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Silver and thallium historical trends in the Seine River basin

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Abstract

Records on pollution by metals of minor economic importance (e.g. silver, thallium) but which prove to be toxic are rarely documented in river sediment. This study used two sediment cores collected downstream of the Seine River to describe the temporal evolution of Ag and Tl concentrations in an urban catchment. Radionuclide analysis (i.e. Cs-137 and Pb-210) allowed dating sediment deposition within the cores (1933-2003). Ag concentration reached maximum values of 14.3 – 24.6 mg kg⁻¹ in the 1960s and 1970s, before gradually decreasing up to values which approximated 4 mg kg⁻¹ in 2003. In contrast, Tl concentrations remained roughly constant throughout the core (median value of 0.86 mg kg⁻¹). Suspended solids was collected at upstream locations in the catchment to derive the background concentrations in Ag and Tl. Very high Ag concentrations were measured in the upstream Seine River sites (0.33 – 0.59 mg kg⁻¹), compared to the values reported in the literature (0.055 mg kg⁻¹). This suggests the presence of a widespread and ancient Ag pollution in the Seine River basin, as demonstrated by the very high Ag enrichment ratios recorded in the cores. Annual flux of particulate Ag in the Seine River was estimated at 1.7 t yr⁻¹ in 2003. In

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34 contrast, Tl concentrations remained in the same order of magnitude as the natural
35 background signal ($0.3 - 0.5 \text{ mg kg}^{-1}$). This study suggests that the Seine River basin is free of
36 Tl contamination. Future concerns should hence mostly rely on Ag contamination, in a
37 context of increasing Ag uses and possible releases to the environment.

38

39

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40 **Introduction**

41 The presence of metals in the environment is known to be harmful and dangerous for
42 fauna, biota and even for human health ^{1,2}. So far, research effort has focused on the
43 behaviour of economically important trace metals (Cr, Hg, Ni, Pb, Zn). Nevertheless, other
44 metals such as silver (Ag) and thallium (Tl) are also particularly toxic. Silver and thallium
45 were assigned to the highest toxicity class, together with cadmium and mercury. Still, the
46 environmental impacts of Ag and Tl anthropogenic emissions are poorly documented, which
47 is probably due to their low abundance in the environment.

48 Whereas silver and thallium are rather scarce in the crust (0.08 mg kg⁻¹ for silver and
49 0.1 – 1.7 mg kg⁻¹ for thallium ³), they can concentrate in sediment and bio-accumulate in
50 organisms (e.g. in benthic invertebrates) ⁴. Silver has been used by people and extracted from
51 argentiferous lead ores since ancient times. People first considered it as a precious metal and
52 used it to make currency coins and jewellery. Its use has now greatly diversified and Ag is
53 found in photographic films, electrical devices, batteries, brazing alloys and electroplating,
54 coins and metals ⁵. In 1995, photographic manufacturing represented 50% of the U.S. silver
55 demand, whereas electrical contacts and conductors only accounted for 15% of the total
56 demand. With the fast development of digital photography, silver applications in this domain
57 sharply decreased (from 26 % in 1999 to 12.5 % in 2008 ⁶), whereas silver use in electronic
58 components greatly increased. Overall, the annual world demand in Ag increased
59 significantly, from 13500 t yr⁻¹ in 1995 ⁷ to 24500 t yr⁻¹ in 2005 ⁸. These authors estimated the
60 global emissions of silver to the environment at 13420 t yr⁻¹, from which ca. 457 t yr⁻¹ were
61 dissipated to water between 1997-2000.

62 Contrary to Ag, thallium was only discovered in 1861 and it mainly served as a rat
63 killer in the past. However, Tl has not been as widely used as Ag. It is for instance used to
64 make thermometers and photocells, and 60% of thallium is used by the US electronics

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65 industry. Tl world production reached only 30 t yr⁻¹ in 1984⁷. Because of the volatile nature
66 of Tl compounds, Tl is readily emitted to the atmosphere by coal combustion, cement
67 production, metal smelting and refining, as well as waste incineration⁹. Furthermore, half of
68 the environmental emission is released to water, as reported in the US Environmental
69 Protection Agency consumer factsheet devoted to thallium in drinking water and its impacts
70 on public health (see
71 http://www.epa.gov/ogwdw000/contaminants/dw_contamfs/thallium.html).

72 The historical evolution of Ag and Tl atmospheric concentrations was documented by
73 several studies carried out in the northern hemisphere. Analyses were carried out on snow and
74 ice samples collected at the Mont Blanc¹⁰; ombrotrophic peat bog samples from Switzerland
75¹¹; sediment cores from boreal and remote, Swedish lakes¹²; and Arctic snow and ice cores¹³.
76 These studies indicate a regional and long-range contamination of ecosystems by atmospheric
77 deposition for both Ag and Tl.

78 In the case of the Swedish boreal and remote lakes, a contribution from the catchment
79 geological background to the Ag concentration was not excluded¹². The authors concluded to
80 an Ag contamination of the recent sediment due to the atmospheric deposition that occurred
81 after the Second World War. Furthermore, analyses of snow and ice collected at the French
82 Alps indicate an increase in Ag atmospheric deposition after 1950¹⁰. This increase is related
83 to the increase in Ag production extracted from argentiferous lead ores. In Arctic snow and ice
84 cores, a huge Ag peak was observed around 1960 and associated it with the economic boom
85 that occurred after the Second World War¹³. A huge Ag peak dating from 1967 was also
86 registered in ombrotrophic peat bog samples from Switzerland¹¹. Even though Ag
87 concentration has continuously increased since the beginning of last century, the average
88 concentration found in samples of Arctic snow and ice in recent times are in the same order of

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89 magnitude of the enrichments already observed during the Medieval, Roman and
90 Greek/Phoenician periods.

91 Data on Tl historical trends are even scarcer than for Ag, and the conclusions are
92 somewhat different from one study to another. Tl concentrations have been increasing since
93 the mid-1800s, but the most prominent increase took place after the Second World War, as it
94 is recorded in lake sediment cores ¹². This increase is consistent with the 1967 peak observed
95 in peat bogs ¹¹. The highest Tl concentrations were observed for the years 1870 and 1920 in
96 Artic ice core ¹³ but a similar peak as the one observed for Ag concentrations in the 1960s was
97 not identified for Tl. Ag and Tl experienced hence different historical evolutions. A decrease
98 in both Ag and Tl concentrations was nevertheless observed during the last decade.

99 Overall, the former studies observed the occurrence of a significant Ag and Tl
100 contamination in the environment after the Second World War, and they related it to the
101 industrialisation of Europe. Ag contamination was observed in ancient archives (8000-300
102 BP). A decrease in Ag and Tl environmental concentrations was only detected during the last
103 decade in archives exhibiting the highest temporal resolution (i.e. ice cores). These studies
104 suggest that Ag and Tl release to the environment are controlled by independent sources
105 and/or processes.

