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1 Persisting impact of historical mining activity to metal (Pb, Zn, Cd,
2 Tl, Hg) and metalloid (As, Sb) enrichment in sediments of the Gardon
3 River, Southern France

4

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14

1 **Abstract**

2 In this study, we assessed past and present influence of ancient mining activity on metal(loid)
3 enrichment in sediments of a former mining watershed (Gardon River, SE France), that is
4 now industrialized and urbanized. A sedimentary archive and current sediments were
5 characterized combining geochemical analyses, zinc isotopic analyses and sequential
6 extractions. The archive was used to establish local geochemical background and recorded (i)
7 increasing enrichment factors (EF) for Pb, Zn, Cd, Tl, Hg, As and Sb throughout the industrial
8 era, (ii) a contamination peak in 1976 attributed to a tailings dam failure, and (iii) current
9 levels in 2002 and 2011 similar to those of 1969, except for Sb and Hg, reflecting a persisting
10 contamination pattern. Inter-element relationships and spatial distribution of EF values of
11 current sediments throughout the watershed suggested that both ancient and current
12 contamination had a common origin for Pb, Zn, Cd, Tl and As related to the exploitation of
13 Pb/Zn mineralization while old Sb mines and coal extraction area were the main sources for
14 Sb and Hg respectively. This prevailing mining origin was reflected for Zn by a relatively
15 uniform isotopic composition at $\delta^{66}\text{Zn} = 0.23 \pm 0.03\text{‰}$, although slight decrease from 0.23‰
16 to 0.18‰ was recorded from upstream to downstream sites along the river course in relation
17 with the contribution of the lighter $\delta^{66}\text{Zn}$ signature ($\sim 0.08\text{‰}$) of acid mine drainage impacted
18 tributaries. Results from sequential extractions revealed that the potential mobility of the
19 studied metal(loid)s varied in the order $\text{Sb} < \text{Tl} \approx \text{As} < \text{Zn} < \text{Pb} < \text{Cd}$, with an increase of the mobile
20 pool for Cd, Pb, Zn and to a lesser extent for As and Tl associated to increased enrichment.
21 Altogether, these results tend to demonstrate that ancient mining activity still contributes to
22 metal enrichment in the sediments of the Gardon River and that some of these metals may be
23 mobilized toward the water compartment.

24 **Keywords**

25 Mining-affected river; Metal and metalloid; Sedimentary archive; Zinc isotopes; Sequential
26 extraction

1 Introduction

2 Mining activity is one of the most important sources of harmful metals (Pb, Zn, Cd, Tl, Hg)
3 and metalloids (As, Sb) to rivers (Byrne et al., 2012; Hudson-Edwards, 2003; Johnson and
4 Hallberg, 2005; Nriagu and Pacyna, 1988; Schwarzenbach et al., 2010). Damage to surface
5 water ecosystems has been recognized in many areas in the United States (Caruso et al., 2008;
6 Cherry et al., 2001; Peplow and Edmonds, 2005), the United Kingdom (Gray, 1997; Jarvis
7 and Younger, 1997), France (Audry et al., 2004a; Monna et al., 2011), Spain (Bonilla-
8 Valverde et al., 2004), with dramatic accidents such as those of Aznalcollar in Spain (Grimalt
9 et al., 1999) or Maramureş County in Romania (Macklin et al., 2003). A peculiarity of mining
10 related pollution is that tailings, waste piles, ochre sediments and contaminated floodplains
11 continue acting as secondary sources for pollutants to downstream watershed throughout
12 hundreds of years after the mine closure (Byrne et al., 2012; Johnson and Hallberg, 2005;
13 MacKenzie and Pulford, 2002; Macklin et al., 1997; Younger and Wolkersdorfer, 2004).
14 Furthermore, the extent of contamination is not strictly limited to the vicinity of mines;
15 contaminated material (i.e. tailings, contaminated river bed and floodplain sediments) may be
16 physically remobilized in high flow conditions (Hudson-Edwards, 2003; Hudson-Edwards et
17 al., 1997; Miller, 1997; Moore and Langner, 2012), thus dispersing pollutants over hundreds
18 of kilometers away from historical mining sites (Grosbois et al., 2012; Moore and Luoma,
19 1990; Salomons, 1995).

20 In Europe, the Water Framework Directive (2000/60/EC) aimed to achieve good ecological
21 status of water bodies by 2015 and has reinforced the need for management of streams and
22 rivers at the catchment scale (Kimball and Runkel, 2009; Mayes et al., 2009; Mighanetara et
23 al., 2009). While metal discharges from industrial activities have decreased as a result of more
24 stringent controls, pollution from historical mining persists and its relative contribution to
25 anthropogenic emissions of metals and metalloids to downstream watersheds has become
26 more important over recent years (Macklin et al., 2006). In the perspective of optimizing
27 remediation strategies at the river basin scale, achieving maximum improvements of
28 downstream water quality, it is essential to develop approaches allowing evaluation of the
29 impact of abandoned mining sites on metal enrichment to downstream river systems and to
30 distinguish metals from such sources from natural geochemical background and other
31 anthropogenic (industrial, urban) point sources. In environmental studies, metal isotope
32 geochemistry may be useful to complement traditional geochemical data to track metal
33 sources and elucidate processes affecting their transport and fate in rivers (Cloquet et al.,

1 2008; Weiss et al., 2008). Zn has five stable isotopes, ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn , and ^{70}Zn , with
2 average natural abundances of 48.63%, 27.90%, 4.10%, 18.75% and 0.62% respectively
3 (Rosman and Taylor, 1998). Previous studies have reported Zn isotope variations (expressed
4 as $\delta^{66}\text{Zn}$ unit) of 2.5‰ in terrestrial samples (Cloquet et al., 2006). In mining environments
5 related studies, Zn isotopic composition of the main Zn-ore (sphalerite, ZnS) was shown to
6 cover a large range of $\delta^{66}\text{Zn}$ from -0.17‰ to 0.64‰ with an average of $+0.16\pm 0.20\text{‰}$ (Sonke
7 et al., 2008). Borrok et al., (2008) reported $\delta^{66}\text{Zn}$ values between 0.02‰ and 0.46‰ for
8 dissolved Zn in streams draining historic mining districts in the United States and Europe.
9 Several physical and biogeochemical reactions including evaporation, inorganic and organic
10 adsorption, diffusion and biological uptake can induce Zn isotope fractionation (Cloquet et al.,
11 2008). Largest Zn isotopic variations are observed associated with smelting industry;
12 atmospheric emissions are enriched in the lighter Zn isotopes while slag are enriched in the
13 heavier Zn isotopes (Mattielli et al., 2009; Sivry et al., 2008; Sonke et al., 2008). The potential
14 of Zn isotopes to track pollution sources has already been demonstrated in urban, mining and
15 smelting impacted environments (Borrok et al., 2009; Chen et al., 2008, 2009; Dolgoplova et
16 al., 2006; Mattielli et al., 2009; Sivry et al., 2008; Sonke et al., 2008; Thapalia et al., 2010).

17 In the present study, we investigated the impact of abandoned mines localized in the
18 Cevennes Mountains to metal (Pb, Zn, Cd, Tl, Hg) and metalloid (As, Sb) enrichment in the
19 sediments of the Gardon River watershed, which is a tributary of the Rhône River. The River
20 Gardon catchment is around 2,000 km^2 with 180,000 people. Multiple mining sites are
21 referenced on this catchment (BRGM, SIG Mines website; Vincent, 2006), including
22 scattered metal mines (Pb, Zn, Ag, Sb) and a coal production district (La Grand-Combe).
23 Besides, one mid-size town (Ales, 40,000 inhabitants) and a chemical and industrial center
24 (Salindres) constitute other possible point sources of metals and metalloids to the watershed.
25 The impact of ancient mining activity on global contamination of the watershed by metals and
26 metalloids has never been evaluated (SMAGE des Gardons, 2011), although severe local
27 pollution was evidenced in the vicinity of some of these mining sites (Casiot et al., 2009).

28 In this study, we propose a methodological framework allowing catchment-scale assessment
29 of in-stream mining-related pollution. For this, a sedimentary archive was used to establish
30 the natural geochemical background levels of metals and metalloids of the watershed and
31 reconstruct a historical record of metal and metalloid enrichment. Enrichment factors were
32 determined for current sediments of the Gardon River and for those of its main tributaries.
33 Inter-element correlations and zinc isotope ratios were used to track the contribution of
34 disused mining sites to sediment contamination. Geochemical associations of Pb, Zn, Cd, Tl,

1 As and Sb, evaluated using the BCR sequential extraction procedure, allowed assessment of
2 the potential mobility of these contaminants in the sediments.

3 **2 Material and methods**

4 **2.1 Study area**

5 The Gardon River watershed is located at the southeast of the Massif Central Mountains in
6 France. This tributary of the Rhône River is 144 km long and drains an area of 2,014 km². The
7 watershed includes three main geological areas (1) Primary metamorphic (schists and
8 micaschists) and igneous (granite) rocks in the upstream part of the watershed (Cevennes
9 Mountains region), (2) Jurassic carbonate formations (limestone and dolomite) along the
10 Cevennes Mountains boundary, (3) Cretaceous limestone formation (Gardon River gorges)
11 and Quaternary alluvium deposits of the Rhône River in the downstream watershed (Figure
12 1a, BRGM, Info Terre website). In the area of Ales-La Grand-Combe, a graben filled with
13 Tertiary detrital sediments represents the most important coalfield of the Cevennes
14 Mountains. Hydrologically, the Gardon River is characterized by high seasonal variability
15 including severe low water during summer and extreme floods with peak reaching 100 times
16 the average discharge mainly in autumn.

17 The upstream watershed drains many disused mining sites (Figure 1b, Table 1). Mining
18 activity began on the Gardon River watershed during Roman Times for Ag and Middle Ages
19 for Ag, Pb and coal (Rolley website; Vincent, 2006). The large-scale production started from
20 the middle of the 19th century and declined after 1960. During this period, we estimated that
21 about 4Mt of pyrite, 85,000t of Zn, 50,000t of Pb and 2,570t of Sb were produced on the
22 Gardon River watershed leaving several millions of tons of wastes close to ore extraction and
23 processing sites (BRGM, SIG Mines website). Exploited ores were in the form of sulfide
24 minerals (galena and argentiferous galena for Pb and Ag, sphalerite for Zn and stibnite for
25 Sb). These minerals were associated to other unexploited sulfide minerals such as pyrite and
26 marcasite (FeS₂), tetradrite (Cu₁₂Sb₄S₁₃), pyrargyrite (Ag₃SbS₃) and proustite (Ag₃AsS₃)
27 described for the Carnoulès mine drained by the Amous River (AF9) (Alkaaby, 1986). On the
28 Gardon of Anduze River subwatershed, the most important Pb/Zn mining districts were those
29 of Carnoulès and Pallières, drained respectively by the Amous River (AF9) and the Ourne and
30 Aiguesmortes Rivers (AF8 and AF10). Antimony mines are localized on the upstream
31 subwatershed of the Gardon of Ales River and they are drained by the Ravin des Bernes and

1 the Richaldon Rivers (AF1 and AF2). Downstream, in the area of Ales-La Grand-Combe,
2 coal has been exploited intensively. Finally, the Grabieux River (AF4), the Alzon River (AF5)
3 and the Avène River (AF6), on the Gardon of Ales River subwatershed, drain old
4 Pb/Zn/pyrite mining sites. Most of these tributaries are impacted by metal and metalloid
5 contamination downstream from these mining sites (SMAGE des Gardons, 2011). Pollution
6 from the abandoned Pb/Zn mine of Carnoulès was already mentioned in 1970 (Michard and
7 Faucherre, 1970) and to date, the Amous River remains highly impacted (Casiot et al., 2009).
8 In addition to the extractive activity, three smelters have been in activity on the watershed; a
9 Zn smelter at La Grand-Combe town with a period of activity from 1846 to 1899 (Ministère
10 de la Culture) and two small Sb smelters located on the upstream Gardon of Ales River near
11 Sb mining sites which had worked from 1822 to 1858 and from 1896 to 1951 (BRGM,
12 BASIAS website).
13 Nowadays, the chemical industrial center of Salindres and the urban area of Ales (40,000
14 inhabitants) can also contribute to metals and metalloids enrichment of the Gardon River. The
15 Avene River (AF 6) is both impacted by industrial and mining discharges. According to the
16 French Water Agency, 27kg d⁻¹ of metals and metalloids were released in 2007 in the Gardon
17 River by industrial activities and urban wastewater treatment plants (SMAGE des Gardons,
18 2011).

