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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

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HIGHLIGHTS

- Metal(loid) contamination in sediments was investigated in multi-source context.
- Metal(loid) enrichment during the 19th century and a peak of pollution were recorded.
- Metal(loid) correlations, Zn isotopes and spatial distribution allowed to identify main sources.
- Historic mining activity remained the prevailing metal(loid) source in sediment.
- Cd, Zn and Pb may be mobilized under changing environmental conditions.

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ABSTRACT

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

1. Introduction

Mining activity is one of the most important sources of harmful metals (Pb, Zn, Cd, Tl, Hg) and metalloids (As, Sb) to rivers (Byrne et al., 2012; Hudson-Edwards, 2003; Johnson and Hallberg, 2005; Nriagu and Pacyna, 1988; Schwarzenbach et al., 2010). Damage to surface water ecosystems has been recognized in many areas in the

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United States (Caruso et al., 2008; Cherry et al., 2001; Peplow and Edmonds, 2005), the United Kingdom (Gray, 1997; Jarvis and Younger, 1997), France (Audry et al., 2004a; Monna et al., 2011), Spain (Bonilla-Valverde et al., 2004), with dramatic accidents such as those of Aznalcollar in Spain (Grimalt et al., 1999) or Maramureş County in Romania (Macklin et al., 2003). A peculiarity of mining related pollution is that tailings, waste piles, ochre sediments and contaminated floodplains continue acting as secondary sources for pollutants to downstream watershed throughout hundreds of years after the mine closure (Byrne et al., 2012; Johnson and Hallberg, 2005; MacKenzie and Pulford, 2002; Macklin et al., 1997; Younger and Wolkersdorfer, 2004). Furthermore, the extent of contamination is not strictly limited to the vicinity of mines; contaminated material (i.e. tailings, contaminated river bed and floodplain sediments) may be physically remobilized in high flow conditions (Hudson-Edwards, 2003; Hudson-Edwards et al., 1997; Miller, 1997; Moore and Langner, 2012), thus dispersing pollutants over hundreds of kilometers away from historical mining sites (Grosbois et al., 2012; Moore and Luoma, 1990; Salomons, 1995).

In Europe, the Water Framework Directive (2000/60/EC) aimed to achieve good ecological status of water bodies by 2015 and has reinforced the need for management of streams and rivers at the catchment scale (Kimball and Runkel, 2009; Mayes et al., 2009; Mighanetara et al., 2009). While metal discharges from industrial activities have decreased as a result of more stringent controls, pollution from historical mining persists and its relative contribution to anthropogenic emissions of metals and metalloids to downstream watersheds has become more important over recent years (Macklin et al., 2006). In the perspective of optimizing remediation strategies at the river basin scale, achieving maximum improvements of downstream water quality, it is essential to develop approaches allowing evaluation of the impact of abandoned mining sites on metal enrichment to downstream river systems and to distinguish metals from such sources from natural geochemical background and other anthropogenic (industrial, urban) point sources. In environmental studies, metal isotope geochemistry may be useful to complement traditional geochemical data to track metal sources and elucidate processes affecting their transport and fate in rivers (Cloquet et al., 2008; Weiss et al., 2008). Zn has five stable isotopes, ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, and ^{70}Zn, with average natural abundances of 48.63%, 27.90%, 4.10%, 18.75% and 0.62% respectively (Rosman and Taylor, 1998). Previous studies have reported Zn isotope variations (expressed as δ^{66}Zn unit) of 2.5‰ in terrestrial samples (Cloquet et al., 2006). In mining environments related studies, Zn isotopic composition of the main Zn-ore (sphalerite, ZnS) was shown to cover a large range of δ^{66}Zn from −0.17‰ to 0.64‰ with an average of +0.16 ± 0.20‰ (Sonke et al., 2008). Borrok et al. (2008) reported δ^{66}Zn values between 0.02‰ and 0.46‰ for dissolved Zn in streams draining historic mining districts in the United States and Europe. Several physical and biogeochemical reactions including evaporation, inorganic and organic adsorption, diffusion and biological uptake can induce Zn isotope fractionation (Cloquet et al., 2008). Largest Zn isotopic variations are observed associated with smelting industry; atmospheric emissions are enriched in the lighter Zn isotopes while slag are enriched in the heavier Zn isotopes (Mattielli et al., 2009; Sivry et al., 2008; Sonke et al., 2008). The potential of Zn isotopes to track pollution sources has already been demonstrated in urban, mining and smelting impacted environments (Borrok et al., 2009; Chen et al., 2008, 2009; Dolgopolova et al., 2006; Mattielli et al., 2009; Sivry et al., 2008; Sonke et al., 2008; Thapalia et al., 2010).