106 The availability of techniques to detect Tl at very low concentrations is recent ¹⁴. Data
107 on Tl concentrations in lakes are rather alarming (e.g. at the Great Lakes ¹⁵). However, similar
108 data are scarce for rivers. Still, obtaining information on the historical evolution of Tl and Ag
109 concentrations in urban catchments is crucial, given river water is used as a supply source for
110 human consumption in densely urbanised areas. Furthermore, the secondary mobilisation of
111 heavy metals from overbank sediment has been demonstrated ¹⁶.

112 Ag is found to be mostly bound to sulphides and organic matter. It is strongly sorbed
113 to suspended particles. In river systems, it is rapidly incorporated into sediment and most of

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114 the dissolved silver (<0.45µm filtration) is associated with colloids ¹⁷. This high affinity for
115 suspended matter would explain why 90 % of Ag are found in the solid phase once they reach
116 the estuary because of dissolved Ag scavenging by organic matter ¹⁸. In this context, analysis
117 of sediment cores sampled in river floodplains can offer a solution to determine the
118 concentrations in this metal. With respect to Tl, the partitioning between the dissolved and
119 solid phases remains the subject of lively debate ¹⁹. Nevertheless, it seems reasonable to
120 hypothesise that the occurrence of a severe pollution in Tl would be recorded in sediment
121 despite the dominance of the dissolved fraction. We propose hence to analyse two sediment
122 cores collected in the Seine River basin, which is one of the most polluted areas in the world
123 in terms of metal contamination ^{20,21}.

124 This study aims to derive the historical trends of Ag and Tl contamination in the Seine
125 River basin. Ag and Tl concentrations in sediment will be compared to the natural
126 geochemical background concentrations. Sediment samples collected at upstream sites
127 considered as only slightly impacted by human activities will be analysed to define the local
128 geochemical background level. Scandium (Sc) will be used as a reference element, because of
129 its conservative behaviour, to evaluate the anthropogenic impact of Ag and Tl on river
130 contamination ^{11,13}. Finally, the main sources of Ag and Tl delivery to the river will also be
131 outlined.

132

133 **Experimental**

134 **Study area and selection of the coring sites**

135 Two cores were collected in the Seine River floodplain, about 100 km downstream of Paris
136 and its main waste water treatment plant (Seine – Aval waste water treatment plant at
137 Achères). The sampling sites drain 96% of the Seine River basin and are located within the
138 last major meander of the Seine River before it reaches its estuary.

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139 The first site (i.e. Bouafles) is located just upstream of a dam, in ‘Les Andelys’ (Fig.
140 1), in an oxbow lake located on the right bank of the Seine River. It corresponds to a recent
141 accretion area as indicated by the recent burial of trees. This undisturbed sampling area has
142 remained under grassland for 30 years, and gradual sediment deposition has occurred. Local
143 inhabitants confirmed indeed that the site has been flooded at least once each year until 2004.
144 The analysis of eleven cores collected in the area between 2003-2008 demonstrated that they
145 correspond to the sedimentation that occurred during the last 60 years (see ²¹ for details).

146 The second site (i.e. Muids) is located in the same meander and on the same bank of
147 the Seine River, but 12 km further on downstream. This site is composed by four islands
148 which experienced regular flooding during winter.

149

150 **Core sampling**

151 Three cores were sampled in each site on April 9, 2003 using an Eijkelkamp device
152 equipped with a percussion drill bit (with 10-cm diameter and 1-m length). The soil corer
153 could be opened laterally, which allowed an immediate transfer of the core into a PVC tube to
154 prevent its contamination by metals.

155

156 **Core dating**

157 Dating of the sediment cores relied on the measurement of two radionuclides (i.e. Cs-
158 137 and Pb-210) that strongly sorb to fine sediment ^{22,23}. Cs-137 was used as an event-tracer,
159 whereas Pb-210 provided the sediment age.

160 Both radionuclides are gamma emitters and they can be detected in small quantities of
161 soil (ca. 50-100 g, typically) without any previous chemical treatment. Sediment was dried at
162 115°C, sieved (< 2 mm), ground to a fine powder and placed in air-tight counting boxes.
163 Counting was conducted during ca. 10⁵ s using Germanium gamma-ray detectors

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164 (Germanium hyperpure – GeHP, N-type, coaxial model) available at the *Laboratoire des*
165 *Sciences du Climat et de l'Environnement* (Gif-sur-Yvette, France). Efficiencies and
166 background of the detectors were periodically controlled with internal soil and sediment
167 standards, pure KCl samples, and IAEA standards (i.e. Soil-6, -135 and -375). Activity decay
168 was corrected taking account of the sediment collection period.

169 Cs-137 is an artificial radionuclide ($t_{1/2} = 30$ years) produced by the thermonuclear
170 bomb testing conducted between the 1950s and the 1980s (with a maximum input in 1964)
171 and the Chernobyl accident in 1986. Measurement of Cs-137 activity in sediment allowed
172 determining the location of three events: the fallout due to the first significant input in the
173 atmosphere in 1954, the maximum input in 1964 and the fallout due to the Chernobyl
174 catastrophe in 1986. Cs-137 is now stored in soils, and this Cs-137 stock decreases by
175 radioactive decay and by fine sediment transfer to the rivers. Cs-137 is easily identified in
176 gamma spectrometry by a peak at 661 keV. Uncertainty on measurements was ca. 0.5%, and
177 the detection limits reached 0.3 Bq kg^{-1} .

178 Pb-210 is a natural radionuclide ($t_{1/2} = 22.3$ years) which is a decay product of U-238
179 ($t_{1/2} = 4.5 \cdot 10^9$ years). U-238 decays through a series of short-lived nuclides (e.g. Ra-226, Rn-
180 222). Rn-222 is a gas that partly remains *in situ*, forming “supported” Pb-210, and that partly
181 escapes to the atmosphere, forming “excess” Pb-210, which reaches the soil surface by wet
182 and dry fallout. It then strongly sorbs to soil particles. The activity in “excess” Pb-210 was
183 calculated by subtracting the supported activity (determined using a U-238 daughter, i.e. Bi-
184 214) from the total activity of Pb-210²⁴. Uncertainty on measurements was thus higher than
185 for Cs-137 (ca. 10%).

186

187 **Suspended matter sampling**

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188 In order to determine the background values for Ag and Tl in the river, suspended
189 matter (SM) was collected in the Seine and Marne rivers at upstream locations (i.e. at
190 Marnay-sur-Seine and Méry-sur-Marne; Fig. 1a). At Méry-sur-Marne, water was collected on
191 two field campaigns (April 2006 and January 2007) by grab sampling with PVC buckets from
192 the river bank. Twenty-liter samples were stored in PVC jerrycans thoroughly rinsed with
193 alkaline detergent TFD-4[®]. SM was obtained by gravitational settling of the samples during
194 several days. Uplying water was eliminated and approximately two litres of water were
195 centrifuged at 3000 rpm. Finally, recovered SM was freeze-dried. At Marnay-sur-Seine, SM
196 was collected in sediment traps from December 2008 to February 2009. These traps consisted
197 in 1.5-liter PET water bottles²⁵. They were emptied once a month, providing SM data at a
198 monthly time step. Samples were collected in polyethylene bottles thoroughly rinsed with 1 M
199 HNO₃ for several days. Samples were then centrifuged at 14000 rpm and vacuum-dried.