19 **2.2 Sampling**

20 **2.2.1 Sedimentary archive**

21 The sedimentary archive (GE) was sampled in March 2010 in the downstream part of the
22 watershed (Figure 1b), in a zone of canyon. This flooding terrace, situated between 6.20 and
23 9.50 m above the riverbed level, was formed by the accumulation of extreme flood deposits
24 (Dezileau et al., 2013; Dezileau et al., in review). These flood events have resulted in one
25 sedimentary layer each. The terrace was composed of 20 layers corresponding to 20 extreme
26 flood events; these layers were identified in the field through a close inspection of deposition
27 breaks and/or indicators of surficial exposure (e.g. presence of a paleosol, clay layers at the
28 top of a unit, detection of erosional surfaces, bioturbation features, angular clast layers
29 deposits in local alcove or slope materials accumulation between flood events, fireplaces and
30 anthropogenic occupation layers between flood events). Sedimentary layers were numbered
31 from the bottom to the top of the terrace and named GE1 to GE20. Samples were excavated
32 directly from the terrace using a Teflon spatula and collected in PP-jars. Sieving was not

1 necessary because all particles were finer than 2mm. Then, samples were air-dried, crushed in
2 an agate mortar and homogenized before further processing. Dating of sedimentary layers was
3 based on an original method using a multi-dating approach described in Dezileau et al. (in
4 review). Radionuclide analyses (^{210}Pb , ^{137}Cs) and geochemical analyses (total Pb) were used
5 to determine age controls. Maximum ^{137}Cs activity in layers GE17 and GE18 was associated
6 to the maximum atmospheric emission in the mid-1960s. ^{210}Pb activity results indicated that
7 layers GE15 to GE20 were deposited after the end-1930s. Pb concentration was constant in
8 layers GE1 to GE9 and increased from the layer GE10 showing that layers GE1 to GE9 dated
9 back the beginning of large-scale mining activity on the watershed around 1870. These age
10 controls were combined with the continuous record of Gardon River flow since 1890, the
11 combined records allow to assign ages to the most recent layers, from GE9 to GE20 (Dezileau
12 et al., 2013; Dezileau et al., in review).

13 **2.2.2 Current stream sediments**

14 Active stream sediments in contact with stream water were studied; this sampling medium
15 integrates both natural geochemical characteristics and recent anthropogenic contamination of
16 the whole watershed upstream from the sampling station over time (Ettler et al., 2006; Gosar
17 and Miler, 2011). Six surveys were carried out from 2010 to 2012 in low flow and high flow
18 conditions; stream sediments were sampled on the upper part of the watershed, along the
19 Gardon River and on the tributaries of interest i.e. main tributaries and tributaries impacted by
20 mining, industrial or urban activities. The location of the sampling stations is shown in Figure
21 1b. Stream sediments were collected in PP-jars using a Teflon spatula, in the first centimeter
22 of the riverbed surface, as far as possible from the riverbank. Back in the laboratory, the
23 sediment samples were sieved <2 mm, freeze-dried and powdered in an agate mortar.

24 **2.3 Sample preparation**

25 **2.3.1 Bulk mineralization**

26 Total digestion of sediment samples was carried out in a clean room. All material was acid-
27 cleaned before use; reagents were Merck Suprapur quality. For each set of samples, method
28 blanks and international certified reference materials digestion (Stream sediments LGC6189
29 from United Kingdom Accreditation Service and NCS DC70317 from LGC Standards) were
30 performed. About 100 mg of sediment samples were digested in closed Teflon reactors on
31 hot-plates at 95 °C for 24 h successively with (1) H_2O_2 35% (2) a 4:3:0.13 mL concentrated

1 HNO₃-HF-HClO₄ mixture and (3) a 1:3 mL concentrated HNO₃-HCl mixture (aqua regia).
2 Samples were cooled and evaporated to dryness between each step and at the end of the
3 procedure. Samples were brought to 30mL using 3mL HNO₃ and double deionized water
4 (Milli-Q®). Finally samples were filtered to remove possible residues.

5 **2.3.2 Chemical purification for zinc isotopic analyses**

6 Zn isotopic analyses were carried out on the sedimentary archive samples and on the current
7 sediments samples of the November 2011 sampling campaign. Digested solution aliquots
8 containing approximately 1000ng of Zn were used for Zn separation and isotopic
9 measurement. Zn was separated from the matrix elements by ion chromatography using AG1-
10 MP1 anion-exchange resin (Biorad) and the elution sequence from Maréchal et al. (1999).
11 The protocol was repeated twice to ensure Zn purity. The total procedural blank of ≈15ng was
12 negligible compared to the amount of Zn in samples (1000ng). Column yields were checked
13 for each sample by ICP-MS, X Series II (Thermo Fisher Scientific) and found to be >96%.
14 After the purification, samples were evaporated to dryness at 60°C. Then samples were taken
15 up in 3.3mL of HNO₃ 0.05N and doped with a Cu standard (Cu NIST-SRM 976); final Zn
16 and Cu concentrations were 300ng.g⁻¹.

17 **2.3.3 Selective sequential extraction procedure**

18 Total metal and metalloid concentrations are insufficient to evaluate the potential mobility of
19 these contaminants in stream sediments. Therefore, selective sequential extractions were
20 performed to characterize the distribution of Pb, Zn, Cd, Tl, As and Sb in sediment samples.
21 Selected samples from the sedimentary archive and current sediments were subjected to a
22 four-step sequential extraction procedure using the standardized method of the European
23 Community Bureau of Reference (BCR) described by Rauret et al. (1999). Metals and
24 metalloids were extracted into the following four operationally defined fractions:
25 exchangeable and carbonate fraction (F1), reducible fraction (bound to Fe and Mn
26 oxides/hydroxydes) (F2), oxidisable fraction (bound to organic matter and sulfides) (F3) and
27 residual fraction (F4). The fraction F4 was determined using a procedure of mineralization
28 assisted by microwaves; 100mg of the residual solid was digested by a 2:4 mL concentrated
29 HF:HNO₃ mixture. Then samples were cooled, evaporated to dryness and brought to 30mL
30 using 3mL HNO₃ and double deionized water (Milli-Q®).

1 2.4 Analyses

2 Metal (Pb, Zn, Cd, Tl), metalloid (As, Sb) and Al concentrations in sediments (total and
3 selective extractions) were determined after an adequate dilution using an ICP-MS, X Series
4 II (Thermo Fisher Scientific) equipped with a CCT (Collision Cell Technology) chamber. The
5 quality of analytical methods was checked by analyzing international certified reference
6 waters (SLRS-5, NIST1643e) and was generally better than 5% relative to the certified
7 values. Analytical error (relative standard deviation) was better than 5% for concentrations ten
8 times higher than the detection limits. Accuracy was within 10% of the certified values for
9 method standards (Stream sediments LGC6189 from United Kingdom Accreditation Service
10 and NCS DC70317 from LGC Standards, n=7) with recoveries of 95±7% for As, 100±4% for
11 Cd, 95±7% for Pb, 101±4% for Sb, 95±4% for Tl and 100±10% for Zn except for Al for
12 which recovery was 86±6%.

13 For total Hg determination, about 0.1g of crushed air-dried sediments was analyzed using a
14 Direct Mercury Analyzer (DMA-80 Milestone) following the 7473 EPA standard method. To
15 ensure analytical results precision, a certified reference material (Stream Sediment NCS
16 DC70317 from LGC Standards) was analyzed every ten samples, accuracy was better than
17 10% for certified Hg concentration (34.4±3.3 ng.g⁻¹, n=12). The procedural blank represents
18 at most 2.7% of Hg measured in samples.

19 Zn isotopic analyses were performed on a multiple-collector inductively coupled plasma mass
20 spectrometer (MC-ICP-MS) during several sessions at GET (Toulouse, France) on a Neptune
21 (Thermo-Scientific) and at ENS Lyon (Lyon, France) on a Nu Plasma 500 HR. Each sample
22 was analyzed three times and was bracketed with the Lyon reference solution JMC 3-0749-L.
23 Zn isotopes (⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn), Cu isotopes (⁶³Cu, ⁶⁵Cu) and Ni isotope (⁶²Ni) were
24 monitored simultaneously. Measurements of ⁶²Ni signal allowed correcting the possible
25 isobaric interference of ⁶⁴Ni on ⁶⁴Zn. Instrumental mass bias was corrected using Cu internal
26 standard NIST-SRM 976 and the exponential law coupled with the method of sample-
27 standard bracketing (Maréchal et al., 1999). Zn isotopic results are given as δ⁶⁶Zn notation (in
28 units of ‰), δ⁶⁶Zn is the deviation relative to a standard, the Lyon reference solution JMC 3-
29 0749-L :

$$30 \quad \delta^{66}\text{Zn} = \left(\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{reference}}} - 1 \right) \times 1000$$

31

1 Results are also given normalized to the standard IRMM-3702 calibrated by Moeller et al.
2 (2012) in supplementary information (SI Table 2 and 3).
3 The external analytical reproducibility (standard deviation) calculated from replicate
4 measurements of the certified stream sediments LGC6189 from United Kingdom
5 Accreditation Service (including column duplicate, n=6) over multiple analytical sessions was
6 0.02‰ and $\delta^{66}\text{Zn}$ was determined at 0.18‰.

7 **2.5 Data treatment**

8 Metal (Pb, Zn, Cd, Tl, Hg) and metalloid (As, Sb) concentration in the sediment was
9 normalized to Al concentration. Indeed, Al is a conservative element and a major constituent
10 of the fine fraction (clay and fine silt) of sediments, which includes the particles most
11 enriched in metals and metalloids (Owens et al., 2005). Al was used as a grain-size proxy and
12 thus the normalization allowed taking into account the dilution effect by silica or calcite and
13 compensating for the effect of grain size distribution (Bouchez et al., 2011). The Enrichment
14 Factor (EF) was then calculated to assess the level of contamination relatively to a reference
15 level:

$$16 \text{EF} = (\text{Me}/\text{Al})_{\text{sample}} / (\text{Me}/\text{Al})_{\text{reference}}$$

17 where $(\text{Me}/\text{Al})_{\text{sample}}$ is the concentration ratio of a metal to Al in the sediment sample and
18 $(\text{Me}/\text{Al})_{\text{reference}}$ is the same ratio in the reference. To detect possible anthropogenic
19 contamination, the reference should be representative of the local geochemical background
20 (Meybeck, 2013). In this study, the selected reference was the average Me/Al ratio in the
21 samples from the bottom of the sedimentary archive (layer GE1 to layer GE6) which
22 represented the pre-industrial metal and metalloid content (Dezileau et al., 2013; Dezileau et
23 al., in review). This approach allows to integrate the geological variability of the whole
24 upstream watershed and to avoid local anomalies.

