

Silver and thallium historical trends in the Seine River basin

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Records on pollution by metals of minor economic importance (*e.g.* silver and 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 contrast, Tl concentrations remained in the same order of magnitude as the natural background signal (0.3–0.5 mg kg^{−1}). This study suggests that the Seine River basin is free of Tl contamination. Future concerns should hence mostly rely on Ag contamination, in a context of increasing Ag uses and possible releases to the environment.

Introduction

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

Whereas silver and thallium are rather scarce in the crust (0.08 mg kg^{−1} for silver and 0.1–1.7 mg kg^{−1} for thallium³), they can concentrate in sediment and bio-accumulate in organisms (*e.g.* in

benthic invertebrates).⁴ Silver has been used by people and extracted from argentiferous lead ores since ancient times. People first considered it as a precious metal and used it to make currency coins and jewellery. Its use has now greatly diversified and Ag is found in photographic films, electrical devices, batteries, brazing alloys and electroplating, coins and metals.⁵ In 1995, photographic manufacturing represented 50% of the US silver demand, whereas electrical contacts and conductors only accounted for 15% of the total demand. With the fast development of digital photography, silver applications in this domain sharply decreased (from 26% in 1999 to 12.5% in 2008⁶), whereas silver use in electronic components greatly increased. Overall, the annual world demand in Ag increased significantly, from 13 500 t yr^{−1} in 1995⁷ to 24 500 t yr^{−1} in 2005.⁸ These authors estimated the global emissions of silver to the environment at 13 420 t yr^{−1}, from which *ca.* 457 t yr^{−1} were dissipated to water between 1997–2000.

Contrary to Ag, thallium was only discovered in 1861 and it mainly served as a rat killer in the past. However, Tl has not been as widely used as Ag. It is for instance used to make

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Environmental impact

This manuscript reports the temporal evolution of silver (Ag) and thallium (Tl) concentrations in sediment cores. These cores, issued from downstream Seine River floodplains, represent extraordinary archives of the sediments flowing across Paris conurbation. Ag and Tl are two toxic metals, released to the environment by human activities and scarcely documented in river sediment. The present work shows a huge Ag sediment contamination around 1960. In contrast, no contamination was registered for Tl. These findings increase the understanding of Ag and Tl environmental cycles in urban environments. In addition, the Ag and Tl geochemical background concentrations in the Seine River were documented. Ag concentrations were tenfold higher than the Ag background values reported for the upper continental crust. This emphasizes the need to increase the research efforts on silver and thallium that have been understudied in an environmental context, whereas the uses of Ag are dramatically increasing.

thermometers and photocells, and 60% of thallium is used by the US electronics industry. Tl world production reached only 30 t yr⁻¹ in 1984.⁷ Because of the volatile nature of Tl compounds, Tl is readily emitted to the atmosphere by coal combustion, cement production, metal smelting and refining, as well as waste incineration.⁹ Furthermore, half of the environmental emission is released to water, as reported in the US Environmental Protection Agency consumer factsheet devoted to thallium in drinking water and its impacts on public health (see http://www.epa.gov/ogwdw000/contaminants/dw_contamfs/thallium.html).

The historical evolution of Ag and Tl atmospheric concentrations was documented by several studies carried out in the northern hemisphere. Analyses were carried out on snow and ice samples collected at the Mont Blanc;¹⁰ ombrotrophic peat bog samples from Switzerland;¹¹ sediment cores from boreal and remote, Swedish lakes;¹² and Arctic snow and ice cores.¹³ These studies indicate a regional and long-range contamination of ecosystems by atmospheric deposition for both Ag and Tl.