200

201 **Elemental analysis.**

202 Sc and Ag concentrations were measured using INAA (Instrumental Neutron
203 Activation Analysis) analyses conducted on bulk sediment powder. Fifty-mg samples were
204 irradiated during 30 minutes by a flux of $2.3 \cdot 10^{13}$ neutrons $\text{cm}^{-2} \text{s}^{-1}$ in the experimental reactor
205 *Orphée* (Commissariat à l'Energie Atomique, Saclay, France), using the irradiation facilities
206 of the *Laboratoire Pierre Süe*. Four successive gamma spectrometry measurements were then
207 conducted using Germanium gamma-ray detectors (Germanium hyperpure – GeHP, N-type,
208 coaxial model). Ag and Sc concentrations were determined using the 10-h counting after a 30
209 days-decay.

210 Ag and Tl concentrations were measured using ICP-MS (Inductively Coupled Plasma
211 – Mass Spectrometry) on totally digested samples. One hundred mg-samples were totally
212 dissolved by successive additions of HNO₃ and HCl mixture, HF, and HClO₄ in Teflon

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213 vessels using a heating block (Digiprep, SCP Science). Ultra pure reagents were used
214 (Normatom grade, VWR, France for HNO₃, and HCl, “for trace metal analyses”, Baker,
215 SODIPRO, France, for HF, and HClO₄). The solutions were evaporated to dryness, retaken 3
216 times in 2 ml of HNO₃ and then diluted with 50 mL of MilliQ water. The concentrations were
217 determined by Inductively Coupled Plasma – Quadrupolar Mass Spectrometry ICP-QMS (X
218 Series, ThermoElectron, France). To correct for instrumental drifts and plasma fluctuations,
219 all solutions were spiked with rhodium (Rh) and rhenium (Re) standard solutions (SPEX, SCP
220 Science, France) to a final concentration of 10 µg L⁻¹ for Rh and 1 µg L⁻¹ for Re. The
221 solutions were weighted at each step of the dilution and spiking operations.

222 We only provide the Ag ICP-MS results for the suspended sediment collected at
223 Méry-sur-Marne and Marnay-sur-Seine, because this technique offers lower detection limits
224 than INAA (Table 1). The combined errors of the concentration measurements (Ag INAA, Sc
225 INAA, Ag and Tl ICP-MS) were estimated to be in the order of 10%, 8% and 5%,
226 respectively. The accuracy of the analytical data was checked by analysing the GXR-1
227 reference material (jasperoid, USGS) by both methods. The measured concentrations in
228 GXR-1 agreed with the recommended Ag and Sc concentration values, and with the Tl
229 provisional concentration value (Table 1).

230 The enrichment factors (EF) in both Ag and Tl were calculated based on the
231 methodology developed by Wedepohl²⁶ (Eq. 1).

$$232 \quad EF = ([M]/[Sc])_{\text{Sample}} / ([M]/[Sc])_{\text{Natural background}} \quad (1)$$

233 where *M* represents Ag or Tl and using the natural background values of Ag/Sc (0.08) and
234 Tl/Sc (0.10)²⁶.

235

236 **Results and discussion**

237 **Dating of sediment cores**

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238 The cores (i.e. B2 for the Bouafles site and M1 for the Muids site) used in this study
239 were selected because of their reliable record of sedimentation.

240 The depth profile of Cs-137 in the B2-core is shown in Fig. 2a. The events
241 corresponding to the 1986 and 1964 fallout were clearly recorded. In depth, no Cs-137 was
242 detected anymore, indicating that the core includes sediment deposited before 1954.
243 Sedimentation rate derived from the excess Pb-210 profile appeared to be constant throughout
244 the core, and the sedimentation rate derived from the chronology of the core reached 1.8 cm
245 yr⁻¹.

246 With respect to the M1-core, sedimentation rates appeared to have varied throughout
247 time (Fig. 2b). Chernobyl fallout is located at 14-cm depth, whereas the maximum Cs-fallout
248 that occurred in 1964 is located at 43-cm depth (Fig. 2c). Calculated sedimentation rates
249 sharply decreased throughout time, from 2.5 cm yr⁻¹ before 1964, to 1.3 cm yr⁻¹ between 1964
250 and 1986, and only 0.8 cm yr⁻¹ between 1986 and 2003. This gradual decrease in
251 sedimentation was due to the progressive burial of the river bed by [suspended matter](#)
252 deposition at this location.

253

254 **Ag and Tl concentrations at upstream sites of the Seine River basin**

255 Mean concentrations in Ag measured in the sediment collected [at](#) Marnay-sur-Seine
256 (0.33 ± 0.15 mg kg⁻¹) and [at](#) Méry-sur-Marne (0.59 ± 0.01 mg kg⁻¹) are about tenfold higher
257 than the Ag [upper continental crust](#) background values (0.055 mg kg⁻¹) ([Table 2](#))^{3,26}.

258 Three explanations can be put forward to explain this difference. First, the high Ag
259 concentrations measured in the Seine River could indicate that the geochemical background
260 values are exceptionally high in this river. However, we rule out this hypothesis, because of
261 the dominant sedimentary origin of the rocks in the Seine River basin. Second, they could
262 indicate that the Seine River basin underwent a general and very ancient pollution. This

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263 second hypothesis seems more likely. Such a large contamination by atmospheric deposition
264 has also been observed in remote environmental archives ¹³. Third, this contamination could
265 be explained by Ag released by lead (Pb) industries present in the Upper Seine and the Marne
266 catchments. Pb and Ag are indeed strongly associated in Pb-ores. Even though the activity of
267 lead industrial facilities strongly decreased after 1970 in the Seine River basin ²⁷, there are
268 still a dozen [plants](#) in activity in the Upper Seine and the Marne catchments (Fig. 1b) ²⁸.

269 Overall, data are still too scarce to draw conclusions about the high Ag geochemical
270 background signal in the Seine River basin. Sediment deposited before the proto-
271 industrialisation in the region needs to be collected and analysed to derive this signal.