25 Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) and enrichment factors (EF) are given for the sedimentary archive and
26 the whole dataset of current stream sediments in supplementary information (SI Table 4 and
27 5).

28 Data analysis R software was used for all statistical analyses. Correlation factors (R^2) were
29 calculated with Spearman method.

1 **3 Results**

2 **3.1 Enrichment factors for the sedimentary archive and current stream** 3 **sediments**

4 In order to distinguish metals and metalloids of anthropogenic origin from natural sources, it
5 is necessary to assess the local geochemical background, especially in a mining watershed
6 where the concentrations in soils and sediments can be naturally high. The bottom of the
7 sedimentary archive was considered as the geochemical background for the Gardon River
8 watershed and used for further EF determination. This local geochemical background value
9 was higher than the Upper Continental Crust average (Taylor and McLennan, 1995 for As,
10 Sb, Cd, Pb, Zn and Tl; Wedepohl, 1995 for Hg) used in some studies as the reference level, by
11 ~23-times for As, ~21-times for Sb, ~3-times for Cd, ~2.5-times for Pb, ~1.7-times for Zn and
12 Tl and lower by ~2.3 times for Hg (Table 2).

13 **3.1.1 Sedimentary archive**

14 Enrichment factors (EF) of Pb, Zn, Cd, Tl, Hg, As and Sb in sediments of the archive are
15 presented in Figure 2. For all these elements, EF values increased from the layer GE10 to
16 upper layers, showing metal enrichment throughout time. For As and Pb, EF reached a plateau
17 at 1.4 (As) and 1.8 (Pb) in the layers GE10 to GE17, and then increased substantially up to 1.9
18 (As) and 3.5 (Pb) in the layer GE18, assigned to 1969-dated flood event (Dezileau et al.,
19 2013; Dezileau et al., in review). For Hg, EF value continuously increased from GE10 to
20 GE17, the latter layer matching the 1963-dated flood event (Dezileau et al., 2013; Dezileau et
21 al., in review), and then increased drastically in the layer GE18. For other elements (Zn, Cd,
22 Tl and Sb), a general increase of EF value was observed from GE10 to GE18, reaching 2.1 for
23 Zn, 3.5 for Cd, 1.9 for Tl, and 2.5 for Sb, although important variations were recorded from
24 one layer to another and even within a single layer. For Sb, a peak was recorded in the layer
25 GE7 whose deposition date was anterior to the beginning of large-scale mining activity on the
26 catchment (Dezileau et al., 2013; Dezileau et al., in review).

27 The GE19 layer was particularly remarkable; a peak was recorded for all studied metals and
28 metalloids and most markedly for As, Pb and Hg with EF value reaching respectively 9.9,
29 10.5 and 18. This layer was ascribed to an exceptional flood event in 1976 that caused
30 important damage on tailings impoundment at the Pb/Zn Carnoulès mine (BRGM, BASOL

1 website). The most recent layer GE20, which corresponded to the latest exceptional flood
2 event in 2002 (Delrieu et al., 2005), presented drastically lower EF values compared to those
3 recorded in the 1976-dated layer; these values were similar to those recorded in 1969 for Pb,
4 Zn, Cd, Tl and As. The order of metal and metalloid enrichment in the sedimentary archive
5 was $Hg > Cd > Sb > Pb > As > Zn \geq Tl$ except for the layer GE19 for which As and Pb were more
6 enriched than Cd, Sb, Tl and Zn.

7 **3.1.2 Current stream sediments**

8 EF values for current stream sediment sample collected at station 25, close to the location of
9 the sedimentary archive are labeled in Figure 2, for comparison to historical record. For this
10 sample, EF values were similar or slightly lower (for Cd) than the 2002 flood event layer
11 values (Figures 2 and 3), thus reflecting comparable contamination level. In order to have an
12 overview of spatial distribution of the contamination, EF values of sediments sampled in
13 December 2012 (the most complete campaign) are mapped on the figure 4 using bar charts for
14 sediments of the main stream and a dot with EF value for sediments of the tributaries.
15 However, the whole dataset which is used for interpretation is presented in supplementary
16 information (SI Table 5). Similar EF values were obtained at the station 25 and at the next
17 upstream station 24, located downstream from the junction between the rivers Gardon of Ales
18 and Gardon of Anduze (Figure 4). Upstream from this junction, at the station 11 in the
19 Gardon of Ales River and station 23 in the Gardon of Anduze River, EF values were
20 drastically higher for Hg (EF=6.6) and Sb (EF=5.7) and to a lesser extent for Zn (EF=4.9) and
21 Cd (EF=4.6) in the Gardon of Ales River than in the Gardon of Anduze River (EF≈1.5, 1.5,
22 1.9 and 2.3 respectively). For other studied elements (Pb, As, Tl), EF values were similar at
23 both stations, with average values EF of 3.7 ± 0.7 for Pb, 2.3 ± 0.1 for As, 1.7 ± 0.3 for Tl. This
24 indicated a significantly higher enrichment of Sb, Hg, Zn and Cd on the Gardon of Ales
25 subwatershed compared to the Gardon of Anduze subwatershed while Pb, As, and Tl were
26 slightly enriched on both subwatersheds.

27 For Sb and Hg, EF values for the main stream of the Gardon of Ales River increased from
28 background level up to 7 (Sb) and 11.6 (Hg) from upstream to downstream stations below the
29 Sb mine-impacted tributaries (AF1 and AF2) and the coal extraction area of La Grand-Combe
30 respectively and then decreased downflow. This reflected a contribution of these sites to Sb
31 and Hg enrichment in the main stream sediments of the Gardon of Ales River. Conversely, EF
32 values for Sb and Hg in the main stream sediments of the Gardon of Anduze River was lower

1 than 2, which did not denote a significant contribution of the following Sb- and Hg-affected
2 tributaries AF8 (EF = 57 for Sb, EF = 174 for Hg), AF9 (EF = 16 for Sb, EF = 35 for Hg) and
3 AF10 (EF = 9.6 for Sb and EF = 24 for Hg). For other elements (Pb, Zn, As, Cd and Tl), a
4 two-fold increase of EF values was observed for As, Zn, Cd, Tl and three-fold increase for Pb
5 in the main stream sediments of the Gardon of Anduze downstream the tributaries AF8, AF9
6 and AF10 draining old Pb/Zn mines. Moreover, a two-fold increase was observed for As, Pb
7 and Tl, a three-fold increase for Zn and five-fold increase for Cd in main stream sediments of
8 the Gardon of Ales River downstream the town of Ales and the Grabieux River (AF4) which
9 drained both Pb/Zn mines and urban area. An additional increase was also evidenced at
10 downstream site (station 10) for Cd, reflecting the contribution of diffuse or unidentified point
11 source.

12 **3.2 Inter-element metal/aluminum ratio correlations**

13 Inter-element Me/Al correlations may be used to characterize different groups of chemical
14 elements with similar geochemical patterns. In the sedimentary archive, Me/Al values for Pb,
15 Zn, Cd, Tl and As were highly correlated with each other ($0.71 < R^2 < 0.87$) from GE1 to GE18
16 and in GE20 (Table 3); furthermore three groups of points representing (i) pre-industrial era
17 (GE1 to GE9) (ii) industrial era until 1963 (GE10 to GE17) and (iii) industrial era in 1969 and
18 2002 (GE18 and GE20), were distributed along a dilution line in relation with the
19 contamination level (Figure 3). This suggested a common origin for these elements over time.
20 The correlation was slightly lower between these elements and Sb ($0.60 < R^2 < 0.75$) or Hg
21 ($0.56 < R^2 < 0.77$). In the layer GE19 corresponding to the extreme 1976 flood event, the data did
22 not follow the same dilution line as the other layers (Figure 3); showing a different
23 geochemical signature.

24 In current main stream sediments, correlations were generally lower than in the sedimentary
25 archive (Table 4). On the Gardon of Anduze River, positive correlations were observed
26 between Pb, Zn, Cd, Tl, As and Hg ($0.23 < R^2 < 0.93$). On the Gardon of Ales River, Pb, Zn, Cd,
27 Tl and As were also correlated ($0.42 < R^2 < 0.90$), while Hg was correlated only with As, Tl and
28 Pb ($0.49 < R^2 < 0.69$). Among these elements, Zn and Cd were highly correlated on both the
29 Gardon of Anduze and the Gardon of Ales Rivers subwatersheds ($R^2 = 0.93$ and 0.91
30 respectively). No correlation was observed between Sb and the 6 other elements
31 ($0.00 < R^2 < 0.17$) on any of the subwatersheds indicating a different predominant source for Sb.

1 **3.3 Zinc isotopes**

2 Zinc isotopic composition was determined in the sedimentary archive (Figure 5a) and in
3 current sediments from the Gardon River including some of its tributaries (Figure 5b). In the
4 sedimentary archive, the range of variation of $\delta^{66}\text{Zn}$ was quite narrow, from 0.20 to 0.26‰
5 (Figure 5a). Extremely homogeneous values ($\delta^{66}\text{Zn}=0.26 \pm 0.02\text{‰}$) were obtained in the
6 bottom of the sedimentary archive, from GE1 to GE7, whereas significant variations occurred
7 in upper layers.

8 Current stream sediments from the main stream of the Gardon River exhibited $\delta^{66}\text{Zn}$ values
9 from 0.18 to 0.25‰, thus matching the range of the sedimentary archive (Figure 5b). The
10 values tended to decrease from upstream to downstream sites along the main stream of the
11 Gardon River. Zn-contaminated tributaries exhibited significantly lower ($\delta^{66}\text{Zn} = 0.07\text{‰}$ for
12 AF9 and 0.08‰ for AF10) or higher ($\delta^{66}\text{Zn} = 0.31\text{‰}$ for AF6) $\delta^{66}\text{Zn}$ values.

13 **3.4 Chemical partitioning of metals and metalloids**

14 The chemical partitioning of Cd, Zn, Pb, Tl, As and Sb in the sedimentary archive is
15 presented in Figure 6. The proportion of Cd, Zn, Pb, Tl and As contained in the most reactive
16 fractions (F1+F2+F3) increased from the bottom to the top of the archive, following the
17 increase of EF value. However, these metals and metalloids showed different distribution
18 pattern. Cd was largely associated with the most reactive fractions ($48\% < \text{F1} + \text{F2} + \text{F3} < 86\%$)
19 and exhibited the highest proportion in exchangeable/carbonates fraction (F1), from $18 \pm 3\%$
20 on average in the bottom layers (GE1 to GE9) up to 36.5% in the most contaminated layer
21 (GE19). For Zn, the sum of the most reactive fractions (F1+F2+F3) increased gradually from
22 $11 \pm 2\%$ on average in the bottom layers (GE1 to GE9) to $49 \pm 5\%$ on average in upper layers
23 (GE19 to GE20), the distribution among fraction F1, F2 and F3 remaining homogeneous. The
24 partitioning of Pb was dominated by Fe/Mn oxyhydroxides fraction ($26\% < \text{F2} < 59\%$) with low
25 exchangeable/carbonates and organic matter/sulfides fractions ($\text{F1} < 6\%$ and $\text{F3} < 17\%$). Tl, As
26 and Sb were mainly associated with the residual fraction ($\text{F4} \geq 65.5\%$). For Tl and As, the
27 Fe/Mn oxyhydroxides fraction (F2) represented up to 19% (Tl) and 25% (As).