In the case of the Swedish boreal and remote lakes, a contribution from the catchment geological background to the Ag concentration was not excluded.¹² The authors concluded to an Ag contamination of the recent sediment due to the atmospheric deposition that occurred after the Second World War. Furthermore, analyses of snow and ice collected at the French Alps indicate an increase in Ag atmospheric deposition after 1950.¹⁰ This increase is related to the increase in Ag production extracted from argentiferous lead ores. In Arctic snow and ice cores, a huge Ag peak was observed around 1960 and the authors associated it with the economic boom that occurred after the Second World War.¹³ A huge Ag peak dating from 1967 was also registered in ombrotrophic peat bog samples from Switzerland.¹¹ Even though Ag concentration has continuously increased since the beginning of last century, the average concentration found in samples of Arctic snow and ice in recent times is in the same order of magnitude of the enrichments already observed during the Medieval, Roman and Greek/Phoenician periods.

Data on Tl historical trends are even scarcer than for Ag, and the conclusions are somewhat different from one study to another. Tl concentrations have been increasing since the mid-1800s, but the most prominent increase took place after the Second World War, as it is recorded in lake sediment cores.¹² This increase is consistent with the 1967 peak observed in peat bogs.¹¹ The highest Tl concentrations were observed for the years 1870 and 1920 in Arctic ice core¹³ but a similar peak as the one observed for Ag concentrations in the 1960s was not identified for Tl. Ag and Tl experienced hence different historical evolutions. A decrease in both Ag and Tl concentrations was nevertheless observed during the last decade.

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

The availability of techniques to detect Tl at very low concentrations is recent.¹⁴ Data on Tl concentrations in lakes are

rather alarming (*e.g.* at the Great Lakes¹⁵). However, similar data are scarce for rivers. Still, obtaining information on the historical evolution of Tl and Ag concentrations in urban catchments is crucial, given river water is used as a supply source for human consumption in densely urbanised areas. Furthermore, the secondary mobilisation of heavy metals from overbank sediment has been demonstrated.¹⁶

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

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

Experimental

Study area and selection of the coring sites

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

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

The second site (*i.e.* Muids) is located in the same meander and on the same bank of the Seine River, but 12 km further on

