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# 1 **Lead contamination of the Seine River, France: geochemical** 2 **implications of a historical perspective.**

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## 13 14 **Abstract**

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

25 The dominating Pb signature in the Paris conurbation that is currently sampled through  
26 incinerators fumes (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.1550 ± 0.0005) and waste water treatment plant  
27 (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.154 ± 0.002), represents a mixture of highly recycled lead from the Rio Tinto  
28 mine and lead from leaded gasoline (imprinted by the low <sup>206</sup>Pb/<sup>207</sup>Pb of the Broken Hill  
29 mine). This signature is called “urban” rather than “industrial”, because it is clearly distinct  
30 from the Pb that is found in areas contaminated by heavy industry, i.e. the heavy industries  
31 located on the Oise River which used lead from European ores characterized by high  
32 <sup>206</sup>Pb/<sup>207</sup>Pb ratios (~1.18-1.19) and possibly a minor amount of North American lead  
33 (<sup>206</sup>Pb/<sup>207</sup>Pb ratios > 1.20). The “urban” signature is also found in a rural area upstream of  
34 Paris in the 1970's. At the Seine River mouth in 2003, Pb with an urban signature represents  
35 70% of the total Pb sediment content, with the 30% remaining corresponding to natural Pb.

36

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

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39

## 40 **1. Introduction.**

41

42 The Seine river basin (67,500 km<sup>2</sup>) drains one of the most urbanised areas in Europe.  
43 It covers 14% of the French territory but accounts for 25% of the agriculture production, 25 to  
44 30% of the industrial activity and 23% of the French population. In the Paris conurbation  
45 (2,740 km<sup>2</sup>, 9.5 million inhabitants), the Seine water and sediments are heavily contaminated  
46 by metals. Unfortunately, the sources and pathways of these contaminations are not well  
47 understood (Thévenot et al., 2007; Meybeck et al. 2007; Le Cloarec et al., 2009).

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

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

63 Gasoline lead additives were the main source of Pb to the road dust (<sup>206</sup>Pb/<sup>207</sup>Pb =  
64 1.101 ± 0.001), but were less important for indoor dust accumulated from 1971 to 1981  
65 (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.120 ± 0.001) and even lower for the Seine River sediment (<sup>206</sup>Pb/<sup>207</sup>Pb =  
66 1.152 ± 0.002) sampled in 1979 (Elbaz-Poulichet et al., 1986). The contribution of gasoline  
67 lead additives to the Seine River decreased from 1979 to 2000 (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.169; Millot et  
68 al., 2004). In 1997, the lead contained in the street dust of Paris (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.151) came

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

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

81 Sediment cores represent valuable archives of the anthropogenic river contamination  
82 (Alfonso et al., 2001; Chillrud et al., 2003; Arnaud et al., 2004; Soster et al., 2007; Le Cloarec  
83 et al., 2009), provided that they are sampled in undisturbed sites with continuous  
84 sedimentation. Unfortunately, navigation and channel dredging prevent continuous  
85 accumulation of sediments in the Seine River bed. The Seine River has no delta where marsh  
86 cores (Alfonso et al., 2001) can be sampled. Floodplains offer an alternative, but undisturbed  
87 floodplains are extremely rare along the Seine River. It was very difficult to find deposit sites  
88 allowing temporal reconstructions over the last 100 years (Le Cloarec et al., in press).

89 Here, we report the Pb concentration and isotopic signature in four cores covering different  
90 periods determined with the  $^{137}\text{Cs}$ - and  $^{210}\text{Pb}$  method, and three sites. This allows to:

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

96

## 97 **2. Materials and methods.**

98

### 99 **2.1. Sampling sites and sediment core dating**

100

101

## **Figure 1**

102

103 The core TR01 was collected in an upstream Seine River site (Fig.1). This sampling  
104 site is located on an oxbow lake of the “Canal de la Haute Seine” that was built between 1806  
105 and 1851 in order to connect Paris with agricultural and coal mining areas. This site drains an  
106 area of 3577 km<sup>2</sup>, and the population density is low, 40 inhabitants km<sup>-2</sup>. Agriculture and  
107 forestry are the major activities. The 80-cm long TR01 core was collected during March 2002.  
108 Bed soft sediments were cored using a hand pushed 10-cm diameter plastic tube, at a depth of  
109 1 meter below the water surface.

110 Two cores, B2 and M1, were collected in the Seine River floodplain, about 100 km  
111 downstream of Paris and its main waste water treatment plant (WWTP Seine Aval at Achères,  
112 see Fig. 1). These two sampling sites drain 96% of the Seine River basin and are situated  
113 within the last major meander of the Seine River before it reaches its estuary. “Bouafles” is  
114 located just upstream of a dam, in ‘Les Andelys’ (Fig. 1), in an oxbow lake located on the  
115 right bank of the Seine River. It corresponds to a young accretion area as indicated by the  
116 recent burial of trees. This undisturbed sampling area has remained grassland for 30 years,  
117 and gradual sediment deposition has occurred. Inhabitants confirmed that this site has been  
118 flooded until 2004 at least once a year. Eleven cores collected in this area between 2003 and  
119 2008 indicated a continuous sedimentation during the last 60 years (see Le Cloarec et al., in  
120 press).

