



HAL
open science

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

Sophie Ayrault, Matthieu Roy-Barman, Marie-Françoise Le Cloarec, Cindy
Rianti Priadi, Philippe Bonté, Christa Göpel

► To cite this version:

Sophie Ayrault, Matthieu Roy-Barman, Marie-Françoise Le Cloarec, Cindy Rianti Priadi, Philippe Bonté, et al.. Lead contamination of the Seine River, France: Geochemical implications of a historical perspective. *Chemosphere*, 2012, 87 (8), pp.902-910. 10.1016/j.chemosphere.2012.01.043 . cea-02615666

HAL Id: cea-02615666

<https://cea.hal.science/cea-02615666>

Submitted on 29 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

3 Sophie Ayrault ^{a,*}, Matthieu Roy-Barman ^a, Marie-Françoise Le Cloarec ^a, Cindy
4 Rianti Priadi ^a, Philippe Bonté ^a, Christa Göpel ^b

5
6 ^a Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), UMR 1572
7 (CEA/CNRS/UVSQ), Domaine du CNRS – Bâtiment 12, Avenue de la Terrasse, F-91198
8 Gif-sur-Yvette Cedex (France)

9 ^b IGP, Laboratoire de Géochimie et Cosmochimie, 1 rue Jussieu, 75238 Paris (France)

10
11 *Corresponding author. Dr Sophie Ayrault, sophie.ayrault@lsce.ipsl.fr, Tel +33 1 69824354;
12 Fax +33 1 69823568

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⁻¹) lies significantly above the natural
18 background (27-40 mg.kg⁻¹), although a significant decrease (down to 75 mg.kg⁻¹) was
19 observed during the second half of the 20th century which can be explained by the reduction
20 of lead emissions. The ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb = 1.1634 ± 0.0001). A high contribution, up to 25%, from the leaded gasoline
23 (characterized by ²⁰⁶Pb/²⁰⁷Pb = 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 (²⁰⁶Pb/²⁰⁷Pb = 1.1550 ± 0.0005) and waste water treatment plant
27 (²⁰⁶Pb/²⁰⁷Pb = 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 ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb ratios (~1.18-1.19) and possibly a minor amount of North American lead
33 (²⁰⁶Pb/²⁰⁷Pb 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.*

39

40 **1. Introduction.**

41

42 The Seine river basin (67,500 km²) 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 km², 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⁻¹ (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 (²⁰⁶Pb/²⁰⁷Pb =
64 1.101 ± 0.001), but were less important for indoor dust accumulated from 1971 to 1981
65 (²⁰⁶Pb/²⁰⁷Pb = 1.120 ± 0.001) and even lower for the Seine River sediment (²⁰⁶Pb/²⁰⁷Pb =
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 (²⁰⁶Pb/²⁰⁷Pb = 1.169; Millot et
68 al., 2004). In 1997, the lead contained in the street dust of Paris (²⁰⁶Pb/²⁰⁷Pb = 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}Cs - and ^{210}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 km², and the population density is low, 40 inhabitants km⁻². 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 23rd, 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 km² 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}Cs -
149 and ^{210}Pb . Both are strongly adsorbed on the fine fraction of the sediment (Wang and Cornett,
150 1993; Gil-García et al., 2009). Artificial ^{137}Cs is used as an event-tracer, whereas natural ^{210}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°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}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}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}Cs stock stored in soils decreases by radioactive decay and fine sediment transfer to
167 the rivers. ^{137}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 Bq.kg^{-1} .
169 ¹.

170 ^{210}Pb , a natural radionuclide ($t_{1/2} = 22.3$ years), is a decay product of ^{238}U ($t_{1/2} = 4.5 \cdot 10^9$
171 years). ^{238}U decays through a series of short-lived nuclides (e.g. ^{226}Ra , ^{222}Rn). ^{222}Rn is a gas
172 that partly remains *in situ*, forming “supported” ^{210}Pb , and that partly escapes to the
173 atmosphere, forming “excess” ^{210}Pb . Excess ^{210}Pb is deposited on the soil surface via wet and
174 dry fallout and strongly sticks to the soil particles. The ^{210}Pb activity in “excess” is calculated
175 by subtracting the supported activity (determined using a ^{238}U daughter, i.e. ^{214}Bi from the
176 total activity of ^{210}Pb (Bonté et al., 2000). The uncertainty of the measurements (ca. 10%) is
177 higher than that for ^{137}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% HNO_3 (3 mL) and 30% HCl (7 mL) mixture, 65% HNO_3 and 40% HF (5 mL
184 each), and 65% HNO_3 and 69-72% 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 HNO_3 , and HCl , “for trace metal analyses”, Baker, SODIPRO, France, for HF , and
187 HClO_4). The solutions were evaporated to dryness, retaken 3 times in 2 mL of 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 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 mg.L^{-1} of dry residue) from the
200 Seine-Aval WWTP were evaporated, the residues were totally dissolved with a mixture of
201 HNO_3 , HCl , HF and HClO_4 (Normatom grade, VWR) in Teflon vessels using a heating block
202 (Digiprep, SCP Science). The solutions were evaporated and 2 ml of 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 2σ -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 ± 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