272 In contrast, thallium concentrations measured [at Marnay-sur-Seine](#) (0.30 mg kg⁻¹) and
273 [Méry-sur-Marne](#) (0.45 mg kg⁻¹) ([Table 2](#)) are in good agreement with the median Tl
274 concentration in European floodplain sediment ²⁹. They were even lower than the Tl
275 geochemical background concentrations reported in the upper continental crust (0.75 mg kg⁻¹).
276 The low Tl concentrations that we observed could be explained by the dilution of the
277 geological Tl input by autochthonous calcite and/or organic matter. Scandium (Sc)
278 concentrations were measured in all the samples. Normalising Tl concentrations to Sc allows
279 taking account of this dilution effect. The Tl/Sc ratio for the reference geochemical
280 background varies between 0.068 and 0.107. According to our data, the Tl/Sc ratio reached
281 0.046 ± 0.005 [at Marnay-sur-Seine](#) and 0.062 ± 0.001 [at Méry-sur-Marne](#). These low Tl
282 concentrations measured at upstream sites of the Seine River basin cannot be explained by a
283 dilution effect. It is more reasonable to attribute these low concentrations to the sedimentary
284 origin of the rocks in the Seine River basin. [Moreover, the Tl concentration observed at](#)
285 [Marnay-sur-Seine lower than the Tl concentration at Méry-sur-Marne may be partly explained](#)
286 [by a possible metal release from the suspended sediments trapped during one month periods](#)
287 [at Marnay-sur-Seine.](#)

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288

289 **Depth profiles of Ag and Tl concentrations**

290 Sc, Ag and Tl concentrations measured along the sediment profiles of the B2 and M1
291 cores as well as the estimated chronology of deposition are shown in Tables 3 and 4.

292 The Ag concentration showed strong variations along the profile of the B2 core (from
293 4 to 25 mg kg⁻¹) (Table 3). The highest concentration (24.6 mg kg⁻¹) was recorded in 1960.
294 The lowest concentration (3.8 mg kg⁻¹) was measured in the uppermost superficial layer
295 which corresponds to the sediment deposited in 2003. Moreover, the peaks in Ag
296 concentrations (observed in 1960 and, to a lesser extent, in 1994) correspond to similar peaks
297 in Zn, Sb, Hg and Pb concentrations²¹. The 1960 peak probably reflects the industrial boom
298 after the Second World War.

299 The depth profile of Ag concentration in the M1 core is similar to the one obtained in
300 the other core, even though it is systematically characterised by slightly lower concentrations
301 (Table 4). Similar observations can be made for Sc concentrations. This indicates the presence
302 of a less abundant clay fraction in M1 compared to B2.

303 To document the influence of anthropogenic activities, temporal variations of the Ag
304 and Tl enrichment factors (EF) ratios were calculated, taking account of the upper continental
305 crust (UCC) concentrations as a reference (Table 5). The following EF values should be
306 interpreted with some caution, keeping in mind the shortcomings of the EF approach, EF
307 being calculated relative to the crust composition or to local background values³⁰. Ag EF
308 recorded in both B2 and M1 cores were extremely high. EF in Ag ranged between 51 and 300
309 in B2 and between 73 and 263 in M1, when using UCC concentrations as reference values.
310 After normalising Ag concentrations to Sc, the Ag EF depth profiles were much more similar
311 in both cores (Fig. 3). Ag EF obtained taking the concentrations measured at Marnay-sur-
312 Seine as a reference ranged from 8 to 47 in the B2 core and from 12 to 39 in the M1 core.

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313 When using the concentrations at Méry-sur-Marne, Ag EF fluctuated similarly between 12
314 and 44 in the B2 core, and 12 and 26 in the M1 core. These results demonstrate a significant
315 enrichment of sediment in Ag and Tl during its transfer from the upper catchment sites to the
316 downstream sites. This enrichment is clearly associated with contemporary anthropogenic
317 impacts, whereas the enrichment observed at the upstream sites was probably induced by
318 more ancient human activities.

319 Given it is widely known that Pb-ores constitute an important Ag source ³¹, it is
320 particularly relevant to compare the Ag concentrations with the ones obtained for Pb ²¹. Both
321 profiles were found to be synchronous (results not shown). Examination of the Pb/Ag ratio
322 can provide valuable insights about the dominant emission processes ¹¹. The Pb/Ag ratio
323 decreased from ca. 50 in sediment deposited in 1930, up to 20 in the 2003 sediment. The
324 higher enrichment in Pb than in Ag observed in the Swiss peat bog ¹¹ level corresponding to
325 1967 is not observed in the Seine River sediment. In addition, the Pb/Ag ratios observed in
326 the Seine sediment cores are significantly lower than those observed in peat bog ¹¹ and even
327 lower than the Pb/Ag ratio reported in UCC (i.e. 400 ³). Overall, we can confidently state that
328 the Seine River sediment is enriched in Ag compared to Pb.

329 Tl concentrations in the B2 core ranged between 0.66 and 1.01 mg kg⁻¹, with a median
330 concentration of 0.86 ± 0.12 mg kg⁻¹ all throughout the depth profile. No significant peak can
331 be detected in the profile (Table 3). The lowest Tl concentration in sediment was measured in
332 the sediment deposited in 1979. Furthermore, Tl EF mean values were close to 1 (0.9 in
333 average) (Table 5) when taking the UCC concentrations as a reference, indicating an absence
334 of enrichment. Tl EF calculated using concentrations measured at Marnay-sur-Seine and
335 Méry-sur-Marne reached 2.1 and 1.5, respectively. The low but constant enrichment in Tl
336 measured in the downstream sediment suggests the potential existence of a natural Tl source
337 in the Seine River basin. We suspect that the Yonne river sediment could be responsible for

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338 this Seine sediment enrichment in Tl. The Yonne river flows indeed into the Seine River at a
339 junction located downstream of Marnay-sur-Seine (Fig. 1a), after having flown across
340 granites exposed in the Morvan region. Granites are known to be enriched in Tl⁷.

341

342 **Thallium pollution records in the sediment cores**

343 Atmospheric archives are characterised by an important Tl pollution, which is even
344 more important than Ag pollution^{11,12,13}. Our results clearly point out that the increase in Tl
345 atmospheric source(s) measured in atmospheric archives did not impact the composition of
346 the Seine River sediment. The geochemical behaviour of Tl is similar to the one of potassium
347 and other alkali metal cations^{31,32}. The lability of Tl may bring into question the relevance of
348 a sediment core to record a Tl pollution signal. However, this issue remains the object of a
349 lively debate in the literature. On the one hand, mobilisation of Tl from the solid phase to pore
350 waters was observed in lacustrine sediment cores^{12,33}. Laforte et al. (2005)³³ concluded that
351 the significant post-depositional Tl mobility must be taken into account to interpret Tl profiles
352 in sediment. On the other hand, it was also shown that Tl sorbed strongly on layered illitic and
353 vermiculite clays¹⁹. Moreover, no Tl desorption was observed from clay-rich soils when
354 adding NH₄⁺ and K⁺ competitive cations. Tl is even considered to be enough **stable** to allow
355 its chronological evaluation³⁴. The strong sorption of Tl from atmospheric origin on silty and
356 silty-clay soils of France was demonstrated³². **It was** also showed that Tl present in the
357 French soils had a pedological origin.