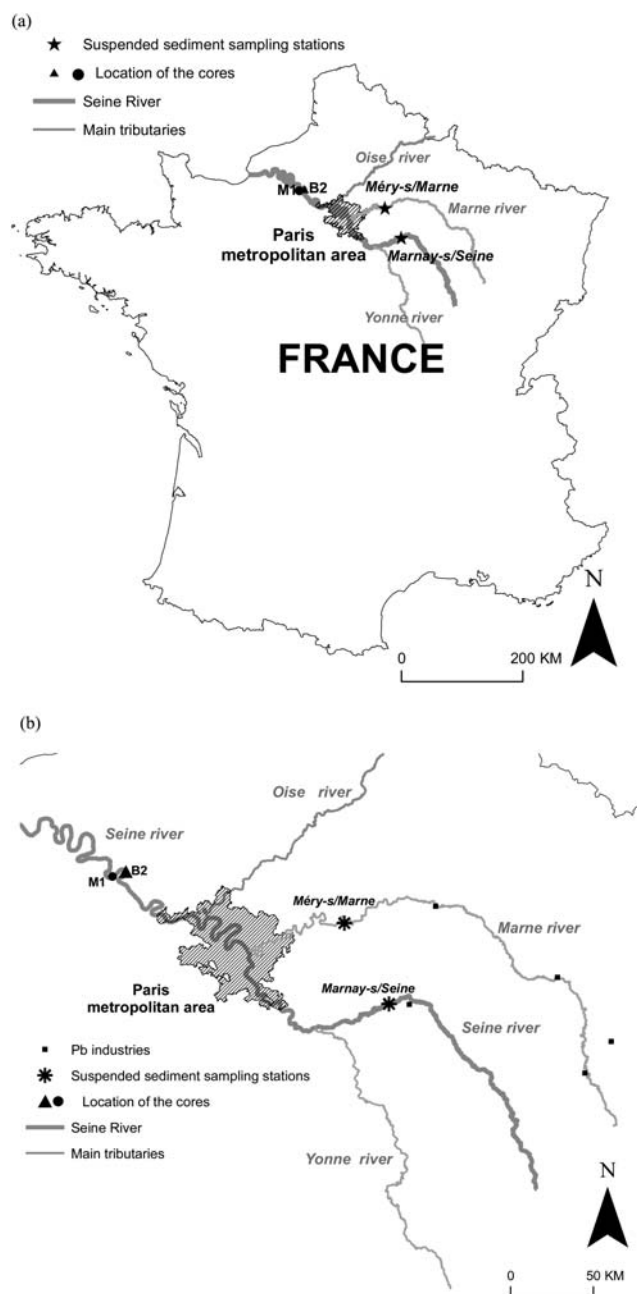


Fig. 1 (a) Location of the B2 and M1 sediment cores and the suspended sediment sampling sites (Marnay-sur-Seine and Méry-sur-Marne) in the Seine River basin. (b) Location of the currently operational Pb industries in the upstream part of the Seine catchment and in the Marne catchment (source: IREP, 2009).

downstream. This site is composed by four islands which experienced regular flooding during winter.

Core sampling

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

Core dating

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

Both radionuclides are γ emitters and they can be detected in small quantities of soil (*ca.* 50–100 g, typically) without any previous chemical treatment. Sediment was dried at 115 °C, sieved (<2 mm), ground to a fine powder and placed in airtight counting boxes. Counting was conducted during *ca.* 10⁵ s using Germanium γ -ray detectors (Germanium hyperpure—GeHP, N-type, coaxial model) available at the *Laboratoire des Sciences du Climat et de l'Environnement* (Gif-sur-Yvette, France). Efficiencies and background of the detectors were periodically controlled with internal soil and sediment standards, pure KCl samples, and IAEA standards (*i.e.* Soil-6, -135 and -375). Activity decay was corrected taking account of the sediment collection period.

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

Pb-210 is a natural radionuclide ($t_{1/2} = 22.3$ years) which is a decay product of U-238 ($t_{1/2} = 4.5 \times 10^9$ years). U-238 decays through a series of short-lived nuclides (*e.g.* Ra-226 and Rn-222). Rn-222 is a gas that partly remains *in situ*, forming “supported” Pb-210, and that partly escapes to the atmosphere, forming “excess” Pb-210, which reaches the soil surface by wet and dry fallout. It then strongly sorbs to soil particles. The activity in “excess” Pb-210 was calculated by subtracting the supported activity (determined using a U-238 daughter, *i.e.* Bi-214) from the total activity of Pb-210.²⁴ Uncertainty on measurements was thus higher than for Cs-137 (*ca.* 10%).

Suspended matter sampling

In order to determine the background values for Ag and Tl in the river, suspended matter (SM) was collected in the Seine and Marne rivers at upstream locations (*i.e.* at Marnay-sur-Seine and Méry-sur-Marne, Fig. 1a). At Méry-sur-Marne, water was collected on two field campaigns (April 2006 and January 2007) by grab sampling with PVC buckets from the riverbank. Twenty-litre samples were stored in PVC jerrycans thoroughly rinsed with alkaline detergent TFD-4®. SM was obtained by gravitational settling of the samples during several days. Uplifting water was eliminated and approximately two litres of water were centrifuged at 3000 rpm. Finally, recovered SM was freeze-dried. At Marnay-sur-Seine, SM was collected in sediment traps from December 2008 to February 2009. These traps consisted in 1.5-litre PET water bottles.²⁵ They were emptied once a month, providing SM data at a monthly time step. Samples were

collected in polyethylene bottles thoroughly rinsed with 1 M HNO₃ for several days. Samples were then centrifuged at 14000 rpm and vacuum-dried.

Elemental analysis

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

Ag and Tl concentrations were measured using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) on totally digested samples. One hundred milligram samples were totally dissolved by successive additions of HNO₃ and HCl mixture, HF, and HClO₄ in Teflon vessels using a heating block (Digiprep, SCP Science). Ultra pure reagents were used (Normatom grade, VWR, France for HNO₃, and HCl, “for trace metal analyses”, Baker, SODIPRO, France, for HF, and HClO₄). The solutions were evaporated to dryness, retaken 3 times in 2 mL of HNO₃ and then diluted with 50 mL of MilliQ water. The concentrations were determined by Inductively Coupled Plasma-Quadrupole Mass Spectrometry ICP-QMS (X Series, Thermo-Electron, France). To correct for instrumental drifts and plasma fluctuations, all solutions were spiked with rhodium (Rh) and rhenium (Re) standard solutions (SPEX, SCP Science, France) to a final concentration of 10 $\mu\text{g L}^{-1}$ for Rh and 1 $\mu\text{g L}^{-1}$ for Re. The solutions were weighted at each step of the dilution and spiking operations.

