline Pb emitted in France in 1986 (Ferrand et al., 1999), the emission flux $F_{gazolinePb\text{-}emission}$ is estimated to1900 tons.

Hence, the river exports only 1.4% of the gasoline Pb deposited annually. It implies that most of the gasoline Pb remains stored in the soils of the Seine River basin. Nevertheless, gasoline Pb is removed much more efficiently than ^{210}Pb, a natural Pb radionuclide supplied homogeneously over the basin by rainfall, for which only 0.7% of the annual deposit reaches the estuary (Le Cloarec et al., 2007). Indeed, natural ^{210}Pb is deposited homogeneously over the whole Seine River Basin, whereas gasoline Pb is mostly deposited around Paris (the bulk of gasoline fallout occurred within a distance of 60-100 km from Paris, Saby, 2006). In this context, gasoline Pb would have 2.0±0.5 times more chance to reach the river than ^{210}Pb, due to the larger proportion of impermeable surfaces directly connected to the river in Paris and in its close suburbs compared to the rest of the basin.

Figure 6

This does not imply that lead from gasoline has been completely and definitely flushed from the Seine River basin, even in urban areas. The fast decrease of leaded gasoline contribution to the river contamination after the emissions stopped may be attributed to the fact that the leaded gasoline was mainly emitted in the most urban areas and along the roads (MacKinnon et al., 2011). Soil erosion affecting areas connected to the river network and runoff on urban surfaces supply fine particles contaminated in Pb to the watercourses during heavy rainfall (Fig. 6). However, because of the strong affinity of Pb for organic matter (e.g., Semlali et al., 2001, Balabane et al., 2002) and the low erosion rates recorded in the Seine River basin, the residence time of this contaminant in soils is very long (up to 10,000 years, Le Cloarec et al., 2007). Together with the in-depth diffusion of Pb in soils (Bacon et al., 1996), this indicates that soil

may constitute a sink for atmospheric anthropogenic Pb which would therefore exert a low but continuous pressure on the river water quality. When the river flows across the Paris megacity, the huge amount of Pb accumulated in the city infrastructure (pipes, roofs, …) imprints the signature of the Rio Tinto ore (the "historical" Pb) on the sediment transiting in the downstream sections of the river.

5. Conclusions

This extensive study of the Pb composition in the river sediments allows to infer the spatial and temporal variability of the anthropogenic Pb sources in the Seine River basin. In the upstream part of basin, before the river flows across the Paris megacity, most of the current Pb river contamination is supplied by soil erosion that stores anthropogenic contamination that has accumulated since the 19^{th} century. Further studies are needed to elucidate the origin of this pervasive soil contamination. The large contamination depth associated with the long residence time of the particles in the soil complicates the detection of any decontamination trend in the basin soils at the decadal scale. To evaluate precisely this "background" contamination, a detailed study of the natural concentration and isotopic signature of the different lithologies and soil types present in the basin is required.

In the downstream part of the river under strong urban influence, the contamination is mainly due to the release of the so-called "urban" Pb whose signature results from a thorough mixing of "historical" and "gasoline" Pb. Urban Pb exhibits a remarkably steady signature over time and space, even though a progressive decrease in the gasoline contribution could have been expected after the ban of leaded additives. It appears that, after the first flush of the gasoline Pb within the decade that followed the ban, a significant part of the gasoline Pb emitted in the basin had transformed into an "urban alloy". Further studies coupling solid speciation tools and isotopic studies at the scale of particles would help in characterizing the bearing phases and availability of the urban lead.