358 Consequently, it seems reasonable to conclude that, if a **significant Tl contamination**
359 **had** affected the Seine River basin, it would have been recorded, at least partly, in the river
360 sediment. Given the absence of any pollution signal in the B2 and M1 sediment cores, we can
361 conclude to the absence of any **significant Tl contamination** in the Seine River sediment
362 between the 1940s and today.

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363 The need to further investigate the partitioning of Tl between the solid and dissolved
364 phases in soils was outlined ¹⁹. Future investigations could also usefully determine Tl
365 partitioning between the sediment and the dissolved phase in rivers. Solid/dissolved
366 partitioning of Tl is of primary importance because of the high toxicity of soluble Tl
367 compounds. Moreover, obtaining this value would allow calculating the dissolved fluxes
368 based on the particulate fluxes which are much easier to measure.

369

370 **Potential sources of Ag to the river**

371 Ag may be released by different sources to the environment. Thouvenin et al. (2005) ¹⁸
372 estimated the silver contribution of the Seine River to its estuary in 2003. Sediments were
373 monthly sampled in Poses, which is the last dam before the estuary. In 2003, the Ag flux in
374 Poses was estimated at 1.5 t yr⁻¹ ¹⁸. Based on the measurements obtained from the B2
375 sediment core sampled in 2003 at Bouafles, which is located 30 km upstream of Poses, we
376 can propose a rough and comparative estimation of the Ag annual flux. The particulate output
377 of the Seine was estimated at 450,000 t yr⁻¹ in 2003 ¹⁸. Ag concentration in the uppermost
378 layers of the B2 core reached 3.8 mg kg⁻¹, we can then estimate the particulate Ag output
379 from the Seine River at 1.7 t yr⁻¹. Similar calculations applied to the M1 uppermost layer
380 concentration result in an Ag particulate flux of 2.0 t yr⁻¹. Both estimations remain in good
381 agreement with the ones obtained previously ¹⁸, given that the concentrations in the
382 uppermost layer of the core are only representative of the solids concentration reached during
383 periods of high water level. Moreover, suspended sediment ¹⁸ and deposited sediment (this
384 work) differ in terms of particle size and organic matter content. Still, these characteristics
385 influence the metal concentration in sediment. Overall, our results suggest that the Ag export
386 to the Seine River estuary (1.7 – 2.0 t yr⁻¹) is at least equivalent to the cadmium and mercury
387 fluxes at the river mouth (1.75 and 1.25 t yr⁻¹, respectively ²⁷). Given the high toxicity of Ag,

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388 Ag concentrations in the solid and the dissolved phases should be monitored to evaluate
389 precisely the Ag particulate and dissolved fluxes from the river and to allow conducting
390 further risk assessment studies.

391 It is necessary to determine the potential sources delivering Ag to the river in order to
392 propose potential remediation regulations. Metal mining and smelting activities are known to
393 constitute the major Ag contaminating sources to atmospheric and aquatic environments.
394 However, there is no sulphide ore exploitation in the Seine River basin. In contrast, municipal
395 waste incinerators could be an important source of Ag contamination in the Seine River. They
396 incinerate domestic waste as well as electronic devices that were not sorted out for recycling.
397 In the Seine River basin, more than 70% of the solid wastes are incinerated. 36% of discarded
398 (not recycled) Ag in Europe are found in municipal solid wastes ⁵. During the incineration
399 process, silver ends up as bottom and fly ashes, and emissions to the atmosphere remain
400 therefore limited ¹⁷. Solid wastes issued from municipal waste incinerators contain the bulk of
401 anthropogenic Ag ⁵. Sewage sludge constitutes the second Ag source. Landfilling of solid
402 wastes issued from thermal treatment incinerators and sewage sludge might constitute a
403 delayed risk of Ag contamination if landfill contaminants were released to the environment by
404 soil erosion.

405 Forty-five percents of the silver used in the film and photo production were not
406 recycled and potentially exposed to the environment in 1997 ⁵. The film photography first
407 developed at the end of the 19th century and became a mass-consumption product throughout
408 the 20th century. This use may have induced a large part of the ancient sediment
409 contamination, not only because of the lack of restrictive waste management regulations, but
410 also because of the spreading of numerous photo laboratories. The exponentially decreasing
411 demand for this use could explain the decrease in Ag concentration measured in the
412 contemporary sediment.

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413 Ag content in domestic waste is likely to increase again in future. A recent study
414 carried out in the Rhine river catchment showed that the production of goods using Ag
415 nanoparticles will increase in future. This will amplify the Ag release to freshwater
416 environments ¹⁷. These products consist in plastics (medical catheters, sanitation tubes,
417 computer keyboards, door handles, car steering wheels and mobile phones) and textiles
418 benefiting from the biocide effect of Ag nanoparticles. The biocidal mechanism of silver-
419 containing products results indeed from a long term release of silver ions (Ag^+) by oxidation
420 of metallic silver (Ag^0) in contact with aqueous media. Up to 15% of the total silver emitted
421 to water in Europe may be released from biocidal plastics and textiles in 2010 ¹⁷.

422

423 **Conclusions**

424 Very few records were available to document the contamination by metals of minor
425 economic importance such as Ag and Tl in river catchments strongly modified by human
426 activities. These metals prove nevertheless to be very toxic. This study demonstrated that the
427 Seine River sediment was not contaminated by Tl during the last 60 years. However, the
428 question of its partition between the solid and the dissolved phases remains a subject of lively
429 debate. In contrast, the Seine River sediment was severely contaminated by Ag.
430 Concentration in this metal started decreasing in the 1960s, but it is still present in the
431 environment. Nowadays, the main source of Ag to the river sediment appears to originate
432 from the waste incinerators. However, the sources of Ag may have changed throughout the
433 last decades. Moreover, the increasing Ag demand and the growth of its uses demonstrate the
434 necessity to understand the biogeochemical cycle of Ag, which can partly be investigated
435 through the analysis of environmental archives.

436

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Table 1 Analytical information. Instrumental detection limits (including digestion blanks for ICP-MS; mg kg^{-1}). Analysis of certified material GXR-1 (USGS). INAA: Instrumental Neutron Activation Analysis. ICP-MS: Inductively Coupled Plasma – Mass Spectrometry.

	Quantification limits		Reference material		
	INAA	ICP-MS	Certified value	Measured value INAA (n=3)	Measured value ICP-MS (n=3)
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Sc	0.1	n.d.	1.58 ± 0.20	1.7 ± 0.1	n.d.
Ag	1	0.005	31 ± 4	33 ± 3	31 ± 3
Tl	n.d.	0.001	0.39 ± 0.20^a	n.d.	0.40 ± 0.02

(a) Provisional concentration value; n.d. not determined

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Table 2 Scandium (Sc), silver (Ag) and thallium (Tl) geochemical background values in the upper continental crust (literature) and in suspended sediment collected at upstream stations of the Seine River basin (mg kg^{-1}).

