



Dynamics of metallic contaminants at a basin scale – Spatial and temporal reconstruction from four sediment cores (Loire fluvial system, France)



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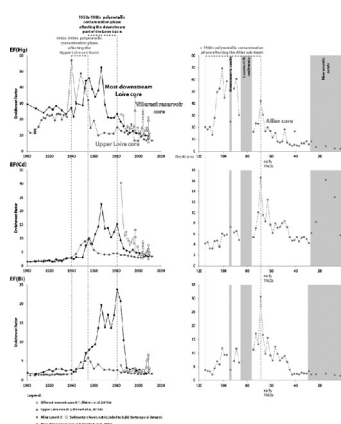
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HIGHLIGHTS

- Dynamic of metals over 100 years at 4 stations of the Loire basin is described.
- Metal source characterization was estimated with river bank sediment composition.
- Hydrosedimentary dynamic and industrial history highly influence archiving processes.
- Upstream–downstream shifts of recorded contamination periods are identified.
- Sediment quality is locally affected (Sb) or more widely impacted (Bi, Cd, Hg).

GRAPHICAL ABSTRACT



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ABSTRACT

From the 19th century, the Loire basin (France) presents potentially pollutant activities such as mining and heavy industries. This paper shows spatio-temporal distribution of trace elements in sediments at a basin-scale, based on a comparison of archived temporal signals recorded in four sedimentary cores. Anthropogenic sources contributing to sediment contamination are also characterized, using geochemical signatures recorded in river bank sediments of the most industrialized tributaries. This study highlights upstream–downstream differences concerning recorded contamination phases in terms of spatial influence and temporality of archiving processes. Such differences were related to (i) various spatial influences of contamination sources and (ii) polluted sediments dispersion controlled by transport capacity of metal-carrier phases and hydrosedimentary dynamics.

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1. Introduction

Industrial Revolutions of the 19th and 20th centuries mark a transition in the European river basin history. From this epoch, a new geological era can be defined – the Anthropocene – corresponding to a period when Human imprint on the global environment largely concurrences natural processes (Crutzen and Stoermer, 2000; Steffen et al., 2007). At basin-scale, dramatic intensification of anthropogenic pressures on the environment result in important disturbances like among others on: (i) geochemical quality of water and sediments (e.g. for trace elements: Martin and Meybeck, 1979; Meybeck and Helmer, 1989; Vink et al., 1999; Meybeck, 2002; Viers et al., 2009) and (ii) the sedimentary transport (e.g. Arnaud-Fassetta, 2003; Vörösmarty et al., 2003; Knox, 2006; Hoffmann et al., 2010; Hughes et al., 2010). Hence, in highly anthropized basins, the major part of metal inputs has been stored in soils and sediments and they are still retained (Walling and Owens, 2003; Audry et al., 2004a; Meybeck et al., 2007; Lestel et al., 2007; Thévenot et al., 2007).

As trace elements (TE) are mostly associated with fine-grained sediments during the sedimentary transport, the spatial distribution of

contaminants is largely controlled by settling capacities of fluvial environments (Horowitz and Elrick, 1987; Walling et al., 2003). In detailed, storage of fine-grained sediments can be more or less long in dam reservoirs (Ye et al., 2011; Vukovic et al., 2014; Dhivert et al., 2015a) and in floodplain (Bradley and Cox, 1990; Martin, 2000; Heaven et al., 2000; Walling et al., 2003; Lecce and Pavlowsky, 2014; Dhivert et al., 2015b). Archiving capacities of these two last storage compartments are often used to build temporal dynamics of pollutants at basin scale (e.g. for French neighboring basins: Grousset et al., 1999; Gocht et al., 2001; Audry et al., 2004b; Castelle et al., 2007; Le Cloarec et al., 2011; Berner et al., 2012; Desmet et al., 2012; Ferrand et al., 2012; Mourier et al., 2014).

The Loire basin contains important coal and TE-mining districts which constituted ones of foci for the industrial development in France (Woronoff, 1994). Associated production activities were mostly implanted in the upstream part of the Loire basin (i.e. mining, heavy industries and urban areas; Fig. 1). In other basins, such anthropogenic activities also constitute important contamination sources during the industrial period (e.g. Audry et al., 2004b; Maclin et al., 2006; Castelle et al., 2007; Grosbois et al., 2007; Meybeck et al., 2007; Thévenot

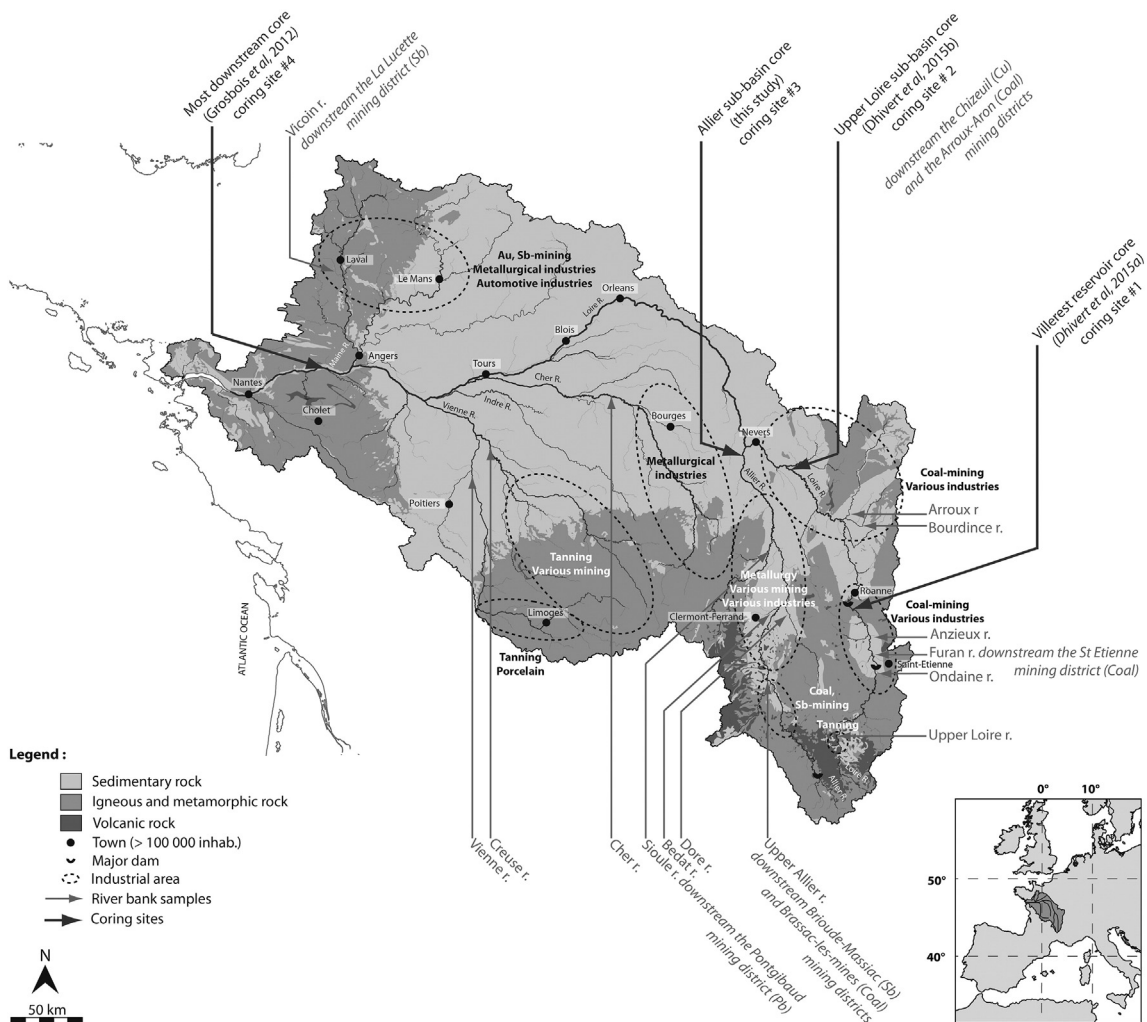


Fig. 1. Map of the Loire basin showing the main geological domains, the localization of major dams (>50 m high), main urban areas (>100,000 inhab.), major industrial and mining areas, coring sites and river bank sediment sampling sites of this study.

et al., 2007; Jasminka and Robert, 2011; Le Cloarec et al., 2011; Louriño-Cabana et al., 2011; Wang et al., 2011; Lecce and Pavlowsky, 2014). Sedimentary cores of the Loire River attest old metallic contaminations (Grosbois et al., 2012; Dhivert et al., 2015b) and additional studies must be done at the entire basin scale in order to characterize historical contamination sources influencing the geochemical composition of sediments.