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Figure

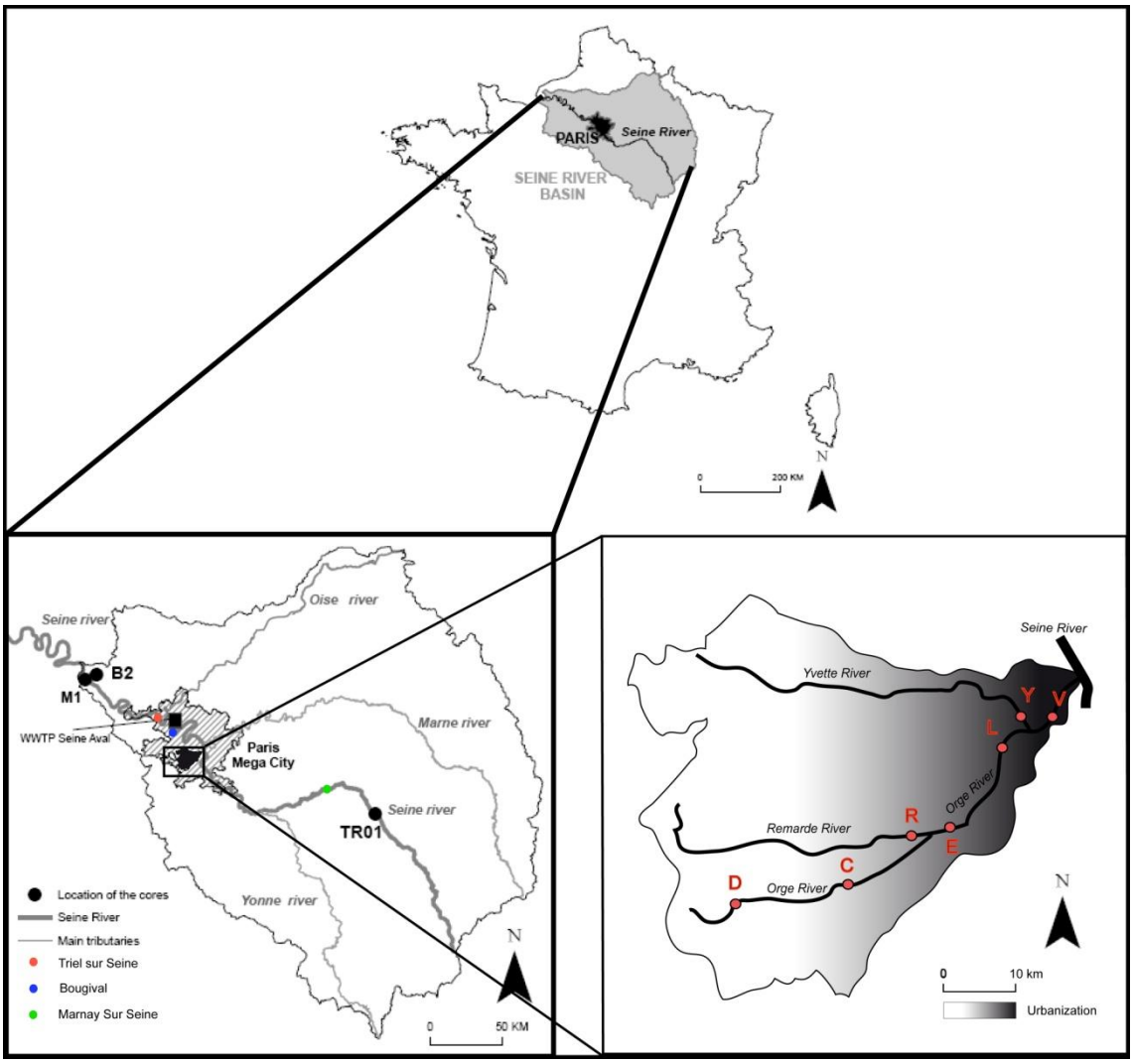

Figure 1. Location of the studied catchments. The Orge River catchment (900 km²) (down, right) is a sub-catchment of the Seine River basin (64,700 km²) (down, left). See Table 1 for the sampling sites labels.