		Sc	Ag	Tl
<i>Upper continental crust</i>				
	Taylor and McLennan (1985)	11	0.050	0.75
	Wedepohl (1995)	7	0.055	0.75
<i>Local background stations</i>				
Marnay-sur-Seine	Dec 08	$6.6^a \pm 0.1$	$0.24^b \pm 0.01$	$0.32^b \pm 0.02$
	Jan 09	$6.6^a \pm 0.1$	$0.25^b \pm 0.01$	$0.31^b \pm 0.02$
	Feb 09	$6.7^a \pm 0.1$	$0.50^b \pm 0.02$	$0.27^b \pm 0.01$
Méry-sur-Marne	Apr 06	$7.0^a \pm 0.1$	$0.59^b \pm 0.03$	$0.43^b \pm 0.02$
	Jan 07	$7.6^a \pm 0.1$	$0.59^b \pm 0.03$	$0.48^b \pm 0.02$

(a) INAA determinations

(b) ICP-MS determinations

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550**Table 3** Scandium (Sc), silver (Ag) and thallium (Tl) concentrations values in the B2 core (mg kg⁻¹). (n.d. not determined)

Year	Sc			Ag			Tl		
2003	9.5	±	0.8	3.8	±	0.4	n.d.		
1997	7.2	±	0.6	7.9	±	0.8	0.70	±	0.04
1994	8.0	±	0.6	13.1	±	1.3	0.95	±	0.05
1989	9.3	±	0.7	10.7	±	1.1	0.92	±	0.05
1986	10.3	±	0.8	7.4	±	0.7	n.d.		
1985	9.8	±	0.8	9.2	±	0.9	0.84	±	0.04
1983	9.6	±	0.8	10.5	±	1.0	0.87	±	0.04
1979	9.5	±	0.8	11.3	±	1.1	0.66	±	0.03
1974	9.1	±	0.7	15.5	±	1.5	0.77	±	0.04
1967	9.6	±	0.8	22.4	±	2.2	0.97	±	0.05
1963	10.5	±	0.8	24.6	±	2.5	0.80	±	0.04
1960	9.7	±	0.8	20.8	±	2.1	1.01	±	0.05
1956	10.1	±	0.8	20.4	±	2.0	n.d.		
1949	9.0	±	0.7	8.8	±	0.9	n.d.		
1943	9.2	±	0.7	9.9	±	1.0	0.99	±	0.05

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558**Table 4** Scandium (Sc) and silver (Ag) concentrations values in the M1 core (mg kg⁻¹) (n.d. not determined).

Year	Sc			Ag			Tl		
2002	7.7	±	0.6	4.4	±	0.4	0.54	±	0.03
1995	6.0	±	0.5	4.6	±	0.5	0.50	±	0.03
1988	6.9	±	0.6	6.1	±	0.6	0.56	±	0.03
1986	6.7	±	0.5	6.1	±	0.6	n.d.		
1983	5.7	±	0.5	6.8	±	0.7	0.49	±	0.02
1980	5.7	±	0.5	6.7	±	0.7	n.d.		
1970	6.9	±	0.6	14.3	±	1.4	0.64	±	0.03
1968	6.4	±	0.5	11.9	±	1.2	0.49	±	0.02
1961	8.0	±	0.6	13.6	±	1.4	0.64	±	0.03
1957	8.9	±	0.7	8.7	±	0.9	0.68	±	0.03
1951	7.4	±	0.6	4.7	±	0.5	n.d.		
1943	9.0	±	0.7	9.6	±	1.0	1.36	±	0.07
1936	8.6	±	0.7	9.1	±	0.9	n.d.		
1933	7.5	±	0.6	6.2	±	0.6	0.67	±	0.03

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562 **Table 5** Silver (Ag) and thallium (Tl) enrichment factors in the B2 and M1 cores, and in the
 563 upstream sites. Ref: upper continental crust reference concentrations used for the calculation
 564 of enrichment factors (Wedepohl, 1995). See text for details.
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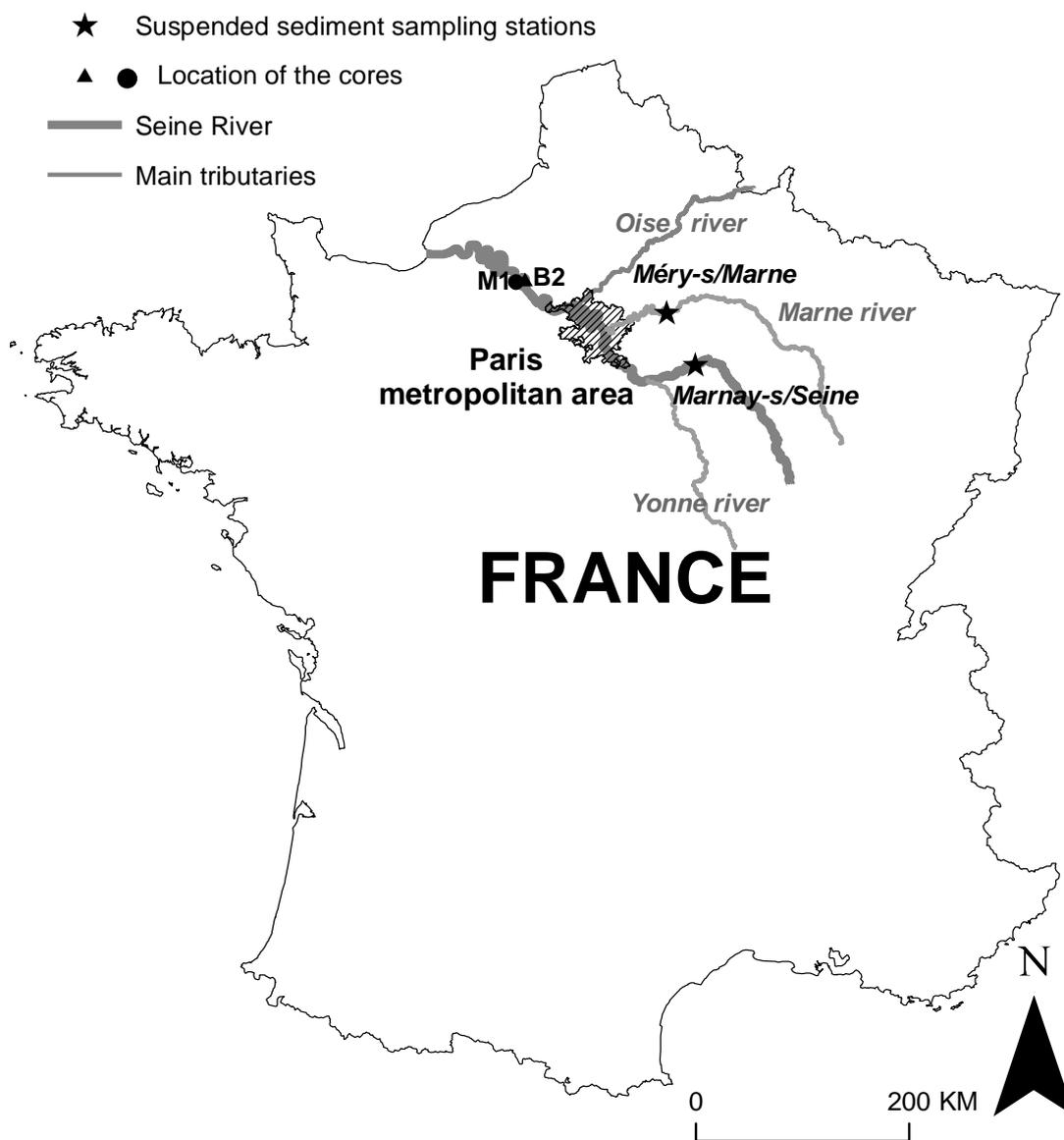
B2 core			M1 core		
Year	Ag	Tl	Year	Ag	Tl
2003	51		2002	73	0.65
1997	140	0.91	1995	98	0.78
1994	208	1.11	1988	112	0.76
1989	146	0.93	1986	116	
1986	92		1983	152	0.79
1985	119	0.79	1980	151	
1983	139	0.84	1970	263	0.86
1979	153	0.65	1968	235	0.71
1974	217	0.79	1961	217	0.75
1967	296	0.94	1957	124	0.72
1963	300	0.72	1951	81	
1960	272	0.97	1943	136	1.41
1956	256		1936	135	
1949	124		1933	105	0.84
1943	137	1.01			
Marnay (Dec 08)	4.6	0.45			
Marnay (Jan 09)	4.9	0.45			
Marnay (Feb 09)	9.5	0.37			
Méry (Apr 06)	10.7	0.57			
Méry (Jan 07)	9.9	0.59			
<i>Ref (mg kg⁻¹)</i>	<i>0.055</i>	<i>0.75</i>		<i>0.055</i>	<i>0.75</i>