230 **Figure 2**

231

232 **3. Results.**

233 Results are reported in Figure 3. Pb concentrations range from 76 mg.kg^{-1} up to 460
234 mg.kg^{-1} in B2 (Bouafles), 73 mg.kg^{-1} to 421 mg.kg^{-1} in M1 (Muids), from 36 mg.kg^{-1} to 342
235 mg.kg^{-1} in S01 (Oise) and from 41 mg.kg^{-1} to 90 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⁻¹.

244

245

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

247 - the ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb ratio decreases to 1.144 ± 0.003

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

252 After 2000, the ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb ratio increases from 1.1521 ± 0.0015 in the 1970's to 1.175 ±
256 0.001 in 2001.

257 In S01, the ²⁰⁶Pb/²⁰⁷Pb 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 ²⁰⁶Pb/²⁰⁷Pb ratio
260 (²⁰⁶Pb/²⁰⁷Pb = 1.173 ± 0.003). This higher ²⁰⁶Pb/²⁰⁷Pb ratio then decreases until 1981
261 (²⁰⁶Pb/²⁰⁷Pb = 1.1693 ± 0.0015) and increases again (²⁰⁶Pb/²⁰⁷Pb = 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⁻¹. This value lies close to the geochemical background (27-40
264 mg.kg⁻¹; Thévenot et al., 2007; Meybeck et al., 2007), while in 1960, concentration up to 342
265 mg.kg⁻¹ 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 18th 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}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 (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}Cs profile and the ^{137}Cs fallout history precludes mixing of the
- 358 sediments (both ^{137}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 ± 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 (Milot 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 (~ 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 ± 0.001 and 1.101 ± 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 ± 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_{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 ± 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 kg^{-1} and the total lead sediment concentration is 77 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 t y^{-1} , 14 t y^{-1} come from erosion (22%). The anthropogenic

534 sources of lead to the river (51 t y^{-1}) are mainly located in urban areas (48 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 19th 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 19th century could account for the general
558 decrease of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio during the 19th and early 20th 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

564 *Acknowledgements.* We thank G. Varrault and B. Pernet-Coudrier for their help for the
565 collection of WWTP sediment, and O. Evrard for mapping and land cover data collection. J.-
566 M. Mouchel is thanked for his active participation to the sediment core collection and his
567 continuous support to this work. We thank the 2 anonymous reviewers for their thoughtful

568 comments. This work has been made possible thanks to funding from the Piren-Seine
569 programme coordinated by J.-M. Mouchel. This is the LSCE contribution number 4517.