Figure

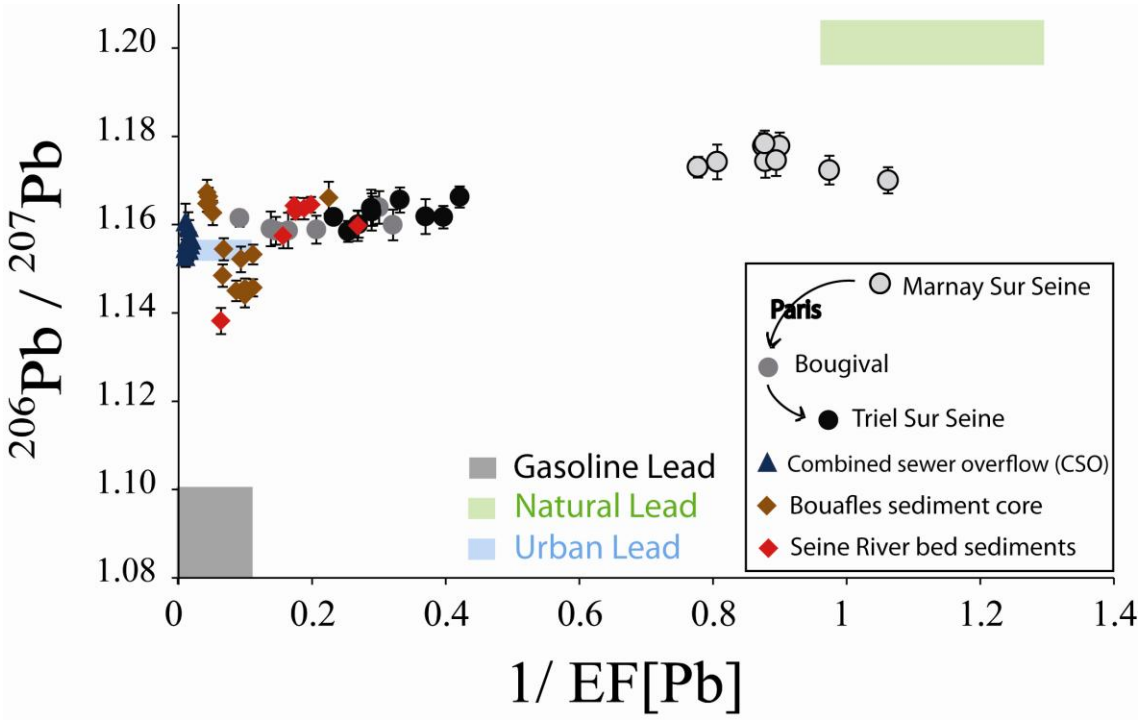

Figure 2. Isotopic Pb signature versus 1/EF. EF : enrichment factor (see text). The colored arrays delimited end-member areas (blue for "urban" Pb, gray for "gasoline" Pb, green for "natural" Pb).