The aim of this paper is to study spatial and temporal distribution of TE archived in sediments at the whole Loire basin-scale. A comparison of TE signals archived in sedimentary cores sampled throughout the basin will help to understand the metallic contaminant dynamics for the last century and possibly identify natural and anthropogenic sources under the hydrosedimentary dynamic influence.

2. Study area

2.1. Physical and hydrological characteristics of the Loire basin

The Loire River is the largest French basin with a total surface area of 117,800 km² (the tenth largest of W-European basins) and 1013 km long from the spring to the estuary. In its upstream part, the basin is composed of the Upper Loire (480 km long, 17,570 km² of surface area) and the Allier sub-basins (421 km, 14,310 km²). The downstream part of the Loire basin drains three main tributaries as the Cher (368 km, 13,920 km²), the Vienne (372 km, 21,161 km²), the Indre sub-basins (279 km, 3428 km²) on the left bank and the Maine (23,314 km²) sub-basin on the right bank (Fig. 1).

Hydrology of the Loire basin is influenced by a balance of oceanic and Mediterranean rainfalls during autumn and winter completed by snow-melt in spring (Dacharry, 1974). Hydrology is very similar between the Upper Loire and the Allier sub-basins, presenting at their most downstream gauging stations, maximum monthly discharges of 325 m³·s⁻¹ in February and minimum of 48 m³·s⁻¹ in August (calculated over 60 years). During the second part of the 20th century, water discharge was controlled by important dams in the upstream part of the Loire basin (dams >50 m high, Fig. 1, built since 1957 and 1984 for the Grangent and the Villerest dams respectively in the Upper Loire River and since 1983 for the Naussac dam, located in the Allier River). At the most downstream gauging station of the entire Loire basin, the annual hydrological cycle is characterized by a high flow period from November to May (maximum averaged monthly discharge of 1530 m³·s⁻¹ in February) and a low flow during summer time (minimum of 250 m³·s⁻¹ in August; calculated over 147 years, www.hydro.eaufrance.fr, 2015). Hydrology of the main tributaries of the Loire basin is quite similar to the upstream basin (averaged monthly discharges ranged from 28 to 196 m³·s⁻¹ for the Cher River, from 62 to 362 m³·s⁻¹ for the Vienne River and from 35 to 267 m³·s⁻¹ for the Maine River; www.hydro.eaufrance.fr, 2015).

Geology of the Loire basin is very contrasted (Fig. 1). The upstream part of the hydrosystem drains the eastern part of the French Massif Central (Fig. 1). This old massif is inherited from the Variscan orogeny (480–290 Ma) and it is composed of (i) Variscan plutonic bedrocks (granites, gneiss and micaschists), (ii) volcanic areas dating from the Tertiary to the Holocene (65 Ma and 3.5 ka), and (iii) sedimentary facies from Carboniferous and Oligocene-Miocene (mainly sandstones, marls and clays). Downstream the confluence between the Upper Loire and the Allier Rivers, the Loire River runs over the southern part of the Paris basin, a sedimentary basin infilled from the Trias to the Tertiary and composed of limestone, chalk, marl and detrital siliceous rocks. Springs of main tributaries are all located in the French Massif Central. The Cher, Indre and the Vienne Rivers start in the central part of the massif essentially composed of Variscan plutonic bedrocks. The Maine basin drains the eastern part of the Armorican Massif composed of a mix of plutonic bedrocks and Primary sedimentary facies (mostly sandstones and partially metamorphized marls) and the central part of the Paris basin.

2.2. Brief history of the Loire basin industrialization

From the 16th century, proto-industrial activities were present in the Loire basin, essentially based on textile, leather and fur tanning and manufacturing (Woronoff, 1994). The industrialization of the Loire basin fully began in the second part of the 19th with the industrial exploitation of geological resources in the French Massif Central. Old mining districts, in the upstream part of the basin, constitute emergence points of this industrial development (Fig. 1). Indeed, three of major coal-mining districts at the French-scale were implanted in Carboniferous sedimentary facies of the eastern part of the massif *i.e.* (i) the Saint Etienne district located in the Upper Loire sub-basin (Furan tributary), (ii) the Blanzy-Epinac-La Machine districts located downstream of the Upper Loire sub-basin (Bourdince and Arroux tributaries) and (iii) the Brassac-les-Mines district located in the upstream part of the Allier sub-basin (Fig. 1). From the Middle-Age to the early 1980s, they produced more than 1.5 Gt of coal, corresponding to 30% of the national production. In details, industrial coal extraction really began in the 1830s and strongly increased at the end of the 19th century to reach a maximum production between the 1940s and the late 1950s. After then, coal-mining activities slowly decreased down to the early 1980s, the last mine closing in 1983 (www.charbonnagesdefrance.fr, 2015). Smaller coal-mining sites were also in activities between the second part of the 19th century and the late 1950s in similar geological units located in the central and the NW part of the massif.

Between the second part of the 19th and the end of the 1950s, TE-mining constituted the second factor of industrial development in the Loire basin. As a result of hydrothermal mineralization during the Variscan orogeny, TE enrichments are present in bedrock of the French Massif Central (Delfour et al., 1984; Sizaret, 2002). TE-ores due to sulfide mineralization were largely exploited in the upstream basin (notably pyrite deposits) as the Cu-mining district of Chizeuil (about 1 kt extracted between 1854 and 1963; in the Upper Loire sub-basin) and the Ag–Pb-mining district of Pontgibaud (50 kt extracted between 1826 and 1897; in the Allier sub basin; Fig. 1). In addition, during the first part of the 20th century, the Loire basin contained two of the most important Sb-mining districts in the world, exploiting stibine deposits in the upstream part of the Allier basin (Brioude-Massiac district, 40 kt extracted between the 1880s and 1968) and in the Maine basin (La Lucette district, 42 kt extracted between 1900 and 1934, Vicoin sub-basin, Fig. 1). Both of them provided more than 60% of the total French production (www.sigminesfrance.brgm.fr, 2015; www.societechimiquedefrance.fr, 2015).

Associated with coal and TE-mining, raw materials and energy production were locally used for heavy industrial activities. Extracted TE-ores were locally smelted, in complement of imported ores from other European countries, using coal extracted nearby (Garçon, 1995). Steel, glass and ceramic factories were also implanted near geological resources (Fig. 1). After the mining production slowdown in the early 1960s, many heavy industries were relocated near to international harbors on seashores.

Since the late 19th, industrial and mining foci correspond to the oldest and the most important urban areas of the Loire basin (Woronoff, 1994). Nowadays, the main urban centers of the basin are located in Saint Etienne (508,847 inhabitants in 2010) and Clermont-Ferrand agglomerations (468,891 inhab.; Fig. 1). Four smaller urban areas are located further downstream *i.e.* Limoges (282,873 inhab., in the Vienne sub-basin), Tours and Orléans (477,438 and 419,271 inhab., respectively, in the Middle Loire stretch) and Angers (397,435 inhab., in the Maine sub-basin; www.insee.fr, 2015).

3. Materials and methods

3.1. Sampling areas and sediment core description

In order to study spatial and temporal variability of TE contamination archived in sediments, TE temporal signals were compared in several sediment archives sampled: (i) downstream the oldest and the most important industrial and mining complexes on the Upper Loire stretch (Dhivert et al., 2015a, b) and on the Allier river and (ii) in the most downstream part of the fluvial domain (Grosbois et al., 2012).