570

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

573

574 **REFERENCES.**

- 575 Alfonso, S., Grousset, F., Massé, L., Tastet, J.P. A European lead isotope signal recorded
576 from 6000 to 300 years BP in coastal marshes (SW France). *Atmos. Environ.* 35 (2001)
577 3595-605.
- 578 Arnaud, F., Revel-Rolland, M., Bosch, D., Winiarski, T., Desmet, M., Tribovillard, N.,
579 Givelet, N. A 300 year history of lead contamination in northern French Alps
580 reconstructed from distant lake sediment records. *J. Environ. Monit.* 6 (2004) 448-56.
- 581 Arribas, A., Tosdal, R.M. Isotopic composition of Pb in ore deposits of the Betic Cordillera,
582 Spain: Origin and relationship to other European deposits. *Econ. Geol.* 88 (1994) 1074-
583 93.
- 584 Ayrault, S., Rianti, C., Evrard, O., Lefèvre, I., Bonté, P. Silver and thallium historical trends
585 in the Seine River basin. *J. Environ. Monit.* 12 (2010) 2177-85.
586 doi:10.1039/C0EM00153H.
- 587 Bonté, P., Mouchel, J.M., Thomas, A.J., Le Cloarec, M.F., Dumoulin, J.P., Sogon, S., Tessier,
588 L. Buffering of suspended sediment transport in lowland river during low water stages:
589 quantification in river Seine using environmental radionuclides. *Acta Geol. Hisp.* 35
590 (2000) 339-55.
- 591 Buzier, R., Tusseau-Vuillemin, M.H., Martin dit Meriadec, C., Rousselot, O., Mouchel, J.M.
592 Trace metal speciation and fluxes within a major French wastewater treatment plant:
593 Impact of the successive treatments stages. *Chemosphere* 65 (2006) 2419–26.
- 594 Carignan, J., Libourel, G., Cloquet, C., Le Forestier, L. Lead Isotopic Composition of Fly Ash
595 and Flue Gas Residues from Municipal Solid Waste Combustors in France :
596 Implications for Atmospheric Lead Source Tracing. *Environ. Sci. Technol.* 39 (2005)
597 2018-24.
- 598 Chillrud, S.N., Bopp, R.F., Ross, J.M., Chaky, D.A., Hemming, S., Shuster, E.L., Simpson,
599 H.J., Estabrooks, F. Radiogenic lead isotopes and time stratigraphy in the Hudson
600 River, New York. *Water, Air, Soil Pollut.* (2003) 469-82.
- 601 Cloquet, C., Carignan, J., Libourel, G. Atmospheric pollutant dispersion around an urban area
602 using trace metal concentrations and Pb isotopic compositions in epiphytic lichens.
603 *Atmos. Environ.* 40 (2006) 574–87.
- 604 Cuming, G.L., Kesler, S.E., Krstic, D. Isotopic composition of lead in Mexican mineral
605 deposits. *Econ. Geol.* 74 (1979) 1395-407.
- 606 Dejonghe, L., Boulègue, J., Demaiffe, D., Létolle, R. Isotope geochemistry (S, C, O, Sr, Pb)
607 of the Chaudfontaine mineralization (Belgium). *Miner. Deposita* 24 (1989) 132-40.
- 608 Deloule, E., Allègre, C.J., Doe, B.R. Lead and sulfur isotope microstratigraphy in galena
609 crystals from Mississippi valley-type deposits. *Econ. Geol.* 81 (1986) 1307-21.
- 610 De Vleeschouwer, F., Gérard, L., Goormaghtigh, C., Mattielli, N., Le Roux, G., Fagel, N.
611 Atmospheric lead and heavy metal pollution records from a Belgian peat bog spanning
612 the last two millennia: Human impact on a regional to global scale. *Sci. Total Environ.*
613 377 (2007) 282-95.
- 614 Doucelance, R., Manhès, G. Reevaluation of precise lead isotope measurements by thermal
615 ionization mass spectrometry: comparison with determinations by plasma source mass
616 spectrometry. *Chem. Geol.* 176 (2001) 361–77.
- 617 Elbaz-Poulichet, F., Holliger, P., Martin, J.M., Petit, D. Stable lead isotopes ratios in major
618 French rivers and estuaries. *Sci. Total Environ.* 54 (1986) 61-76.
- 619 Fletcher, S. Lead Mining in Pain in the 19th century: Spanish industry or British adventure?
620 *Bulletin Peak District Mines Historical Society* 11(4) (1991) 195-202.
- 621 Ferrand, J.L., Hamelin, B., Monaco, A. Isotopic tracing of anthropogenic Pb inventories and
622 sedimentary fluxes in the Gulf of Lions (NW Mediterranean sea). *Cont. Shelf Res.* 19
623 (1999) 23-47.

624 Gallon, C., Tessier, A., Gobeil, C. Historical perspective of industrial lead emissions to the
625 atmosphere from a Canadian Smelter. *Environ. Sci. Technol.* 40 (2006) 741-747.

626 Gil-García, C., Rigol, A., Vidal, M. New best estimates for radionuclide solid-liquid
627 distribution coefficients in soils, Part 1: radiostrontium and radiocaesium. *J. Environ.*
628 *Radioact.* 100 (2009) 690-6.

629 Kabata-Pendias, A., Pendias, H. *Trace Elements in Soils and Plants*, 2nd ed. CRC Press, Boca
630 Raton, 1992.

631 Kesler, S.E., Cumming, G.L., Krstic, D., Appold, M.S. Lead Isotope Geochemistry of
632 Mississippi Valley-Type Deposits of the Southern Appalachians. *Econ. Geol.* 89 (1994)
633 307-21.

