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### ► To cite this version:

Eleonore Resongles, Corinne Casiot, Remi Freydier, Laurent Dezileau, Jerome Viers, et al.. Persisting impact of historical mining activity to metal (Pb, Zn, Cd, Tl, Hg) and metalloid (As, Sb) enrichment in sediments of the Gardon River, Southern France. *Science of the Total Environment*, 2014, 481, pp.509-521. 10.1016/j.scitotenv.2014.02.078 . hal-01054163

**HAL Id: hal-01054163**

**<https://hal.science/hal-01054163v1>**

Submitted on 31 May 2021

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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

5 Eléonore Resongles<sup>a\*</sup>, Corinne Casiot<sup>a</sup>, Rémi Freydier<sup>a</sup>, Laurent Dezileau<sup>b</sup>, Jérôme Viers<sup>c</sup> and  
6 Françoise Elbaz-Poulichet<sup>a</sup>

7

8 <sup>a</sup> HydroSciences UMR 5569, CNRS, Universités Montpellier I & II, IRD, Place Eugène  
9 Bataillon, CC MSE, 34095 Montpellier Cedex 5, France

10 <sup>b</sup> Géosciences UMR 5243, CNRS, Universités Montpellier II, Place Eugène Bataillon, CC 60,  
11 34095 Montpellier Cedex 5, France

12 <sup>c</sup> Géosciences Environnement Toulouse UMR 5563, Université Paul Sabatier, CNRS, IRD, 14  
13 Avenue Edouard Belin, 31400 Toulouse, France

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,  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  $^{67}\text{Zn}$ ,  $^{68}\text{Zn}$ , and  $^{70}\text{Zn}$ , 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,  $\text{ZnS}$ ) 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<sup>2</sup> 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 km<sup>2</sup>. 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 19<sup>th</sup> 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 (FeS<sub>2</sub>), tetradrite (Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>), pyrargyrite (Ag<sub>3</sub>SbS<sub>3</sub>) and proustite (Ag<sub>3</sub>AsS<sub>3</sub>)  
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<sup>-1</sup> 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 ( $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ) and geochemical analyses (total Pb) were used  
5 to determine age controls. Maximum  $^{137}\text{Cs}$  activity in layers GE17 and GE18 was associated  
6 to the maximum atmospheric emission in the mid-1960s.  $^{210}\text{Pb}$  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)  $\text{H}_2\text{O}_2$  35% (2) a 4:3:0.13 mL concentrated



1 HNO<sub>3</sub>-HF-HClO<sub>4</sub> mixture and (3) a 1:3 mL concentrated HNO<sub>3</sub>-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 HNO<sub>3</sub> 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 HNO<sub>3</sub> 0.05N and doped with a Cu standard (Cu NIST-SRM 976); final Zn  
16 and Cu concentrations were 300ng.g<sup>-1</sup>.

### 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:HNO<sub>3</sub> mixture. Then samples were cooled, evaporated to dryness and brought to 30mL  
30 using 3mL HNO<sub>3</sub> 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<sup>-1</sup>, 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 (<sup>64</sup>Zn, <sup>66</sup>Zn, <sup>67</sup>Zn, <sup>68</sup>Zn), Cu isotopes (<sup>63</sup>Cu, <sup>65</sup>Cu) and Ni isotope (<sup>62</sup>Ni) were  
24 monitored simultaneously. Measurements of <sup>62</sup>Ni signal allowed correcting the possible  
25 isobaric interference of <sup>64</sup>Ni on <sup>64</sup>Zn. 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 δ<sup>66</sup>Zn notation (in  
28 units of ‰), δ<sup>66</sup>Zn 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 $\approx$ 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  $3.7 \pm 0.7$  for Pb,  $2.3 \pm 0.1$  for As,  $1.7 \pm 0.3$  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  $2100\text{m}^3/\text{s}$  (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 19<sup>th</sup> 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 19<sup>th</sup> 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 m<sup>3</sup>/s in 2002 (Dezileau et al., 2013; Dezileau et al., in  
2 review)) and moderate (1140 m<sup>3</sup>/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 FeS<sub>2</sub>), in sulfosalts (proustite Ag<sub>3</sub>AsS<sub>3</sub>) and in galena (PbS), antimony in sulfosalts (pyrargyrite Ag<sub>3</sub>SbS<sub>3</sub>) 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  $0.18\text{‰}$  (unpublished data) which is close to the  $\delta^{66}\text{Zn}$  average of  
14  $0.16\text{‰}$  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  $0.20\text{‰}$  in the sedimentary archive and  $0.18\text{‰}$  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  $1.35\text{‰}$ ), 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  $0.46\text{‰}$  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

## 6 **6 Acknowledgments**

7 The authors would like to thank Sophie Delpoux for fieldwork and analysis and Daniel Cossa  
8 for mercury analysis. Jérôme Chmeleff and Philippe Télouk are gratefully acknowledged for  
9 zinc isotopic analysis at Toulouse and Lyon. This study was supported by the EC2CO-INSU  
10 program and OSU OREME (<http://www.oreme.univ-montp2.fr>).

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## References

- 1
- 2 Alkaaby, A. (1986). Conglomérats minéralisés (Pb-Ba-Fe) du Trias basal sur la bordure sud-  
3 est des Cévennes : exemple du système fluvial en tresse de Carnoulès (Gard). Thesis.  
4 Université des Sciences et Techniques du Languedoc. p.154.
- 5 Aranda, S., Borrok, D. M., Wanty, R. B., & Balistrieri, L. S. (2012). Zinc isotope  
6 investigation of surface and pore waters in a mountain watershed impacted by acid rock  
7 drainage. *The Science of the Total Environment*, 420, 202–213.
- 8 Audry, S., Schäfer, J., Blanc, G., Bossy, C., & Lavaux, G. (2004a). Anthropogenic  
9 components of heavy metal (Cd, Zn, Cu, Pb) budgets in the Lot-Garonne fluvial system  
10 (France). *Applied Geochemistry*, 19(5), 769–786. doi:10.1016/j.apgeochem.2003.10.002
- 11 Audry, S., Schäfer, J., Blanc, G., & Jouanneau, J.-M. (2004b). Fifty-year sedimentary record  
12 of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France).  
13 *Environmental Pollution*, 132(3), 413–426. doi:10.1016/j.envpol.2004.05.025
- 14 Audry, S., Grosbois, C., Bril, H., Schäfer, J., Kierczak, J., & Blanc, G. (2010). Post-  
15 depositional redistribution of trace metals in reservoir sediments of a mining/smelting-  
16 impacted watershed (the Lot River, SW France). *Applied Geochemistry*, 25(6), 778–794.  
17 doi:10.1016/j.apgeochem.2010.02.009
- 18 Ayrault, S., Roy-Barman, M., Le Cloarec, M.-F., Priadi, C. R., Bonté, P., & Göpel, C. (2012).  
19 Lead contamination of the Seine River, France: geochemical implications of a historical  
20 perspective. *Chemosphere*, 87(8), 902–910. doi:10.1016/j.chemosphere.2012.01.043
- 21 Balistrieri, L. S., Borrok, D. M., Wanty, R. B., & Ridley, W. I. (2008). Fractionation of Cu  
22 and Zn isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: Experimental  
23 mixing of acid rock drainage and ambient river water. *Geochimica et Cosmochimica*  
24 *Acta*, 72(2), 311–328.
- 25 Banque Hydro, Eaufrance. Last accessed on 11/26/2013. <http://www.hydro.eaufrance.fr/>
- 26 Bird, G., Brewer, P. A., Macklin, M. G., Balteanu, D., Driga, B., Serban, M., & Zaharia, S.  
27 (2003). The solid state partitioning of contaminant metals and As in river channel  
28 sediments of the mining affected Tisa drainage basin, northwestern Romania and eastern  
29 Hungary. *Applied Geochemistry*, 18(10), 1583–1595. doi:10.1016/S0883-  
30 2927(03)00078-7
- 31 Bonilla-Valverde, D., Ruiz-Laguna, J., Muñoz, A., Ballesteros, J., Lorenzo, F., Gómez-Ariza,  
32 J. L., & López-Barea, J. (2004). Evolution of biological effects of Aznalcóllar mining  
33 spill in the Algerian mouse (*Mus spretus*) using biochemical biomarkers. *Toxicology*,  
34 197(2), 123–138. doi:10.1016/j.tox.2003.12.010
- 35 Borrok, D. M., Nimick, D. A., Wanty, R. B., & Ridley, W. I. (2008). Isotopic variations of  
36 dissolved copper and zinc in stream waters affected by historical mining. *Geochimica et*  
37 *Cosmochimica Acta*, 72(2), 329–344. doi:10.1016/j.gca.2007.11.014