In the Upper Loire sub-basin, 2 cores were collected. One in the Villerest reservoir in 2010 (45°58'54"N, 4°2'15"E) is 84 cm long (coring site #1; Fig. 1). It has registered the temporal evolution of TE contaminations since 1984, downstream the most important industrial and mining area of the basin (Dhivert et al., 2015a) and the influence of three flood sequences was shown for specific TE remobilization. A second core was sampled in 2012 in a paleochannel at Decize (46°49'37"N, 3°27'38"E; Dhivert et al., 2015b; coring site #2; Fig. 1). More than two centuries were registered in this sedimentary archive of 160 cm long.

In the Allier sub-basin, just upstream of the confluence with the Upper Loire stretch, another core was sampled in 2012 in a water supply canal (46° 55' 36" N, 03° 03' 29" E; coring site #3; Fig. 1; Fig. S1a). Since 1840, this hydraulic structure supplies water from the Allier River to the Loire lateral shipping canal. In the 1940s, this structure was equipped to retain the coarsest particles in the lock. In order to limit the influence of biomass deposits, the coring site was located close to the supply lock. According to canal managers, sediments have never been dredged.

Some description details are given below as this core has not been previously described. According to a visual and textural sedimentary analysis, the #3 core can be divided in two sedimentary units (Fig. S1b). The deepest unit (116–28 cm) is dark and composed of very poorly sorted sediments in a balanced proportion of very fine-grained sands and silts. The 78–88 cm sedimentary layer is composed of compacted leaves and brushwood and therefore could not be integrated in this study. The median grain-size of this unit averages 88 μm ($n = 44$) but the grain-size variability is high (RDS = 58%) because of heterometric sandy layers archived at 116–114, 110–108, 98–88, 74–72 and 40–36 cm deep. The upper unit (28–0 cm) is homogeneously composed of sands, moderately sorted, with a median grain-size equal to 298 μm (RDS = 12%, $n = 14$).

Sandy sedimentary layers at 96–92 cm and the upper unit (28–0 cm) contain high Hf concentrations ranging from 40 to 139 mg/kg of dry mass compared to the lower unit (median = 21 ± 8 mg/kg; data not shown). In general in the Loire basin, Hf concentrations are due to the presence of heavy minerals and are used as a tracer of detrital inputs, especially during floods (Dhivert et al., 2015a). The <63 μm fraction being negligible and TE signal being potentially influenced by these detrital inputs, these sandy layers (96–92 and 28–0 cm deep) could not be considered to build long-term evolution of sedimentary contaminations in this core. A detailed age-model was not possible to build because of a non-linear sedimentation rate resulting of undated sandy layers (S11b). These layers should be attributed to overfull episodes for the sand retention structure, when the coarsest particles could be spread in the water supply canal. Unfortunately, any information about such events was recorded by the canal manager.

The ^{137}Cs measurements show that any ^{137}Cs was detected below 96 cm deep attesting sediment deposits before 1950, date of the first significant Nuclear Weapon Test (NWT; S11b). A ^{137}Cs extended peak was detected between 86 and 54 cm deep with a maximum at 64–62 cm (39 ± 1.1 Bq.kg $^{-1}$) and a lower activity from 38 cm deep to the surface ($< 4 \pm 0.4$ Bq.kg $^{-1}$; S11b). According to this ^{137}Cs vertical profile and the low influence of the Chernobyl Nuclear Power Plant Disaster in the study area (Dhivert et al., 2015b), the ^{137}Cs maximum can be attributed to the maximum fallout of NWT in the early 1960s.

The most downstream core of the Loire basin was sampled in 2009 in an alluvial island (47°23'34"N, 0°51'23"O; Grosbois et al., 2012;

coring site #4; Fig. 1). The time interval covers from the early 20th at 198 cm deep to 2009. In addition, first estimation of preindustrial TE concentrations in the Loire basin were measured in a clayey layer sampled between 400 and 360 cm deep.

Unfortunately, some highly industrialized sub-basins such as the Cher, the Vienne and the Maine sub-basins could not have been sampled as any appropriate coring site, combining good settling spots, downstream representative sites under anthropogenic influence, could be identified because of embankments and river channel canalization.

Coal and TE-mining activities being no longer in operation in the Loire basin, historical contamination sources are not necessary active nowadays. However, their geochemical signatures can be partially or totally archived in sedimentary storage areas. Information was found in various databases to select representative stations with a potential anthropogenic impact (BASIAS, BASOL and SIGMines databases www.basias.brgm.fr, 2015; www.basol.developpement-durable.gouv.fr, 2015 and www.sigminesfrance.brgm.fr, 2015), in industrialist websites (www.acier.org, 2015; www.societechimiquedefrance.fr, 2015; www.charbonnagedefrance.fr, 2015; www.atelierdeprojet.loire.equipement.gouv.fr, 2015) and in local municipal services and museums (St Etienne, Chazelles-sur-Lyon, Gueugnon, Decize, Le Puy Guillaume municipal archives).

After identifying the station, river bank sediments were sampled downstream important mining districts or/and industrialized areas (Fig. 1) in the outer part of meanders, after refreshing the erosion surface. Two situations were selected for this sampling campaign: (i) when the river bank was visually homogenous, sediments were sampled continuously on 20 cm - slices over the vertical profile, and (ii) when the river bank presents visual transitions, each layer was individually sampled. All across the Loire basin, 14 sub basins were sampled (Fig. 1). River bank sediments used in this study are mostly composed of fine-grained sediments.

3.2. Analytical methods

Material and method are all detailed in Dhivert et al. (2015a). Grain-size, dating and geochemical analyses were performed with 2 cm-slices of core sediments.

Briefly, grain-size measurements were performed using a laser microgranulometer (Mastersizer 2000, Malvern). For dating, ^{137}Cs was measured by gamma spectrometry with very low-background detectors, coaxial HP Ge N-type (8000 channels, low back-ground).

Sediments of the Loire basin can be very heterometric (Valverde et al., 2013; Dhivert et al., 2015b). Therefore, all geochemical analyses were carried out on the <63 μm fraction in order to limit grain-size influence. Geochemical analyses were carried by the SARM-CRPG laboratory (France; www.helium.crpq.cnrs-nancy.fr/SARM, 2015). Sediments were completely digested with $\text{LiBO}_2\text{-Li}_2\text{B}_4\text{O}_7$ on a tunnel oven and placed in an acid solution before to be analyzed by ICP-OES (ICap 6500, Thermo Scientific) for total contents of major and minor elements, by ICP-MS (Thermo Elemental X7, Thermo Scientific) for trace elements, except for Hg done by DMA-80 (Milestone). Total organic carbon (TOC) after a HCl attack and total sulfur (TS) were analyzed by O_2 flow combustion at 1350°C with a SC 144-DRPC (Leco). Analytical error tacking into account accuracy of digestion process and analyses was within 1% for major elements and within 10% for trace elements.

4. Results and discussion

In this study, the spatio-temporal distribution of TE throughout the Loire basin is based on several sediment cores. This approach allows to discriminate local contamination phases to those affecting the upstream like the downstream part of the basin. Contamination periods are defined according to the temporal evolution of enrichment factors and to TE associations with similar behaviors. Concentrations in preindustrial

samples were similar in sediments of the upstream and the downstream part of the Loire River, except local influences of geochemical anomalies (Grosbois et al., 2012; Dhivert et al., 2015b). Hence, by calculating enrichment factors (EF) with a double normalization to Al concentrations and to preindustrial concentrations, a comparison of contamination levels has been performed according to defined contamination periods.