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

recommended Ag and Sc concentration values, and with the Tl provisional concentration value (Table 1).

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

$$EF = ([M]/[Sc])_{\text{sample}} / ([M]/[Sc])_{\text{natural background}} \quad (1)$$

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

Results and discussion

Dating of sediment cores

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

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

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

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

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

Three explanations can be put forward to explain this difference. First, the high Ag concentrations measured in the Seine River could indicate that the geochemical background values are

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	Measured value	
	INAA/mg kg ⁻¹	ICP-MS/mg kg ⁻¹		INAA (<i>n</i> = 3)/mg kg ⁻¹	ICP-MS (<i>n</i> = 3)/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.

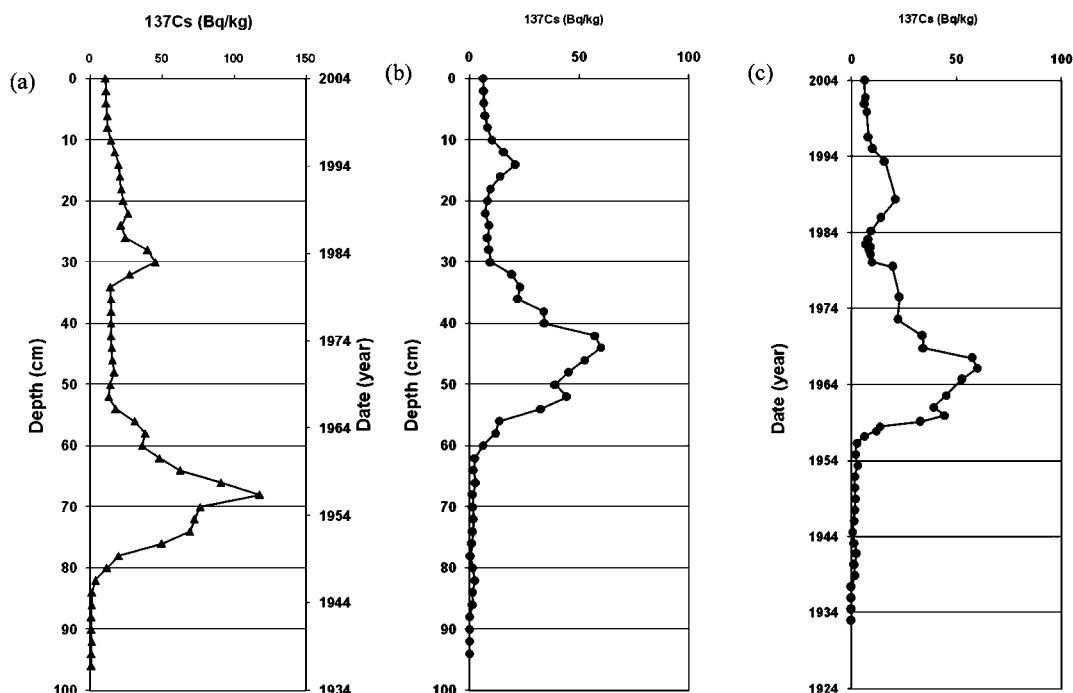


Fig. 2 Depth profiles of the Cs-137 activity. (a) (▲) B2 core (Bouafles); (b) (●) M1 core (Muids). (a) The chronology derived from the measured activities is indicated on the right axis of the graph for the B2 core. (c) Due to changes in the deposition rate along the depth profile of the M1 core, its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