28 Chemical partitioning of Cd, Zn, Pb, Tl, As and Sb in current stream sediments from the
29 Gardon River was similar to that of the sedimentary archive (Table 5). Cd and Zn exhibited
30 the highest proportion in exchangeable/carbonates fraction F1, ranging from 25% to 62% for
31 Cd and from 6% to 37% for Zn, with the most reactive fractions (F1+F2+F3) accounting

1 respectively for $71\pm 12\%$ and $40\pm 16\%$ (Table 5). For Pb, the reactive fractions represented
2 $44\pm 12\%$ and were dominated by the Fe/Mn oxyhydroxides fraction ($F_2=30\pm 8\%$). Tl and As
3 were largely bound to the residual fraction ($F_4>56\%$ and 75% respectively) with Fe/Mn
4 oxyhydroxides fraction accounting for the majority of the remaining content. Sb was
5 essentially contained in the residual fraction ($F_4>94\%$).

6 For Cd, Zn, Pb and to a lesser extent for Tl and As, the proportion of the most reactive
7 fractions ($F_1+F_2+F_3$) in main stream sediments tended to increase from upstream to
8 downstream sites along the watershed in relation with increased EF value. $F_1+F_2+F_3$
9 represented on average 62% for Cd, 27% for Zn, 40% for Pb, 6% for Tl and 12% for As in
10 sediments of the upstream Gardon River (station 1, 3, 13 and 15) and reached 84% for Cd,
11 54% for Zn, 45% for Pb, 21% for Tl and 22% for As in sediments of downstream watershed
12 at station 24 downstream from the junction between the Gardon of Anduze and the Gardon of
13 Ales Rivers.

14 **4 Discussion**

15 **4.1 Historical record of metal (Pb, Zn, Cd, Tl, Hg) and metalloid (As, Sb)** 16 **contamination**

17 The Gardon River watershed is a typical example of an ancient mining basin with multiple
18 sources of metal contamination. The assessment of anthropogenic metal levels in this
19 watershed and the deciphering of the origin of these contaminants is complex for several
20 reasons: (1) the geology of the watershed, which includes several metal-mineralized areas,
21 contributes to high metal levels in the transported sediments, thus confounding metals from
22 anthropogenic origin, (2) the temporal variability of the hydrological regime, typical of the
23 Mediterranean climate, with flash flood events responsible for most of the transport and
24 deposition of polluted sediments in the riverbed and floodplain away from their contamination
25 sources, making it difficult to acquire representative samples. Therefore, the use of a
26 sedimentary archive, which integrates both anthropogenic metal emissions and geochemical
27 background related to local geology of the whole upstream watershed, combined with current
28 stream sediment analysis, can make sense for a rigorous estimation of the contamination
29 status of the watershed. Sedimentary archives have recently been used to reconstruct
30 watershed contamination histories in several European river basins (Audry et al., 2004b;

1 Ayrault et al., 2012; Ferrand et al., 2012; Gocht et al., 2001; Grosbois et al., 2012; Grousset et
2 al., 1999; Le Cloarec et al., 2011; Monna et al., 2000; Müller et al., 2000; Winkels et al.,
3 1998); these archives are generally floodplain cores (Ayrault et al., 2012; Gocht et al., 2001;
4 Grosbois et al., 2012; Le Cloarec et al., 2011) or reservoir cores (Audry et al., 2004b; Müller
5 et al., 2000). On the Gardon River watershed, there is no reservoir downstream from mining
6 sites and it is very difficult to find intact continuous record in the floodplain mainly due to
7 possible remobilization of sediments during flash floods which affect the watershed (Dezileau
8 et al. in review; Delrieu et al. 2005). For these reasons, the sedimentary archive used was a
9 high-standing flooding terrace which recorded only extreme flood events with a minimum
10 discharge of 2100m³/s (Dezileau et al., 2013; Dezileau et al., in review); the recording is thus
11 discontinuous and provides a low temporal resolution. Nevertheless, the archive has recorded
12 (i) pre-industrial floods allowing to determine the geochemical background of the watershed
13 and (ii) 12 floods from the late 19th century to 2002 allowing to study the evolution of
14 contamination level throughout the industrial era. Pre-industrial levels of Pb, Zn, Cd, Tl, Hg,
15 As, and Sb in the archive allowed to characterize the local geochemical background of the
16 Gardon River watershed, which was highly enriched for As, Sb and to a lesser extent for Cd,
17 Pb, Zn and Tl relatively to the Upper Continental Crust, while being slightly depleted in Hg.
18 These results point out the importance to assess the local reference level in mine-impacted
19 watersheds for estimation of anthropogenic status as also highlighted elsewhere (Audry et al.,
20 2004b; Dolgoplova et al., 2006; Lapworth et al., 2012). This high geochemical background
21 for As, Sb, Cd, Pb, Zn and Tl in the Gardon watershed was related to the presence of several
22 mineralized areas containing pyrite, galena, sphalerite and stibnite (BRGM, SIG Mines
23 website; Alkaaby, 1986; European Commission 1988) on the Gardon of Ales and the Gardon of
24 Anduze subwatersheds.

25 Since the late 19th century, 12 floods have been recorded by the sedimentary archive (layer
26 GE9 to layer GE20), revealing a global enrichment of metals (Pb, Zn, Cd, Tl, Hg) and
27 metalloids (As, Sb) in sediments of the Gardon River over time, until 1969, together with a
28 contamination peak related to tailing dam failure in 1976 and a latest record in 2002 that
29 presented levels similar to those of 1969 except for enrichment in Hg and Sb which was lower
30 in 2002 than in 1969. This latest sedimentary record in 2002 might reflect remobilization of
31 ancient floodplain sediments, acting as secondary contamination source during exceptional
32 flooding events (Hudson-Edwards, 2003). However, the similarity of EF values in the 2002
33 sedimentary record and in current stream sediments (station 25), characterized by respectively

1 high (maximum discharge of 7200 m³/s in 2002 (Dezileau et al., 2013; Dezileau et al., in
2 review)) and moderate (1140 m³/s in 2011, Banque Hydro website) intensity floods rather
3 points out limited improvement of sediment quality over recent years. This historical pattern
4 contrasted with that of large French Rivers such as the Loire River (Grosbois et al., 2012), the
5 Seine River (Le Cloarec et al., 2011) or the Rhône River (Ferrand et al., 2012) where a
6 gradual decrease was observed for most contaminants in sediments after 1980. This general
7 decontamination has been explained by improvement of waste water treatment, de-
8 industrialization and industrial processes changes and generally by more stringent
9 environmental regulations (Ferrand et al., 2012; Grosbois et al., 2012; Le Cloarec et al., 2011;
10 Meybeck, 2013).

11 **4.2 Current sediment contamination**

12 According to the classification of pollution level based on the enrichment factor method
13 proposed by Sutherland (2000), current stream sediments were extremely polluted (EF>40),
14 very highly polluted (20<EF<40) or significantly polluted (5<EF<20) for all studied elements
15 (Pb, Zn, As, Cd, Tl, Sb and Hg) in sediments of mining/urban impacted tributary (AF4),
16 mining/industrial impacted tributary (AF6) and Pb/Zn mines impacted tributaries (AF8, AF9
17 and AF10). Tributaries which drain old Sb mines (AF1 and AF2) were extremely polluted
18 (AF1) and very highly polluted (AF2) with Sb.

19 In the sediments of the Gardon of Ales River, Hg and Sb were significantly (5<EF<20) to
20 moderately (2<EF<5) enriched. In both the Gardon of Anduze and the Gardon of Ales Rivers,
21 Pb, Zn, As and Cd were moderately enriched (2<EF<5) downstream from polluted tributaries
22 (AF4, AF6, AF8, AF9, AF10) while EF values for Tl reflected no or minimal pollution signal
23 in sediments. Variation of EF values along the Gardon of Ales and the Gardon of Anduze
24 Rivers downstream from the uppermost affected tributaries differed for the following two
25 groups of elements. For Pb, Zn, Cd, As and Tl, EF values remained almost constant,
26 suggesting a continuous input of these elements by several polluted tributaries along the main
27 stream (AF8, AF9 and AF10 on the Gardon of Anduze River and AF4, AF6 on the Gardon of
28 Ales River). For Sb and Hg, the decrease of EF values along the flowpath may reflect the
29 prevailing contribution of sources located on the upstream watershed and then the dilution by
30 less contaminated sediments, hydraulic sorting or storage in reservoir and floodplain (Byrne et
31 al., 2012; Hudson-Edwards, 2003).

4.3 Sources of metals and metalloids in the sedimentary archive and current stream sediments

Metal/aluminum ratios Pb, As, Zn, Cd and Tl in the sedimentary archive were found to be correlated, suggesting a common origin for these elements from the pre-industrial era until the present day. Such correlation could be ascribed to the association of these elements within the Pb/Zn mineralization that has been exploited in several mines on the Gardon of Ales and the Gardon of Anduze subwatersheds. This mineralization contained traces of cadmium in sphalerite (ZnS), arsenic in Fe-sulfides (pyrite, marcasite FeS₂), in sulfosalts (proustite Ag₃AsS₃) and in galena (PbS), antimony in sulfosalts (pyrargyrite Ag₃SbS₃) and in galena, mercury in Fe-sulfides and in sphalerite and thallium in Fe-sulfides (Alkaaby, 1986; Casiot et al., 2011; European Commission, 1988). In particular, the strong relationship between Zn and Cd both in the archive and in current stream sediments might reflect a homogeneous Cd content in Zn-ore in the area. The 1976 layer exhibited a different geochemical signature, with enrichment of As and Pb compared to previous layers; this was a local characteristic of flotation residues stored behind a dam at the abandoned Carnoulès site located 60 km upstream from the archive location (Leblanc et al., 1996); the impoundment contained As-rich pyrite and galena, the wastes having exceptionally high As (~0.2%) and Pb (~0.7%) content. Correlations of metal/aluminum ratios for Sb and Hg with other studied metal or metalloid were lower than for the other elements, suggesting a contribution of multiple sources including the Pb/Zn mineralization (Alkaaby, 1986) and Pb/Zn mine-impacted tributaries (AF4, AF6, AF8, AF9 and AF10). However, the spatial distribution of EF values for Sb in current stream sediments suggested that extraction of Sb ore and smelting works on the upstream subwatershed of the Gardon of Ales River were responsible for the Sb enrichment in main stream sediments of the Gardon River. The contamination peak at the bottom of the sedimentary archive probably reflected ancient mining works dating back to the early 19th century; first extraction (1810-1858) and smelting activities (1833-1858) were operating near the tributary AF2. Then the largest Sb mine was active between 1906 and 1948 resulting in 38,000T of tailings drained by the tributary AF1 and an associated smelter that worked between 1896 and 1951 (BRGM, BASIAS website). For Hg, important enrichment evidenced in current main stream sediments of the Gardon of Ales River downstream from the coal production area of La Grand-Combe suggests the predominance of this source over Pb-Zn mineralization.