4.1. Local Sb contamination in the upper Loire and the Allier sub-basins for the 1900–1950 period

Results obtained in the Upper Loire sub-basin show a non-contaminated period defined before the late 1870s in the core #2, with EF between 1 and 2 for all TE except for Sb. In this core #2, Sb is enriched and stays constant until the 1900s ($4 < EF < 6$). Between the 1900s and the 1950s, Sb enrichments are gradually amplified, up to 13 (Fig. 2). During this time interval, Sb is significantly correlated with TOC, TS and also with some TE like As, Bi, Cd, Cu, Mo, Ni, Pb, U, W and Zn ($r \geq 0.8$, $p < 0.05$, $n = 19$). From the late 1950s up to late 1970s, Sb enrichments started to decrease, being significantly correlated with Al, TS and with other TE like Bi, Cd, Cr, Cu, Mo, Ni, Sn and Zn ($r \geq 0.8$, $p < 0.05$, $n = 18$) but not with TOC anymore ($r < 0.6$, $p > 0.05$). After the early 1980s, EF (Sb) levels recover close to 5 like before the late 1870s. In the core #1, sediments older than 1984 present lower EF than core #2, ranging between 1 and 3 without any significant temporal evolution (Fig. 2). The studied sites are located downstream the most important coal-mining district of the Loire basin (the St. Etienne coal mining district; Fig. 1). Bank sediments of the tributary draining this coal mining district, the Furan river, were also sampled in our study and present important Sb and TOC concentrations (Table 2). In dark layers, coal particles were identified and therefore, their chemical composition could be considered as representative of a local coal-mining effluent (Fig. 3, Fig. S2a).

The coal mining period occurred between the 1900s and the 1950s in the Loire basin and was maximum between the 1940s and 1950s (www.charbonnagedefrance.fr, 2015). Coals and more especially their pyrite contents can be important host for chalcophil TE (Finkelman, 1993; Mishra et al., 2008; Seredin and Finkelman, 2008; Kolker, 2012). Sb concentrations in coals are very variable and locally very important (Querol et al., 1995; Karayigit et al., 2000; Seredin and Finkelman, 2008, Qi et al., 2008). However, any specific information about TE contents in coals of the French Massif Central has been described in this

area. As shown by Querol et al. (1995), the geochemical composition of coals depends on the selected fraction density, the richest in Sb being the densest. For these authors, Sb-TOC relationship also depends on the selected fraction, from $Sb/Al = 1.10^{-6} \cdot TOC$ in the less dense fraction (density equal to 1.3–1.4) to $Sb/Al = 2.10^{-5} \cdot TOC$ in the densest fraction (> 2.8). During sedimentary archiving processes, coal particles are subjected to be stored according to density like other minerals, and associated geochemical signals depend on depositional environments (Dhivert et al., 2015b). Therefore, the difference between geochemical signatures archived in Furan river bank sediments and the core #2 shown in this study can be explained by: (i) the local influence of various industries accompanying coal-mining in the Upper Loire sub-basin and/or (ii) by controlled depositional environment of the coring site selecting archived coal particles and thus archiving only a partial geochemical signature of coal-mining effluents.

In the present study, very high Sb enrichments were recorded between 116 and 68 cm deep in the core #3 of the Allier sub-basin, corresponding to the period <1960s with EF ranging between 21 and 56 (Fig. 2). In this sequence, Sb is significantly correlated with As, Pb, Sn and Zn ($r = 0.7$, $p < 0.05$, $n = 17$). From 68 cm to 28 cm deep, Sb enrichments decreased exponentially but stayed still high (between 12 and 21; Fig. 2). They are not significantly correlated with other TE or major elements. The ratio Sb/Al does not present significant correlations with TOC ($r = 0.5$, $p > 0.05$, $n = 37$). However, before the 1960s, Sb is very highly enriched (Fig. 3). Antimony sources could be at least double in the Allier basin. A potential source is one the most important coal-mining districts at national scale, located upstream the sampling site (the Brassac les Mines district; Fig. 1). Another source can be one of the most important Sb-mining and smelting complexes at a national scale (the Brioude-Massiac district; Fig. 1). Like coal mining activities, Sb-mining and smelting were maximum between the 1940s–1950s (www.sigmines.fr, 2015). In Sb-mining districts of the Loire basin Sb is associated to sulfide mineralization, mostly as stibnite (Sb_2S_3). This is the case for the Brioude-Massiac district in the Allier sub-basin and also for the La Lucette district (the two most important Sb mining sites in France, Fig. 1). River bank sediments were sampled downstream of these mining sites in our research. Sediments are very rich in Sb and their geochemical composition can be characteristic of Sb-mining effluents (Fig. 3; Fig. S2b).

These results show a local and synchronous Sb important contamination phase in the Upper Loire and Allier sub-basins, registered before the 1960s and related to local coal and Sb-mining activities. However,

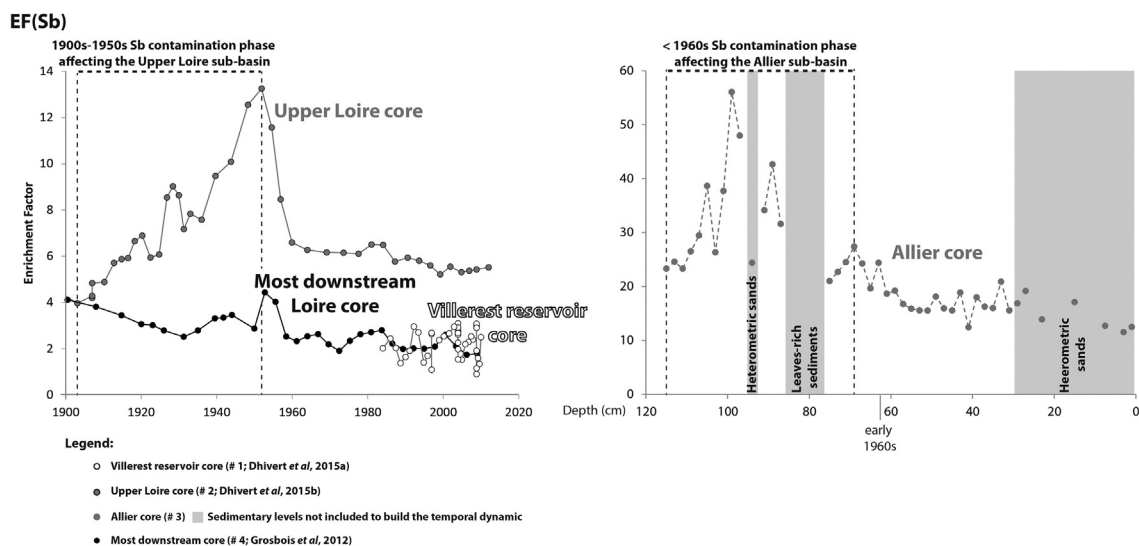


Fig. 2. Spatio-temporal evolution of Sb enrichment factor in all the studied cores of the Loire basin. Enrichment factors are calculated in the $<63 \mu m$ fraction after normalization to Al contents and preindustrial concentrations.