Figure

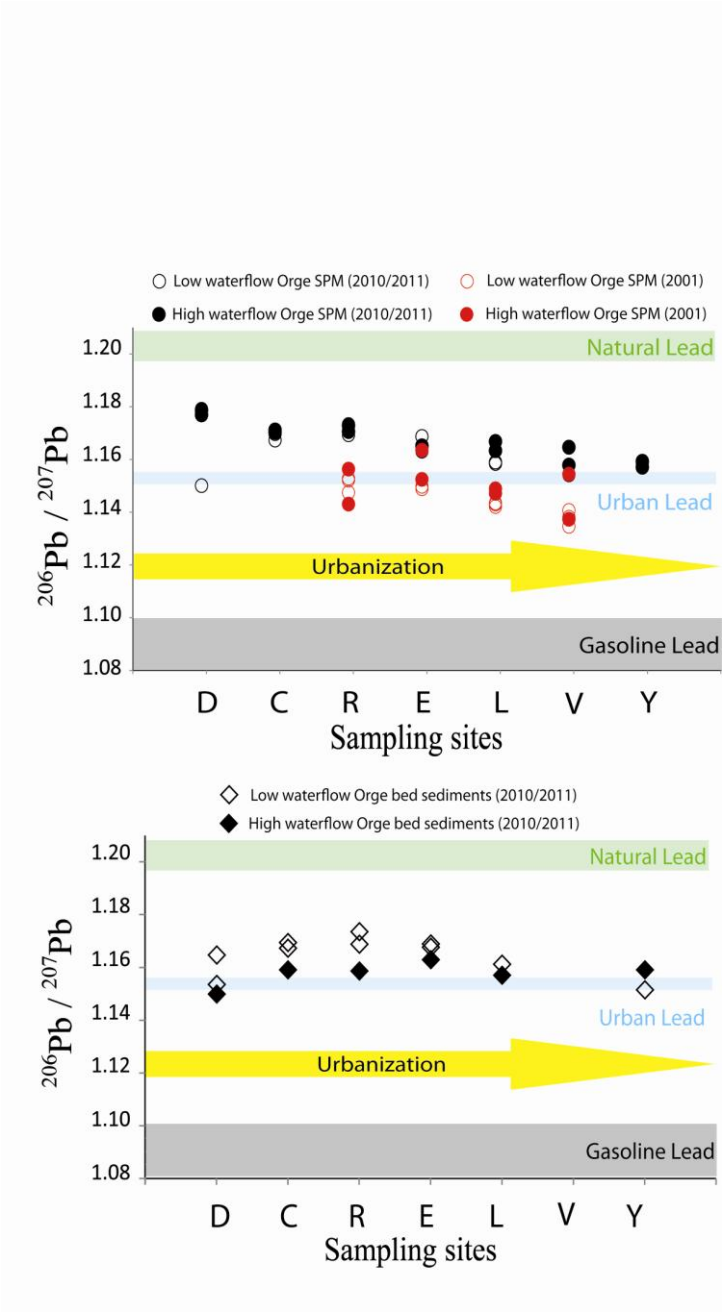

Figure 3. Isotopic Pb signature in suspended particle matter (SPM) (top) and bed sediments (BS) (down) of the Orge River. Open circles are for low water flow samplings. Closed circles are for high waterflow samplings. The symbol size matches the error amplitude.

Figure

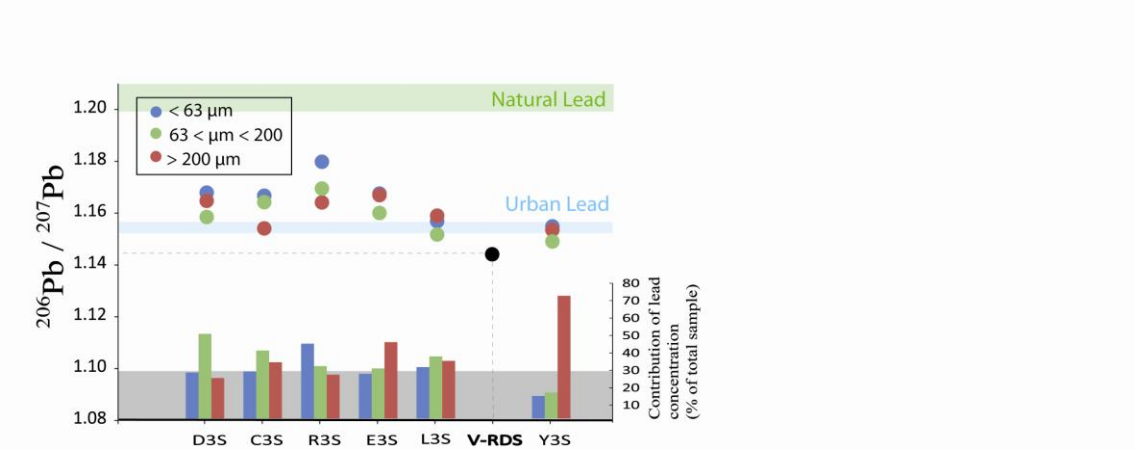

Figure 4. Isotopic Pb signature of the sieved bed sediments of the Orge River. RDS: road-side sediment sampled at V site. See Table 1 for the sites label. The symbol size matches the error amplitude.