- 1 Borrok, D. M., Wanty, R. B., Ridley, W. I., Lamothe, P. J., Kimball, B. A., Verplanck, P. L.,  
2 & Runkel, R. L. (2009). Application of iron and zinc isotopes to track the sources and  
3 mechanisms of metal loading in a mountain watershed. *Applied Geochemistry*, 24(7),  
4 1270–1277. doi:10.1016/j.apgeochem.2009.03.010
- 5 Bouchez, J., Lupker, M., Gaillardet, J., France-Lanord, C., & Maurice, L. (2011). How  
6 important is it to integrate riverine suspended sediment chemical composition with  
7 depth? Clues from Amazon River depth-profiles. *Geochimica et Cosmochimica Acta*,  
8 75(22), 6955–6970.
- 9 BRGM, SIG Mines. Last accessed on 11/26/2013. <http://sigminesfrancebrgmfr/>
- 10 BRGM, InfoTerre. Last accessed on 11/26/2013. <http://infoterre.brgm.fr/>
- 11 BRGM, BASIAS. Inventaire historique de sites industriels et activités de service. Last  
12 accessed on 11/26/2013. <http://basias.brgm.fr/>
- 13 BRGM, BASOL. Last accessed on 11/26/2013. <http://basol.developpement-durable.gouv.fr/>
- 14 Byrne, P., Wood, P. J., & Reid, I. (2012). The Impairment of River Systems by Metal Mine  
15 Contamination: A Review Including Remediation Options. *Critical Reviews in*  
16 *Environmental Science and Technology*, 42(19), 2017–2077.  
17 doi:10.1080/10643389.2011.574103
- 18 Caruso, B., Cox, T., Runkel, R., Velleux, M., Bencala, K., Nordstrom, D., Julien, P.Y., Butler,  
19 B.A., Alpers, C.N., Marion, A., & Smith, K. (2008). Metals fate and transport modelling in  
20 streams and watersheds: state of the science and USEPA workshop review. *Hydrological*  
21 *Processes*, 22, 4011–4021. doi:10.1002/hyp
- 22 Casiot, C., Egal, M., Bruneel, O., Verma, N., Parmentier, M., & Elbaz-Poulichet, F. (2011).  
23 Predominance of aqueous Tl (I) species in the river system downstream from the  
24 abandoned Carnoules Mine (Southern France). *Environmental Science & Technology*,  
25 45(I), 2056–2064.
- 26 Casiot, C., Egal, M., Elbaz-Poulichet, F., Bruneel, O., Bancon-Montigny, C., Cordier, M.-A.,  
27 Gomez, E., & Aliaume, C. (2009). Hydrological and geochemical control of metals and  
28 arsenic in a Mediterranean river contaminated by acid mine drainage (the Amous River,  
29 France); preliminary assessment of impacts on fish (*Leuciscus cephalus*). *Applied*  
30 *Geochemistry*, 24(5), 787–799. doi:10.1016/j.apgeochem.2009.01.006
- 31 Chen, J., Gaillardet, J., & Louvat, P. (2008). Zinc Isotopes in the Seine River Waters, France:  
32 A Probe of Anthropogenic Contamination. *Environmental Science & Technology*,  
33 42(17), 6494–6501. doi:10.1021/es800725z
- 34 Chen, J., Gaillardet, J., Louvat, P., & Huon, S. (2009). Zn isotopes in the suspended load of  
35 the Seine River, France: Isotopic variations and source determination. *Geochimica et*  
36 *Cosmochimica Acta*, 73(14), 4060–4076. doi:10.1016/j.gca.2009.04.017

- 1 Cloquet, C., Carignan, J., & Libourel, G. (2006). Isotopic composition of Zn and Pb  
2 atmospheric depositions in an urban/Periurban area of northeastern France.  
3 *Environmental Science & Technology*, 40(21), 6594–600.
- 4 Cloquet, C., Carignan, J., Lehmann, M. F., & Vanhaecke, F. (2008). Variation in the isotopic  
5 composition of zinc in the natural environment and the use of zinc isotopes in  
6 biogeosciences: a review. *Analytical and bioanalytical chemistry*, 390(2), 451–63.  
7 doi:10.1007/s00216-007-1635-y
- 8 Cherry, D. S., Currie, R. J., Soucek, D. J., Latimer, H. A., & Trent, G. C. (2001). An  
9 integrative assessment of a watershed impacted by abandoned mined land discharges.  
10 *Environmental Pollution*, 111(3), 377–88.
- 11 Delrieu, G., Ducrocq, V., Gaume, E., Nicol, J., Payrastre, O., Yates, E., Kirstetter, PE.,  
12 Andrieu, H., Ayrat, PA., Bouvier, C., Creutin, JD., Livet, M., Anquetin, S., Lang, M.,  
13 Neppel, L., Obled, C., Parent-Du-Chatelet, J., Saulier, GM., Walpersdorf, A., &  
14 Wobrock, W. (2005). The catastrophic flash-flood event of 8-9 September 2002 in the  
15 Gard region, France: a first case study for the Cévennes-Vivarais Mediterranean  
16 Hydrometeorological. *Journal of Hydrometeorology*, 6, 34–52.
- 17 Dezileau, L., Terrier, B., Berger, J. F., Blanchemanche, P., Freydier, R., Bremond, L.,  
18 Latapie, A., Paquier, A., Lang, M., & Delgado, J. (in review). A multi-dating approach  
19 applied to historical slackwater flood deposits of the Gardon River, SE France.  
20 *Geomorphology*.
- 21 Dezileau, L., Terrier, B., Berger, J. F., Blanchemanche, P., Freydier, R., Latapie, A., Paquier,  
22 A., Lang, M., & Delgado, J. (2013). Reconstitution des crues extrêmes du Gardon à  
23 partir d'une analyse paléohydrologique. In *Société Hydrotechnique de France* (pp. 1–12).
- 24 Dolgoplova, A., Weiss, D. J., Seltmann, R., Kober, B., Mason, T. F. D., Coles, B., &  
25 Stanley, C. J. (2006). Use of isotope ratios to assess sources of Pb and Zn dispersed in  
26 the environment during mining and ore processing within the Orlovka–Spokoinoe  
27 mining site (Russia). *Applied Geochemistry*, 21(4), 563–579.  
28 doi:10.1016/j.apgeochem.2005.12.014
- 29 Ettler, V., Mihaljevic, M., Sebek, O., Molek, M., Grygar, T., & Zeman, J. (2006).  
30 Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination  
31 in stream sediments from the mining and smelting district of Příbram, Czech Republic.  
32 *Environmental Pollution*, 142(3), 409–417. doi:10.1016/j.envpol.2005.10.024
- 33 European Commission. (1988). Summary reports of the subprogramme: metals and mineral  
34 substances (1982-85): Volume 1. (M. Donato & L. Van Wambeke, Eds.) (Commission.,  
35 Vol. 1, p. 552).
- 36 Fernandez, A., & Borrok, D. M. (2009). Fractionation of Cu, Fe, and Zn isotopes during the  
37 oxidative weathering of sulfide-rich rocks. *Chemical Geology*, 264, 1–12.  
38 doi:10.1016/j.chemgeo.2009.01.024
- 39 Ferrand, E., Eyrolle, F., Radakovitch, O., Provansal, M., Dufour, S., Vella, C., Raccasi, G., &  
40 Gurriaran, R. (2012). Historical levels of heavy metals and artificial radionuclides