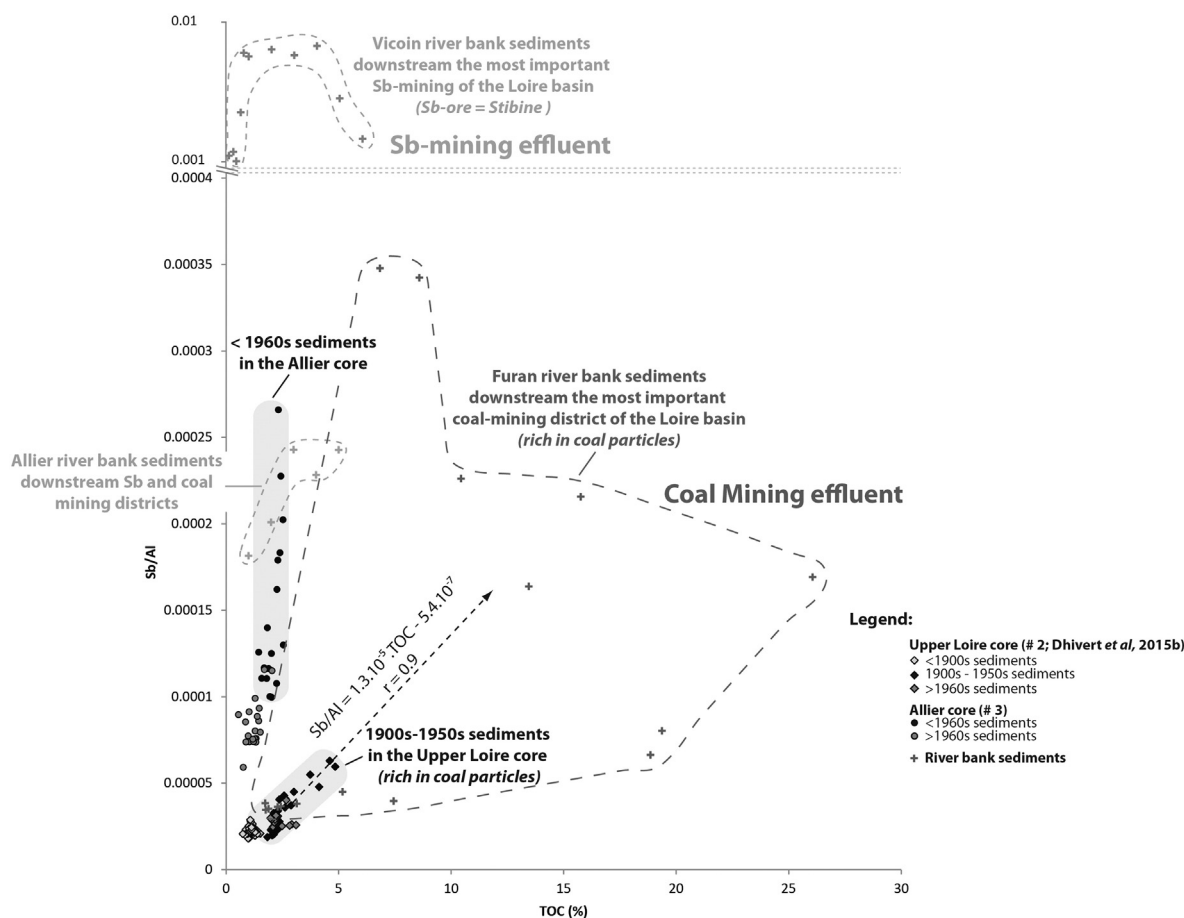


Fig. 3. Sb-TOC relationship, normalized to Al contents, in the <63 μm fraction of sedimentary cores of the Upper Loire (# 2), the Allier sub-basin (# 3) and selected river bank sediments.

such high Sb enrichments are not observed in the most downstream part of the Loire basin, EF ranging between 2 and 6 (Fig. 2).

4.2. Bi, Cd, Hg contaminations recorded at the entire Loire basin scale between 1940s and 1980s

Results obtained in this study show important increases of TE enrichments in sediments of the Loire basin from the 1940s to the 1980s. The most enriched TE were Bi, Cd and Hg in all the studied cores of the Loire basin (Fig. 4).

In the Upper Loire stretch, Hg is the most enriched TE in the core #2, especially during the 1940–1950 period, with maximum EF of 57 in the 1940s (Fig. 4). This TE is not correlated with any other TE nor any major element. Bi and Cd are also very enriched, presenting EF close to 1 before the 1940s but reaching moderate to high enrichments in the 1950s (range between 6 and 10; Fig. 4). Between the 1940s and the 1950s, other TE reach low enrichments ($\text{EF} < 4$) like As, Cr, Ni to moderate enrichments (EF range between 5 and 7) for Cu, Pb, Sn and Zn. During the 1940s–1950s time interval, a strong correlation can be highlighted between Bi, Cd, Cr, Ni, W and Zn ($r > 0.9$, $p > 0.05$, $n = 6$). However, they do not present any significant correlation with major element. From the early 1960s, temporal trajectories of TE contaminations are reversed, following an exponential decrease (Fig. 4). Bi like As, Cr, Cu, Ni, Pb, Sn, U, W or Zn recover EF range between 1 and 2 in the early 1980s, while Cd and Hg present enrichments respectively close to 3 and 8.

Upstream, in the core #1, Cd and Hg are the most enriched TE of this group ($\text{EF} > 30$) in the early 1980s and then, they also follow an exponential decrease. However, they are strongly enhanced in flood

sequences. Bi like other TE presents low enrichments in this core, ranging between 2 and 7 (Fig. 4).

For the Allier sub-basin, in the core #3 Bi, Cd and Hg enrichments are maximum between 116 and 68 cm deep, before the 1960s. Hg shows the highest enrichment (EF range between 20 and 69), while Bi and Cd present moderate to high EF (ranging between 4 and 31; Fig. 4). Other TE are low to moderately enriched in this interval (between 2 and 5; Table 1) and significant correlations can be highlighted between Bi, Cd, Cr and Cu ($r > 0.7$, $p < 0.05$, $n = 17$). From 68 cm to 28 cm deep, TE enrichments exponentially decrease like in the Upper Loire sites (Fig. 4). Arsenic, Al, Bi, Cd, Cu, Hg, Pb, TOC and Zn are all significantly correlated in this interval ($r > 0.8$, $p < 0.05$, $n = 17$). Bismuth like As, Cr, Cu, Ni, Pb, Sn, U, W and Zn recover EF ranging between 2 and 4 while Cd and Hg are still moderately enriched with EF ranging between 4 and 8.

At the most downstream station of the Loire basin (core #4), Hg is also the most enriched TE, reaching maximum EF up to 53, in the same range than upstream Hg signals but a little later, in the late 1960s (Fig. 4). Once again, Hg is not correlated with other TE nor major elements. Bi and Cd enrichments start to increase later than the Hg signals, at the beginning of the 1950s (Fig. 4). From the 1950s to the early 1980s, Bi and Cd show maximum peaks (EF ranging from 10 to 24 for both TE) and their EF levels are always higher than the upstream signals. Significant correlations are registered between Bi, Cd, Cr, Cu, Ni, Pb and Zn ($r < 0.7$, $p < 0.05$, $n = 21$) in post 1950s sediments. These EF variations draw a polymetallic contamination phase between the 1950s and the 1980s before to exponentially decline (Fig. 4). After the 1990s, TE enrichment are low, ranging between 1 and 3 excepted for Cd and Hg presenting EF respectively close to 4 and 10.

These results highlight a common Bi, Cd and Hg contamination phase in the Loire sediments at the basin scale. However, an important