Figure

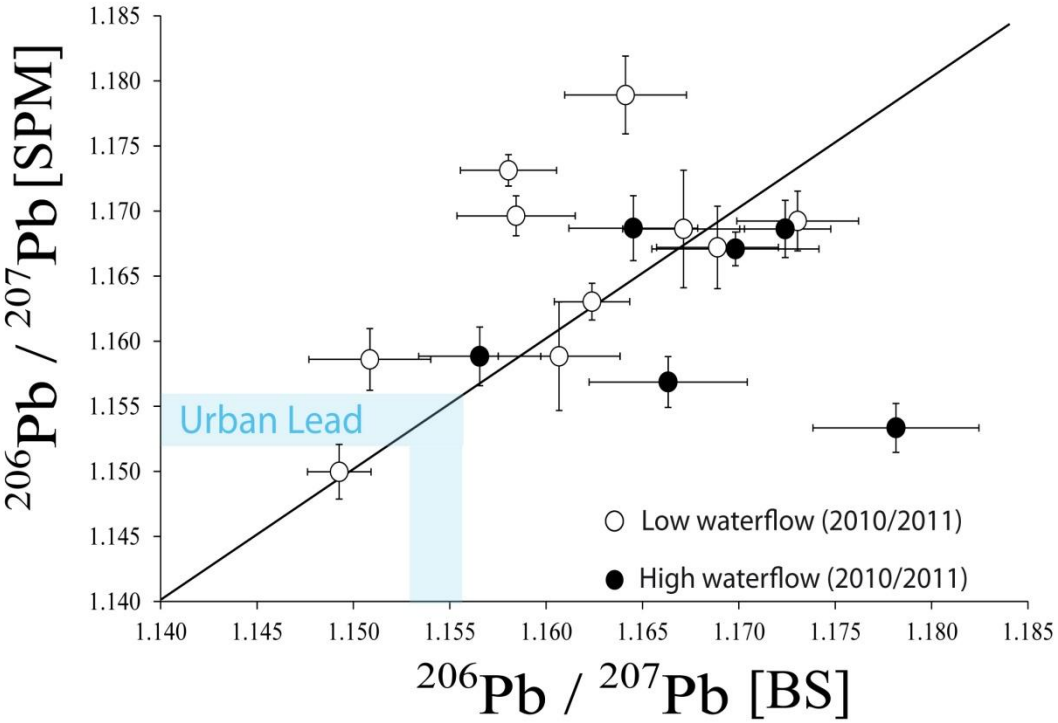

Figure 5. Isotopic Pb signature of the suspended particle matter (SPM) and bed sediments (BS) of the Orge River. Open circles are for low water flow samplings. Closed circles are for high waterflow samplings.