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

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

128 The 1-meter long core S01 was collected in at Pontoise-les-Noyon, March 23<sup>rd</sup>, 2005,  
129 in a meander of the Oise River (Fig. 1). The site is located in an annually flooded pasture  
130 downstream the city of Chauny. The core was sampled with the same equipment as the  
131 samples from Bouafles and Muids. The sampling site drains an area of 4044 km<sup>2</sup> that was  
132 dominated by rural and low density urban areas. The Oise River basin has been industrialized  
133 since the beginning of the 1800’s. This led to an increase of local urbanization beginning  
134 shortly after the Second World War and continuing until 1975 (Le Cloarec et al., in press).  
135 Today many Oise industrial plants are no longer in activity. The Saint Gobain (glass industry)  
136 plant in Chauny (Fig 1), situated a few km above the sampling site, is particularly interesting

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

139

140 In addition, treated wastewater issued from the Seine – Aval waste water treatment plant  
141 (WWTP) at Achères (Fig. 1) was sampled during December 2006 (Pernet-Coudrier et al,  
142 2008). The Seine – Aval WWTP is connected to 80% of the Paris conurbation area combined  
143 sewers (9.5 million inhabitants).

144

## 145 **2. 2. Core dating**

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

148 The sediment cores are dated through the measurement of two radionuclides,  $^{137}\text{Cs}$ -  
149 and  $^{210}\text{Pb}$ . Both are strongly adsorbed on the fine fraction of the sediment (Wang and Cornett,  
150 1993; Gil-García et al., 2009). Artificial  $^{137}\text{Cs}$  is used as an event-tracer, whereas natural  $^{210}\text{Pb}$   
151 provides the sediment age.

152 Both radionuclides are gamma emitters and can be analyzed in small quantities of  
153 sediments (ca. 50-100 g) without any previous chemical treatment. The sediments are dried at  
154  $115^{\circ}\text{C}$ , sieved ( $< 2$  mm), powdered and then placed into air-tight counting boxes. Counting  
155 was conducted during ca.  $10^5$  s using Germanium gamma-ray detectors (High purity  
156 germanium – GeHP, N-type, coaxial model) at the *Laboratoire des Sciences du Climat et de*  
157 *l'Environnement* (Gif-sur-Yvette, France). Efficiencies and background of the detectors are  
158 controlled with internal soil and sediment standards, pure KCl samples, and IAEA standards  
159 (i.e., Soil-6, -135 and -375). Activity decay was corrected taking the sediment collection  
160 period into account.

161  $^{137}\text{Cs}$ , an artificial radionuclide ( $t_{1/2} = 30$  years), was produced by the thermonuclear  
162 bomb testing conducted between the 1950's and the 1980's (the maximum input occurred in  
163 1964) and the Chernobyl accident in 1986. Measurement of the  $^{137}\text{Cs}$  activity in the sediment  
164 allows one to distinguish three events: fallout due to the first significant input in the  
165 atmosphere in 1954, maximum input in 1964 and fallout due to the Chernobyl accident in  
166 1986.  $^{137}\text{Cs}$  stock stored in soils decreases by radioactive decay and fine sediment transfer to  
167 the rivers.  $^{137}\text{Cs}$  is easily identified in gamma spectrometry by a peak at 661 keV. The  
168 uncertainty on measurements corresponds to ca. 0.5%. The detection limit reaches  $0.3 \text{ Bq.kg}^{-1}$ .  
169 <sup>1</sup>.

170  $^{210}\text{Pb}$ , a natural radionuclide ( $t_{1/2} = 22.3$  years), is a decay product of  $^{238}\text{U}$  ( $t_{1/2} = 4.5 \cdot 10^9$   
171 years).  $^{238}\text{U}$  decays through a series of short-lived nuclides (e.g.  $^{226}\text{Ra}$ ,  $^{222}\text{Rn}$ ).  $^{222}\text{Rn}$  is a gas  
172 that partly remains *in situ*, forming “supported”  $^{210}\text{Pb}$ , and that partly escapes to the  
173 atmosphere, forming “excess”  $^{210}\text{Pb}$ . Excess  $^{210}\text{Pb}$  is deposited on the soil surface via wet and  
174 dry fallout and strongly sticks to the soil particles. The  $^{210}\text{Pb}$  activity in “excess” is calculated  
175 by subtracting the supported activity (determined using a  $^{238}\text{U}$  daughter, i.e.  $^{214}\text{Bi}$  from the  
176 total activity of  $^{210}\text{Pb}$  (Bonté et al., 2000). The uncertainty of the measurements (ca. 10%) is  
177 higher than that for  $^{137}\text{Cs}$ .

178

### 179 **2.3. Determination of lead concentration**

180

181 Details of the determination of lead concentration in totally digested sediment samples  
182 are given in Le Cloarec et al. (2009). Samples of about 100 mg are dissolved by successive  
183 addition of 65%  $\text{HNO}_3$  (3 mL) and 30%  $\text{HCl}$  (7 mL) mixture, 65%  $\text{HNO}_3$  and 40%  $\text{HF}$  (5 mL  
184 each), and 65%  $\text{HNO}_3$  and 69-72%  $\text{HClO}_4$  (6 mL each) in Teflon vessels using a heating  
185 block (Digiprep, SCP Science). Ultra pure reagents were used (Normatom grade, VWR,  
186 France for  $\text{HNO}_3$ , and  $\text{HCl}$ , “for trace metal analyses”, Baker, SODIPRO, France, for  $\text{HF}$ , and  
187  $\text{HClO}_4$ ). The solutions were evaporated to dryness, retaken 3 times in 2 mL of  $\text{HNO}_3$  and then  
188 diluted with 50 mL of MilliQ water. Three different analytical techniques were used to  
189 determine the lead content: atomic absorption spectrometry (AAS), inductively coupled  
190 plasma – atomic emission spectrometry (ICP-AES) and inductively coupled plasma – mass  
191 spectrometry (ICP-MS) (Table 1). The accuracy of the Pb concentration determination was  
192 evaluated through the analysis of the certified reference material SL-1 (lake sediment, AIEA,  
193 Vienna, Austria). The obtained value,  $36.6 \pm 2.0 \text{ mg.kg}^{-1}$  ( $n=15$ ), agreed with the certified  
194 concentration ( $37.7 \text{ mg.kg}^{-1}$ , certification interval:  $30.3 - 45.5 \text{ mg.kg}^{-1}$ ). For all these methods,  
195 the lead concentration determination uncertainty was up to 5%. The procedural “blank”  
196 contribution to the Pb concentration ranges from 0.06 % for sediments with high Pb  
197 concentration up to 0.4% for sediments with low Pb content.