1 The potential of Zn isotopes to track the sources of zinc have been investigated in the present
2 study because Zn enrichment in current main stream sediments was evidenced downstream
3 various sources (Pb/Zn mine-impacted tributaries AF8, AF9 and AF10; both urban and mine-
4 impacted tributary AF4, both industrial and mine-impacted tributary AF6; Ales town).
5 However, considering the prevailing Pb/Zn mining origin for Zn in sediments of the Gardon
6 River watershed, the relatively uniform isotopic composition of the sedimentary archive and
7 current main stream sediments ($\delta^{66}\text{Zn}=0.23\pm 0.03\text{‰}$) was consistent. Nevertheless, significant
8 differences were evidenced between the relatively homogeneous values at the bottom of the
9 sedimentary archive and upper layers, also between current main stream sediments and
10 tributaries. $\delta^{66}\text{Zn}$ value of the natural geochemical background of the Gardon River watershed
11 was $0.26\text{‰}\pm 0.02\text{‰}$, lying within background values determined at $0.31\pm 0.06\text{‰}$ for the Lot
12 River watershed (Sivry et al., 2008), also located in the Massif Central Mountains in France.
13 Local Zn-ore was found at 0.18‰ (unpublished data) which is close to the $\delta^{66}\text{Zn}$ average of
14 0.16‰ proposed by Sonke et al. (2008) for sphalerite. $\delta^{66}\text{Zn}$ values in upper layers (from GE8
15 to GE20) of the sedimentary archive and in current main stream sediments impacted by
16 anthropogenic activities deviated slightly from the background value, with an average of
17 0.20‰ in the sedimentary archive and 0.18‰ in current main stream sediments. This was
18 consistent with the contribution of Pb/Zn mine-impacted tributaries (AF9, AF10),
19 characterized by lower $\delta^{66}\text{Zn}$ value ($\sim -0.07\text{‰}$), to Zn enrichment in main stream sediments.

20 Conversely, the higher $\delta^{66}\text{Zn}$ value of tributary AF4 ($\delta^{66}\text{Zn} = 0.31\text{‰}$), both influenced by
21 industrial and mining sites, did not significantly increase the $\delta^{66}\text{Zn}$ value of the main stream,
22 showing little impact of industrial Zn source on Zn load. $\delta^{66}\text{Zn}$ values of polluted sediments
23 from this study were drastically lower than in reservoir sediments of the Lot River
24 downstream from the mining and smelting area of Decazeville ($\delta^{66}\text{Zn}=0.75$ to 1.35‰), where
25 the smelting process favored enrichment in the heavier isotopes in the remaining waste (Sivry
26 et al., 2008). In the present study, ancient smelting activities on the Gardon of Ales
27 subwatershed, at La Grand-Combe (Ministère de la Culture) did not appear to significantly
28 influence $\delta^{66}\text{Zn}$ value in the sediments from this watershed.

29 To our knowledge, the $\delta^{66}\text{Zn}$ data presented in this study are the first for riverbed sediments
30 from AMD-impacted streams. They showed an isotopic composition at $\delta^{66}\text{Zn}\sim 0.07\text{‰}$, thus
31 within the range of 0.02 to 0.46‰ measured for the water compartment in a variety of streams
32 draining historical mining district in United States and Europe (Borrok et al., 2008). This

1 lower value for AMD-impacted sediments compared to the local Zn-ore ($\delta^{66}\text{Zn}=0.18\text{‰}$) was
2 unexpected considering the low isotopic fractionation during Zn sulfide dissolution
3 (Fernandez and Borrok, 2009) and the preferential uptake of heavier Zn isotopes during
4 adsorption on ferrihydrite, which precipitates in AMD-impacted rivers (Aranda et al., 2012;
5 Balistrieri et al., 2008; Borrok et al., 2008). However, it probably reflects the complex
6 processes leading to enrichment either in the heavier or in the lighter isotopes depending on
7 the mineral phase onto which Zn is sorbed (Pokrovsky et al., 2005). Moreover, Borrok et al.
8 (2008) highlighted that lighter isotopes are enriched in the solid reservoir during important
9 diel fluctuations of dissolved Zn concentrations. Considering the variety of processes
10 involved in the cycle of Zn in AMD-impacted streams, further research would be required to
11 elucidate those controlling Zn isotopic composition in our mine-impacted streambed
12 sediments.

13 **4.4 Environmental significance of metal partitioning in sediments**

14 Considering the relatively high enrichment factors for the studied metals and metalloids in the
15 sediments of the Gardon River watershed, it is important to evaluate the potential mobility of
16 these elements in the sediments that can act as a chemical sink or a potential source of
17 pollutants to the overlying water. The three first fractions (F1, F2 and F3) defined as
18 exchangeable, reducible and oxidisable fractions are supposed to contain metals that may be
19 mobilized toward the aqueous phase by changing redox conditions i.e. from reducing to
20 oxidizing (floods, dredging), and conversely from oxidizing to reducing (early diagenesis) or
21 pH conditions (Byrne et al., 2012). Subsequently to their release, metals may be transported
22 downstream in the dissolved phase or they might re-distribute to another solid phase in the
23 sediment (Audry et al., 2010; Byrne et al., 2012). Considering the percentage of metals and
24 metalloids extracted in the fractions F1+F2+F3, the order of potential mobility in the
25 sedimentary archive and in current stream sediments was Sb (1-7%) < Tl (3-34%) = As (4-
26 35%) < Zn (9-65%) < Pb (25-77%) < Cd (48-88%). Comparison with other studies is limited
27 due to the diversity of the extraction protocols used (Byrne et al., 2012; Filgueiras et al.,
28 2002). Nevertheless, other authors using BCR procedure or a similar one also reported an
29 important potential mobility for Cd, Zn and Pb in mine affected rivers. For As and Sb,
30 geochemical associations and subsequent estimation of their potential mobility in mine-
31 affected stream sediments differed widely through studies. Galán et al. (2003) showed that As
32 was mainly bound to the relatively mobile pool in poorly crystallized Fe and Mn

1 oxyhydroxides (fraction F2) in acidic Odiel and Tinto Rivers (Spain) affected by AMD while
2 other studies reported low mobility for As in other mining impacted environments (Bird et al.,
3 2003; Grosbois et al., 2001; Rapant et al., 2006). Association of Sb to the residual fraction
4 evidenced in other mine-impacted watersheds (Grosbois et al., 2001; Kraus and Wiegand,
5 2006; Rapant et al., 2006) was ascribed to its presence in stibnite which is an insoluble sulfide
6 phase (Kraus and Wiegand, 2006).

7 An increase of the proportion of the most reactive fractions (F1+F2+F3) was observed in
8 relation with EF increase for Cd, Zn, Pb and to a lesser extent for As and Tl both in the
9 sedimentary archive and in current main stream sediments of the Gardon River. Such an
10 increase of metal mobility associated to anthropogenic contamination was already observed in
11 other mining environments (Byrne et al., 2012) and industrial or urban affected rivers
12 (Gagnon et al., 2009; Kim et al., 2009) showing that sediments may not act as a permanent
13 sink for these metals.

14 **5 Conclusion**

15 This study provided evidence of the gradual enrichment of Pb, Zn, Cd, Tl, Hg, As and Sb in
16 the sediments of the Gardon watershed since the late 19th century related to the beginning of
17 the industrial era and a remaining contamination pattern in recent decades, in contrast to the
18 general decontamination observed for large French Rivers.

19 The combination of inter-element relationships and spatial distribution of EF values allowed
20 to point out the main sources of metals and metalloids in sediments, i.e. Pb/Zn ore
21 exploitation (Pb, Zn, As, Tl, Cd), antimony mining (Sb) and coal extraction (Hg). Zinc
22 isotopic composition provided modestly useful complement to the traditional geochemistry
23 results, in this particular context. The contribution of lighter $\delta^{66}\text{Zn}$ value of AMD-impacted
24 streams decreases only slightly the isotopic composition of the Gardon River sediments.
25 Anthropogenic enrichment of metals and metalloids from mining origin in sediments of the
26 Gardon River was associated to increased potential mobility, as estimated by sequential
27 extraction, for Cd, Pb, Zn and to a lesser extent for As and Tl.

28 Altogether, these results showed that about fifty years after the closure of mines, the former
29 mining sites remained the prevailing sources of Pb, Zn, Cd, Tl, Hg, As and Sb in sediments of
30 the Gardon River, some of these contaminants initially trapped in the sediment being

1 potentially mobilizable toward the aqueous medium by changing environmental conditions.
2 Further studies are necessary to quantify the contribution of specific mining sites to global
3 metal and metalloid enrichment in sediments of the Gardon River and to determine if these
4 sediments may actually become a source of contaminant to the overlying water.

5

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1 **7 Figure and table captions**

2 **Figure 1** a) Simplified geological map (simplified from BRGM, Info Terre website); b) Map
3 of the study area showing the main mining sites and the sampling stations (current stream
4 sediments sampling stations : numbers represent stations on the main stream and AFx
5 represents stations on the tributaries (AF1 Ravin des Bernes River, AF2 Richaldon River,
6 AF3 Galeizon River, AF4 Grabieux River, AF5 Alzon River, AF6 Avène River, AF7
7 Salindrenque River, AF8 Aiguesmortes River, AF9 Amous River, AF10 Ourne River);
8 Locations of sampling stations are available in supplementary information, SI Table 1

9 **Figure 2** Enrichment Factors (EF) of As, Pb, Hg, Cd, Zn, Tl and Sb in sediments of the
10 archive (♦) and in current stream sediments (●) sampled on November 2011 at the station 25.
11 Datation from Dezileau et al., 2013 and Dezileau et al., in review

12 **Figure 3** Temporal evolution of a) EF Tl vs. EF As and b) EF Pb vs. EF Zn in the
13 sedimentary archive and in the current stream sediment sampled at the station 25 in 2011

14 **Figure 4** Enrichment Factors (EF) of As, Cd, Hg, Pb, Sb, Tl and Zn in sediments sampled
15 during the most complete campaign (December 6-7, 2012). EF are represented using bar
16 charts for sediments of the main stream and a dot with EF value for sediments of the
17 tributaries

18 **Figure 5** a) $\delta^{66}\text{Zn}$ (‰) variations in the sedimentary archive and b) $\delta^{66}\text{Zn}$ (‰) in current
19 stream sediments of the campaign of November 2011

20 **Figure 6** Chemical partitioning of Cd, Zn, Pb, Tl, As and Sb in sediments of the archive
21 between operationally defined fractions F1, F2, F3 and F4, expressed as percentage of total
22 metal content and enrichment factor EF values. F1: exchangeable and bound to carbonates,
23 F2: bound to Fe/Mn oxyhydroxides, F3: bound to organic matter (OM) and sulfides and F4:
24 residual fraction

25 **Table 1** Gardon River tributaries characteristics. Station number AFx indicate the sampling
26 station location on the tributaries