Figure

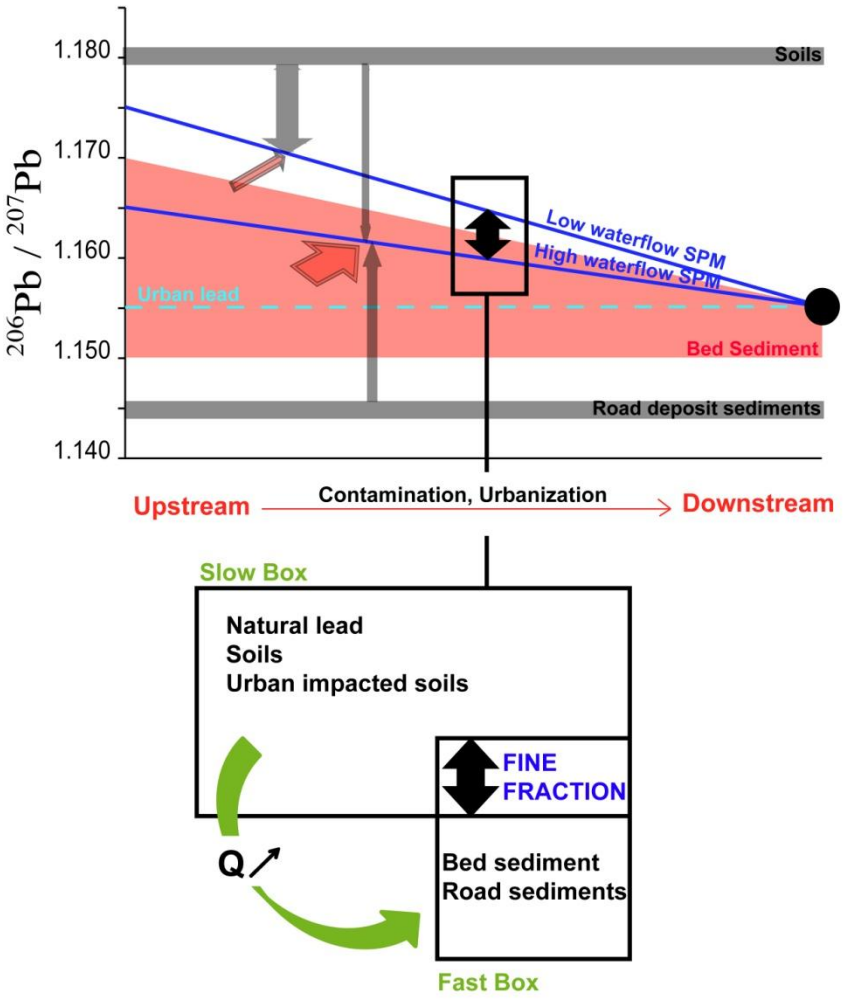

Figure 6. Scheme of the Pb contamination pathways along an urban river.

Table 1. Sample types, location and period of collection.

Site	Label	Lambert II coordinates		Sampling date
Seine				
Bed sediments (provided by SNS)				
Paris, Pt Tolbiac	Tol	595770	2427906	Sep 2007
Suresnes	Sur	592144	2429828	Sep 2007; Aug 2009
Sartrouville	Sar	586939	2438517	Jul 2008; Sep 2009
Colombes	Col	591484	2435843	Aug 2009
Clichy	Cli	598131	2434990	Aug 2009
Cores (Ayrault et al., 2012)				
Troyes	TR01	726238	2372883	Mar 1998
Muids	M1	525581	2470343	Apr 2003
Bouafles	B2	529698	2468611	Apr 2003
SPM (Priadi et al., 2011 a, b)				
Marnay-sur-Seine	M	690279	2391403	Dec 2008 - Sept 2009
Bougival	B	583671	2431778	Jan 2009 - Sept 2009
Triel-sur-Seine	T	575458	2442308	Dec 2008 - Aug 2009
Combined sewer overflow (Passerat et al., 2013)				
Clichy	CSO	598131	2434990	Aug 2008
Orge (Le Pape et al., 2012 and 2013)				
SPM and bed sediment				
Dourdan	D	575202	2392697	Jun 2010; Sep 2010; Jan 2011; Apr 2011
St Chéron	C	584428	2394522	Jun 2010; Sep 2010; Jan 2011; Apr 2011
Rémarde	R	589402	2398180	Jun 2010; Sep 2010; Jan 2011; Apr 2011
Egly	E	591912	2398466	2001; Jun 2010; Sep 2010; Jan 2011; Apr 2011
Longpont-sur-Orge	L	597093	2405080	2001; Jun 2010; Sep 2010; Jan 2011; Apr 2011
Yvette	Y	599432	2408855	Jun 2010; Sep 2010; Jan 2011; Apr 2011
Viry-Chatillon	V	603074	2408773	2001; Jun 2010; Sep 2010; Jan 2011; Apr 2011
Road side dust				
Viry-Chatillon	RDS	603074	2408773	Jan 2011

Table 2. Seine River bed sediment data. The three first letters correspond to the label of the sampling site (see Table 1), the two last figures refer to the sampling year (see Table 1). EF: enrichment factor (see text).

	$^{206}Pb / ^{207}Pb$ ± 2s	Al (mg/kg)	Pb (mg/kg)	EF
Tol 07	1.1645 ± 0.0019	30870 ± 4320	99.7 ± 5.0	5.8
Sur 07	1.1600 ± 0.0034	36145 ± 5060	75.2 ± 3.8	3.7
Sar 08	1.1632 ± 0.0017	29360 ± 4110	93.8 ± 4.7	5.8
Sur 09	1.1639 ± 0.0024	24885 ± 3485	74.0 ± 3.7	5.4
Col 09	1.1384 ± 0.0030	31580 ± 4420	281.7 ± 14.1	16.1
Cli 09	1.1647 ± 0.0018	33910 ± 4750	95.5 ± 4.8	5.1
Sar 09	1.1577 ± 0.0028	30370 ± 4252	108.5 ± 5.4	6.4

Table

Table 3. Seine River trapped SPM. EF: enrichment factor (see text).