- 1 reconstructed from overbank sediment records in lower Rhône River (South-East  
2 France). *Geochimica et Cosmochimica Acta*, 82, 163–182.  
3 doi:10.1016/j.gca.2011.11.023
- 4 Filgueiras, A. V., Lavilla, I., & Bendicho, C. (2002). Chemical sequential extraction for metal  
5 partitioning in environmental solid samples. *Journal of Environmental Monitoring*, 4(6),  
6 823–857. doi:10.1039/b207574c
- 7 Gagnon, C., Turcotte, P., & Vigneault, B. (2009). Comparative study of the fate and mobility  
8 of metals discharged in mining and urban effluents using sequential extractions on  
9 suspended solids. *Environmental Geochemistry and Health*, 31(6), 657–671.  
10 doi:10.1007/s10653-008-9223-4
- 11 Galán, E., Gómez-Ariza, J., Gonzales, I., Fernandez-Caliani, J., Morales, E., & Giraldez, I.  
12 (2003). Heavy metal partitioning in river sediments severely polluted by acid mine  
13 drainage in the Iberian Pyrite Belt. *Applied Geochemistry*, 18, 409–421.
- 14 Gocht, T., Moldenhauer, K., & Püttmann, W. (2001). Historical record of polycyclic aromatic  
15 hydrocarbons (PAH) and heavy metals in floodplain sediments from the Rhine River  
16 (Hessisches Ried, Germany). *Applied Geochemistry*, 16, 1707–1721.
- 17 Gosar, M., & Miler, M. (2011). Anthropogenic metal loads and their sources in stream  
18 sediments of the Meža River catchment area (NE Slovenia). *Applied Geochemistry*,  
19 26(11), 1855–1866. doi:10.1016/j.apgeochem.2011.06.009
- 20 Gray, N. (1997). Environmental impact and remediation of acid mine drainage: a management  
21 problem. *Environmental Geology*, 30, 62–71.
- 22 Grimalt, J. O., Ferrer, M., & Macpherson, E. (1999). The mine tailing accident in Aznalcollar.  
23 *The Science of the Total Environment*, 242, 3–11.
- 24 Grosbois, C, Meybeck, M., Lestel, L., Lefèvre, I., & Moatar, F. (2012). Severe and contrasted  
25 polymetallic contamination patterns (1900-2009) in the Loire River sediments (France).  
26 *The Science of the Total Environment*, 435-436, 290–305.  
27 doi:10.1016/j.scitotenv.2012.06.056
- 28 Grosbois, Cecile, Horowitz, A. J., Smith, J. J., & Elrick, K. A. (2001). The effect of mining  
29 and related activities on the sediment-trace element geochemistry of Lake Coeur  
30 d’Alene, Idaho, USA. Part III. Downstream effects: the Spokane River Basin.  
31 *Hydrological Processes*, 15(5), 855–875.
- 32 Grousset, F. E., Jouanneau, J. M., Castaing, P., Lavaux, G., & Latouche, C. (1999). A 70 year  
33 Record of Contamination from Industrial Activity Along the Garonne River and its  
34 Tributaries (SW France). *Estuarine, Coastal and Shelf Science*, 48(3), 401–414.  
35 doi:10.1006/ecss.1998.0435
- 36 Hudson-Edwards, K. (2003). Sources, mineralogy, chemistry and fate of heavy metal-bearing  
37 particles in mining-affected river systems. *Mineralogical Magazine*, 67(2), 205–217.  
38 doi:10.1180/0026461036720095

- 1 Hudson-Edwards, K., Macklin, M., & Taylor, M. (1997). Historic metal mining inputs to Tees  
2 river sediment. *The Science of the Total Environment*, 194/195, 437–445.
- 3 Jarvis, A., & Younger, P. (1997). Dominating chemical factors in mine water induced  
4 impoverishment of the invertebrate fauna of two streams in the Durham Coalfield, UK.  
5 *Chemistry and Ecology*, 13(4), 249–270.
- 6 Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: a review.  
7 *The Science of the Total Environment*, 338, 3–14. doi:10.1016/j.scitotenv.2004.09.002
- 8 Kim, Y., Kim, B.-K., & Kim, K. (2009). Distribution and speciation of heavy metals and their  
9 sources in Kumho River sediment, Korea. *Environmental Earth Sciences*, 60(5), 943–  
10 952. doi:10.1007/s12665-009-0230-2
- 11 Kimball, B. A., & Runkel, R. L. (2009). Spatially Detailed Quantification of Metal Loading  
12 for Decision Making: Metal Mass Loading to American Fork and Mary Ellen Gulch,  
13 Utah. *Mine Water and the Environment*, 28(4), 274–290. doi:10.1007/s10230-009-0085-  
14 5
- 15 Kraus, U., & Wiegand, J. (2006). Long-term effects of the Aznalcóllar mine spill-heavy metal  
16 content and mobility in soils and sediments of the Guadiamar river valley (SW Spain).  
17 *The Science of the Total Environment*, 367, 855–71. doi:10.1016/j.scitotenv.2005.12.027
- 18 Lapworth, D., Knights, K., Key, R., Johnson, C., Ayoade, E., Adekanmi, M., Arisekola, T.,  
19 Okunlola, O., Backman, B., Eklund, M., Everett, P., Lister, R., Ridgway, J., Watts, M.,  
20 Kemp, S.J., & Pitfield, P. (2012). Geochemical mapping using stream sediments in west-  
21 central Nigeria: Implications for environmental studies and mineral exploration in West  
22 Africa. *Applied Geochemistry*, 27(6), 1035–1052. doi:10.1016/j.apgeochem.2012.02.023
- 23 Le Cloarec, M.-F., Bonte, P. H., Lestel, L., Lefèvre, I., & Ayrault, S. (2011). Sedimentary  
24 record of metal contamination in the Seine River during the last century. *Physics and  
25 Chemistry of the Earth, Parts A/B/C*, 36(12), 515–529. doi:10.1016/j.pce.2009.02.003
- 26 Leblanc, M., Achard, B., Othman, D. Ben, & Luck, J. (1996). Accumulation of arsenic from  
27 acidic mine waters by ferruginous bacterial accretions (stromatolites). *Applied  
28 Geochemistry*, 11(96), 541–554.
- 29 MacKenzie, A., & Pulford, I. (2002). Investigation of contaminant metal dispersal from a  
30 disused mine site at Tyndrum, Scotland, using concentration gradients and stable Pb  
31 isotope ratios. *Applied Geochemistry*, 17(8), 1093–1103. doi:10.1016/S0883-  
32 2927(02)00007-0
- 33 Macklin, M., Brewer, P., & Balteanu, D. (2003). The long term fate and environmental  
34 significance of contaminant metals released by the January and March 2000 mining  
35 tailings dam failures in Maramureş County, upper Tisa Basin, Romania. *Applied  
36 Geochemistry*, 18, 241–257.
- 37 Macklin, M. G., Brewer, P. A., Hudson-Edwards, K. A., Bird, G., Coulthard, T. J., Dennis, I.  
38 A., Lechler, P.J., Miller, J.R., & Turner, J. N. (2006). A geomorphological approach to

- 1 the management of rivers contaminated by metal mining. *Geomorphology*, 79, 423–447.  
2 doi:10.1016/j.geomorph.2006.06.024
- 3 Macklin, M. G., Hudson-Edwards, K. A., & Dawson, E. J. (1997). The significance of  
4 pollution from historic metal mining in the Pennine orefields on river sediment  
5 contaminant fluxes to the North Sea. *The Science of The Total Environment*, 194-  
6 195(96), 391–397. doi:10.1016/S0048-9697(96)05378-8
- 7 Maréchal, C., Télouk, P., & Albarède, F. (1999). Precise analysis of copper and zinc isotopic  
8 compositions by plasma-source mass spectrometry. *Chemical Geology*, 156, 251–273.
- 9 Mattielli, N., Petit, J. C. J., Deboudt, K., Flament, P., Perdrix, E., Taillez, A., Rimetz-  
10 Planchon J. & Weiss, D. (2009). Zn isotope study of atmospheric emissions and dry  
11 depositions within a 5 km radius of a Pb–Zn refinery. *Atmospheric Environment*, 43(6),  
12 1265–1272. doi:10.1016/j.atmosenv.2008.11.030
- 13 Mayes, W. M., Johnston, D., Potter, H. A. B., & Jarvis, A. P. (2009). A national strategy for  
14 identification, prioritisation and management of pollution from abandoned non-coal mine  
15 sites in England and Wales. I. Methodology development and initial results. *The Science  
16 of the Total Environment*, 407(21), 5435–47. doi:10.1016/j.scitotenv.2009.06.019
- 17 Meybeck, M. (2013). Heavy metal contamination in rivers across the globe : an indicator of  
18 complex interactions between societies and catchments. In *Proceedings of H04  
19 Understanding Freshwater Quality Problems in a Changing World* (Vol. 361, pp. 3–16).
- 20 Michard, G., & Faucherre, J. (1970). Étude géochimique de l'altération des minerais sulfurés  
21 de St. Sébastien d'Aigrefeuille. *Chemical Geology*, 6, 63–84.
- 22 Mighanetara, K., Braungardt, C. B., Rieuwerts, J. S., & Azizi, F. (2009). Contaminant fluxes  
23 from point and diffuse sources from abandoned mines in the River Tamar catchment,  
24 UK. *Journal of Geochemical Exploration*, 100, 116–124.  
25 doi:10.1016/j.gexplo.2008.03.003
- 26 Miller, J. (1997). The role of fluvial geomorphic processes in the dispersal of heavy metals  
27 from mine sites. *Journal of Geochemical Exploration*, 58, 101–118.
- 28 Ministère de la Culture, Inventaire général du patrimoine culturel, base de donnée Mérimée.  
29 Last accessed on 11/26/2013. <http://www.inventaire.culture.gouv.fr/>
- 30 Moeller, K., Schoenberg, R., Pedersen, R.-B., Weiss, D., & Dong, S. (2012). Calibration of  
31 the New Certified Reference Materials ERM-AE633 and ERM-AE647 for Copper and  
32 IRMM-3702 for Zinc Isotope Amount Ratio Determinations. *Geostandards and  
33 Geoanalytical Research*, 36(2), 177–199. doi:10.1111/j.1751-908X.2011.00153.x
- 34 Monna, F., Camizuli, E., Revelli, P., Biville, C., Thomas, C., Losno, R., Scheifler, R.,  
35 Bruguier, O., Baron, S., Chateau, C., Ploquin, A., & Alibert, P. (2011). Wild brown trout  
36 affected by historical mining in the Cévennes National Park, France. *Environmental  
37 science & technology*, 45(16), 6823–30. doi:10.1021/es200755n