634 Kober, B., Wessels, M., Bollhöfer, A., Mangini, A. Pb isotopes in sediments of Lake
635 Constance, Central Europe constrain the heavy metal pathways and the pollution history
636 of the catchment, the lake and the regional atmosphere. *Geochim. Cosmochim. Acta* 63,
637 9 (1999) 1293-1303.

638 Kumar, M., Furumai, H., Kurisu, F., Kasuga, I. Understanding the partitioning processes of
639 mobile lead in soakaway sediments using sequential extraction and isotope analysis.
640 *Water Sci. Technol.* 60.8 (2009) 2085-2091.

641 Krahn, L., Baumann, A. Lead isotope systematics of epigenetic lead-zinc mineralization in the
642 western part of the Rheinisches Schiefergebirge, Germany. *Miner. Deposita* 31 (1996)
643 225-237.

644 Laurensot, F. Importance de la qualité de l'eau sur l'imprégnation saturnine. Identification des
645 sources prépondérantes d'exposition au plomb. Utilisation de l'isotopie. Rapport d'étude.
646 LHRSP, Agence de l'eau Seine-Normandie. (2001) 52 p.

647 Large, D., Schaeffer, R., Höhndorf, A. Lead Isotope Data from Selected Galena Occurrences
648 in the North Eifel and North Sauerland, Germany. *Miner. Deposita* 18 (1983) 235-43.

649 Le Cloarec, M.F., Bonté, P., Mouchel, J.M., Lefèvre, I., Colbert, S. Distribution of ^{210}Pb , ^7Be
650 and ^{137}Cs in watersheds of different scales in the Seine basin: inventories and residence
651 times. *Sci. Total Environ.* 375 (2007) 125-39.

652 Le Cloarec, M.F., Bonté, P., Lestel, L., Lefèvre, I., Ayrault, S. Sedimentary record of metal
653 contamination in the Seine River during the last century. *Phys. Chem. Earth, in press.*

654 Lestel, L. Le cycle du plomb. 2007; hal-00199344, version 1, [http://hal.archives-](http://hal.archives-ouvertes.fr/hal-00199344/en/)
655 [ouvertes.fr/hal-00199344/en/](http://hal.archives-ouvertes.fr/hal-00199344/en/) (in French).

656 Meybeck, M., Lestel, L., Bonté, P., Moilleron, R., Colin, J.L., Rousselot, O., et al. Historical
657 perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River
658 basin (France) following a DPSIR approach (1950-2005). *Sci. Total Environ.* 375
659 (2007) 204-31.

660 Millot, R., Allègre, C.J., Gaillardet, J., Roy, S. Lead isotopic systematics of major river
661 sediments: a new estimate of the Pb isotopic composition of the Upper Continental
662 Crust. *Chem. Geol.* 203 (2004) 75-90

663 Monna, F., Clauer, N., Toulkeridis, T., Lancelot, J. R. Influence of anthropogenic activity on
664 the lead isotope signature of Thau Lake sediments (southern France): origin and
665 temporal evolution. *Appl. Geochem.* 15 (2000) 1291-1305.

666 Nageotte, S., Day, J.P. Lead concentrations and isotope ratios in street dust determined by
667 electrothermal atomic absorption spectrometry and inductively coupled plasma mass
668 spectrometry. *Analyst* 123 (1998) 59-62.

669 Pernet-Coudrier, B., Clouzot, L., Varrault, G., Tusseau-Vuillemin, M.H., Verger, A.,
670 Mouchel, J.M. Dissolved organic matter from treated effluent of a major wastewater
671 treatment plant: characterization and influence on copper toxicity. *Chemosphere* 73
672 (2008) 593-9.

673 Marcoux, E. Lead isotope systematics of the giant massive sulphide deposits in the Iberian
674 Pyrite Belt. *Miner. Deposita* 33 (1998) 45-58.

675 Rabinowitz, M.B. Lead isotopes in soils near five historic American lead smelters and
676 refineries. *Sci. Total Environ.* 346 (2005) 138– 48.

677 Rosman, K.J.R., Ly, C., Van de Velde, K., Boutron, C.F. A two century record of lead
678 isotopes in high altitude Alpine snow and ice. *Earth Planet. Sci. Lett.* 176 (2000) 413-
679 24.