.

Sampling date	^{206}Pb / ^{207}Pb ± 2s	Al (mg/kg)	Pb (mg/kg)	EF
Marnay (M)				
20/12/2008	1.1777 ± 0.0033	36954 ± 5174	23.5 ± 1.2	1.14
20/01/2009	1.1781 ± 0.0028	34735 ± 4863	22.1 ± 1.1	1.14
20/02/2009	1.1744 ± 0.0039	29556 ± 4138	20.4 ± 1.0	1.24
20/03/2009	1.1703 ± 0.0030	38998 ± 5460	20.4 ± 1.0	0.94
20/04/2009	1.1725 ± 0.0033	32687 ± 4576	18.7 ± 0.9	1.03
10/06/2009	1.1746 ± 0.0037	30757 ± 4306	19.5 ± 1.0	1.14
22/06/2009	1.1781 ± 0.0030	31796 ± 4451	19.7 ± 1.0	1.11
20/07/2009	1.1786 ± 0.0030	31552 ± 4417	20.0 ± 1.0	1.14
20/08/2009	1.1748 ± 0.0036	31723 ± 4441	19.7 ± 1.0	1.12
20/09/2009	1.1733 ± 0.0023	32090 ± 4493	23.0 ± 1.1	1.29
Median ± SD	1.1752 ± 0.0028		20.7 ± 1.6	
Bougival (B)				
20/01/2009	1.1591 0.0039	38862 5441	105.2 5.3	4.87
20/02/2009	1.1601 0.0042	54900 7686	95.4 4.8	3.13
20/03/2009	1.1633 0.0028	41725 5842	80.0 4.0	3.45
20/04/2009	1.1641 0.0024	46881 6563	87.1 4.4	3.34
10/06/2009	1.1617 0.0026	39883 5584	245.2 12.3	11.07
20/07/2009	1.1593 0.0041	43563 6099	176.7 8.8	7.30
20/08/2009	1.1588 0.0030	36609 5125	140.7 7.0	6.92
20/09/2009	1.1589 0.0024	43416 6078	148.0 7.4	6.14
Median ± SD	1.1607 0.0021		134.8 2.8	
Triel (T)				
20/12/2008	1.1621 0.0032	38909 5447	58.7 2.9	2.71
20/01/2009	1.1631 0.0035	42411 5938	81.8 4.1	3.47
20/02/2009	1.1658 0.0033	32886 4604	55.3 2.8	3.03
20/03/2009	1.1665 0.0037	38273 5358	50.7 2.5	2.38
20/04/2009	1.1619 0.0019	45352 6349	63.7 3.2	2.53
10/06/2009	1.1640 0.0040	43473 6086	84.1 4.2	3.48

22/06/2009	1.1603	0.0031	39913	5588	82.7	4.1	3.73
20/07/2009	1.1587	0.0040	40782	5709	89.6	4.5	3.96
20/08/2009	1.1619	0.0041	40981	5737	98.5	4.9	4.33
Median ± SD	1.1627	±0.0025			75.8	±0.9	

Table

Table 4. Combined sewer overflow (CSO) particulate matter composition. EF: enrichment factor (see text).