198

199 Fifty millilitres of bulk water samples (containing  $50 \text{ mg.L}^{-1}$  of dry residue) from the  
200 Seine-Aval WWTP were evaporated, the residues were totally dissolved with a mixture of  
201  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HF}$  and  $\text{HClO}_4$  (Normatom grade, VWR) in Teflon vessels using a heating block  
202 (Digiprep, SCP Science). The solutions were evaporated and 2 ml of  $\text{HNO}_3$  were added  
203 afterwards (addition and evaporation sequence repeated three times) and then diluted with 50

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

208

#### 209 **2.4. Lead isotopic measurements.**

210 Lead isotope ratios ( $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$ ) were measured in the sediment  
211 solutions that were also used for lead concentration determinations and were made by ICP-  
212 QMS (X Series, ThermoElectron, France), following the conditions defined in Gallon et al.  
213 (2006). The experimental conditions were: three channels reading; dwell time of 30 ms; 100  
214 sweeps; 5 replicates per sample. Mass bias and drift of the isotope ratios were corrected based  
215 on repeated measurements of the Pb reference material NIST SRM-981 that were analysed  
216 between every three samples. The  $2\sigma$ -errors of isotopic ratios are 0.23% for the  $^{206}\text{Pb}/^{207}\text{Pb}$   
217 and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the blank corresponds to  $1.168 \pm 0.003$  (lying in the  
218 range of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of the samples). SRM-981 was also analysed as a sample  
219 (n=25) to control the bracketing correction. Values  $^{206}\text{Pb}/^{207}\text{Pb} = 1.0933 \pm 0.0015$  and  
220  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0084$  were obtained. Certified values for the SRM-981 are  
221  $^{206}\text{Pb}/^{207}\text{Pb} = 1.09333 \pm 0.00039$  and  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0008$ . The lead isotopic  
222 composition of three samples from core B2 were also determined by thermal ionisation mass  
223 spectrometry (TIMS, Finnigan Mat 261 in LSCE), following the method described in  
224 Doucelance and Manhès, 2001. Even though the data obtained using TIMS are more precise  
225 than the data obtained using ICP-QMS, the results obtained with both instruments are  
226 consistent (see Fig. 2).  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios were measured. The data are  
227 presented in the Supporting Information. Since both ratios are linearly correlated, only the  
228  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio is used in the text.

229

230

### Figure 2

231

### 232 **3. Results.**

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



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

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

244

245

246 The <sup>206</sup>Pb/<sup>207</sup>Pb ratio varies similarly in the cores B2 and M1:

247 - the <sup>206</sup>Pb/<sup>207</sup>Pb ratio is rather stable between 1920 to 1960, ranging from 1.163 ± 0.003 up to  
248 1.166 ± 0.003

249 - between 1960 and 1986/1989, the <sup>206</sup>Pb/<sup>207</sup>Pb ratio decreases to 1.144 ± 0.003

250 - starting from 1986/1989 up to the early 2000's, the <sup>206</sup>Pb/<sup>207</sup>Pb ratio increases up to 1.163 ±  
251 0.002 in 2000 and 1.166 ± 0.003 in 2003.

252 After 2000, the <sup>206</sup>Pb/<sup>207</sup>Pb ratios in B2 and M1 are similar to that observed before  
253 1960, the Pb concentration however is much lower. This is due to the above mentioned  
254 general decrease of the Pb concentration.

255 In TR01, the <sup>206</sup>Pb/<sup>207</sup>Pb ratio increases from 1.1521 ± 0.0015 in the 1970's to 1.175 ±  
256 0.001 in 2001.

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

266

267

268

**Figure 3.**

269

**Table 1**

270

271 The Seine-Aval combined sewer system at Achères (SIAAP) collects 80% of the urban water  
272 originating from the Paris conurbation. The Pb concentration is  $0.53 \pm 0.01 \mu\text{g.L}^{-1}$ , this is in  
273 agreement with the detailed study of the Seine-Aval effluents composition by Buzier et al.,  
274 (2006). The treated waste water, sampled during December 2006 (rainy period) is  
275 characterized by  $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$  and may represent a mixture of lead originating  
276 from different sources (roof and road runoff, domestic and industrial wastewaters).

277

278

## 279 **4. Discussion.**

280

### 281 **4.1. Anthropogenic lead sources in the Seine river basin.**

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

292 During the second part of the 18<sup>th</sup> century, the majority of all Pb used in France was  
293 imported from Spain, French ores played only a minor role (Lestel, 2007). The major part of  
294 Pb imported by France from 1900-1914 came from Spain, Belgium-Luxemburg and United  
295 Kingdom, Pb extraction in French mines did not play an important role. Between World War  
296 1 and World War 2, Spain, Mexico and Tunisia provided most of the Pb manufactured in  
297 France, the proportion of Pb furnished by French mines constantly decreased. After 1945, Pb  
298 was mainly imported from Morocco and Tunisia, more recently from the United State of  
299 America and the European Union. Today, all manufactured Pb in France originates from  
300 recycling.