680 Saby, N., Arrouays, D., Boulonne, L., Jolivet, C., Pochot, A. Geostatistical assessment of Pb
681 in soil around Paris, France. *Sci. Total Environ.* 367 (2006) 212-21.

682 Sahnoun, O., Schärer, U., Added, A., Fernex, F., Abdeljaoued, S. Metal origin and Pb
683 isotopes in water of the mine-draining Mejerda river system, north Tunisia. *Geochem.:
684 Explor. Environ. Anal.* 9 (2009) 369-80.

685 Shotyk, W., Weiss, D., Appleby, P., Cheburkin, A., Frei, R., Gloor, M., Kramers, J., Reese,
686 S., Van Der Knapp, W. History of atmospheric lead deposition since 12,370 ¹⁴C yr BP
687 from peat bog, Jura Mountains, Switzerland. *Science* (1998) 281, 1635-40.

688 Soster, F.M., Matisoff, G., Whiting, P.J., Fornes, W., Ketterer, M., Szechenyi, S. Floodplain
689 sedimentation rates in an alpine watershed determined by radionuclide techniques. *Earth
690 Surf. Proces. Landforms* 32 (2007) 2038-51.

691 Thévenot, D.R., Moilleron, R., Lestel, L., Gromaire, M.C., Rocher, V., Cambier, P., Bonté,
692 P., Colin, J.L., de Pontevès, C., Meybeck, M. Critical budget of metal sources and
693 pathways in the Seine River basin (1994-2003) for Cd, Cr, Cu, Hg, Ni, Pb and Zn. *Sci.
694 Total Environ.* 375 (2007) 180-203.

695 Townsend, A.T., Yu, Z., McGoldrick, P., Hutton, J.A. Precise lead isotope ratios in Australian
696 galena samples by high resolution inductively coupled plasma mass spectrometry. *J.
697 Anal. At. Spectrom.* 13 (1998) 809-13.

698 Véron, A., Flament, P., Bertho, M.L., Alleman, L., Flegal, R., Hamelin, B. Isotopic evidence
699 of pollutant lead sources in Northwestern France. *Atmos. Environ.* 33 (1999) 3377-88.

700 Wang, K., Cornett, R.J. Distribution coefficients of ²¹⁰Pb and ²¹⁰Po in laboratory and natural
701 aquatic systems. *J. Paleolimnol.* 9 (1993) 179-88.

702 Widory, D., Roy, S., Le Moullec, Y., Toupil, G., Cocherie, A., Guerrot, C. The origin of
703 atmospheric particles in Paris: a view through carbon and lead isotopes. *Atmos.
704 Environ.* 38 (2004) 953-61.

705 Widory, D. Development of a method for characterising contributions of point sources to
706 atmospheric emissions of particles using a multi-isotopic approach: Application to the
707 urban area of Paris. Report BRGM/RP-53335-FR (2004).

708

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 (2σ error bars).