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571 **Figure 1** (a) Location of the B2 and M1 sediment cores and the suspended sediment sampling
572 sites (Marnay-sur-Seine and Méry-sur-Marne) in the Seine River basin. (b) Location of the
573 currently operational Pb industries in the upstream part of the Seine catchment and in the
574 Marne catchment (Source: IREP, 2009).

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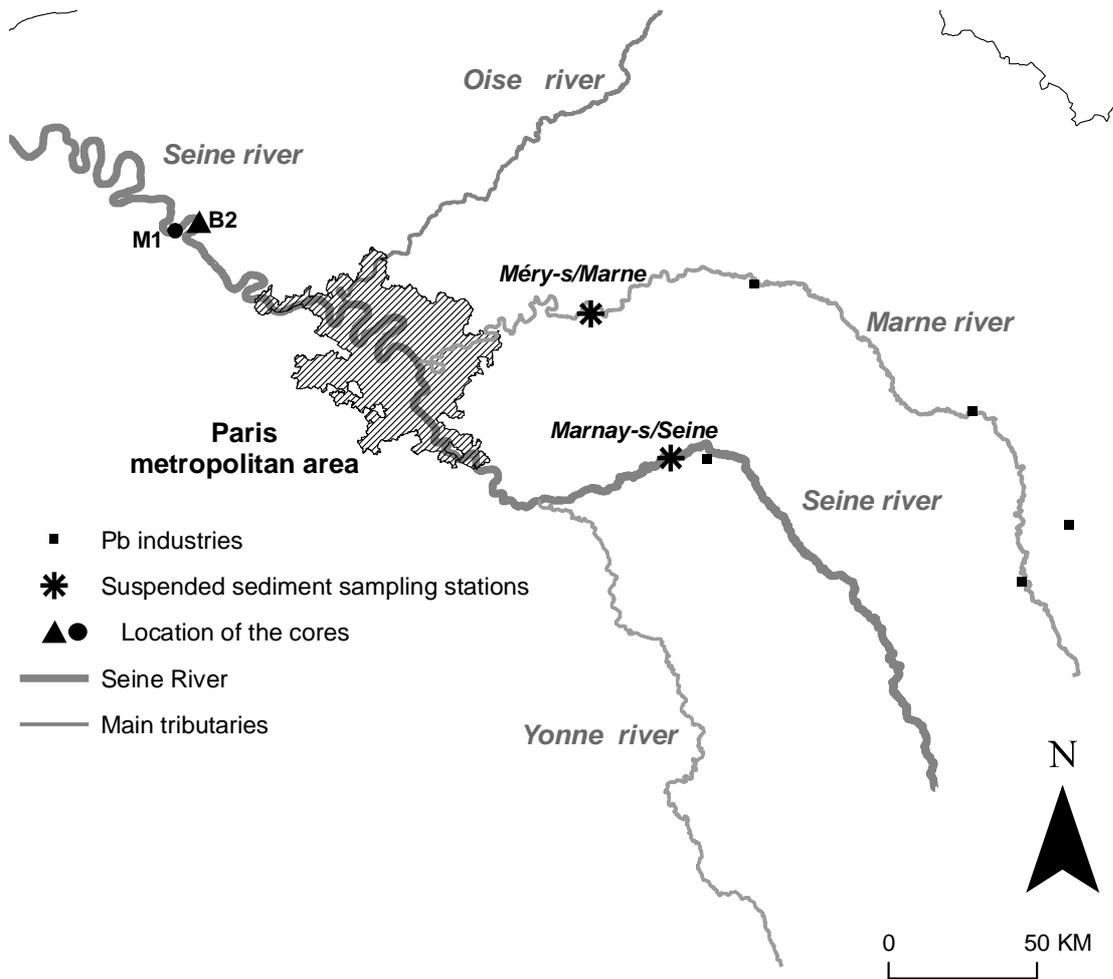