In the present study, we investigated the impact of abandoned mines localized in the Cevennes Mountains to metal (Pb, Zn, Cd, Tl, Hg) and metalloid (As, Sb) enrichment in the sediments of the Gardon River watershed, which is a tributary of the Rhône River. The River Gardon catchment is around 2000 km^2 with 180,000 people. Multiple mining sites are referenced on this catchment (BRGM, SIG Mines website; Vincent, 2006), including scattered metal mines (Pb, Zn, Ag, Sb) and a coal production district (Ales—La Grand-Combe). Besides, one mid-size town (Ales, 40,000 inhabitants) and a chemical and industrial center (Salindres) constitute other possible point sources of metals and metalloids to the watershed. The impact of ancient mining activity on global contamination of the watershed by metals and metalloids has never been evaluated (SMAGE des Gardons, 2011), although severe local pollution was evidenced in the vicinity of some of these mining sites (Casiot et al., 2009).

In this study, we propose a methodological framework allowing catchment-scale assessment of in-stream mining-related pollution. For this, a sedimentary archive was used to establish the natural geochemical background levels of metals and metalloids of the watershed and reconstruct a historical record of metal and metalloid enrichment. Enrichment factors were determined for current sediments of the Gardon River and for those of its main tributaries. Inter-element correlations and zinc isotope ratios were used to track the contribution of disused mining sites to sediment contamination. Geochemical associations of Pb, Zn, Cd, Tl, As and Sb, evaluated using the BCR sequential extraction procedure, allowed assessment of the potential mobility of these contaminants in the sediments.

2. Material and methods

2.1. Study area

The Gardon River watershed is located at the southeast of the Massif Central Mountains in France. This tributary of the Rhône River is 144 km long and drains an area of 2014 km^2. The watershed includes three main geological areas (1) Primary metamorphic (schists and micaschists) and igneous (granite) rocks in the upstream part of the watershed (Cevennes Mountains region), (2) Jurassic carbonate formations (limestone and dolomite) along the Cevennes Mountains boundary, (3) Cretaceous limestone formation (Gardon River gorges) and Quaternary alluvium deposits of the Rhône River in the downstream watershed (Fig. 1a, BRGM, Info Terre website). In the area of Ales–La Grand-Combe, a graben filled with Tertiary detrital sediments represents the most important coalfield of the Cevennes Mountains. Hydrologically, the Gardon River is characterized by high seasonal variability including severe low water during summer and extreme floods with peak reaching 100 times the average discharge mainly in autumn.