exceptionally high in this river. However, we rule out this hypothesis, because of the dominant sedimentary origin of the rocks in the Seine River basin. Second, they could indicate that the Seine River basin underwent a general and very ancient pollution. This second hypothesis seems more likely. Such a large contamination by atmospheric deposition has also been observed in remote environmental archives.¹³ Third, this contamination could be explained by Ag released by lead (Pb) industries present in the Upper Seine and the Marne catchments. Pb and Ag are indeed strongly associated in Pb-ores. Even though the activity of lead industrial facilities strongly decreased after 1970 in the Seine River basin,²⁷ there are still a dozen plants in activity in the Upper Seine and the Marne catchments (Fig. 1b).²⁸

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

In contrast, thallium concentrations measured at Marnay-sur-Seine (0.30 mg kg^{-1}) and Méry-sur-Marne (0.45 mg kg^{-1}) (Table 2) are in good agreement with the median Tl concentration in European floodplain sediment.²⁹ They were even lower than the Tl geochemical background concentrations reported in the upper continental crust (0.75 mg kg^{-1}). The low Tl concentrations that we observed could be explained by the dilution of the geological Tl input by autochthonous calcite and/or organic matter. Scandium (Sc) concentrations were measured in all the samples. Normalising Tl concentrations to Sc allows taking account of this dilution effect. The Tl/Sc ratio for the reference geochemical background varies between 0.068 and 0.107. According to our data, the Tl/Sc ratio reached 0.046 ± 0.005 at Marnay-sur-Seine and 0.062 ± 0.001 at Méry-sur-Marne. These low Tl concentrations measured at upstream sites of the Seine River basin cannot be explained by a dilution effect. It is more reasonable to attribute these low concentrations to the sedimentary origin of

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.

the rocks in the Seine River basin. Moreover, the Tl concentration observed at Marnay-sur-Seine lower than the Tl concentration at Méry-sur-Marne may be partly explained by a possible metal release from the suspended sediments trapped during one month periods at Marnay-sur-Seine.

Depth profiles of Ag and Tl concentrations

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

The Ag concentration showed strong variations along the profile of the B2 core (from 4 to 25 mg kg⁻¹) (Table 3). The highest concentration (24.6 mg kg⁻¹) was recorded in 1960. The lowest concentration (3.8 mg kg⁻¹) was measured in the uppermost superficial layer which corresponds to the sediment deposited in 2003. Moreover, the peaks in Ag concentrations (observed in 1960 and, to a lesser extent, in 1994) correspond to similar peaks in Zn, Sb, Hg and Pb concentrations.²¹ The 1960 peak probably reflects the industrial boom after the Second World War.

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

To document the influence of anthropogenic activities, temporal variations of the Ag and Tl enrichment factor (EF) ratios were calculated, taking account of the upper continental crust (UCC) concentrations as a reference (Table 5). The following EF values should be interpreted with some caution, keeping in mind the shortcomings of the EF approach, EF being calculated relative to the crust composition or to local background values.³⁰ Ag EF recorded in both B2 and M1 cores were extremely high. EF in Ag ranged between 51 and 300 in B2 and between 73 and 263 in M1, when using UCC concentrations as reference values. After normalising Ag concentrations to Sc, the Ag EF depth profiles were much more similar in both cores (Fig. 3). Ag EF obtained taking the concentrations measured at Marnay-sur-Seine as a reference ranged from 8 to 47 in the B2

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

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

core and from 12 to 39 in the M1 core. When using the concentrations at Méry-sur-Marne, Ag EF fluctuated similarly between 12 and 44 in the B2 core, and 12 and 26 in the M1 core. These results demonstrate a significant enrichment of sediment in Ag and Tl during its transfer from the upper catchment sites to the downstream sites. This enrichment is clearly associated with contemporary anthropogenic impacts, whereas the enrichment observed at the upstream sites was probably induced by more ancient human activities.