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

304 straightforward (Table 2). The local natural background signature ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.2007 \pm$   
305  $0.0011$ ) was determined using a 8000 BP- $^{14}\text{C}$  dated sediment (Elbaz-Poulichet et al., 1986).

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

309

310

## Table 2

311

312 The determination of the nature and isotopic signature of the “industrial” end-member  
313 is more difficult. Industrial lead is characterized by an isotopic composition that is  
314 intermediate between the end-members of natural and leaded gasoline ( $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.146 -$   
315  $1.162$ ; Monna et al., 2000; Véron et al., 1999; Widory et al., 2004) but at the same time it is  
316 characterized by significantly higher Pb concentrations. Carignan et al. (2005) suggest to use  
317  $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.003$  as the best estimate for the average French industrial atmospheric  
318 signature emission. Paradoxically, several heavy industries use Pb with isotopic signatures  
319 that are quite distinct from the “industrial” Pb signature (Carignan et al., 2005; Nageotte and  
320 Day, 1998; Véron et al., 1999). In this section, we discuss the possible sources and  
321 characteristics of the so-called “industrial” lead of the Seine basin and we compare it to values  
322 from previous studies. While Pb ores with different origins have been used throughout  
323 history, some prevailing ore isotopic signatures are relevant (Table 3):

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

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

329 Broken Hill: this Australian ore (together with other ores) is specifically used for the  
330 production of the leaded gasoline additives. Its low isotopic signature ( $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.040 \pm$   
331  $0.001$ ) is due to the old age of the crust from which the ore was formed.

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

334

335

## Table 3

336

337 *B2 and M1 cores*

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

343 It is possible to discriminate distinct Pb sources in a diagram where the  $^{206}\text{Pb}/^{207}\text{Pb}$   
344 ratio is plotted as a function of  $1/[\text{Pb}]$  ratio, where [Pb] is the lead concentration ( $\text{mg.kg}^{-1}$ ). In  
345 this diagram, all samples representing a mixing of 2 end-members fall on a straight line (Fig.  
346 4).

#### 347 **Figure 4**

348 Between 1927 and 1968, the lead isotopic signature of B2 and M1 plots in a narrow  
349 range that resembles Rio Tinto (and possibly Moroccan) ores, suggesting that these ores  
350 represent the most important Pb sources reaching the river. Significant contribution of other  
351 European or North American ores would raise the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio above the observed values  
352 unless it is exactly compensated by addition of Pb from Broken Hill (see Table 3 for ores  
353 isotopic lead signatures). This hypothesis is unlikely because the oldest samples from Muide  
354 (1927) preceded the introduction of leaded gasoline (1931) and corresponded to a time when  
355 road traffic was marginal. Contamination of the 1930 sediments by younger sediments that  
356 come from the leaded gasoline period is unlikely, since:

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

361  
362 Therefore the Rio Tinto signature probably represents the main lead contribution to the  
363 Seine River basin. This Rio Tinto ore signature may be the best source estimation for Pb that  
364 accumulated over centuries in the Seine River basin and may be called “historical” Parisian  
365 lead. Around 1850, English companies took the control of the major Spanish mines including  
366 Rio Tinto. Spain began to produce large quantities of lead, sold below the price of lead from  
367 British mines, the former biggest provider to Europe. From 1878, with the declining ore  
368 reserves in Britain, Spain became the major lead producer in Europe (Fletcher, 1991).

369 Surprisingly, the contribution of Pb from “heavy industries” characterized by a high  
370  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio cannot be resolved in the average Seine River basin lead, although it can be

371 detected locally (i.e., near the Eiffel Tower; Nageotte and Day (1998)). From 1968 to  
372 1986/1989, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio decreases from 1.165 (Rio Tinto ~ historical Parisian Pb) to  
373  $1.145 \pm 0.001$  (line 1 on Fig. 4). This decrease is clearly coupled with the raise of the leaded  
374 gasoline emission in combination with the new environmental regulations which lead to a  
375 reduction of other than gasoline anthropogenic lead sources. In 1963, a directive on industrial  
376 effluents quality controls was published. Between 1960 and 1980 domestic wastewater  
377 treatment plants (WWTP) were gradually implemented. One important WWTP, the Seine-  
378 Aval combined sewer system at Achères, was operational at the end of the 70's. In addition to  
379 the reduction of industrial effluents, leaded gasoline reduction started in 1986 and leaded  
380 gasoline was completely banned after 2000. This mixing of historical Parisian lead with lead  
381 from leaded gasoline produces an “urban” lead signature (previously called “industrial”) will  
382 be discussed in more details hereafter.

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

391 Previous studies have pointed out the decrease of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in the time  
392 interval between 1900 and 1930 in the Lake Constance sediments (Germany) (Kober et al.,  
393 1999), in the French Alps lake sediments (Arnaud et al., 2004) and in the Mont Blanc ice  
394 record (Rosman et al., 2000). As in the case of the early signatures in the Seine sediments  
395 (M1), this early trend towards low  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios cannot be explained by leaded gasoline  
396 because leaded gasoline was only introduced on 1931 in France, Italy and Germany. In  
397 contrast the increase of industrial Pb uses, combined with the predominant use of Rio Tinto  
398 Pb, results in a source of Pb that is characterized by a low  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio at the European  
399 scale.