The upstream watershed drains many disused mining sites (Fig. 1b, Table 1). Mining activity began on the Gardon River watershed during Roman Times for Ag and Middle Ages for Ag, Pb and coal (Rolley website; Vincent, 2006). The large-scale production started from the middle of the 19th century and declined after 1960. During this period, we estimated that about 4 Mt of pyrite, 85,000 t of Zn, 50,000 t of Pb and 2570 t of Sb were produced on the Gardon River watershed leaving several millions of tons of wastes close to ore extraction and processing sites (BRGM, SIG Mines website). Exploited ores were in the form of sulfide minerals (galena and argentiferous galena for Pb and Ag, sphalerite for Zn and stibnite for Sb). These minerals were associated to other unexploited sulfide minerals such as pyrite and marcasite (FeS_2), tetraedrite ($Cu_{12}Sb_4S_{13}$), pyrargyrite (Ag_3SbS_3) and proustite (Ag_3AsS_3) described for the Carnoulès mine drained by the Amous River (AF9) (Alkaaby, 1986). On the Gardon of Anduze River subwatershed, the most important Pb/Zn mining districts were those of Carnoulès and Pallières, drained respectively by the Amous River (AF9) and the Ourne and Aiguesmortes Rivers (AF8 and AF10). Antimony mines are localized on the upstream subwatershed of the Gardon of Ales River and they are drained by the Ravin des Bernes and the Richaldon Rivers (AF1 and AF2). Downstream, in the area of Ales–La Grand-Combe, coal has been exploited intensively. Finally, the Grabieux River (AF4), the Alzon River (AF5) and the Avène River (AF6), on the Gardon of Ales River subwatershed, drain old Pb/Zn/pyrite mining sites. Most of these tributaries are impacted by metal and metalloid contamination downstream from these mining sites (SMAGE des Gardons, 2011). Pollution from the abandoned Pb/Zn mine of Carnoulès was already mentioned in 1970 (Michard and Faucherre, 1970) and to date, the Amous River remains highly impacted (Casiot et al., 2009). In addition to the extractive activity,