Given it is widely known that Pb-ores constitute an important Ag source,³¹ it is particularly relevant to compare the Ag concentrations with the ones obtained for Pb.²¹ Both profiles were found to be synchronous (results not shown). Examination of the Pb/Ag ratio can provide valuable insights about the dominant emission processes.¹¹ The Pb/Ag ratio decreased from

Table 5 Silver (Ag) and thallium (Tl) enrichment factors in the B2 and M1 cores, and in the upstream sites. Ref: upper continental crust reference concentrations used for the calculation of enrichment factors (Wedepohl, 1995). See text for details

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			
Ref/mg kg ⁻¹	0.055	0.75		0.055	0.75

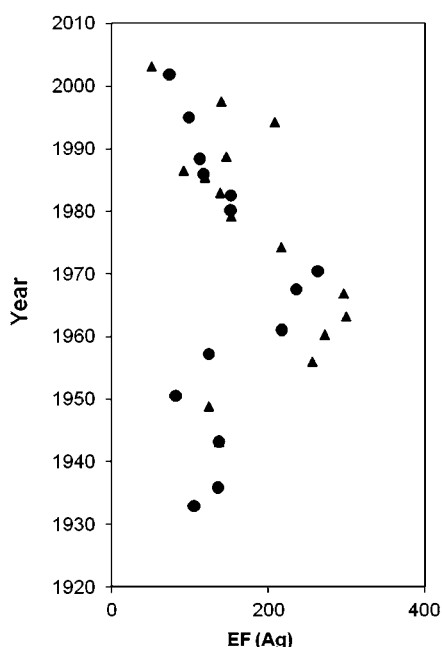


Fig. 3 Enrichment factor (EF) in Ag in the depth profiles of the two analysed cores: (▲) B2 core (Bouafles); (●) M1 core (Muids) using upper continental crust values as reference.

ca. 50 in sediment deposited in 1930, up to 20 in the 2003 sediment. The higher enrichment in Pb than in Ag observed in the Swiss peat bog¹¹ level corresponding to 1967 is not observed in the Seine River sediment. In addition, the Pb/Ag ratios observed in the Seine sediment cores are significantly lower than those observed in peat bog¹¹ and even lower than the Pb/Ag ratio reported in UCC (*i.e.* 400³). Overall, we can confidently state that the Seine River sediment is enriched in Ag compared to Pb.

Tl concentrations in the B2 core ranged between 0.66 and 1.01 mg kg⁻¹, with a median concentration of 0.86 ± 0.12 mg kg⁻¹ all throughout the depth profile. No significant peak can be detected in the profile (Table 3). The lowest Tl concentration in sediment was measured in the sediment deposited in 1979. Furthermore, Tl EF mean values were close to 1 (0.9 in average) (Table 5) when taking the UCC concentrations as a reference, indicating an absence of enrichment. Tl EF calculated using concentrations measured at Marnay-sur-Seine and Méry-sur-Marne reached 2.1 and 1.5, respectively. The low but constant enrichment in Tl measured in the downstream sediment suggests the potential existence of a natural Tl source in the Seine River basin. We suspect that the Yonne River sediment could be responsible for this Seine sediment enrichment in Tl. The Yonne River flows indeed into the Seine River at a junction located downstream of Marnay-sur-Seine (Fig. 1a), after having flown across granites exposed in the Morvan region. Granites are known to be enriched in Tl.⁷

Thallium pollution records in the sediment cores

Atmospheric archives are characterised by an important Tl pollution, which is even more important than Ag pollution.^{11–13} Our results clearly point out that the increase in Tl atmospheric source(s) measured in atmospheric archives did not impact the

composition of the Seine River sediment. The geochemical behaviour of Tl is similar to the one of potassium and other alkali metal cations.^{31,32} The lability of Tl may bring into question the relevance of a sediment core to record a Tl pollution signal. However, this issue remains the object of a lively debate in the literature. On the one hand, mobilisation of Tl from the solid phase to pore waters was observed in lacustrine sediment cores.^{12,33} Laforte *et al.* (2005)³³ concluded that the significant post-depositional Tl mobility must be taken into account to interpret Tl profiles in sediment. On the other hand, it was also shown that Tl sorbed strongly on layered illitic and vermiculite clays.¹⁹ Moreover, no Tl desorption was observed from clay-rich soils when adding NH₄⁺ and K⁺ competitive cations. Tl is even considered to be enough stable to allow its chronological evaluation.³⁴ The strong sorption of Tl from atmospheric origin on silty and silty-clay soils of France was demonstrated.³² It was also showed that Tl present in the French soils had a pedological origin.