- 1 Monna, F., Hamer, K., Lévêque, J., & Sauer, M. (2000). Pb isotopes as a reliable marker of  
2 early mining and smelting in the Northern Harz province (Lower Saxony, Germany).  
3 *Journal of Geochemical Exploration*, 68, 201–210.
- 4 Moore, J., & Luoma, S. (1990). Hazardous wastes from large-scale metal extraction. A case  
5 study. *Environmental Science & Technology*, 24(9), 1278–1285.
- 6 Moore, J. N., & Langner, H. W. (2012). Can a river heal itself? Natural attenuation of metal  
7 contamination in river sediment. *Environmental Science & Technology*, 46(5), 2616–  
8 2623. doi:10.1021/es203810j
- 9 Müller, J., Ruppert, H., Muramatsu, Y., & Schneider, J. (2000). Reservoir sediments—a  
10 witness of mining and industrial development (Malter Reservoir, eastern Erzgebirge,  
11 Germany). *Environmental Geology*, 39(12), 1341–1351.
- 12 Nriagu, J., & Pacyna, J. (1988). Quantitative assessment of worldwide contamination of air,  
13 water and soils by trace metals. *Nature*, 333, 134–139.
- 14 Owens, P. N., Batalla, R. J., Collins, A. J., Gomez, B., Hicks, D. M., Horowitz, A. J.,  
15 Kondolf, G., Marden, M., Page, M., Peacock, D., Petticrew, E., Salomons, W., &  
16 Trustrum, N. (2005). Fine-grained sediment in river systems: environmental significance  
17 and management issues. *River Research and Applications*, 21(7), 693–717.  
18 doi:10.1002/rra.878
- 19 Peplow, D., & Edmonds, R. (2005). The effects of mine waste contamination at multiple  
20 levels of biological organization. *Ecological Engineering*, 24, 101–119.  
21 doi:10.1016/j.ecoleng.2004.12.011
- 22 Pokrovsky, O. S., Viers, J., & Freydier, R. (2005). Zinc stable isotope fractionation during its  
23 adsorption on oxides and hydroxides. *Journal of colloid and interface science*, 291(1),  
24 192–200. doi:10.1016/j.jcis.2005.04.079
- 25 Rapant, S., Dietzová, Z., & Cicmanová, S. (2006). Environmental and health risk assessment  
26 in abandoned mining area, Zlata Idka, Slovakia. *Environmental Geology*, 51(3), 387–  
27 397. doi:10.1007/s00254-006-0334-x
- 28 Rauret, G., López-Sánchez, J. F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., &  
29 Quevauviller, P. (1999). Improvement of the BCR three step sequential extraction  
30 procedure prior to the certification of new sediment and soil reference materials. *Journal*  
31 *of Environmental Monitoring*, 1(1), 57–61.
- 32 Rolley, J., La petite histoire du plomb et du zinc en Cévennes. Last accessed on 11/26/2013.  
33 <http://www.rolley.fr/Geologie.html>
- 34 Rosman, K.J.R., & Taylor, P.D.P. (1998). Isotopic compositions of the elements 1997 (   
35 Technical Report ). *Pure and Applied Chemistry*, 70(1), 217–235.
- 36 Salomons, W. (1995). Environmental impact of metals derived from mining activities:  
37 processes, predictions, prevention. *Journal of Geochemical Exploration*, 52, 5–23.

- 1 Schwarzenbach, R. P., Egli, T., Hofstetter, T. B., von Gunten, U., & Wehrli, B. (2010).  
2 Global Water Pollution and Human Health. *Annual Review of Environment and*  
3 *Resources*, 35(1), 109–136. doi:10.1146/annurev-environ-100809-125342
- 4 Sivry, Y., Riotte, J., Sonke, J., Audry, S., Schafer, J., Viers, J., Blanc, G., Freydier, R., &  
5 Dupre, B. (2008). Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters  
6 The Riou Mort–Lot River system. *Chemical Geology*, 255, 295–304.  
7 doi:10.1016/j.chemgeo.2008.06.038
- 8 SMAGE des Gardons (2011). *Etude de la qualité des eaux du bassin des Gardons* (p. 380).
- 9 Sonke, J., Sivry, Y., Viers, J., Freydier, R., Dejonghe, L., Andre, L., Aggarwal, J., Fontan, F.,  
10 & Dupre, B. (2008). Historical variations in the isotopic composition of atmospheric zinc  
11 deposition from a zinc smelter. *Chemical Geology*, 252, 145–157.  
12 doi:10.1016/j.chemgeo.2008.02.006
- 13 Sutherland, R. (2000). Bed sediment-associated trace metals in an urban stream, Oahu,  
14 Hawaii. *Environmental Geology*, 39(6), 611–627.
- 15 Taylor, S. R., & McLennan, S. M. (1995). The geochemical evolution of the continental crust.  
16 *Reviews of Geophysics*, 33(2), 241–265.
- 17 Thapalia, A., Borrok, D., Van Metre, P., Musgrove, M., & Landa, E. (2010). Zn and Cu  
18 isotopes as tracers of anthropogenic contamination in a sediment core from an urban  
19 lake. *Environmental Science & Technology*, 44(5), 1544–50. doi:10.1021/es902933y
- 20 Vincent, M. (2006). *Les Mines des Cevennes*. (Terre Cevenole, Ed.) (p. 320).
- 21 Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica et*  
22 *Cosmochimica Acta*, 59(7), 1217–1232.
- 23 Weiss, D., Rehkdmper, M., Schoenberg, R., McLaughlin, M., Kirby, J., Campbell, P., Arnold  
24 T., Chapman J., Peel K. & Gioia, S. (2008). Application of nontraditional stable-isotope  
25 systems to the study of sources and fate of metals in the environment. *Environmental*  
26 *Science & Technology*, 42(3), 655–664.
- 27 Winkels, H. J., Kroonenberg, S. B., Lychagin, M. Y., Marin, G., Rusakov, G. V., & Kasimov,  
28 N. S. (1998). Geochronology of priority pollutants in sedimentation zones of the Volga  
29 and Danube delta in comparison with the Rhine delta. *Applied Geochemistry*, 13(5),  
30 581–591. doi:10.1016/S0883-2927(98)00002-X
- 31 Younger, P., & Wolkersdorfer, C. (2004). Mining impacts on the fresh water environment:  
32 technical and managerial guidelines for catchment scale management. *Mine water and*  
33 *the environment*, 23, 2–80.