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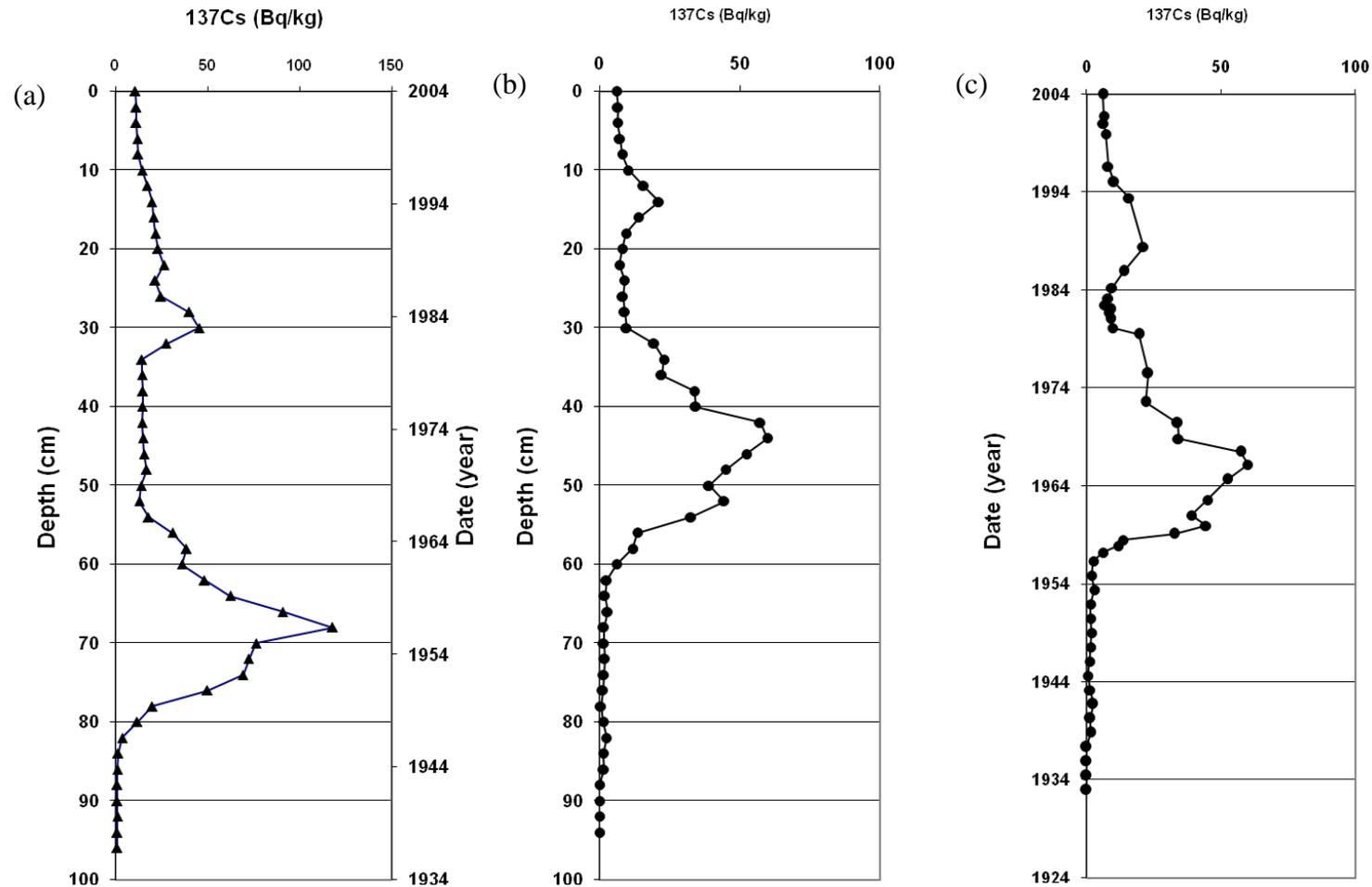
(b)



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596 **Figure 2** Depth profiles of the Cs-137 activity. (a) (\blacktriangle) B2 core (Bouafles); (b) (\bullet) M1 core (Muids). (a) The chronology derived from the
 597 measured activities is indicated on the right axis of the graph for the B2 core. (c) Due to changes in the deposition rate along the depth profile of
 598 the M1 core, its chronological profile is shown in a separated graph.
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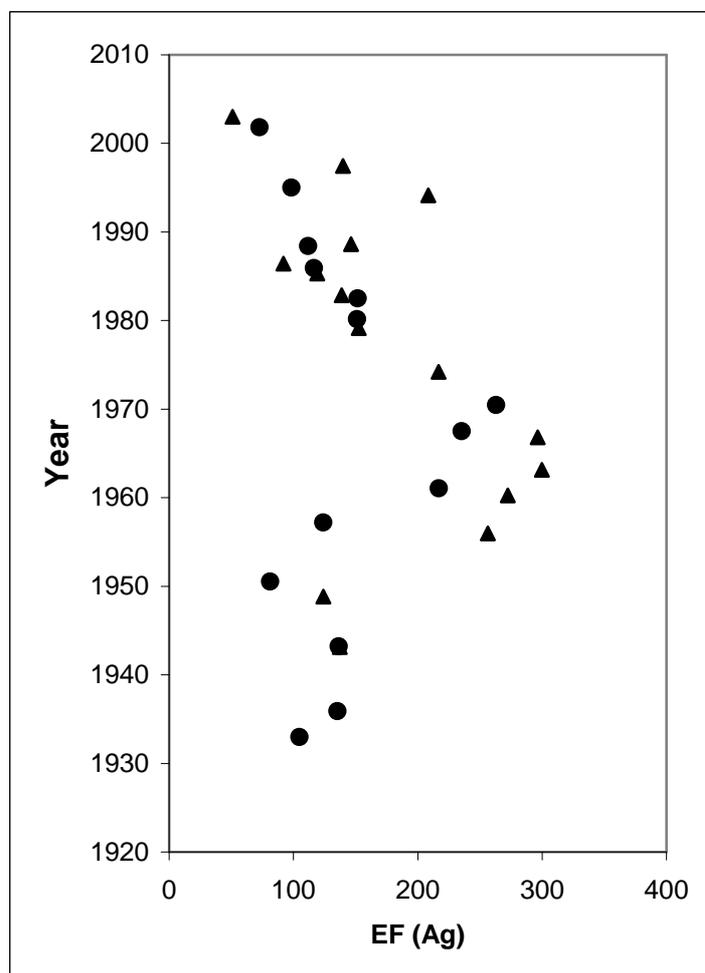


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Figure 3 Enrichment factor (EF) in Ag in the depth profiles of the two analysed cores: (▲) B2 core (Bouafles); (●) M1 core (Muids) using upper continental crust values as reference.



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Impact statement

616 This manuscript reports the temporal evolution of silver (Ag) and thallium (Tl) concentrations
617 in sediment cores. These cores, issued from downstream Seine River flood plains, represent
618 extraordinary archives of the sediments flowing across Paris conurbation. Ag and Tl are two
619 toxic metals, released to the environment by human activities and scarcely documented in
620 river sediment. The present work shows a huge Ag sediment contamination around 1960. In
621 contrast, no contamination was registered for Tl. These findings increase the understanding of
622 Ag and Tl environmental cycles in urban environments. In addition, the Ag and Tl
623 geochemical background concentrations in the Seine River were documented. Ag
624 concentrations were tenfold higher than the Ag background values reported for the upper
625 continental crust. This emphasizes the need to increase the research efforts on silver and

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626 thallium that have been understudied in an environmental context, whereas the uses of Ag are
627 dramatically increasing.
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Environmental archives showed that the Seine River (France) was severely contaminated by silver during the last century.