400

#### 401 *TR01 core*

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

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

407

408 *S01 core*

409 The Oise River had already been strongly polluted in 1916 by heavy industries as  
410 indicated by Pb concentrations above the natural background. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio rapidly  
411 increases several times and this may be caused by changes of the lead ores used by the  
412 industry and/or changes in the industrial activity or recycling. Samples from 1916 to 1952 fall  
413 on a mixing line between the natural and the Rio Tinto signature ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.1634 \pm$   
414  $0.0001$ ). Between 1952 and 1960, there is a clear shift towards higher  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios  
415 ( $\sim 1.17$ ) in agreement with the use of European, Tunisian or north American ores together with  
416 recycled ores. This isotopic shift is associated with the highest Pb concentration in the core.  
417 Subsequently the concentrations decrease. And after 1976, the samples tend to be aligned onto  
418 the urban/natural mixing line, similar to the other sites for the last 35 years, suggesting that  
419 the industrial source characterized by high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio has efficiently been removed.

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

425

#### 426 **4.2. Industrial lead signature revisited.**

427

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

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

440 Considering that Pb rejected by the waste water treatment plant (WWTP) directly  
441 enters the river and that the waste waters combine most contaminant sources of lead for the  
442 river (roofs, pipes, accumulators, and oxide-containing glasses), the signature of the waste  
443 waters constitutes the urban lead signature for the river sediments. Indeed the urban lead  
444 signature defined by the isotopic signature of the WWTP Seine –Aval at Achères sewage  
445 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$ ) is not significantly different from the signature of the three  
446 major Parisian municipal solid waste incinerators ( $1.1550 \pm 0.0005$ ; Widory, 2004), the  
447 leaded paint chips and the tap water contaminated by lead pipes (Table 2).

448 The urban signature measured nowadays after the complete stop of leaded gasoline in  
449 2000 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$ ) is significantly different from the measured signature in  
450 the Seine sediments before 1960 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.167 \pm 0.002$ ). This suggests that leaded  
451 gasoline created an “in-depth” contamination of the environment. As argued in the previous  
452 sections, the lead accumulated in the Parisian conurbation is largely dominated by the Rio  
453 Tinto ores signature. This domination is enforced by recycling. The contribution of recycled  
454 lead in manufacture is significant in France: 50% in 1950 increasing to 70% in 2000 (Lestel,  
455 2007). Today all manufactured Pb that is used in France comes from recycling. The large  
456 amount of lead accumulated in the urban structures tends to buffer the isotopic signature in  
457 the river which is marginally shifted by the leaded gasoline in depth imprint.

458 The “industrial lead” denomination is ambiguous because several heavy industries in  
459 the Seine basin and in France show Pb isotopic signatures that are distinct from the “industrial  
460 Pb” (see section “TR01 core”). The lead signature of the Oise river sediment, directly issued  
461 from industrial activities, is quite distinct ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.174 \pm 0.003$ ). Therefore the  
462 denomination “industrial” attributed to all the signatures but gasoline additives may be  
463 abusive. In order to prevent any confusion, we use the term “urban” ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm$   
464  $0.002$ ) for the most common Parisian Pb signatures and “heavy industries” for the relevant  
465 industries.

466

### 467 **4.3. Impact of leaded gasoline of the Seine sediment contamination.**

468

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

471 2007). At the same time leaded gasoline represents almost 90% of the anthropogenic  
 472 atmospheric lead emission (Ferrand et al., 1999), thus raising the possibility that the Seine  
 473 river catchment suffers from a wide contamination by road traffic. The present data can be  
 474 used to evaluate the contribution of the leaded gasoline to the Seine contamination.

475 The maximum impact of the leaded gasoline in the Seine sediment contamination was  
 476 reached in 1986/1989 (Fig. 3), when the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio was at its lowest value ( $1.146 \pm$   
 477  $0.002$ ). Considering that the lead was a mixture of leaded gasoline ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.08 \pm 0.02$ )  
 478 and historical lead whose signature is defined by the oldest sedimentary deposits ( $^{206}\text{Pb}/^{207}\text{Pb}$   
 479  $= 1.165 \pm 0.002$  in 1943 (B2)), as shown by the mixing line 1 on Fig. 4, the fraction of lead  
 480 issued from the gasoline ( $f_{\text{gasoline}}$ ) in the Seine River sediments is given by Equation 1:

481

$$482 \quad f_{\text{gasoline}} = \frac{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{sample}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{historica}}}{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{gasoline}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{historica}}} \quad (\text{Eq. 1})$$

483

484

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

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

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



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

508 The stock of anthropogenic lead in the soils of Paris area is estimated to lie close to  
509 143,000 t (Saby et al., 2006). This stock includes the fallouts issued from the leaded gasoline  
510 combustion. Therefore, most Pb issued for the leaded gasoline combustion did not (yet) reach  
511 the river. The lead issued from gasoline that is seen in the Seine sediment around 1986 was  
512 probably brought to the river by road and roof runoff. The direct contamination of Pb from  
513 leaded gasoline in the atmosphere compared to the other sources of Pb also explains that the  
514 fraction of Pb from leaded gasoline is lower in the urban lead characterised in the  
515 hydrosystem ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.146 \pm 0.002$ ) than in Parisian aerosols samples approximately at  
516 the same period ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.1187 - 1.1260$  in 1989; Véron et al., 1999).