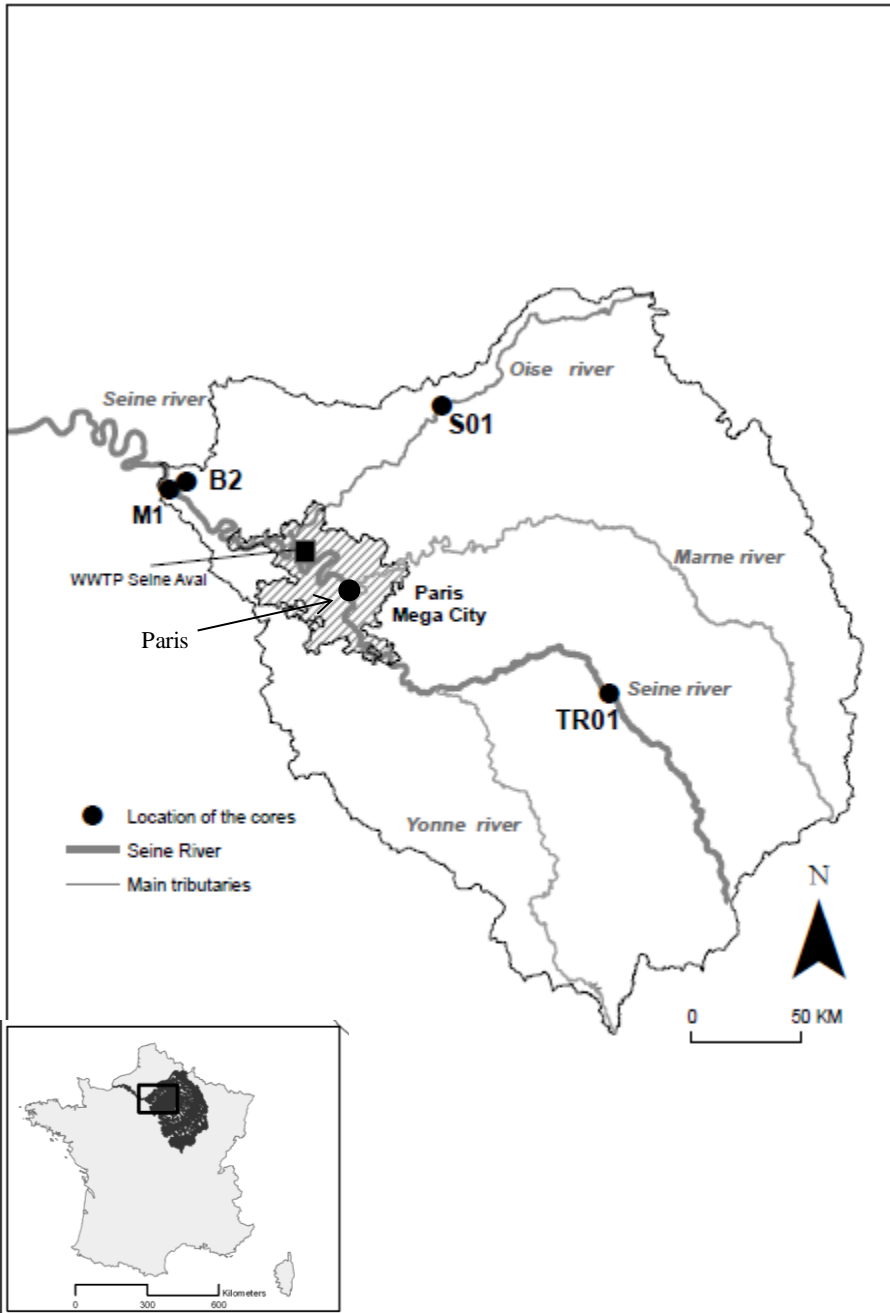
729

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

732

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



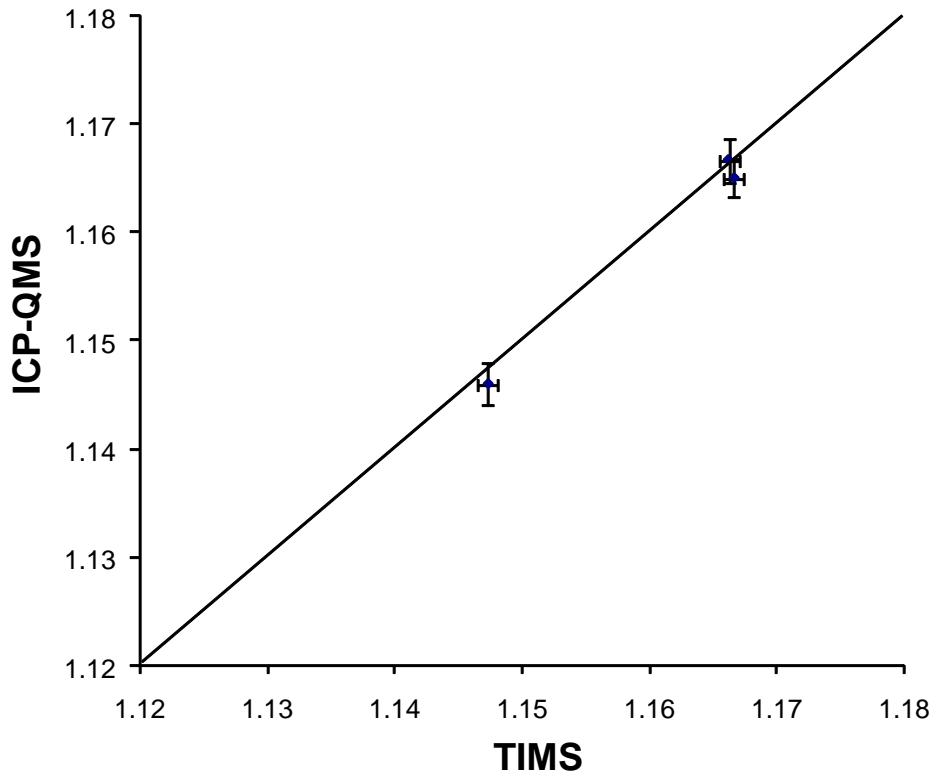
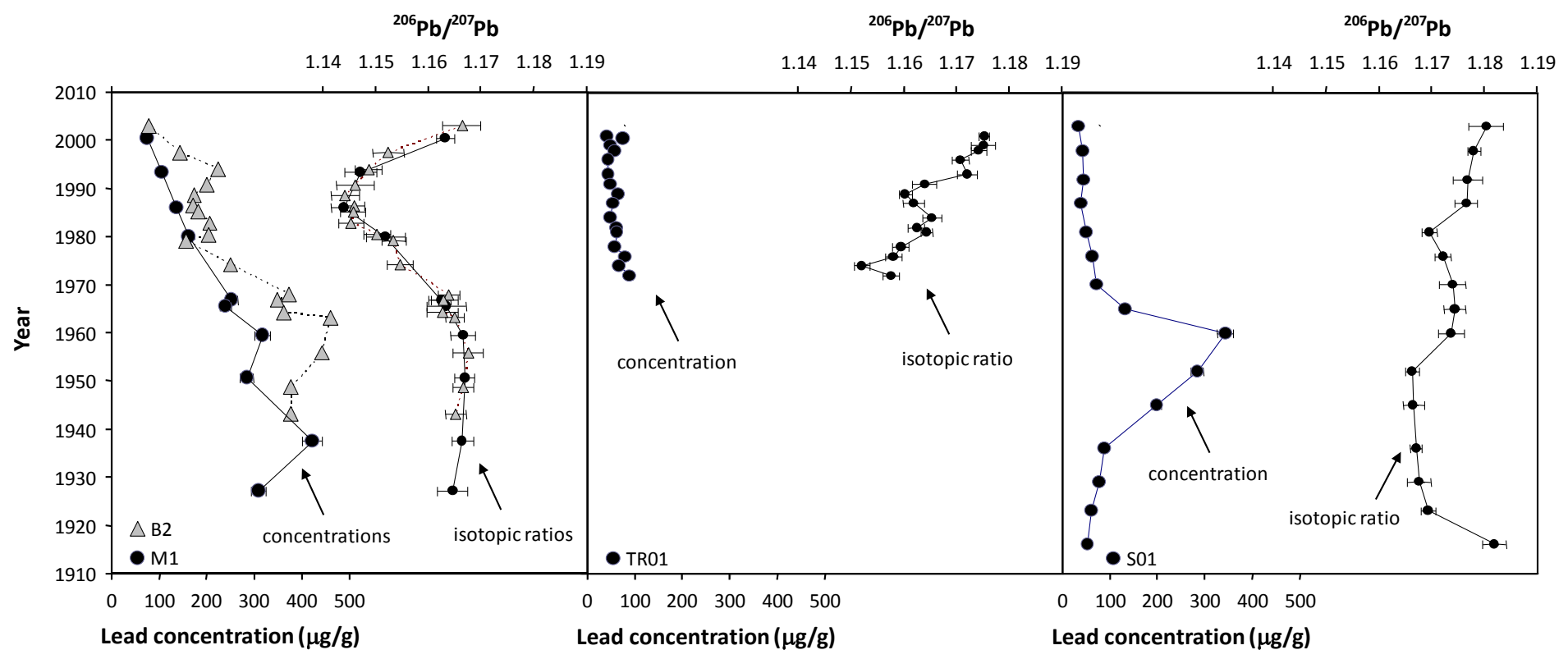


Figure 2. Lead isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$) by thermal ionisation mass spectrometry (TIMS) and inductively coupled plasma – mass spectrometry (ICP-QMS) in three sediment samples (2σ error bars).