## 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

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12

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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

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		As/Al 10 <sup>3</sup>	Cd/Al 10 <sup>3</sup>	Hg/Al 10 <sup>3</sup>	Pb/Al 10 <sup>3</sup>	Sb/Al 10 <sup>3</sup>	Tl/Al 10 <sup>3</sup>	Zn/Al 10 <sup>3</sup>
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 <sup>a</sup>	0.0012 <sup>a</sup>	0.0007 <sup>b</sup>	0.25 <sup>a</sup>	0.002 <sup>a</sup>	0.009 <sup>a</sup>	0.88 <sup>a</sup>

<sup>a</sup> Taylor and Mc Lennan 1995 ; <sup>b</sup> Wedepohl 1995

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

\*\*\*p-value <0.0001

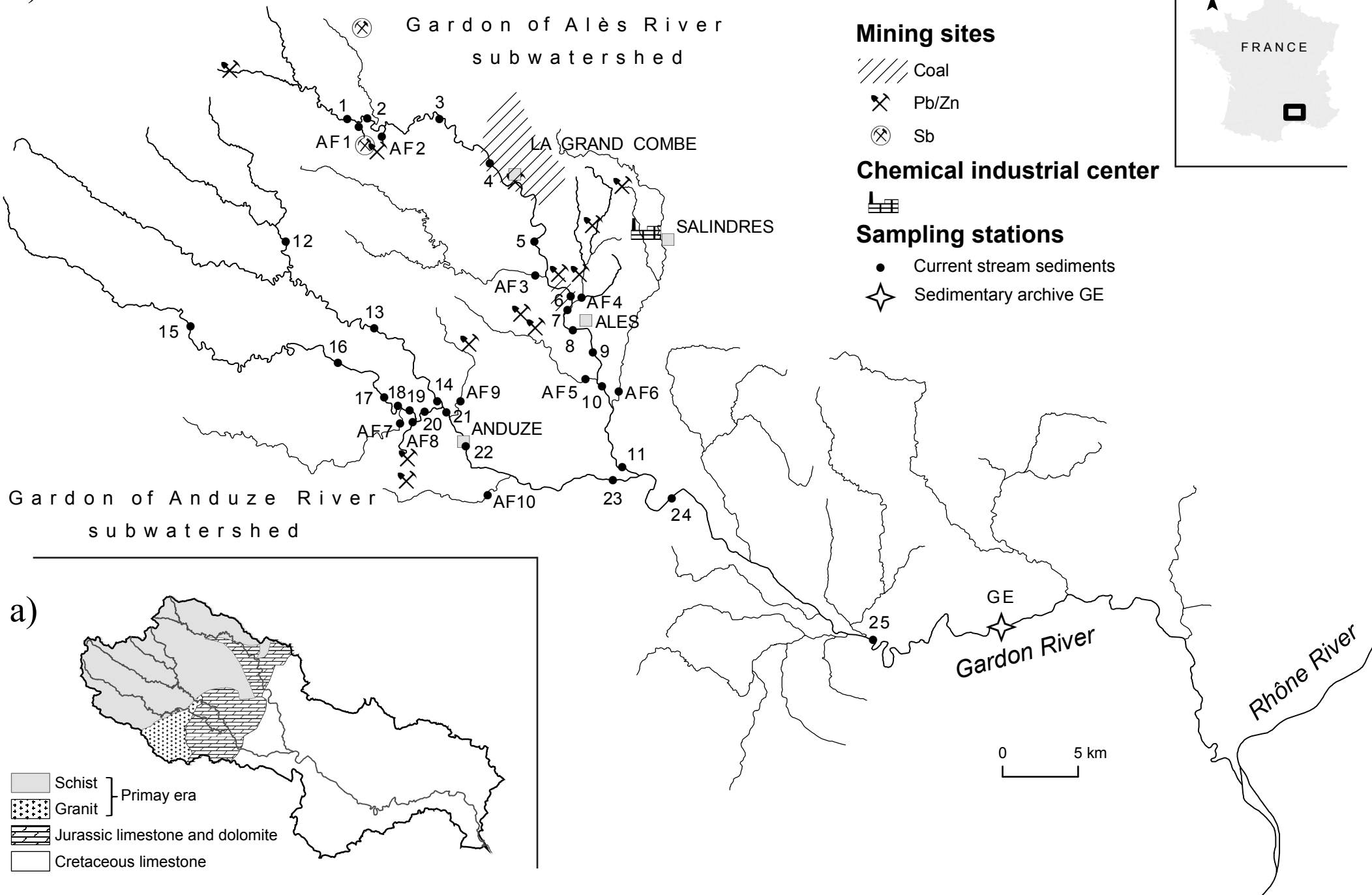
	Zn/Al	As/Al	Cd/Al	Sb/Al	Tl/Al	Pb/Al	Hg/Al
Zn/Al		<b>0.51**</b>	<b>0.93**</b>	0.17	<b>0.23*</b>	<b>0.65**</b>	<b>0.54**</b>
As/Al	<b>0.47*</b>		<b>0.48**</b>	0.07	<b>0.33*</b>	<b>0.65**</b>	<b>0.31*</b>
Cd/Al	<b>0.90**</b>	<b>0.44*</b>		0.15	<b>0.25*</b>	<b>0.67**</b>	<b>0.54**</b>
Sb/Al	0.00	0.04	0.00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

\*p-value<0.05

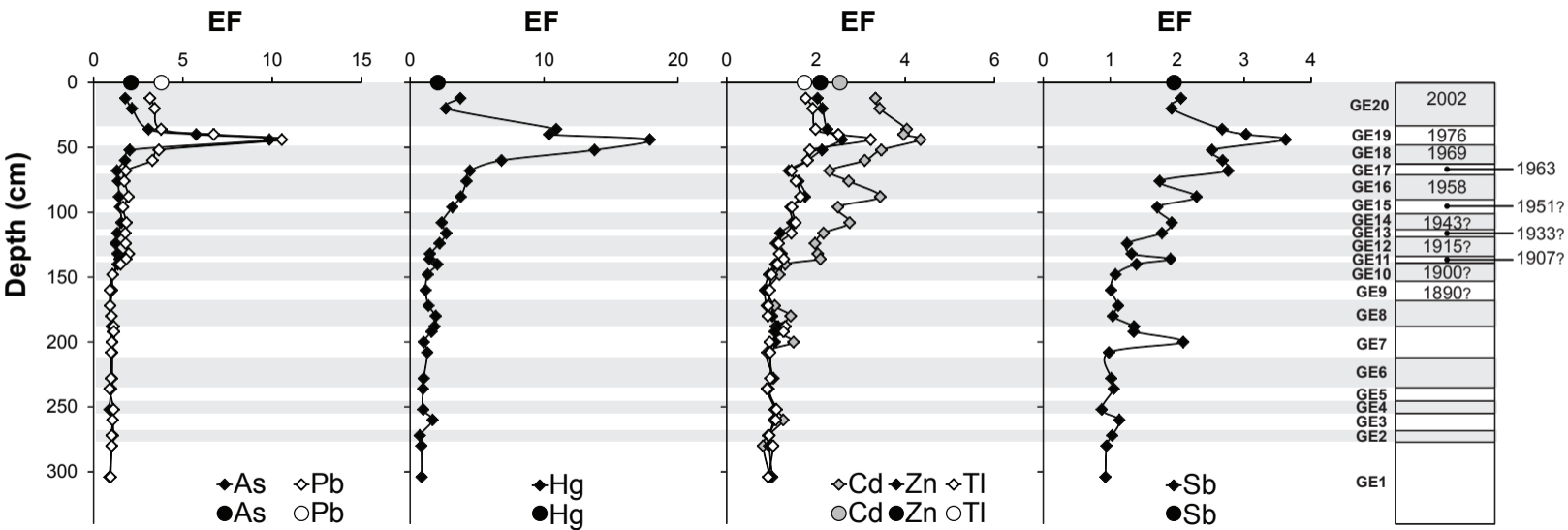
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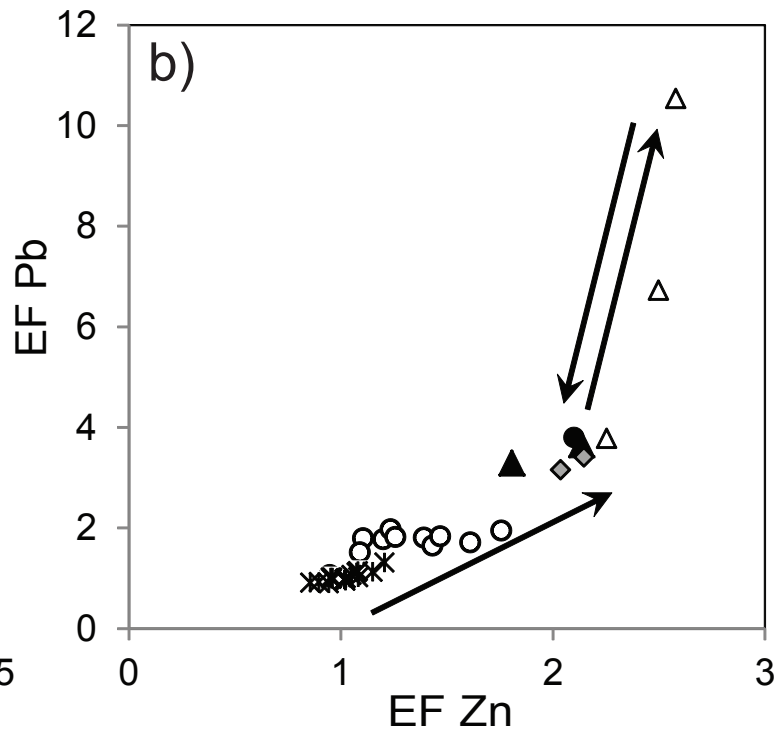
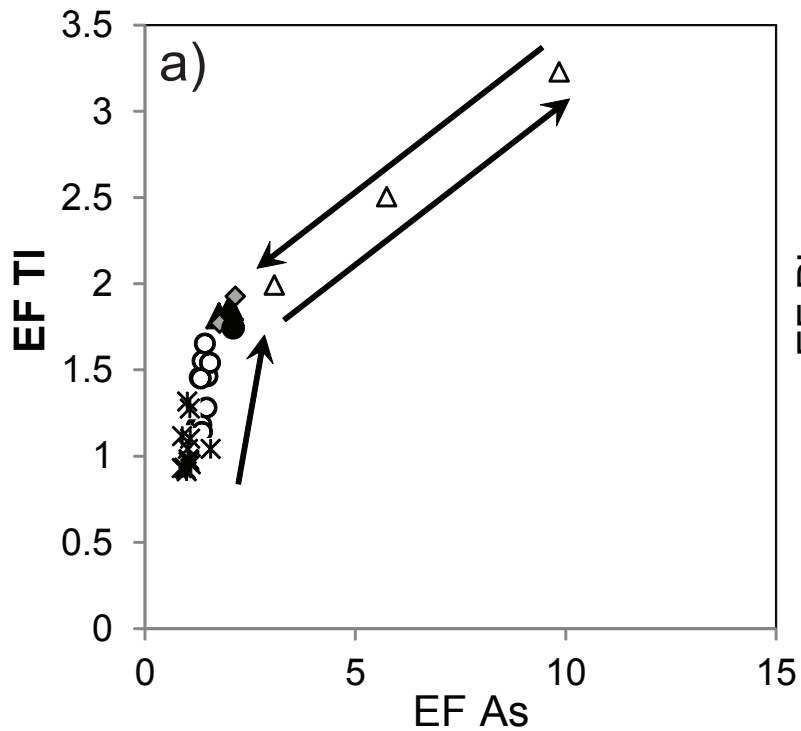
Station number	<i>Gardon of Ales River</i>				<i>Gardon of Anduze River</i>				<i>Gardon River</i>
	1	3	9	11	13	15	22	23	24
<i>Cadmium</i>									
F1	32	40	48	38	25	27	44	62	53
F2	20	16	31	10	16	17	7	11	21
F3	16	11	9	10	17	13	25	11	10
F4	33	33	12	41	42	43	24	16	16
F1+F2+F3	67	67	88	59	58	57	76	84	84
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)