27 **Table 2** Metal/aluminum ratios in samples examined for geochemical background
28 determination

1 **Table 3** Spearman's correlation matrix for the metal(loid)/aluminum ratios in the sedimentary
2 archive

3 **Table 4** Spearman's correlation matrix for the metal(loid)/aluminum ratios in current stream
4 sediments : the left lower part is correlation coefficient (R^2) for the Gardon of Ales River; the
5 right upper part is for the Gardon of Anduze River

6 **Table 5** Chemical partitioning of Cd, Zn, Pb, Tl, As and Sb in current stream sediments
7 between operationally defined fractions F1, F2, F3 and F4, expressed as percentage of total
8 metal content and enrichment factor EF values. F1: exchangeable and bound to carbonates,
9 F2: bound to Fe/Mn oxyhydroxides, F3: bound to organic matter (OM) and sulfides and F4:
10 residual fraction

11

12

1 **8 Supplementary information**

2 **SI Table 1** Sampling station locations

3 **SI Table 2** $\delta^{66}\text{Zn}$ values in the sedimentary archive relative to the standards “JMC Lyon 3-
4 0749-L” and “IRMM 3702”

5 **SI Table 3** $\delta^{66}\text{Zn}$ values in current stream sediments of the campaign of November 2011
6 relative to the standards “JMC Lyon 3-0749-L” and “IRMM 3702”

7 **SI Table 4** As, Cd, Hg, Pb, Sb, Tl and Zn concentrations (in $\mu\text{g}\cdot\text{g}^{-1}$) and enrichment factors in
8 the sedimentary archive

9 **SI Table 5** As, Cd, Hg, Pb, Sb, Tl and Zn concentrations (in $\mu\text{g}\cdot\text{g}^{-1}$) and enrichment factors of
10 the whole dataset of current stream sediments

11

12

Tributaries	Station number	Characteristics
Ravin des Bernes River	AF1	Former Sb mining site drainage
Richaldon River	AF2	Former Sb, Pb, Zn mining site drainage
Galeizon River	AF3	Unimpacted
Grabieux River	AF4	Urban tributary with former coal, pyrite, Pb and Zn mining sites drainage
Alzon River	AF5	Former pyrite, Pb and Zn mining sites drainage
Avene River	AF6	Former pyrite, Pb and Zn mining sites drainage and industrial activity discharge
Salindrenque River	AF7	Unimpacted
Aiguesmortes River	AF8	Former Pb and Zn mining sites drainage
Amous River	AF9	Former Pb and Zn mining sites drainage
Ourne River	AF10	Former Pb and Zn mining sites drainage

		As/Al 10 ³	Cd/Al 10 ³	Hg/Al 10 ³	Pb/Al 10 ³	Sb/Al 10 ³	Tl/Al 10 ³	Zn/Al 10 ³
Sedimentary archive : Bottom layers GE1 to GE6 (n=7)	Mean	0.42	0.0036	0.0003	0.61	0.052	0.016	1.45
	Standard error	0.04	0.0005	0.0001	0.04	0.005	0.001	0.08
Upper Continental Crust		0.02 ^a	0.0012 ^a	0.0007 ^b	0.25 ^a	0.002 ^a	0.009 ^a	0.88 ^a

^a Taylor and Mc Lennan 1995 ; ^b Wedepohl 1995

	Zn/Al	As/Al	Cd/Al	Sb/Al	Tl/Al	Pb/Al	Hg/Al
Zn/Al							
As/Al	0.71***						
Cd/Al	0.87***	0.71***					
Sb/Al	0.69***	0.62***	0.75***				
Tl/Al	0.85***	0.72***	0.73***	0.60***			
Pb/Al	0.87***	0.77***	0.81***	0.63***	0.85***		
Hg/Al	0.69***	0.56***	0.77***	0.66***	0.70***	0.61***	

***p-value <0.0001

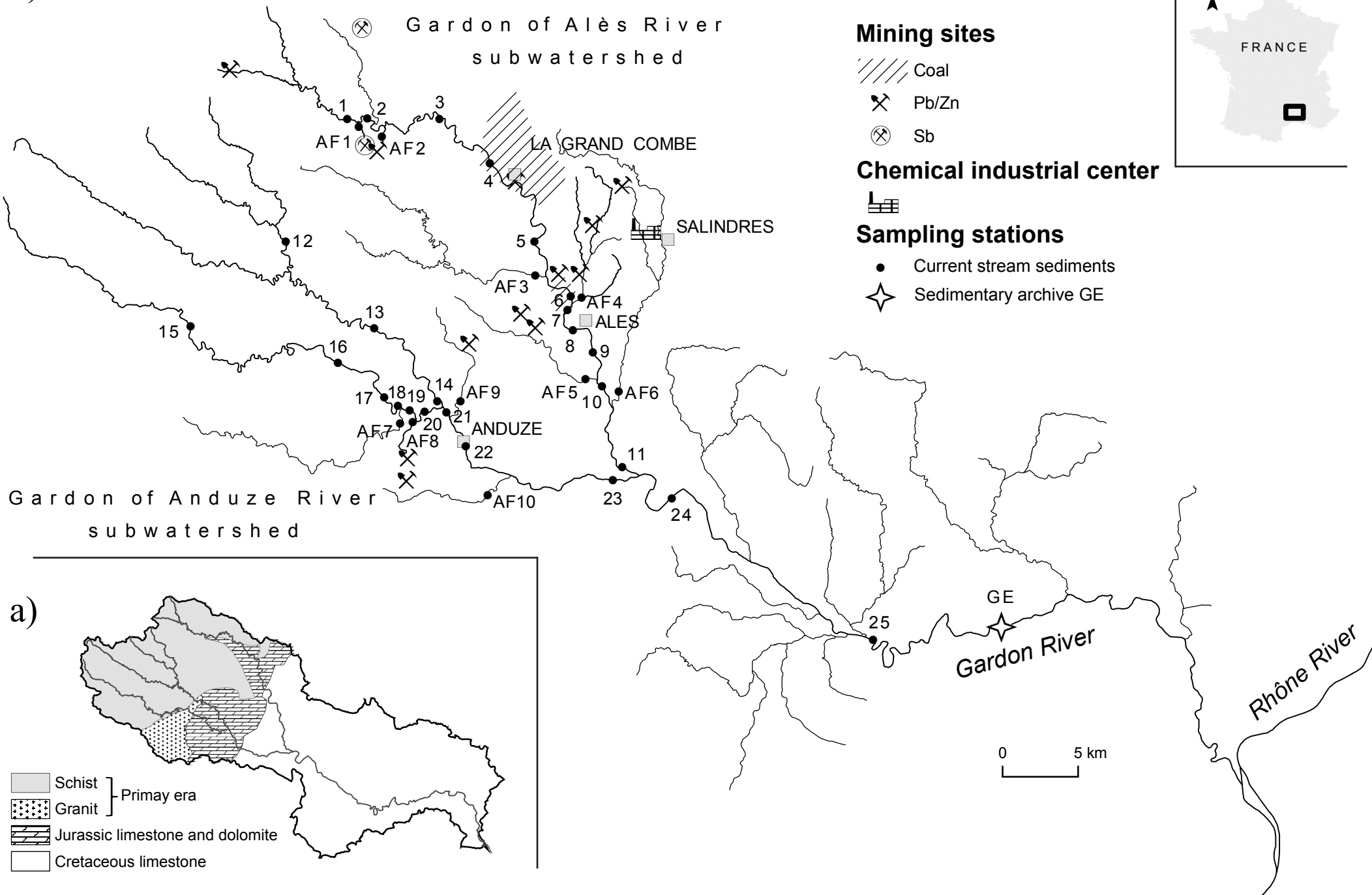
	Zn/Al	As/Al	Cd/Al	Sb/Al	Tl/Al	Pb/Al	Hg/Al
Zn/Al		0.51**	0.93**	0.17	0.23*	0.65**	0.54**
As/Al	0.47*		0.48**	0.07	0.33*	0.65**	0.31*
Cd/Al	0.90**	0.44*		0.15	0.25*	0.67**	0.54**
Sb/Al	0.00	0.04	0.00		0.00	0.04	0.02
Tl/Al	0.56**	0.42*	0.49*	0.08		0.57**	0.39*
Pb/Al	0.70**	0.58**	0.58**	0.00	0.58**		0.77**
Hg/Al	0.11	0.57*	0.10	0.15	0.49*	0.69*	