517

#### 518 **4.4. Lead sources today.**

519

520 Since runoff has probably washed out the labile lead source (i.e., the lead-  
521 contaminated particles on non-permeable surfaces) and since the direct inputs of lead from the  
522 heavy industries are very low, the lead concentration today in the Seine river sediments  
523 represents a mixture of natural and urban lead (line 2 in Fig. 4). Considering the respective  
524 signature of the natural lead ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.2007 \pm 0.0011$ ) and the signature of urban lead  
525 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$ ) (line 2 in Fig. 4), we calculate that the lead today ( $^{206}\text{Pb}/^{207}\text{Pb} =$   
526  $1.166 \pm 0.004$ ) is constituted of 30% of natural lead and 70% of urban lead. This result is  
527 compatible with the concentration data, as the natural background concentration is 27-40 mg  
528  $\text{kg}^{-1}$  and the total lead sediment concentration is 77  $\text{mg kg}^{-1}$ . If the Pb concentration in the  
529 urban end-member is much higher than in the natural one, it corresponds to 34% of natural  
530 lead and 66% of urban lead. Moreover, these findings are also consistent with the study by  
531 Thévenot et al. (2007). These authors evaluate the sources and pathways budget for seven  
532 metals including lead in the Seine River basin for the period, 1994 – 2003. The total lead  
533 inputs to the river reached 65  $\text{t y}^{-1}$ , 14  $\text{t y}^{-1}$  come from erosion (22%). The anthropogenic

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

537

## 538 **5. Conclusion.**

539

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

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

561

562

563

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570

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

573

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709

710 **Tables**

711

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

713

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

715

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

718

719 **Figures**

720

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

725

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

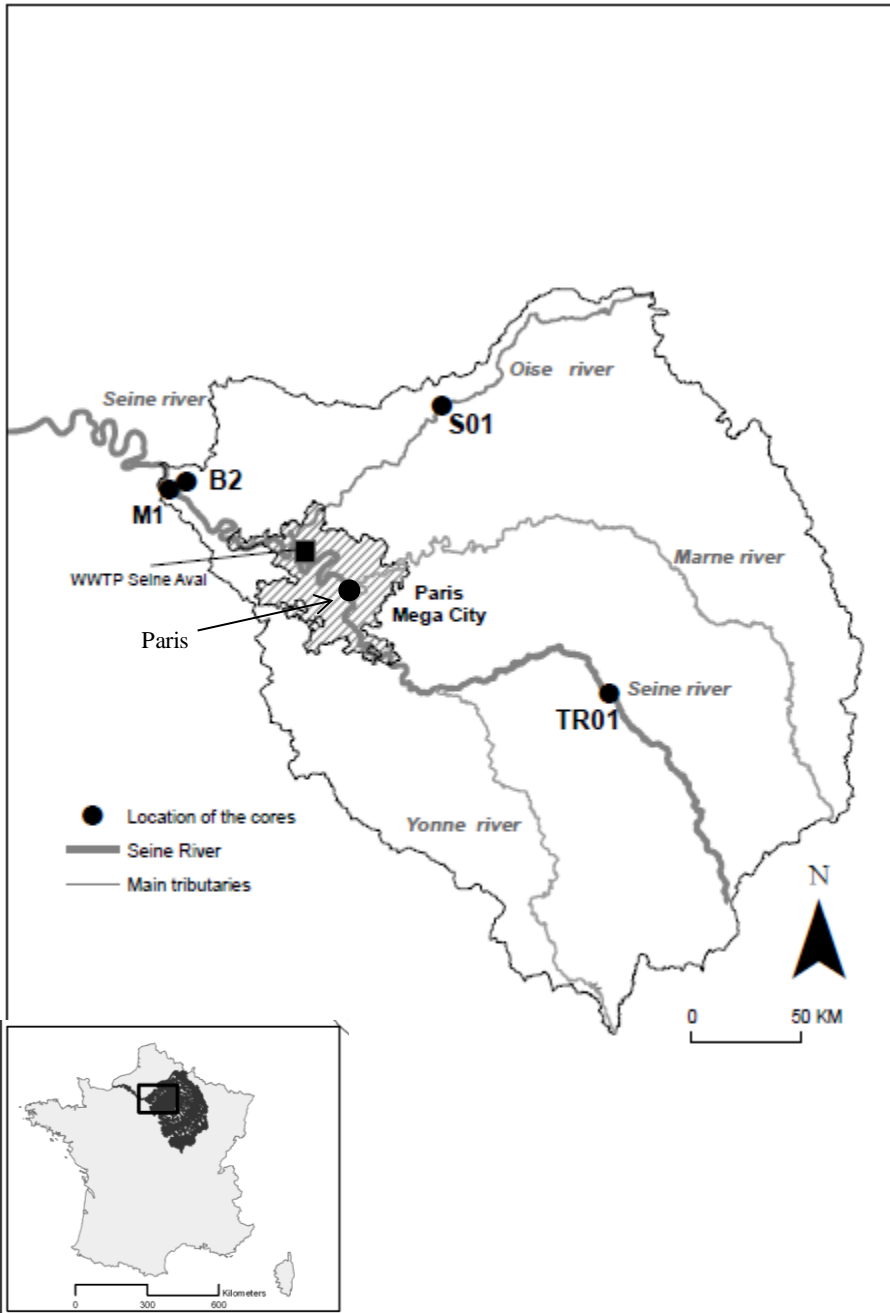
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730 **Figure 3.** Lead concentration and isotope ratio in the dated depth profiles in four cores in the  
731 Seine River basin.