1



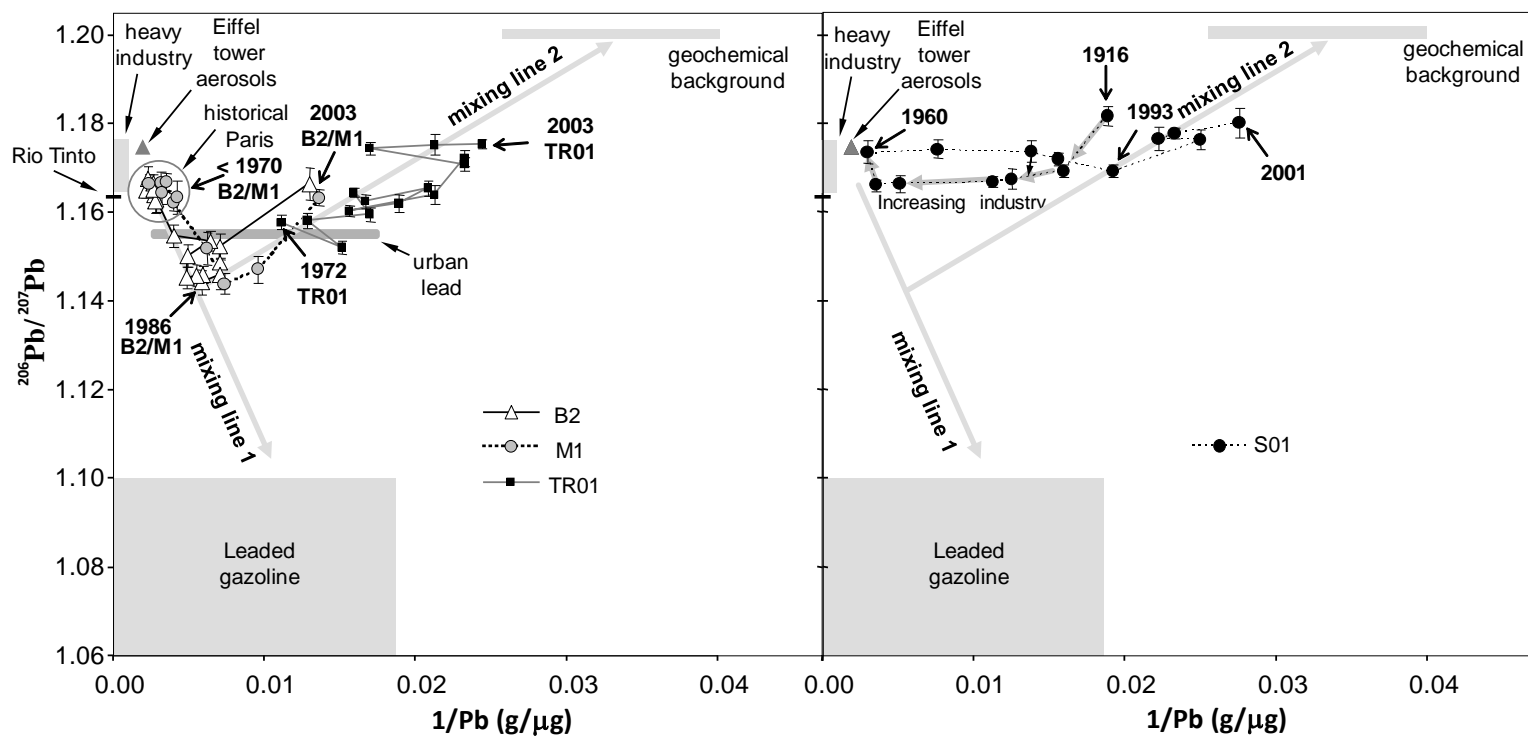
2

3

4

Figure

1
2
3



4

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

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

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

Table 2. $^{206}\text{Pb}/^{207}\text{Pb}$ 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 ± 0.0011	Elbaz-Poulichet et al. (1986)
Road dust (suburbs)	1978	1.101 ± 0.001	id
Indoor dust (Paris)	1971 – 1981	1.120 ± 0.001	id
Street dust (Paris)	1997	1.151	Nageotte and Day (1998)
Eiffel tower paints	1997	1.174	id
Municipal solid waste incinerators	2001	1.1550 ± 0.0005^a	Widory (2004)
Urban heating plants (Paris)	2003		
	burning oil	1.11	id
	burning gas	1.14 – 1.20	id
Leaded gasoline	1980 - 1987	1.10 ± 0.04	Véron et al. (1999)
	1987-1992	1.08 ± 0.03	id
	1993	1.09 ± 0.02	id
	1994-1995	1.06 ± 0.02	id
Unleaded paints ^b	>> 1940	1.1534 ± 0.0066	Laurenst (2001)
Leaded paints ^b	< 1940	1.1596 ± 0.0023	id
Tap water (presence of lead pipes, [Pb] = 25 µg/L)	1996 – 1998	1.1561 ± 0.0031	id
Urban waste waters (combined sewer)	2006	1.154 ± 0.002	This work

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

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

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

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