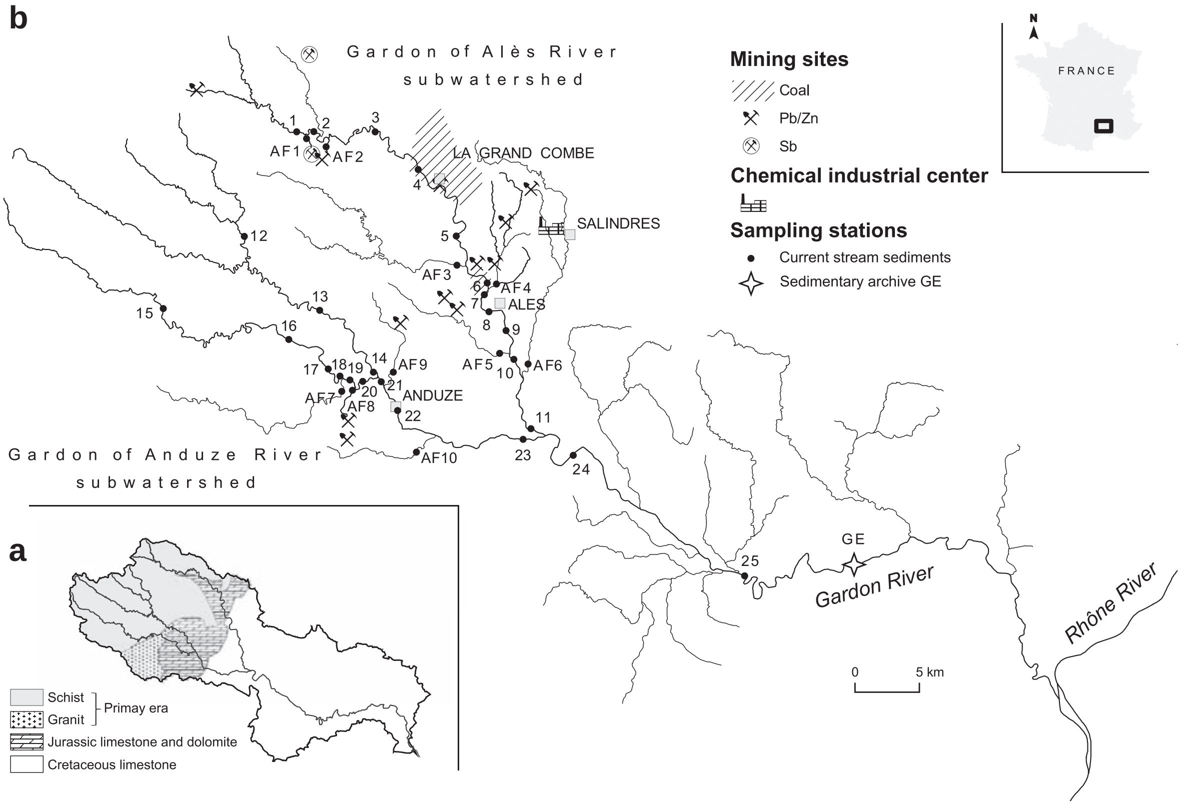

Fig. 1. a) Simplified geological map (simplified from BRGM, Info Terre website); b) Map of the study area showing the main mining sites and the sampling stations (current stream sediments sampling stations: numbers represent stations on the main stream and AFx represents stations on the tributaries;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

three smelters have been in activity on the watershed; a Zn smelter at La Grand-Combe town with a period of activity from 1846 to 1899 (Ministère de la Culture) and two small Sb smelters located on the upstream Gardon of Ales River near Sb mining sites which had worked from 1822 to 1858 and from 1896 to 1951 (BRGM, BASIAS website).

Nowadays, the chemical industrial center of Salindres and the urban area of Ales (40,000 inhabitants) can also contribute to metal and metalloid enrichment of the Gardon River. The Avene River (AF 6) is both impacted by industrial and mining discharges. According to the French Water Agency, 27 kg d^{-1} of metals and metalloids were released in 2007 in the Gardon River by industrial activities and urban wastewater treatment plants (SMAGE des Gardons, 2011).

2.2. Sampling

2.2.1. Sedimentary archive

The sedimentary archive (GE) was sampled in March 2010 in the downstream part of the watershed (Fig. 1b), in a zone of canyon. This flooding terrace, situated between 6.20 and 9.50 m above the riverbed level, was formed by the accumulation of extreme flood deposits (Dezileau et al., 2013, accepted for publication). These flood events have resulted in one sedimentary layer each. The terrace was composed of 20 layers corresponding to 20 extreme flood events; these layers were identified in the field through a close inspection of deposition breaks and/or indicators of surficial exposure (e.g. presence of a paleosol, clay layers at the top of a unit, detection of erosional surfaces, bioturbation features, angular clast layers deposits in local alcove or slope materials accumulation between flood events, fireplaces and anthropogenic occupation layers between flood events). Sedimentary layers were numbered from the bottom to the top of the terrace and named GE1 to GE20. Samples were excavated directly from the terrace using a Teflon spatula and collected in PP-jars. Sieving was not necessary because all particles were finer than 2 mm. Then, samples were air-dried, crushed in an agate mortar and homogenized before further processing. Dating of sedimentary layers was based on an original method using a multi-dating approach described in Dezileau et al.

Table 1
Gardon River tributaries characteristics. Station number AFx indicates the sampling station location on the tributaries.

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

(accepted for publication). Radionuclide analyses (^{210}Pb, ^{137}Cs) and geochemical analyses (total Pb) were used to determine age controls. Maximum ^{137}Cs activity in layers GE17 and GE18 was associated to the maximum atmospheric emission in the mid-1960s. ^{210}Pb activity results indicated that layers GE15 to GE20 were deposited after the end-1930s. Pb concentration was constant in layers GE1 to GE9 and increased from the layer GE10 showing that layers GE1 to GE9 dated back the beginning of large-scale mining activity on the watershed around 1870. These age controls were combined with the continuous record of Gardon River flow since 1890, the combined records allow to assign ages to the most recent layers, from GE9 to GE20 (Dezileau et al., 2013, accepted for publication).