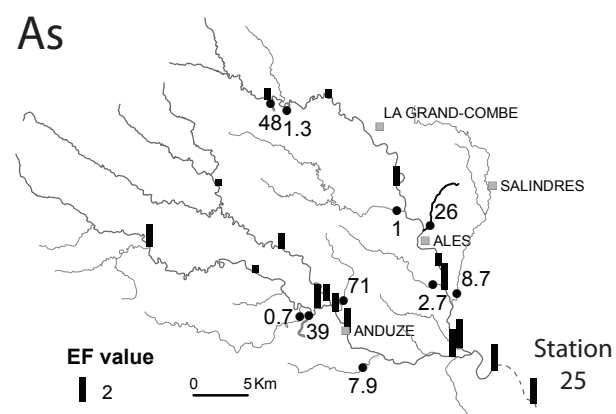
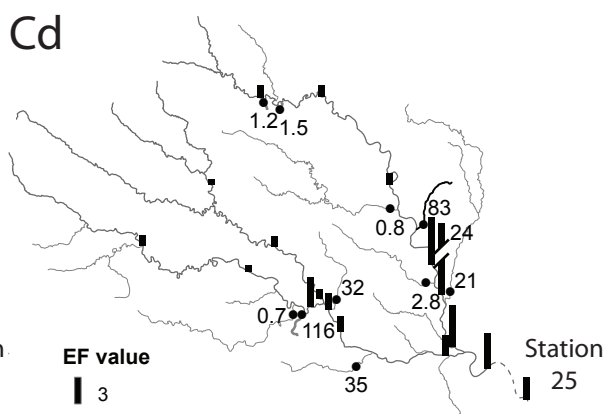
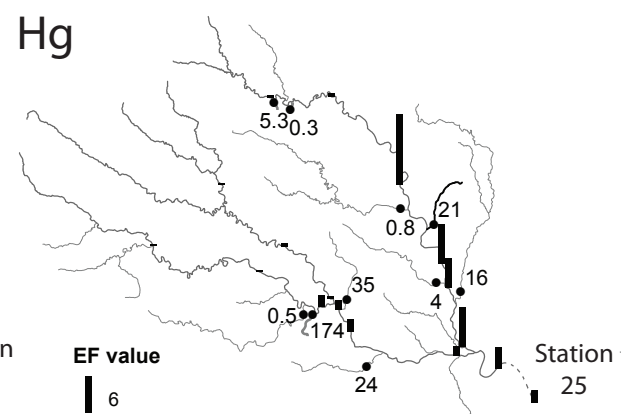
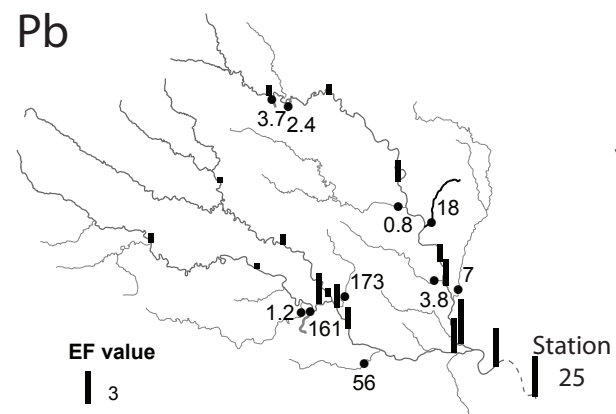
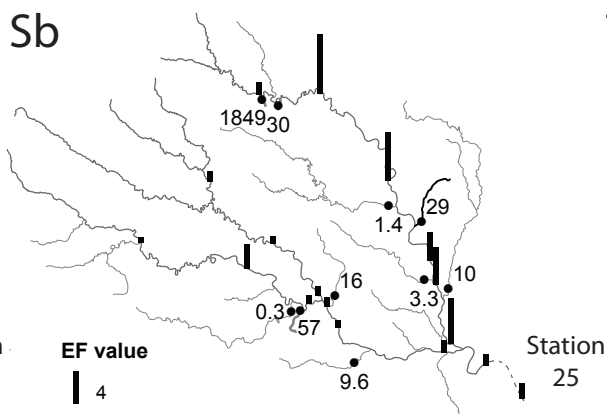
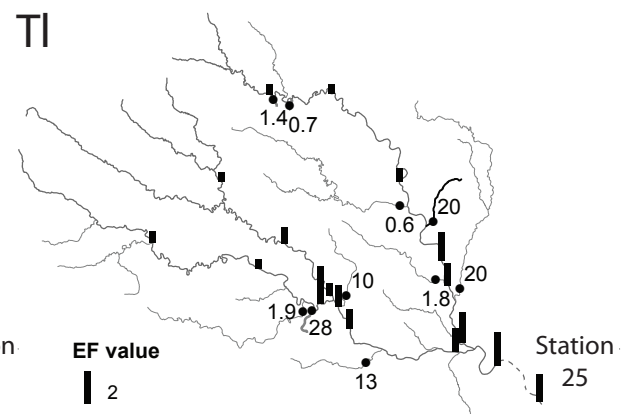
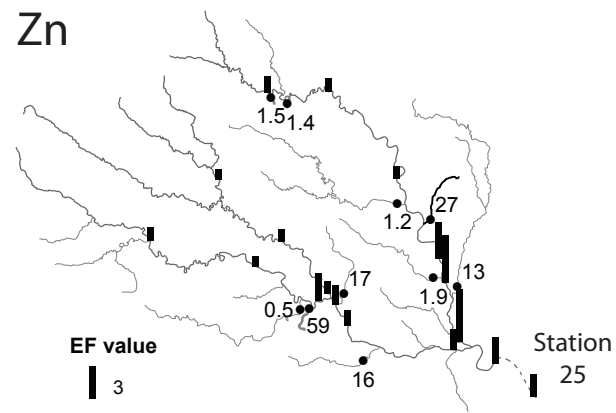