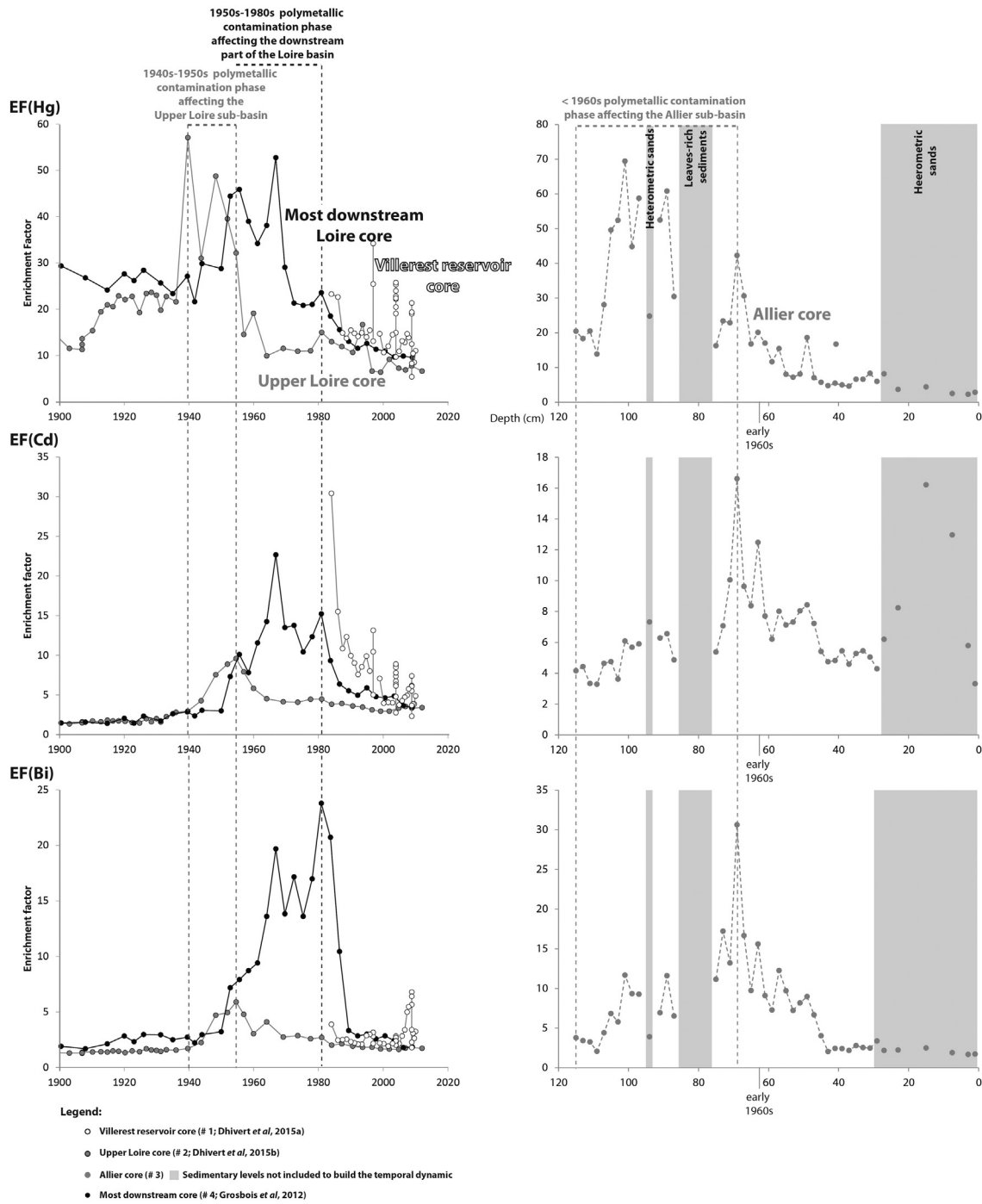


Fig. 4. Spatio-temporal evolution of Bi, Cd and Hg enrichment factors in all the studied cores of the Loire basin. Same EF calculations than Fig. 2.

upstream-downstream difference concerns temporal dynamics of these TE enrichments archived in sediment cores. Maximum EF peaks are recorded: (i) between 1940s and the 1960s in the Upper part of the basin (Loire and Allier stretches) and (ii) between the 1950s and the 1980s in the most downstream part. Therefore, a decade delay can be enhanced for both the registered maxima and the beginning of decline. In the upstream basin when Bi, Cd and Hg enrichments started to decrease from the 1960s, these TE enrichments are maximum in the downstream part of the Loire basin (Fig. 4). Such an upstream-downstream delay in TE contamination phases has been described in the Seine basin for Cd and Hg (Le Cloarec et al., 2011), when enrichment maxima were observed between the 1940s and 1950s in the most industrialized sub-

basin although they were registered between the 1960s and the 1980s at the most downstream station.

In addition, in basins where the density of anthropogenic activities follows an upstream-downstream gradient, the multiplication of source contributions can induce a spatial increasing trend of pollutions levels in suspended matters and in river bank deposits (e.g. for the Seine and the Rhône Rivers: Santiago et al., 1994; Horowitz et al., 1999; Meybeck et al., 2004; Grosbois et al., 2006; Le Cloarec et al., 2011; Le Pape et al., 2012). In our study, this up-downstream gradient does not appear clearly. Contamination levels of Bi and Cd are higher in the downstream than in the upstream part of the Loire basin although while maximum Hg contamination levels are similar in throughout the fluvial domain.

Table 1

Al, TOC and trace element concentrations in the <63 µm fraction of the Allier sub-basin core (# 3). n.d. = not determined, <d.l. = under the detection limit, mg/kg of dry mass.

Depth (cm)	Al %	TOC %	As mg/kg	Bi mg/kg	Cd mg/kg	Cr mg/kg	Cu mg/kg	Hg mg/kg	Mo mg/kg	Ni mg/kg	Pb mg/kg	Sb mg/kg	Sn mg/kg	U mg/kg	W mg/kg	Zn mg/kg
0–2	7.17	1.45	23.5	1.0	1.0	138	22	48	1.1	44	48.3	4.3	19.1	11.5	10.1	137
2–4	6.94	0.76	19.5	0.9	1.7	168	19	49	0.9	50	45.1	3.8	23.8	22.6	16.8	132
4–10	6.77	0.83	17.9	1.0	3.6	196	21	50	1.1	57	47.5	4.1	48.1	42.6	30.9	155
10–20	6.95	1.10	21.2	1.3	4.7	218	28	51	1.5	59	55.4	5.6	75.4	54.4	23.0	191
20–26	6.98	0.78	20.3	1.2	2.4	170	24	52	1.1	50	52.7	4.6	42.7	30.3	10.2	148
26–28	7.25	0.94	22.3	1.2	1.9	161	25	53	1.2	48	52.6	6.6	23.5	21.4	13.0	142
28–30	7.45	1.30	26.9	1.9	1.3	155	31	54	1.2	47	58.0	6.0	18.3	12.8	10.4	162
30–32	7.39	1.05	23.4	1.4	1.5	168	29	55	1.3	49	54.7	5.5	16.2	15.7	10.0	150
32–34	7.37	1.30	25.9	1.4	1.7	162	32	56	1.8	48	57.5	7.3	20.7	12.9	13.2	161
34–36	7.38	1.34	24.7	1.6	1.6	151	30	57	1.4	45	57.9	5.6	16.9	12.2	8.5	161
36–38	7.19	0.99	22.0	1.2	1.4	161	26	58	1.1	46	52.9	5.6	14.4	15.4	8.8	145
38–40	7.27	0.87	22.3	1.4	1.6	158	25	59	1.2	45	57.0	6.2	20.3	14.3	7.2	147
40–42	7.15	0.77	21.0	1.3	1.4	160	24	60	1.1	45	49.7	4.2	18.3	11.8	7.0	147
42–44	7.12	0.56	18.7	1.1	1.4	152	20	61	1.1	43	45.1	6.4	11.8	13.3	9.2	129
44–46	7.38	0.89	25.0	2.3	1.7	173	26	62	1.2	47	52.2	5.4	17.9	13.2	12.7	150
46–48	7.53	1.29	29.7	3.9	2.2	188	36	63	1.5	48	61.1	5.7	13.6	11.8	8.8	187
48–50	7.72	1.46	35.0	5.3	2.7	184	41	64	1.7	50	66.9	6.6	17.7	9.8	9.1	206
50–52	7.59	1.33	32.0	4.8	2.5	188	39	65	1.4	51	63.3	5.6	15.5	10.9	8.8	199
52–54	7.64	1.23	30.4	4.2	2.3	184	38	66	2.2	47	61.4	5.6	15.1	9.8	8.4	189
54–56	7.64	1.20	30.0	5.7	2.3	183	39	67	1.3	47	64.0	5.8	15.1	11.2	9.0	190
56–58	7.82	1.53	33.7	7.4	2.6	165	44	68	1.2	45	67.8	6.2	13.3	8.7	8.7	207
58–60	7.64	1.03	25.2	4.3	2.0	158	33	69	1.3	45	60.2	7.0	14.1	10.7	9.0	176
60–62	7.84	1.39	28.6	5.5	2.5	160	41	70	1.2	46	63.9	6.9	14.8	9.4	9.5	188
62–64	7.68	1.71	40.3	9.2	4.0	166	57	71	1.8	49	75.4	8.9	16.6	10.0	9.6	231
64–66	7.70	1.48	31.7	5.8	2.7	165	44	72	2.4	47	66.9	7.2	17.9	10.4	10.7	200
66–68	7.95	2.05	40.1	10.2	3.2	167	63	73	2.5	46	82.6	9.1	17.3	9.1	11.8	251
68–70	7.00	2.55	51.4	16.5	4.8	150	90	74	2.3	47	94.3	9.1	19.3	8.6	9.1	323
70–72	7.30	1.90	35.2	7.4	3.0	172	65	75	2.7	53	73.7	8.5	18.7	18.4	13.9	264
72–74	7.68	2.25	38.3	10.2	2.2	159	87	76	1.6	53	83.6	8.3	17.6	11.1	11.4	291
74–76	7.67	2.03	32.5	6.6	1.7	147	59	77	1.3	51	72.0	7.6	14.0	9.6	11.3	246
88–90	7.65	2.54	55.0	6.8	2.1	152	85	84	1.5	54	118.0	15.5	21.6	10.0	19.8	381
90–92	7.29	2.27	45.6	3.9	1.9	146	58	85	1.3	51	87.7	11.8	18.6	11.1	19.2	301
92–96	7.51	1.30	32.1	2.3	2.3	167	41	86	1.2	53	81.4	8.7	30.2	20.7	17.4	236
96–98	7.74	2.44	49.0	5.5	1.9	155	76	87	1.2	50	106.0	17.6	23.5	10.0	27.4	366
98–100	7.98	2.33	55.2	5.7	1.9	154	80	88	1.4	54	104.9	21.2	27.6	9.1	42.0	408
100–102	7.24	2.31	53.8	6.5	1.8	152	71	1190	1.2	50	104.0	13.0	29.0	9.4	31.9	329
102–104	8.07	2.02	41.1	3.6	1.2	153	45	1000	1.2	52	85.7	10.1	15.1	8.9	39.4	248
104–106	8.19	2.40	48.5	4.3	1.6	145	54	960	1.4	51	99.5	15.0	20.6	8.4	37.9	286
106–108	7.38	1.84	44.4	2.5	1.4	138	44	490	1.3	51	80.5	10.3	17.1	11.4	8.4	222
108–110	8.09	1.46	35.9	1.3	1.1	143	37	265	1.3	54	73.6	10.2	14.0	8.4	7.2	193
110–112	7.94	1.59	37.0	2.0	1.1	149	36	385	1.3	52	76.6	8.8	13.2	9.0	6.6	205
112–114	7.63	1.70	40.8	2.0	1.4	145	41	330	1.2	50	74.7	8.9	14.7	9.7	8.6	207
114–116	7.45	1.81	40.1	2.2	1.3	138	40	360	1.2	48	71.3	8.2	13.9	9.7	9.4	199
d.l.	0.02	0.01	1.5	0.1	0.2	4	5	1	0.5	5	0.7	0.2	0.5	0.1	0.3	11