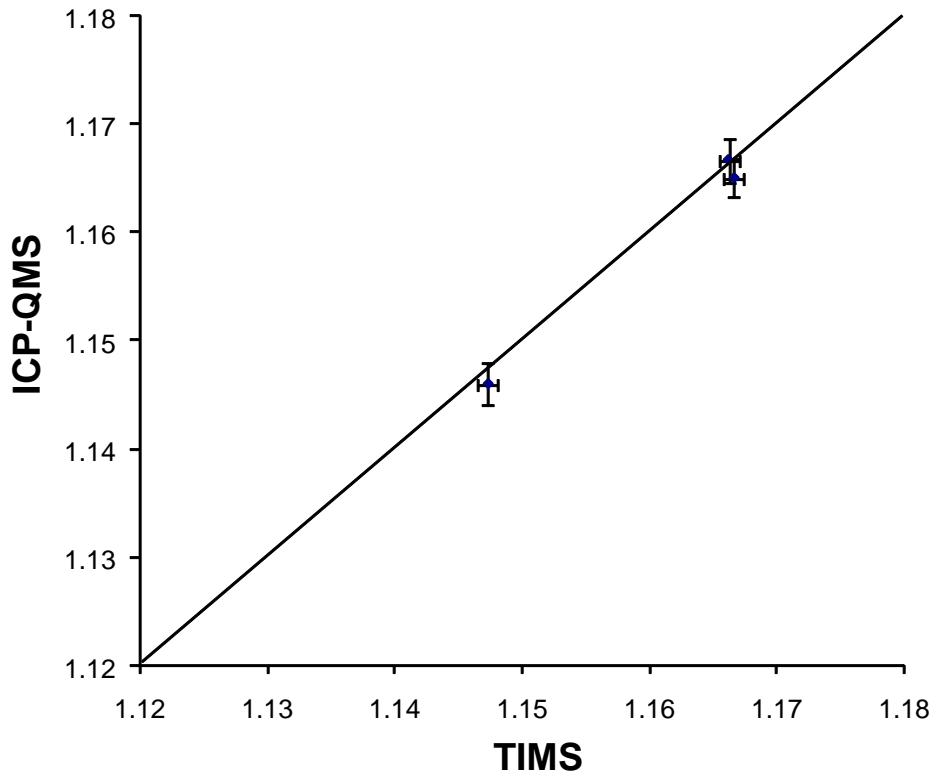
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733 **Figure 4.** Evolution of the lead isotopic composition ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) in the Seine River basin  
734 sediment: influence of geochemical background, leaded gasoline and heavy industries.

Figure

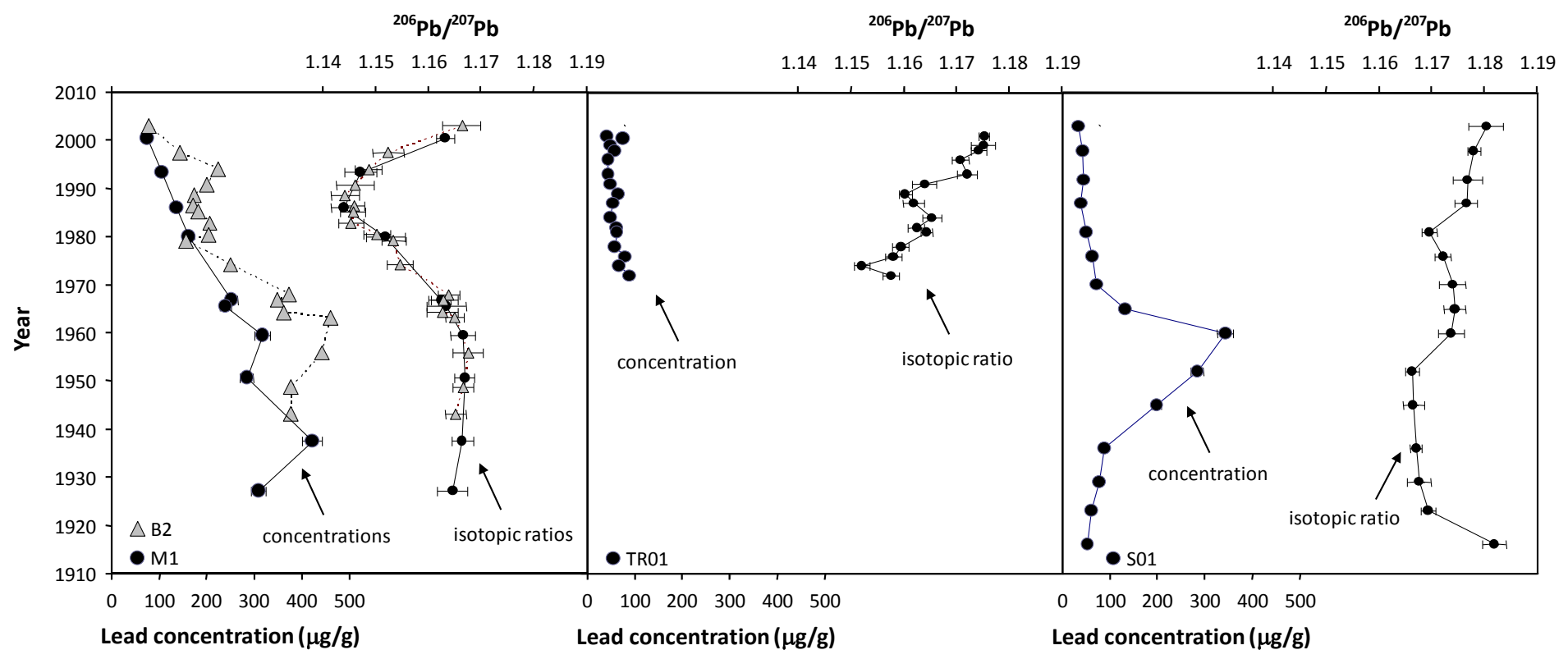






**Figure 2.** Lead isotopic composition ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) by thermal ionisation mass spectrometry (TIMS) and inductively coupled plasma – mass spectrometry (ICP-QMS) in three sediment samples ( $2\sigma$  error bars).