2.2.2. Current stream sediments

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

2.3. Sample preparation

2.3.1. Bulk mineralization

Total digestion of sediment samples was carried out in a clean room. All material was acid-cleaned before use; reagents were Merck Suprapur quality. For each set of samples, method blanks and international certified reference materials digestion (Stream sediments LGC6189 from United Kingdom Accreditation Service and NCS DC70317 from LGC Standards) were performed. About 100 mg of sediment samples were digested in closed Teflon reactors on hot-plates at 95 °C for 24 h successively with (1) H_2O_2 35% (2) a 4:3:0.13 mL concentrated HNO_3–HF–$HClO_4$ mixture and (3) a 1:3 mL concentrated HNO_3–HCl mixture (aqua regia). Samples were cooled and evaporated to dryness between each step and at the end of the procedure. Samples were brought to 30 mL using 3 mL HNO_3 and double deionized water (Milli-Q®). Finally samples were filtered to remove possible residues.

2.3.2. Chemical purification for zinc isotopic analyses

Zn isotopic analyses were carried out on the sedimentary archive samples and on the current sediments samples of the November 2011 sampling campaign. Digested solution aliquots containing approximately 1000 ng of Zn were used for Zn separation and isotopic measurement. Zn was separated from the matrix elements by ion chromatography using AG1-MP1 anion-exchange resin (Biorad) and the elution sequence from Maréchal et al. (1999). The protocol was repeated twice to ensure Zn purity. The total procedural blank of ≈15 ng was negligible compared to the amount of Zn in samples (1000 ng). Column yields were checked for each sample by ICP-MS, X Series II (Thermo Fisher Scientific) and found to be >96%. After the purification, samples were evaporated to dryness at 60 °C. Then samples were taken up in 3.3 mL of HNO_3 0.05 N and doped with a Cu standard (Cu NIST-SRM 976); final Zn and Cu concentrations were 300 $ng \cdot g^{-1}$.

2.3.3. Selective sequential extraction procedure

Total metal and metalloid concentrations are insufficient to evaluate the potential mobility of these contaminants in stream sediments. Therefore, selective sequential extractions were performed to characterize the distribution of Pb, Zn, Cd, Tl, As and Sb in sediment samples. Selected samples from the sedimentary archive and current sediments were subjected to a four-step sequential extraction procedure using the standardized method of the European Community Bureau of Reference (BCR) described by Rauret et al. (1999). Metals and metalloids were extracted into the following four operationally defined fractions: exchangeable and carbonate fraction (F1), reducible fraction (bound to Fe and Mn oxides/hydroxides) (F2), oxidizable fraction (bound to organic matter and sulfides) (F3) and residual fraction (F4). The fraction F4 was determined using a procedure of mineralization assisted by microwaves; 100 mg of the residual solid was digested by a 2:4 mL concentrated HF:HNO_3 mixture. Then samples were cooled, evaporated to dryness and brought to 30 mL using 3 mL HNO3 and double deionized water (Milli-Q®).

2.4. Analyses

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

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

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

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

Results are also given normalized to the standard IRMM-3702 calibrated by Moeller et al. (2012) in Supplementary information (SI Tables 2 and 3).

The external analytical reproducibility (standard deviation) calculated from replicate measurements of the certified stream sediments LGC6189 from United Kingdom Accreditation Service (including column duplicate, $n = 6$) over multiple analytical sessions was 0.02‰ and δ^{66}Zn was determined at 0.18‰.

2.5. Data treatment

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

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

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

Concentrations ($\mu g \cdot g^{-1}$) and enrichment factors (EFs) are given for the sedimentary archive and the whole dataset of current stream sediments in Supplementary information (SI Tables 4 and 5).

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

3. Results

3.1. Enrichment factors for the sedimentary archive and current stream sediments

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

3.1.1. Sedimentary archive

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

The GE19 layer was particularly remarkable; a peak was recorded for all studied metals and metalloids and most markedly for As, Pb and Hg with EF value reaching respectively 9.9, 10.5 and 18. This layer was ascribed to an exceptional flood event in 1976 that caused important damage on tailings impoundment at the Pb/Zn Carnoulès mine (BRGM, BASOL website). The most recent layer GE20, which corresponded to the latest exceptional flood event in 2002 (Delrieu et al., 2005), presented drastically lower EF values compared to those recorded in the 1976-dated layer; these values were similar to those recorded in 1969 for Pb, Zn, Cd, Tl and As. The order of metal and metalloid enrichment in the sedimentary archive was Hg > Cd > Sb > Pb > As > Zn ≥ Tl except for the layer GE19 for which As and Pb were more enriched than Cd, Sb, Tl and Zn.