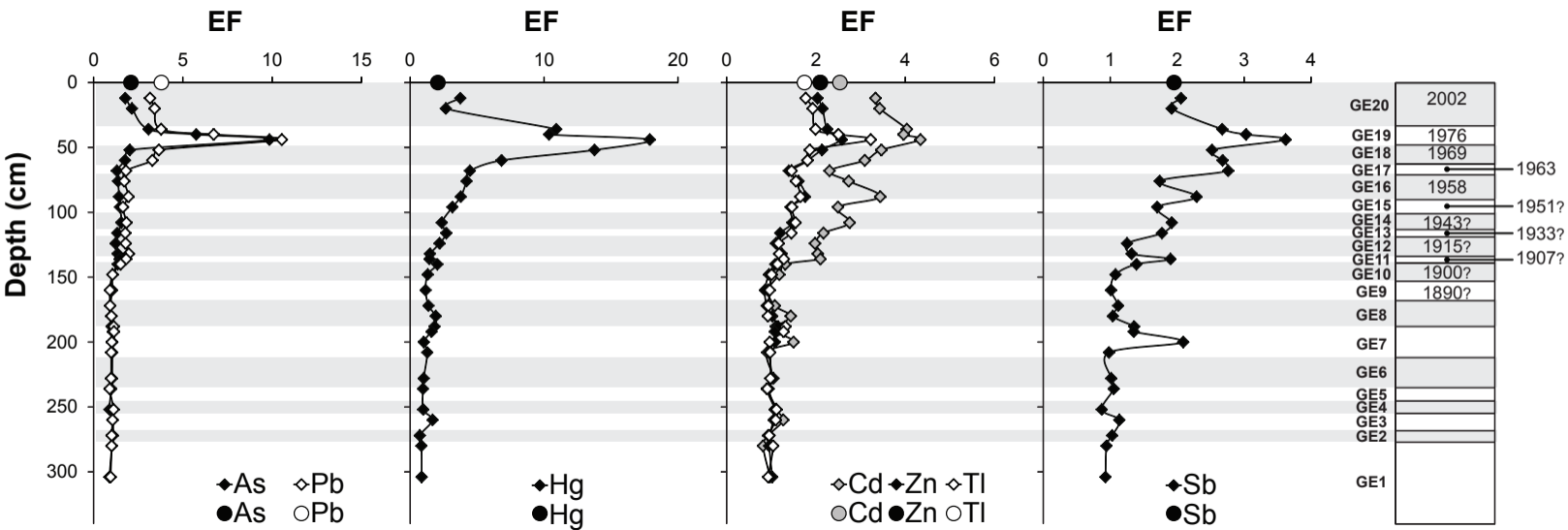
*p-value<0.05

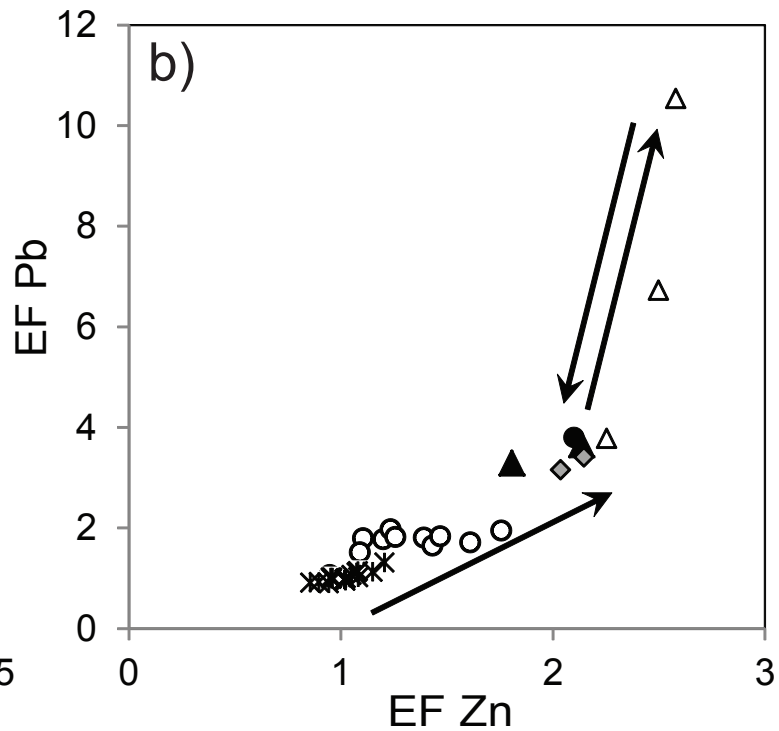
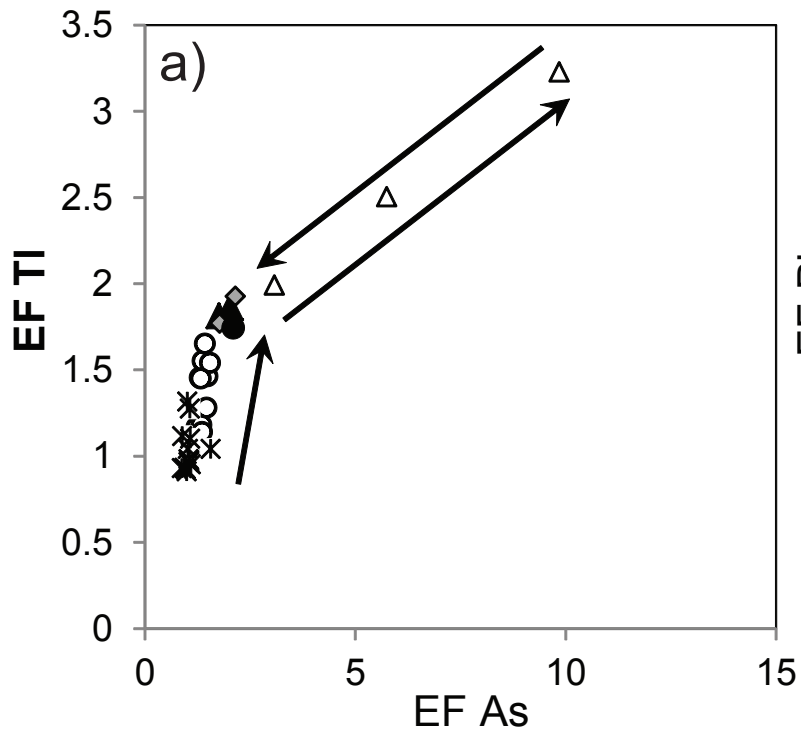
**p-value <0.001

Station number	<i>Gardon of Ales River</i>				<i>Gardon of Anduze River</i>				<i>Gardon River</i>
	1	3	9	11	13	15	22	23	24
<i>Cadmium</i>									
F1	32	40	48	38	25	27	44	62	53
F2	20	16	31	10	16	17	7	11	21
F3	16	11	9	10	17	13	25	11	10
F4	33	33	12	41	42	43	24	16	16
F1+F2+F3	67	67	88	59	58	57	76	84	84
EF	1.4	1.3	5.3	4.6	1.2	1.2	1.8	2.3	4.0
<i>Zinc</i>									
F1	9	11	37	12	6	8	21	22	23
F2	6	6	15	7	5	6	10	12	17
F3	13	12	13	6	13	13	20	22	14
F4	72	71	35	75	75	74	49	44	46
F1+F2+F3	28	29	65	25	25	26	51	56	54
EF	1.6	1.3	3.4	4.9	1.1	1.2	1.5	1.9	2.5
<i>Lead</i>									
F1	13	7	8	3	4	9	14	20	5
F2	28	33	43	19	18	30	34	31	35
F3	5	5	8	4	3	4	6	4	5
F4	54	54	41	74	75	56	46	45	55
F1+F2+F3	46	46	59	26	25	44	54	55	45
EF	1.0	1.0	1.7	4.2	1.0	0.9	2.0	3.2	3.6
<i>Thallium</i>									
F1	1	1	9	4	1	1	1	1	2
F2	6	3	29	17	5	2	7	6	14
F3	1	1	5	4	2	1	4	4	4
F4	92	96	56	75	92	97	89	89	79
F1+F2+F3	8	4	44	25	8	3	11	11	21
EF	0.7	0.6	1.8	1.9	1.0	0.7	1.2	1.5	2.1
<i>Arsenic</i>									
F1	1	2	10	1	1	2	2	2	2
F2	3	8	8	2	8	10	18	13	16
F3	2	4	3	1	3	3	4	3	4
F4	93	86	79	96	87	85	75	82	78
F1+F2+F3	7	14	21	4	13	15	25	18	22
EF	1.0	0.7	1.1	2.4	1.3	1.9	2.0	2.3	2.2
<i>Antimony</i>									
F1	0	0	2	0	1	0	1	1	1
F2	1	2	1	1	2	1	2	2	3
F3	0	1	1	0	0	0	1	0	1
F4	98	97	96	98	97	99	97	97	95
F1+F2+F3	2	3	4	2	3	1	3	3	5
EF	1.6	7.4	3.6	5.7	0.9	0.7	1.0	1.5	1.4

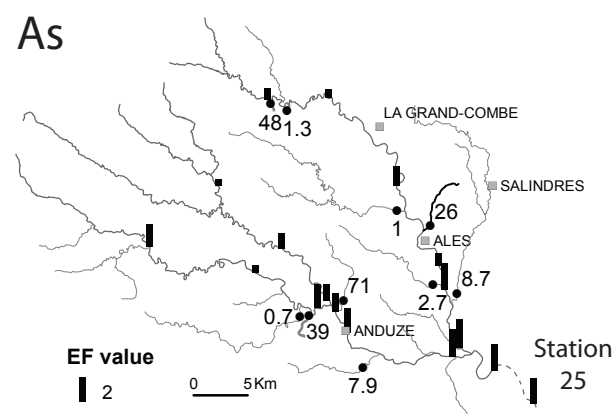
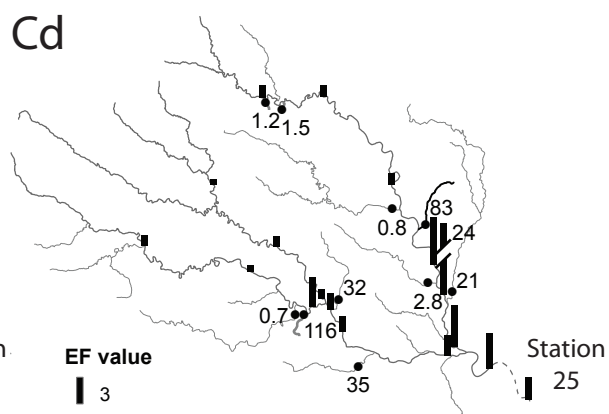
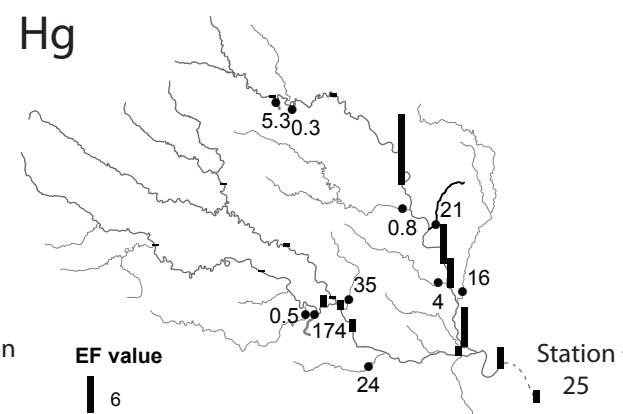
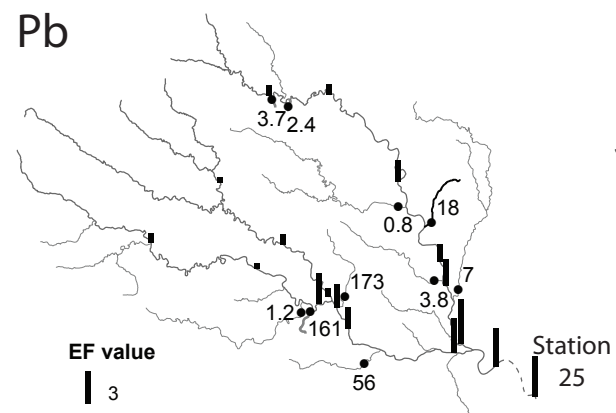
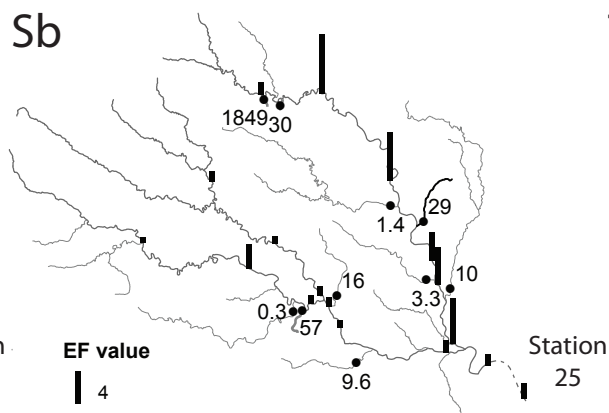
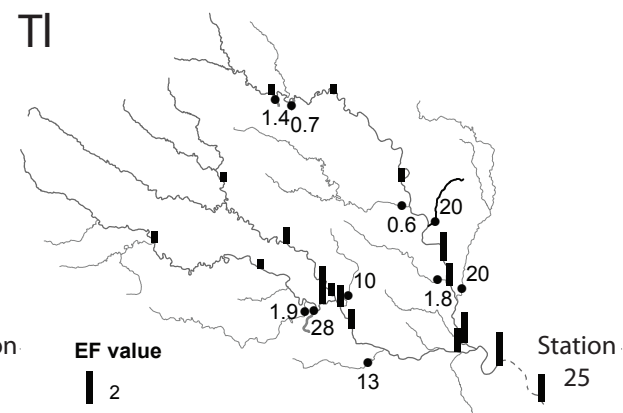
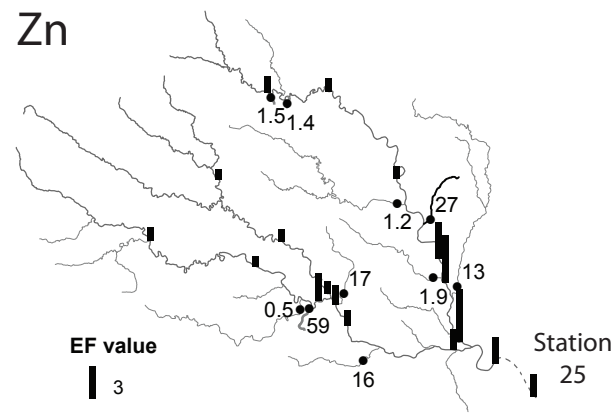
b)