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

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

Potential sources of Ag to the river

Ag may be released by different sources to the environment. Thouvenin *et al.* (2005)¹⁸ estimated the silver contribution of the Seine River to its estuary in 2003. Sediments were monthly sampled in Poses, which is the last dam before the estuary. In 2003, the Ag flux in Poses was estimated at 1.5 t yr⁻¹.¹⁸ Based on the measurements obtained from the B2 sediment core sampled in 2003 at Bouafles, which is located 30 km upstream of Poses, we can propose a rough and comparative estimation of the Ag annual flux. The particulate output of the Seine was estimated at 450 000 t yr⁻¹ in 2003.¹⁸ Ag concentration in the uppermost layers of the B2 core reached 3.8 mg kg⁻¹, we can then estimate the particulate Ag output from the Seine River at 1.7 t yr⁻¹. Similar calculations applied to the M1 uppermost layer concentration result in an Ag particulate flux of 2.0 t yr⁻¹. Both estimations remain in good agreement with the ones obtained previously,¹⁸ given that the concentrations in the uppermost layer of the core are only representative of the solids concentration reached during periods of high water level. Moreover, suspended sediment¹⁸ and deposited sediment (this work) differ in terms of particle size and organic matter content. Still, these characteristics influence the metal concentration in sediment. Overall, our results suggest that the Ag export to the Seine River estuary (1.7–2.0 t yr⁻¹) is at least equivalent to the cadmium and mercury

fluxes at the river mouth (1.75 and 1.25 t yr⁻¹, respectively²⁷). Given the high toxicity of Ag, Ag concentrations in the solid and the dissolved phases should be monitored to evaluate precisely the Ag particulate and dissolved fluxes from the river and to allow conducting further risk assessment studies.

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

Forty-five percents of the silver used in the film and photo-production were not recycled and potentially exposed to the environment in 1997.⁵ The film photography first developed at the end of the 19th century and became a mass-consumption product throughout the 20th century. This use may have induced a large part of the ancient sediment contamination, not only because of the lack of restrictive waste management regulations, but also because of the spreading of numerous photo-laboratories. The exponentially decreasing demand for this use could explain the decrease in Ag concentration measured in the contemporary sediment.

Ag content in domestic waste is likely to increase again in future. A recent study carried out in the Rhine River catchment showed that the production of goods using Ag nanoparticles will increase in future. This will amplify the Ag release to freshwater environments.¹⁷ These products consist in plastics (medical catheters, sanitation tubes, computer keyboards, door handles, car steering wheels and mobile phones) and textiles benefiting from the biocide effect of Ag nanoparticles. The biocidal mechanism of silver-containing products results indeed from a long term release of silver ions (Ag⁺) by oxidation of metallic silver (Ag⁰) in contact with aqueous media. Up to 15% of the total silver emitted to water in Europe may be released from biocidal plastics and textiles in 2010.¹⁷

Conclusions

Very few records were available to document the contamination by metals of minor economic importance such as Ag and Tl in river catchments strongly modified by human activities. These metals prove nevertheless to be very toxic. This study demonstrated that the Seine River sediment was not contaminated by Tl during the last 60 years. However, the question of its partition between the solid and the dissolved phases remains a subject of

lively debate. In contrast, the Seine River sediment was severely contaminated by Ag. Concentration in this metal started decreasing in the 1960s, but it is still present in the environment. Nowadays, the main source of Ag to the river sediment appears to originate from the waste incinerators. However, the sources of Ag may have changed throughout the last decades. Moreover, the increasing Ag demand and the growth of its uses demonstrate the necessity to understand the biogeochemical cycle of Ag, which can partly be investigated through the analysis of environmental archives.

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