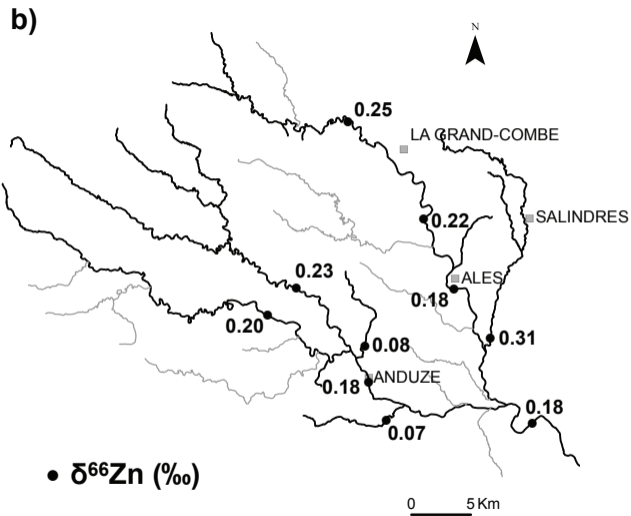
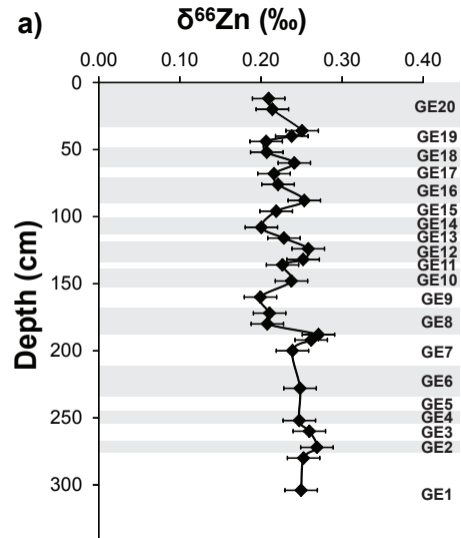


- Current stream sediment sampled at the station 25
- ◆ GE20
- △ GE19
- ▲ GE18
- GE10 to GE17
- ✱ GE1 to GE9

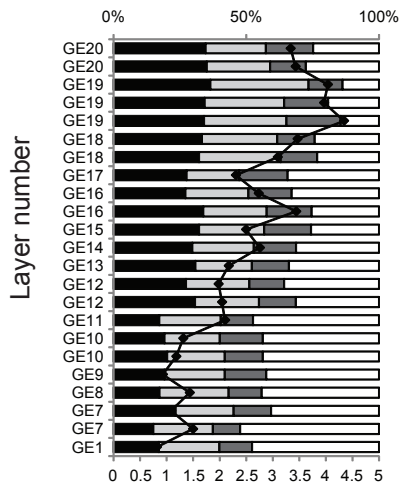
**As****Cd****Hg****Pb****Sb****Tl****Zn**

▬ Main stream EF values

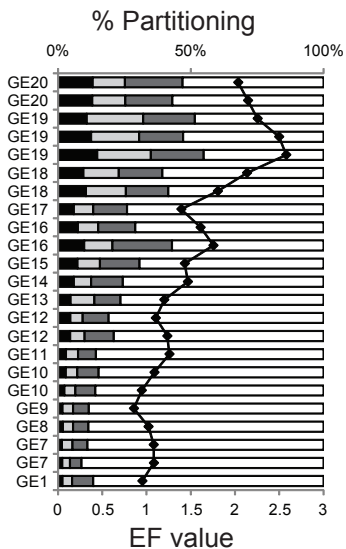
● Tributaries EF values



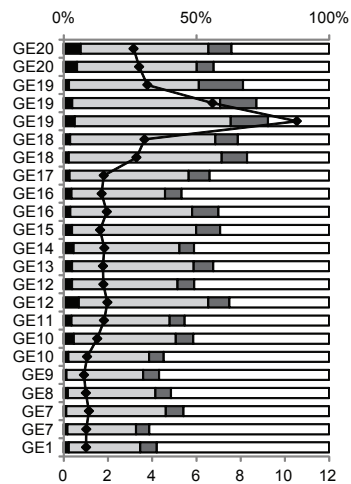
# Cd



# Zn

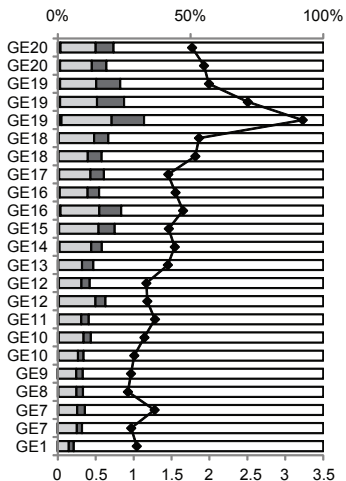


# Pb

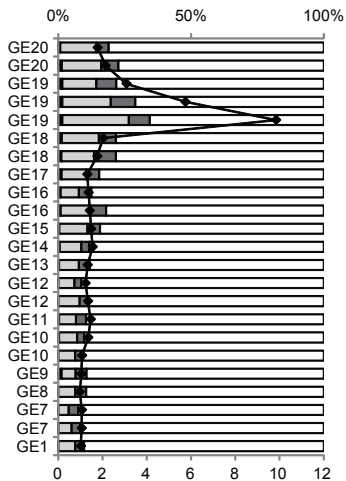


■ F1   ■ F2   ■ F3   ■ F4   ◆ EF

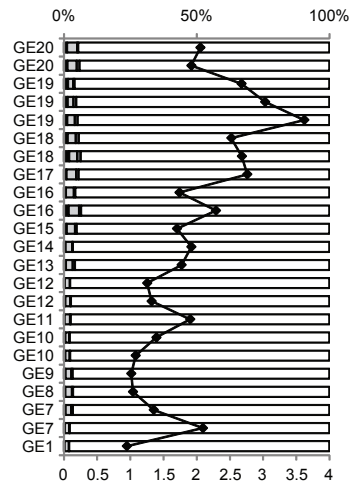
# Tl



# As



# Sb



	<b>Station</b>	<b>Longitude</b>	<b>Latitude</b>
	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 <sup>a</sup> (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

<sup>a</sup>measured from the top of the terrace

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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

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Sampling depth <sup>a</sup> (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		