	^{206}Pb / ^{207}Pb ± 2s	Al (mg/kg)	Pb (mg/kg)	EF
CSO-1	1.1568 ±0.0017	461 ± 23	15442 ±2162	53.8
CSO-2	1.1599 ±0.0031	560 ± 28	13540 ±1896	74.4
CSO-3	1.1531 ± 0.0024	801 ± 40	13641 ±1910	105.7
CSO-4	1.1596 ± 0.0017	452 ± 23	12026 ±1684	67.6
CSO-5	1.1559 ± 0.0018	515 ± 26	12517 ±1752	74.1
CSO-6	1.1609 ± 0.0040	566 ± 28	9398 ±1316	108.5
CSO-7	1.1571 ± 0.0026	478 ± 24	10881 ±1523	79.0
CSO-8	1.1549 ± 0.0026	948 ± 47	15855 ±2220	107.6
CSO-9	1.1557 ± 0.0024	588 ± 29	17547 ±2457	60.3
CSO-10	1.1546 ± 0.0015	684 ± 34	17502 ±2450	70.3
CSO-11	1.1545 ± 0.0024	656 ± 33	17056 ±2388	69.2
CSO-12	1.1563 ± 0.0024	244 ± 12	4668 ± 654	94.0
Median ± SD	1.1573 ± 0.0025	579 ± 181		

Table

Table 5. Orge River bulk and sieved bed sediments. EF: enrichment factor (see text).

	^{206}Pb / ^{207}Pb ± 2s		Pb	(mg/kg)	Mass %	Al (mg/kg)		EF
D1S	1.1497	± 0.0016	70.9	± 3.5	bulk	X		X
C1S	1.1589	0.0031	44.2	2.2	bulk	X		X
R1S	1.1585	0.0025	32.8	1.6	bulk	X		X
E1S	1.1628	0.0020	64.5	3.2	bulk	X		X
D3S	1.1534	0.0043	46.3	2.3	bulk	20055	±2808	4.151
C3S	1.1671	0.0043	10.3	0.5	bulk	8598	1204	2.156
R3S	1.1687	0.0024	37.1	1.9	bulk	32736	4583	2.038
E3S	1.1687	0.0033	64.5	3.2	bulk	39955	5594	2.906
L3S	1.1569	0.0041	39.5	2.0	bulk	17535	2455	4.057
Y3S	1.1589	0.0032	72.2	3.6	bulk	12405	1737	10.483
D3S>200	1.1586	0.0049	28.4	1.4	30.1	11913	1668	4.285
C3S>200	1.1643	0.0032	11.3	0.6	39.7	8158	1142	2.493
R3S>200	1.1696	0.0045	38.5	1.9	23.9	34433	4821	2.013
E3S>200	1.1601	0.0025	69.1	3.5	41.5	44854	6279	2.773
L3S>200	1.1518	0.0050	47.6	2.4	20.3	11819	1655	7.243
Y3S>200	1.1492	0.0037	37.2	1.9	69.8	14431	2020	4.640
63<D3S<200	1.1648	0.0034	35.3	1.8	50.7	23282	3259	2.726
63<C3S<200	1.1542	0.0025	9.9	0.5	54.5	11060	1548	1.619
63<R3S<200	1.1642	0.0050	31.5	1.6	34.9	27727	3882	2.045
63<E3S<200	1.1670	0.0029	74.0	3.7	25.4	44198	6188	3.014
63<L3S<200	1.1591	0.0046	15.3	0.8	68.0	11367	1591	2.424
63<Y3S<200	1.1536	0.0040	21.1	1.1	25.9	10768	1508	3.535
D3S<63	1.1680	0.0044	50.7	2.5	19.1	41577	5821	2.196
C3S<63	1.1668	0.0042	64.7	3.2	5.8	37132	5198	3.138
R3S<63	1.1799	0.0040	37.9	1.9	41.3	43537	6095	1.569
E3S<63	1.1676	0.0044	50.8	2.5	33.1	40678	5695	2.248
L3S<63	1.1570	0.0049	73.6	3.7	11.7	45155	6322	2.936
Y3S<63	1.1550	0.0036	110.0	5.5	4.3	44335	6207	4.467
D4S	1.1646	0.0023	40.5	2.0	bulk	X		X
C4S	1.1693	0.0018	14.6	0.7	bulk	X		X
R4S	1.1735	0.0011	15.8	0.8	bulk	X		X
E4S	1.1676	0.0018	64.7	3.2	bulk	X		X
L4S	1.1611	0.0018	26.8	1.3	bulk	X		X
Y4S	1.1513	0.0025	30.4	1.5	bulk	X		X
RDS	1.1443	0.0028	35.6	1.8	bulk	X		X