In upstream sub-basins of the Loire system, the 1940s–1950s contamination phase for Bi and Cd can be characterized by two significant relationships ($r = 0.9$, $p < 0.05$, $n = 6$ in the core #2 and $r = 0.9$, $p < 0.05$, $n = 17$ in the core #3; Fig. 5). The polymetallic contamination phase, recorded in the core #4 between the 1950s and the 1980s, shows Bi/Cd ratios ranging between those archived during the 1940s–1950s period of the upstream part of the Loire basin (Fig. 5). A significant geochemical signature can be characterized in this sequence ($r = 0.7$, $p < 0.05$, $n = 14$; Fig. 5).

Among all the river bank sediments collected in the present study, some are highly concentrated in both Bi and Cd such as in Furan, Anzieux, Bedat and Vienne sub-basins (Table 2). Their Bi/Cd ratios, ranging from 1 to 4, are close to those recorded in sedimentary core (Fig. 5) and they can represent the geochemical influence of past heavy industrial activities. In mining and industrial complexes of the Upper Loire basin, coal from the Furan tributary was locally used in industry. Coal particles can contain high Cd and Bi concentrations, but during combustion, these TE are largely enriched in fly ashes, contributing to atmospheric and soil pollutions (average Bi/Cd ratio close to 1 in fly ashes; Querol et al., 1995; Querol et al., 2007; Li et al., 2013). Therefore, in the studied case, important fallout of ashes associated to massive coal combustion may constitute a potential contamination source

affecting the entire Loire basin and specifically the most industrialized areas. In addition, extracted coal was also largely used for heavy industries (steel, ceramic and glass factories) in the Furan, Anzieux, Bedat and Vienne sub-basins. Blast furnace sludge are known to contain high TE concentrations, notably for Bi and Cd with an average Bi/Cd ratio close to 3 (Földi et al., 2014). Effluents of heavy industries located in these studied sub-basins should constitute important contamination sources in the Loire basin.

In our research, Hg contamination affected the most part of studied sub-basins in the Loire domain. River bank sediments sampled in the Furan, Anzieux and Vienne rivers present the most important Hg concentrations (> 1 mg/kg in the <63 µm fraction; Table 2).

At basin scale, diffuse local and global Hg emission sources all contribute to Hg sediment contamination (Meybeck et al., 2007; Thévenot et al., 2007; Lestel et al., 2007; Le Cloarec et al., 2011). Indeed, Hg is a highly volatile TE and Hg global fallout has increased by a factor 2 to 10 compared to the preindustrial period because of massive extractions and generalized use in industries from the second part of the 19th century to the 1960s (Lumb, 1995; Hylander and Meili, 2003; Bank, 2012). Moreover, coals can be rich in Hg and the volatilization of Hg during combustion has constituted another major Hg source at global scale from the 19th century (Querol et al., 1995; Mukherjee et al., 2008).

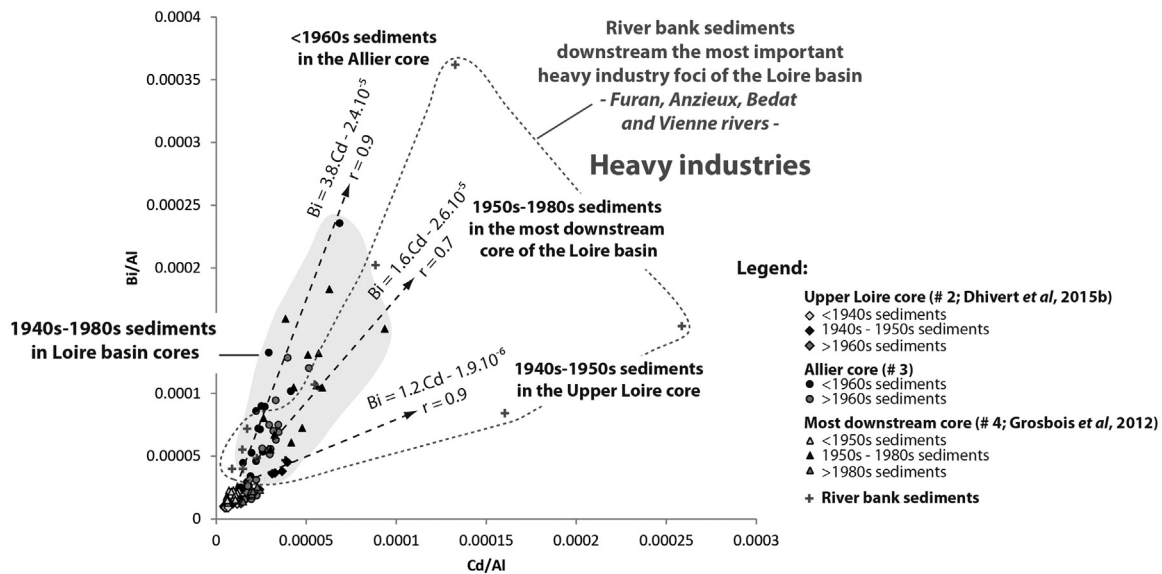


Fig. 5. Cd–Bi relationship, normalized to Al contents, in the $<63 \mu\text{m}$ fraction of the studied cores of the Loire basin (cores # 2, # 3 and # 4) and selected river bank sediments.

Heavy industry effluents also constitute important Hg contamination sources (Castelle et al., 2007; Jasminka and Robert, 2011; Földi et al., 2014). Hg contamination shown in our study can be both related to the global fallout and to local heavy and coal industries. Actually potential Hg sources are present in the studied sub-basins of the Loire domain like weapon industries (in the Furan sub-basin), hat-making (in the Anzieux sub-basin), leather treatments and porcelain decorations (in the Vienne sub-basin; Neal, 1938; Lumb, 1995; Hylander and Meili, 2003; Wang et al., 2004). However, it is difficult to well distinguish local sources from the global signature in sediments without any more discriminant analytical methods like isotopic analyses (Feng et al., 2010).