<sup>a</sup>measured from the top of the terrace

n.d. not determined

Station number	As		Cd		Hg		Pb		Sb		Tl		Zn		Hydrological conditions	Sampling date	River
	$\mu\text{g}\cdot\text{g}^{-1}$	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			
1	27.5	1.0	0.34	1.4	0.009	0.4	40.1	1.0	5.58	1.6	0.72	0.7	153.5	1.6	Low flow	December 6-7, 2012	Gardon of Ales River
2	24.6	0.9	0.63	2.8	n.d.	n.d.	48.3	1.3	19.97	6.1	0.62	0.6	172.9	1.9	High flow	March 17, 2011	
3	26.0	0.8	0.37	1.4	n.d.	n.d.	45.1	1.0	51.72	13.4	0.72	0.6	142.6	1.3	Low flow	March 10, 2011	
	24.8	0.6	0.29	0.8	0.033	1.1	54.7	0.9	29.42	5.7	0.97	0.6	152.4	1.1	High flow	November 7, 2011	
	21.9	0.7	0.33	1.3	0.011	0.5	41.0	1.0	27.22	7.4	0.67	0.6	127.1	1.3	Low flow	December 6-7, 2012	
4	20.5	0.8	0.26	1.3	n.d.	n.d.	26.0	0.7	19.41	6.4	0.64	0.7	82.5	1.0	Low flow	March 10, 2011	
5	20.6	0.7	0.28	1.2	n.d.	n.d.	36.0	0.9	7.85	2.3	0.70	0.7	82.2	0.9	Low flow	March 10, 2011	
	21.8	0.9	0.20	0.9	0.048	2.5	51.1	1.4	12.38	3.9	0.71	0.7	85.3	1.0	High flow	November 7, 2011	
	42.3	1.6	0.28	1.3	0.227	11.6	76.2	2.0	19.68	6.1	0.84	0.8	105.0	1.2	Low flow	December 6-7, 2012	
6	17.4	0.6	0.59	2.5	n.d.	n.d.	67.2	1.7	4.93	1.4	1.00	1.0	194.5	2.1	High flow	March 17, 2011	
7	34.9	1.5	1.13	5.7	n.d.	n.d.	83.1	2.5	13.48	4.7	1.38	1.6	323.0	4.1	High flow	November 16, 2010	
8	29.8	1.2	0.55	2.6	0.092	5.0	58.7	1.7	8.15	2.7	1.53	1.6	192.6	2.3	High flow	November 7, 2011	
9	51.8	3.2	0.92	6.8	n.d.	n.d.	168.3	7.3	14.90	7.5	1.06	1.7	338.3	6.2	Low flow	March 10, 2011	
	24.2	1.1	1.02	5.3	0.112	6.6	54.3	1.7	10.10	3.6	1.56	1.8	265.2	3.4	Low flow	December 6-7, 2012	
10	33.5	2.2	3.11	23.7	0.058	5.0	54.3	2.4	8.92	4.6	0.81	1.4	235.4	4.4	Low flow	December 6-7, 2012	
11	13.3	0.8	0.55	4.0	0.012	1.0	34.4	1.5	4.25	2.1	0.70	1.1	167.6	3.0	Low flow	October 10, 2011	
	40.5	2.4	0.67	4.6	0.084	6.6	102.2	4.2	11.99	5.7	1.25	1.9	284.2	4.9	Low flow	December 6-7, 2012	
12	16.8	0.6	0.16	0.7	0.005	0.2	20.7	0.5	4.78	1.3	0.63	0.6	94.1	1.0	Low flow	December 6-7, 2012	Gardon of Anduze River
13	26.5	1.2	0.19	1.0	0.005	0.3	23.0	0.7	2.87	1.1	0.61	0.7	83.3	1.1	Low flow	October 10, 2011	
	31.9	1.2	0.21	1.0	0.005	0.2	28.7	0.8	2.88	0.9	0.60	0.6	99.9	1.1	High flow	November 7, 2011	
	29.4	1.3	0.23	1.2	0.009	0.5	31.1	1.0	2.47	0.9	0.88	1.0	87.1	1.1	Low flow	December 6-7, 2012	
14	20.6	1.3	0.15	1.1	0.005	0.4	18.6	0.8	2.31	1.2	0.47	0.8	62.3	1.2	Low flow	December 6-7, 2012	
15	57.5	1.9	0.31	1.2	0.005	0.2	39.4	0.9	2.60	0.7	0.80	0.7	130.0	1.2	Low flow	December 6-7, 2012	
16	27.0	1.0	0.28	1.2	0.013	0.6	59.2	1.5	0.97	0.3	0.87	0.9	121.6	1.3	High flow	November 7, 2011	
	19.3	0.6	0.19	0.7	0.007	0.3	24.0	0.6	11.42	3.0	0.67	0.6	98.7	1.0	Low flow	December 6-7, 2012	
17	47.7	2.1	0.11	0.6	0.005	0.3	35.0	1.1	1.34	0.5	1.17	1.3	58.4	0.7	Low flow	October 10, 2011	
18	30.3	1.1	0.23	1.0	0.008	0.4	39.1	1.0	1.77	0.5	1.33	1.3	96.7	1.0	Low flow	October 10, 2011	
19	29.7	1.1	0.11	0.5	0.011	0.6	55.3	1.5	1.70	0.5	1.74	1.7	71.0	0.8	Low flow	October 10, 2011	
20	46.4	2.0	0.68	3.4	0.033	1.8	99.3	2.9	3.04	1.0	2.11	2.3	213.7	2.6	Low flow	December 6-7, 2012	
21	25.3	1.5	0.27	1.9	0.021	1.7	51.4	2.2	2.46	1.2	0.83	1.3	106.0	1.9	Low flow	December 6-7, 2012	
22	35.2	1.7	0.39	2.3	0.044	2.9	68.9	2.4	2.09	0.8	1.05	1.4	109.1	1.6	Low flow	October 10, 2011	
	68.2	3.1	0.45	2.4	0.055	3.3	266.6	8.4	4.98	1.8	1.01	1.2	155.6	2.0	High flow	November 7, 2011	
	45.8	2.0	0.34	1.8	0.036	2.1	65.4	2.0	2.69	1.0	1.04	1.2	115.1	1.5	Low flow	December 6-7, 2012	
23	58.0	3.3	0.20	1.3	0.087	6.5	90.4	3.6	2.32	1.1	0.89	1.3	118.6	1.9	Low flow	October 10, 2011	
	45.5	2.3	0.39	2.3	0.023	1.5	91.7	3.2	3.73	1.5	1.14	1.5	132.6	1.9	Low flow	December 6-7, 2012	
24	52.9	2.3	0.27	1.4	0.024	1.4	120.4	3.7	3.76	1.3	1.23	1.4	159.7	2.0	Low flow	October 10, 2011	Gardon River downstream from the confluence of the Gardon of Anduze and Ales Rivers
	31.5	1.2	0.36	1.7	0.024	1.2	87.4	2.4	1.94	0.6	1.10	1.1	147.9	1.7	High flow	November 7, 2011	
	44.6	2.2	0.70	4.0	0.053	3.5	106.2	3.6	3.69	1.4	1.62	2.1	178.3	2.5	Low flow	December 6-7, 2012	
25	43.9	2.1	0.45	2.5	0.033	2.1	114.4	3.8	5.10	2.0	1.40	1.7	151.3	2.1	High flow	November 7, 2011	
AF1	1461.0	48.4	0.30	1.2	0.120	5.3	160.6	3.7	6942.15	#####	1.56	1.4	157.8	1.5	Low flow	December 6-7, 2012	Gardon of Ales River Tributaries
AF2	155.3	3.8	0.61	1.7	n.d.	n.d.	312.1	5.3	132.50	25.8	1.01	0.6	198.4	1.4	High flow	March 17, 2011	
	47.7	1.3	0.46	1.5	0.009	0.3	124.0	2.4	133.99	30.5	0.93	0.7	167.5	1.4	Low flow	December 6-7, 2012	
AF3	6.5	0.4	0.16	1.0	n.d.	n.d.	12.7	0.5	1.02	0.5	0.38	0.6	65.0	1.1	High flow	November 16, 2010	
	25.2	1.0	0.16	0.8	0.014	0.8	29.7	0.8	4.22	1.4	0.60	0.6	99.6	1.2	Low flow	December 6-7, 2012	
AF4	278.2	29.3	5.06	62.5	n.d.	n.d.	315.8	23.2	31.49	26.6	8.25	22.8	1197.0	36.7	High flow	November 16, 2010	
	240.6	26.0	6.58	83.5	0.143	20.6	238.0	17.9	33.79	29.4	7.05	20.0	855.0	26.9	Low flow	December 6-7, 2012	
AF5	34.4	2.7	0.31	2.8	0.039	4.0	69.8	3.8	5.33	3.3	0.90	1.8	85.5	1.9	Low flow	December 6-7, 2012	
AF6	50.1	6.6	1.21	18.9	n.d.	n.d.	70.8	6.5	9.01	9.6	3.89	13.5	314.0	12.1	High flow	November 16, 2010	
	45.9	4.2	1.48	16.0	0.191	23.5	69.4	4.5	6.27	4.7	7.33	17.8	354.5	9.5	High flow	November 7, 2011	
	55.3	8.7	1.15	21.3	0.074	15.7	63.4	7.0	7.97	10.1	4.91	20.4	288.0	13.3	Low flow	December 6-7, 2012	
AF7	5.4	0.2	0.08	0.3	0.013	0.6	49.4	1.2	0.10	0.0	1.90	1.8	69.0	0.7	Low flow	October 10, 2011	Gardon of Anduze River Tributaries
	15.9	0.7	0.14	0.7	0.009	0.5	40.3	1.2	0.86	0.3	1.68	1.9	42.7	0.5	Low flow	December 6-7, 2012	
AF8	216.7	38.5	5.56	116.1	0.733	173.9	1295.4	160.5	39.91	57.1	5.99	27.9	1148.1	59.5	Low flow	December 6-7, 2012	
AF9	691.8	47.5	2.57	20.8	0.372	34.1	3957.7	189.5	4.59	2.5	4.41	7.9	763.9	15.3	Low flow	October 10, 2011	
	877.9	70.3	3.47	32.6	0.365	39.0	4475.5	249.8	30.59	19.7	4.61	9.7	926.5	21.6	High flow	November 7, 2011	
	833.0	70.6	3.20	31.8	0.313	35.4	2927.2	172.9	24.14	16.5	4.63	10.3	679.8	16.8	Low flow	December 6-7, 2012	
AF10	125.4	20.2	2.83	53.7	0.163	35.1	1021.9	115.0	14.66	19.1	5.25	22.2	576.6	27.1	High flow	November 7, 2011	
	70.7	7.9	2.68	35.2	0.159	23.8	712.6	55.7	10.65	9.6	4.29	12.6	493.9	16.1	Low flow	December 6-7, 2012	

n.d. not determined