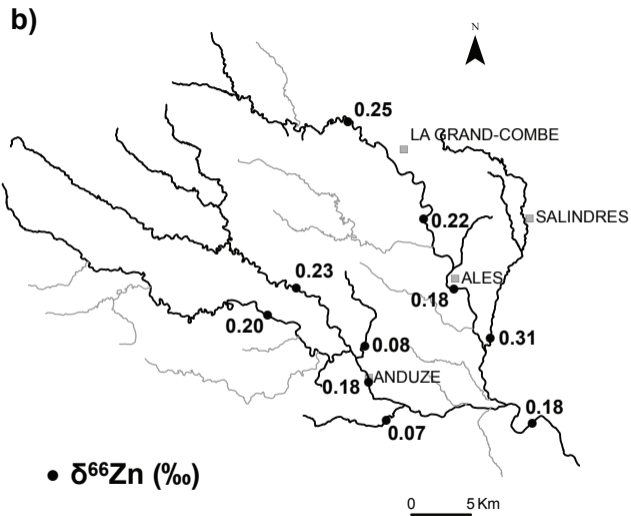
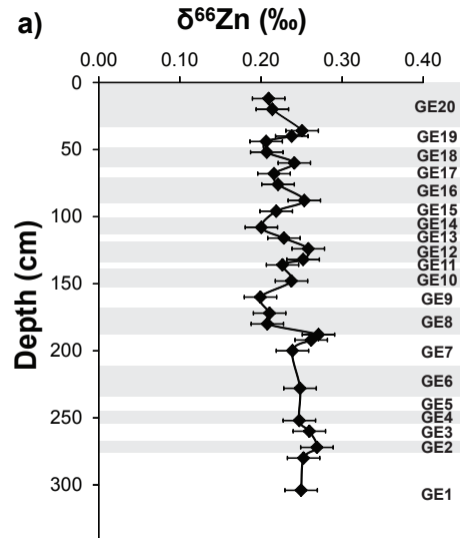


- Current stream sediment sampled at the station 25
- ◆ GE20
- △ GE19
- ▲ GE18
- GE10 to GE17
- ✱ GE1 to GE9

As**Cd****Hg****Pb****Sb****Tl****Zn**

▬ Main stream EF values

● Tributaries EF values



	Station	Longitude	Latitude
	1	3.9015	44.2477
	2	3.9138	44.2474
	3	3.9724	44.2478
	3	3.9148	44.1236
	4	4.0137	44.2208
	5	4.0493	44.1736
	6	4.0783	44.1403
	7	4.0754	44.1322
	8	4.0795	44.1202
	9	4.0956	44.1066
	10	4.1026	44.0863
Main stream	11	4.1180	44.0374
sediments	12	3.8429	44.1763
	14	3.9661	44.0794
	15	3.7626	44.1267
	16	3.8844	44.1034
	17	3.9221	44.0822
	18	3.9333	44.0771
	19	3.9429	44.0743
	20	3.9554	44.0731
	21	3.9735	44.0726
	22	3.9886	44.0521
	23	4.1101	44.0302
	24	4.1585	44.0182
	25	4.3221	43.9309
	AF1	3.9054	44.2439
	AF2	3.9241	44.2381
	AF3	4.0493	44.1531
	AF4	4.0874	44.1394
Tributary	AF5	4.0892	44.0907
sediments	AF6	4.1166	44.0829
	AF7	3.9348	44.0663
	AF8	3.9451	44.0669
	AF9	3.9854	44.0790
	AF10	4.0062	44.0226
Sedimentary	GE	4.4285	43.9369
archive			

Sampling depth ^a (cm)	$\delta^{66}\text{Zn}_{\text{JMC 3-0749-L}}$	$\delta^{66}\text{Zn}_{\text{IRMM 3702}}$
12	0.21	-0.08
20	0.21	-0.08
36	0.25	-0.04
40	0.24	-0.05
44	0.21	-0.08
52	0.21	-0.08
60	0.24	-0.05
68	0.22	-0.07
76	0.22	-0.07
88	0.25	-0.04
96	0.22	-0.07
108	0.20	-0.09
116	0.23	-0.06
124	0.26	-0.03
132	0.25	-0.04
136	0.23	-0.06
148	0.24	-0.05
160	0.20	-0.09
172	0.21	-0.08
180	0.21	-0.08
188	0.27	-0.02
192	0.26	-0.03
200	0.24	-0.05
228	0.25	-0.04
236	0.25	-0.04
252	0.25	-0.04
260	0.26	-0.03
272	0.27	-0.02
280	0.25	-0.04
304	0.25	-0.04

^ameasured from the top of the terrace

Station number	$\delta^{66}\text{Zn}_{\text{JMC 3-0749-L}}$	$\delta^{66}\text{Zn}_{\text{IRMM 3702}}$
3	0.25	-0.04
5	0.22	-0.07
8	0.18	-0.11
13	0.23	-0.06
16	0.20	-0.09
22	0.18	-0.11
24	0.18	-0.11
AF6	0.31	0.02
AF9	0.08	-0.21
AF10	0.07	-0.22

Sampling depth ^a (cm)	As		Cd		Hg		Pb		Sb		Tl		Zn		Layer number	Dating
	$\mu\text{g}\cdot\text{g}^{-1}$	EF	$\mu\text{g}\cdot\text{g}^{-1}$	EF	$\mu\text{g}\cdot\text{g}^{-1}$	EF	$\mu\text{g}\cdot\text{g}^{-1}$	EF	$\mu\text{g}\cdot\text{g}^{-1}$	EF	$\mu\text{g}\cdot\text{g}^{-1}$	EF	$\mu\text{g}\cdot\text{g}^{-1}$	EF		
12	33.2	1.8	0.53	3.3	0.053	3.7	84.8	3.2	4.78	2.1	1.26	1.8	130.7	2.0	GE20	2002
20	46.4	2.1	0.63	3.4	0.043	2.7	106.0	3.4	5.16	1.9	1.59	1.9	159.4	2.1		
36	84.7	3.1	0.95	4.0	0.225	10.9	253.7	3.8	9.14	2.7	2.09	2.0	212.8	2.3	GE19	1976
40	165.2	5.7	0.97	4.0	0.223	10.4	471.3	6.7	10.82	3.0	2.74	2.5	246.2	2.5		
44	275.8	9.8	1.04	4.3	0.376	17.9	720.0	10.5	12.60	3.6	3.45	3.2	247.9	2.6		
52	59.2	2.0	0.86	3.5	0.301	13.8	153.2	3.7	9.15	2.5	2.07	1.9	214.0	2.1	GE18	1969
60	53.1	1.8	0.80	3.1	0.155	6.8	142.6	3.3	10.05	2.7	2.09	1.8	187.2	1.8		
68	39.3	1.3	0.59	2.3	0.101	4.5	78.1	1.8	10.32	2.8	1.67	1.5	143.7	1.4	GE17	1963
76	30.7	1.4	0.52	2.7	0.071	4.2	55.1	1.7	4.84	1.7	1.33	1.6	123.8	1.6	GE16	1958
88	34.9	1.4	0.72	3.4	0.069	3.8	68.5	1.9	6.97	2.3	1.54	1.7	147.5	1.8		
96	47.0	1.5	0.67	2.5	0.075	3.2	74.7	1.6	6.69	1.7	1.76	1.5	155.4	1.4	GE15	1951?
108	38.4	1.5	0.58	2.8	0.044	2.4	65.3	1.8	5.91	1.9	1.46	1.5	124.8	1.5	GE14	1943?
116	38.4	1.3	0.53	2.2	0.058	2.7	73.5	1.8	6.35	1.8	1.60	1.5	118.8	1.2	GE13	1933?
124	31.9	1.2	0.44	2.0	0.043	2.2	66.7	1.8	4.03	1.3	1.15	1.2	98.2	1.1	GE12	1915?
132	43.5	1.3	0.56	2.0	0.036	1.5	91.8	2.0	5.32	1.3	1.46	1.2	137.5	1.2		
136	37.2	1.5	0.45	2.1	0.028	1.5	66.3	1.8	5.99	1.9	1.24	1.3	109.5	1.3	GE11	1907?
140	34.3	1.4	0.28	1.3	0.039	2.0	55.0	1.5	4.37	1.4	1.10	1.1	94.5	1.1	GE10	1900?
148	27.6	1.1	0.26	1.2	0.025	1.3	39.3	1.1	3.46	1.1	0.99	1.0	83.8	0.9		
160	30.4	1.0	0.23	0.9	0.025	1.2	38.3	0.9	3.68	1.0	1.07	1.0	85.8	0.9	GE9	1890?
172	31.5	0.9	0.31	1.1	0.035	1.4	44.7	0.9	4.68	1.1	1.19	0.9	103.3	0.9	GE8	n.d.
180	31.8	1.0	0.40	1.4	0.047	1.9	46.9	1.0	4.22	1.0	1.15	0.9	114.7	1.0		
188	35.5	1.0	0.33	1.1	0.048	1.8	57.3	1.1	5.96	1.4	1.77	1.3	139.6	1.1	GE7	n.d.
192	37.8	1.1	0.33	1.1	0.043	1.6	58.1	1.1	5.97	1.4	1.73	1.3	131.7	1.1		
200	29.0	1.1	0.35	1.5	0.021	1.0	40.3	1.0	7.16	2.1	1.02	1.0	102.3	1.1		
208	36.7	1.0	0.27	0.9	0.034	1.3	49.5	1.0	4.27	1.0	1.30	1.0	114.8	1.0		
228	32.7	1.0	0.28	1.0	0.024	1.0	44.3	1.0	3.99	1.0	1.18	1.0	110.2	1.0	GE6	n.d.
236	32.0	1.0	0.25	0.9	0.023	1.0	41.8	0.9	4.22	1.1	1.12	0.9	104.6	0.9	GE5	n.d.
252	22.5	0.9	0.24	1.1	0.019	1.0	40.6	1.1	2.75	0.9	1.08	1.1	93.5	1.1	GE4	n.d.
260	29.4	1.1	0.30	1.3	0.034	1.7	41.7	1.1	3.87	1.1	1.15	1.1	98.9	1.1	GE3	n.d.
272	33.8	1.1	0.25	0.9	0.017	0.7	45.0	1.0	3.97	1.0	1.13	1.0	102.2	1.0	GE2	n.d.
280	28.9	1.0	0.20	0.8	0.018	0.8	41.0	1.0	3.32	0.9	1.12	1.0	92.2	1.0	GE1	n.d.
304	25.2	0.9	0.24	1.0	0.018	0.9	38.9	0.9	3.30	0.9	1.01	0.9	100.1	1.0		

^ameasured from the top of the terrace

n.d. not determined