4.3. Influence of the sedimentary dynamic on the spatial and temporal distribution of metals in sediments of the Loire basin

This study highlights important differences in TE temporal dynamics archived in sediment cores between upstream sub-basins and the most downstream part of the Loire basin. Maximum activity period for mining and industrial complexes occurred between the end of the World War II and the late 1950s in French continental industrial foci (see Section 2.2). This time interval corresponds to the most polluted period recorded in cores #2 and #3. These two upstream sub-basins plus the Vienne sub-basin present anthropogenic activities impacting largely sediment TE quality during specific temporal contamination phases *i.e.* (i) Sb sources related to mining effluents affecting only the Upper Loire and the Allier sub-basins and (ii) polymetallic sources related to heavy industry effluents affecting the entire Loire basin but with a decade delay in the downstream part.

The local influence of Sb sources can be explained by the spatially limited dispersion of contaminated sediments because of the low transport of heavy TE-carrier phases (influences from 10 to 10^2 km, *e.g.*, Maclin et al., 2006; Courtin-Nomade et al., 2005; Grosbois et al., 2007; Wang et al., 2011; Lecce and Pavlowsky, 2014; Resongles et al., 2014). Moreover, the Sb dispersion in the dissolved fraction is limited because of its behavior to be sorbed to Fe, Al, Mn hydroxides, clays and organic matter (Filella et al., 2002; Wang et al., 2011). Nevertheless, during major hydrosedimentary events, Sb-bearing phases can be transported and altered several km downstream of mining sites (Craw et al., 2004). The present study shows multiple polymetallic contamination phases affecting the upstream as the downstream part of the basin, geochemical signatures recorded in cores are similar and could be related to

common sources *i.e.* heavy industry effluents (Fig. 5). The delay for archiving such a polymetallic contamination phase can be explained by the dispersion time of impacted sediments. Indeed, at basin scale, sediments – and thus associated substances – are transported from eroded bedrocks to estuaries like a sedimentary cascade, by alternate episodes of deposition and erosion (Burt and Allison, 2010). Therefore, the spatial and temporal distribution of sedimentary contaminations do not only depend on the geography and the history of anthropogenic releases but also on geomorphological processes controlling storage/transport conditions and therefore the fate of sediments and associated contaminants (Miller, 1997; Walling et al., 2003; Macklin et al., 2006).

Since the 19th century, embankments and other hydraulic structures controlling water discharge have largely disturbed the continuity of the sedimentary transport by amplifying sediment storage in banks and dam reservoirs (*e.g.* Vörösmarty et al., 2003; Arnaud-Fassetta, 2003). In the Loire basin, the river bed has also been largely managed by longitudinal and lateral hydraulic structures (Dion, 1961; Lino et al., 2000). According to the Loire Water Agency, more than 5 Mm^3 of alluvial sediments were extracted at an annual rate up to the 1990s, 20 times higher than the sedimentary transport. As a result, the river geomorphology has changed and the sediment storage capacity of the Loire basin has been enhanced in banks (Babonaux, 1970; Leteinturier et al., 2000; Rodrigues et al., 2007; Détriché et al., 2010; Grivel and Gauthier, 2012; Dhivert et al., 2015b). In this context, dispersion of contaminated sediments should largely be slowdown.

In addition, incision of the Loire river bed has increased since the 19th century (Gasowski, 1994; Latapie et al., 2014). Currently, this river bed erosion process fosters the reworking of old sediments (Macaire et al., 2013). The Villerest dam reservoir has trapped highly polluted sediments since the early 1980s (Fig. 4). In this reservoir, while a general decrease of TE enrichments is recorded in sediments deposited during linear aggradation rate periods, three flood sequences corresponding to major hydrosedimentary events present the highest TE enrichments (Dhivert et al., 2015a). In the current context of controlled TE releases, this attests the activation of old sources during these hydrosedimentary events. Such a reactivation process was also observed in other basins where erosion of contaminated soils, bank and bed sediments has become one of the major contamination sources in the hydrosystem (Macklin and Klimek, 1992; Lecce and Pavlowsky, 1997; Förstner, 2004; Lecce and Pavlowsky, 2014).

Table 2 (continued)

Sampled river bank	Depth	Al	COT	As	Bi	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	U	W	Zn	
	cm	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Vicoïn	30–35	8.49	4.33	42.2	2.8	2.3	130	85	0.710	1.3	47	87.2	0.7	20.0	12.0	9.1	262	
	60–65	8.85	4.11	51.9	4.3	2.0	137	103	0.880	1.4	45	98.7	0.7	17.0	12.0	8.9	277	
	90–95	8.73	3.79	75.8	3.5	1.3	123	72	1.840	1.2	42	107.4	0.8	25.0	12.6	12.7	296	
	95–125	9.04	2.95	72.0	1.9	0.8	103	56	3.990	0.9	29	109.1	0.8	23.0	10.9	8.4	228	
	125–130	9.16	2.71	68.8	1.4	0.7	96	53	4.780	0.7	27	100.3	0.7	22.0	10.2	6.6	188	
	160–165	9.09	3.2	67.7	1.7	0.7	103	63	4.380	0.9	31	105.9	0.7	23.0	11.4	6.3	212	
	0–20	7.90	1.96	110.0	1.1	1.0	94	36	0.305	2.0	34	48.8	627.4	7.6	3.7	2.5	190	
	20–40	7.78	1.75	136.5	1.9	1.0	99	38	0.325	2.0	36	49.5	656.4	8.0	3.8	2.7	194	
	40–60	7.66	1.54	141.4	1.6	0.7	93	32	0.315	2.0	38	42.4	615.3	7.0	3.8	2.5	172	
	60–80	7.46	1.12	122.9	0.7	1.0	91	31	0.290	2.0	32	41.0	648.6	7.2	3.7	2.7	157	
	80–10	7.56	0.66	70.7	0.4	0.7	90	23	0.195	2.0	31	31.1	373.3	5.0	3.7	2.5	125	
	100–120	7.45	0.42	41.4	0.3	0.6	90	21	0.105	1.5	28	26.4	151.8	4.3	3.7	2.4	105	
	<i>d.l.</i>		0.02	0.01	1.5	0.1	0.2	4	5	0.001	0.5	5	0.7	0.2	0.5	0.1	0.3	11

5. Conclusions

Four sedimentary archives sampled in the upstream and the downstream part of the basin show spatio-temporal variability of TE archived in sediments of the Loire basin. Such a multisite study allows to highlight important upstream-downstream differences between registered contamination phases and sources *i.e.* (i) local Sb-contamination phases affecting the Upper Loire and the Allier sub-basin between the 1900s and the 1950s and (ii) polymetallic contamination phases recorded between the 1940s and 1950s in upstream sub-basin and with a decade delay in the downstream part of the Loire basin (between the 1950s and the 1980s).

In order to explain distribution of metals in sediments of the Loire basin, historical contamination sources were characterized by comparing geochemical signatures archives in river bank sediments, recovered downstream major industrial and mining areas to those recorded in sedimentary cores. Such an approach highlights the respective influence of (i) coal and TE mining activities in upstream sub-basins related to Sb contamination phases and (ii) heavy industries affecting the entire basin and related to polymetallic contaminations phases.

In addition, this basin-scale approach shows the influence of hydrosedimentary dynamic on spatial and temporal distribution of metals in sediments. At basin scale the dispersion of contaminated sediments is controlled by the sedimentary cascade influencing spatially and temporally archiving processes of contamination phases. It also depends on the nature of TE-carrier phases and the residence time of sediments. Nowadays in the Upper Loire sub-basin, the hydrosedimentary dynamic is a factor of old sources reactivation during major flood events.

This paper reveals the importance to consider a multi-site approach to build temporal evolution of pollutants and sources at an entire basin scale. In this context, the characterization of preindustrial references in tributaries constitutes an important scientific issue, especially for basins with heterogeneous geology like the Loire basin. Moreover, the key role of the hydrosedimentary dynamic is important to point out the spatial and temporal distribution of metals in sediments.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.09.146>.

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