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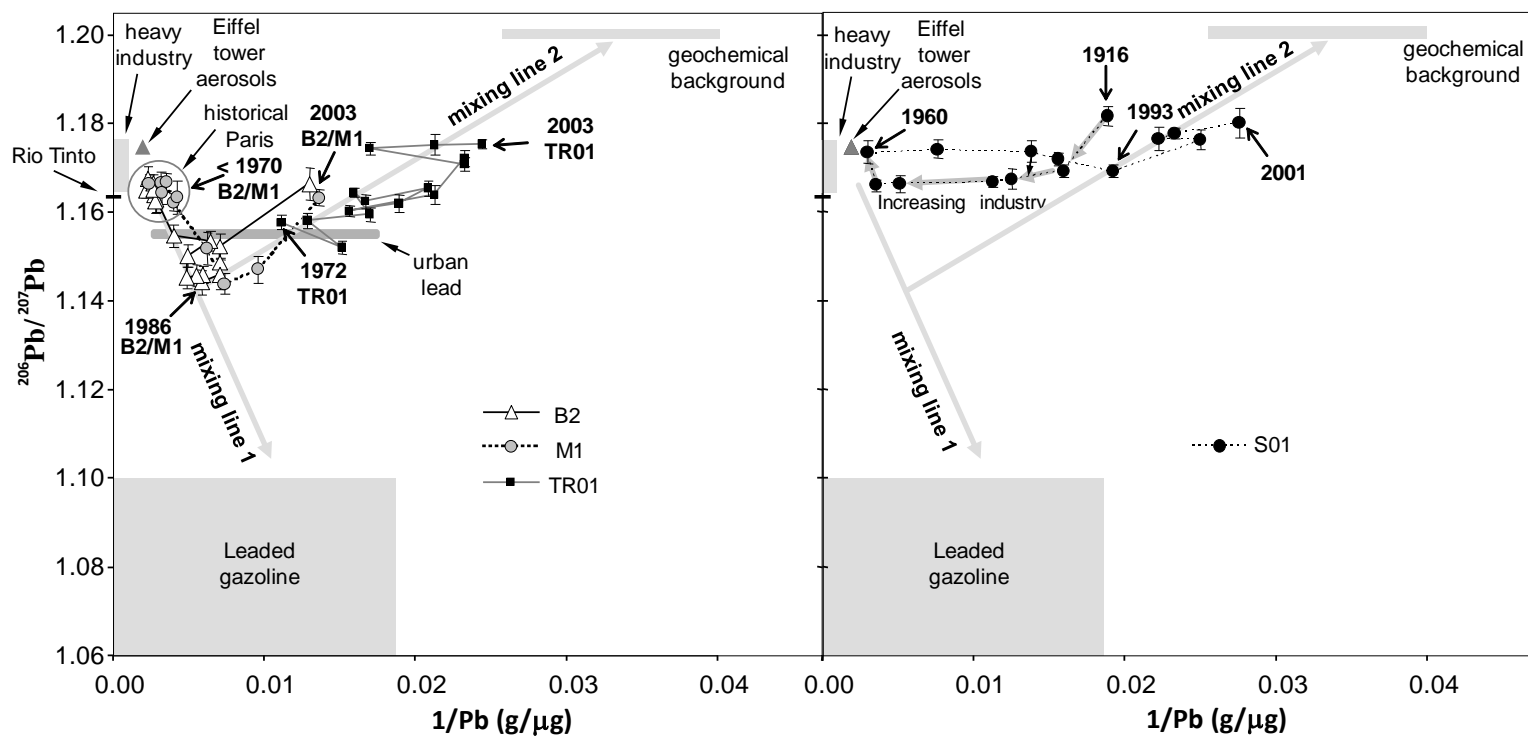
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**Table 1.** Details on the four analysed cores sampled in the Seine River basin.

	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 <sup>-1</sup> )	2.6 <sup>a</sup>	1.1 <sup>b</sup>	1.1 <sup>b</sup>	1.8 <sup>b</sup>
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	

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

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

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

<sup>a</sup> Average of 3 Parisian incinerators (Issy, Ivry-sur-Seine, Saint Ouen).

<sup>b</sup> 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.**  $^{206}\text{Pb}/^{207}\text{Pb}$  signature of lead in ores potentially imported by France from 1900 to today.

	$^{206}\text{Pb}/^{207}\text{Pb}$	Reference
<b>Belgium</b>	1.16 -1.18	De Vleeschouwer et al., 2007 Dejonghe et al., 1989
<b>Germany</b>		
(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
<b>Spain</b>		
(Mazarrón, Cartagena)	1.191 – 1.195	Arribas and Tosdal, 1994
(Rio Tinto)	1.1633 – 1.1635	Marcoux., 1998
<b>France</b>		
(L'Argentière)	1.1701	Arribas and Tosdal, 1994
(La Maligne)	1.1742	Arribas and Tosdal, 1994
<b>United Kingdom</b>		
(Mendips)	1.176 – 1.189	Alfonso et al., 2001
(Debyshire)	1.171 – 1.188	"
<b>Mexico</b>	1.200 ± 0.006 (n=48)	Cuming et al., 1979
<b>Tunisia</b>	1.1971 ± 0.0045 (n=11)	Sahnoun et al., 2009
<b>Morocco</b>	1.1638 ± 0.0071 (n=30)	"
<b>USA</b> (Mississippi valley-type deposits)	> 1.2	Deloule et al., 1986 ; Kesler et al., 1994
<b>Australia</b> (Broken Hill)	1.0412 ± 0.0011	Townsend et al. 1998