3.1.2. Current stream sediments

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

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

Table 2
Metal/aluminum ratios in samples examined for geochemical background determination.

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

[a] Taylor and McLennan (1995).

[b] Wedepohl (1995).

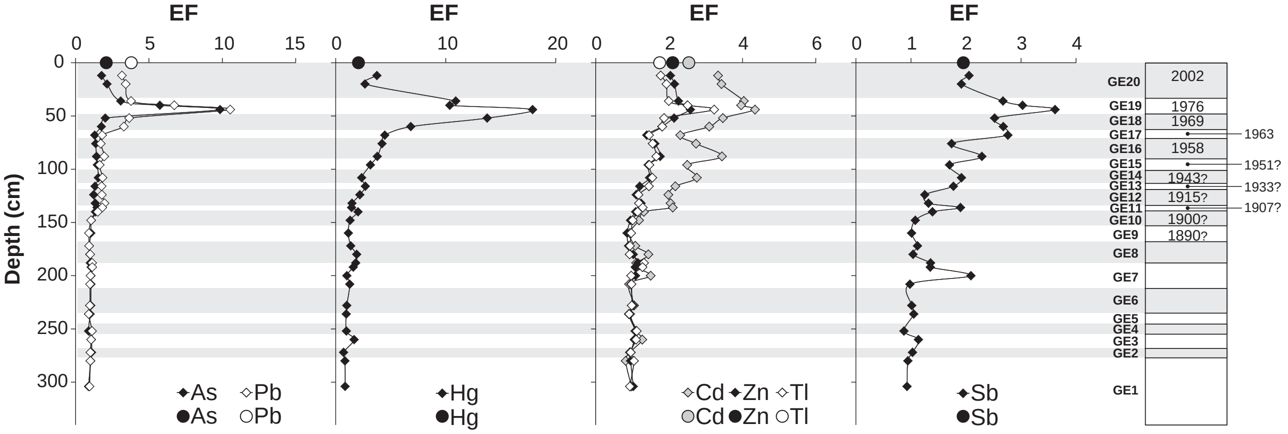

Fig. 2. Enrichment Factors (EFs) of As, Pb, Hg, Cd, Zn, Tl and Sb in sediments of the archive (◆) and in current stream sediments (●) sampled on November 2011 at the station 25. Dating is from Dezileau et al. (2013, accepted for publication).

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

3.2. Inter-element metal/aluminum ratio correlations

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

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

3.3. Zinc isotopes

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

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

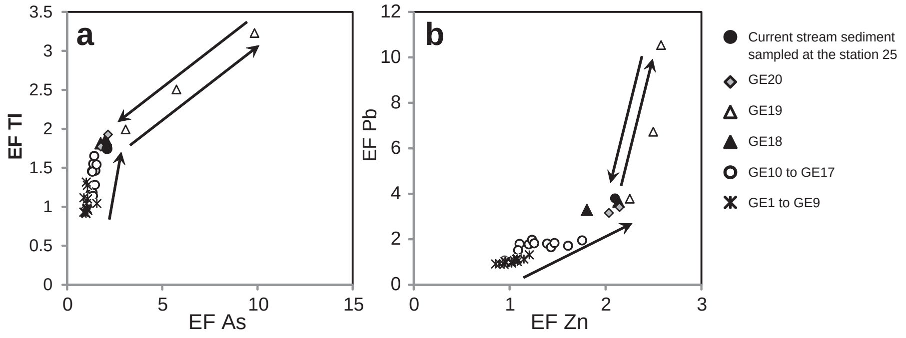

Fig. 3. Temporal evolution of a) EF Tl vs. EF As and b) EF Pb vs. EF Zn in the sedimentary archive and in the current stream sediment sampled at the station 25 in 2011.

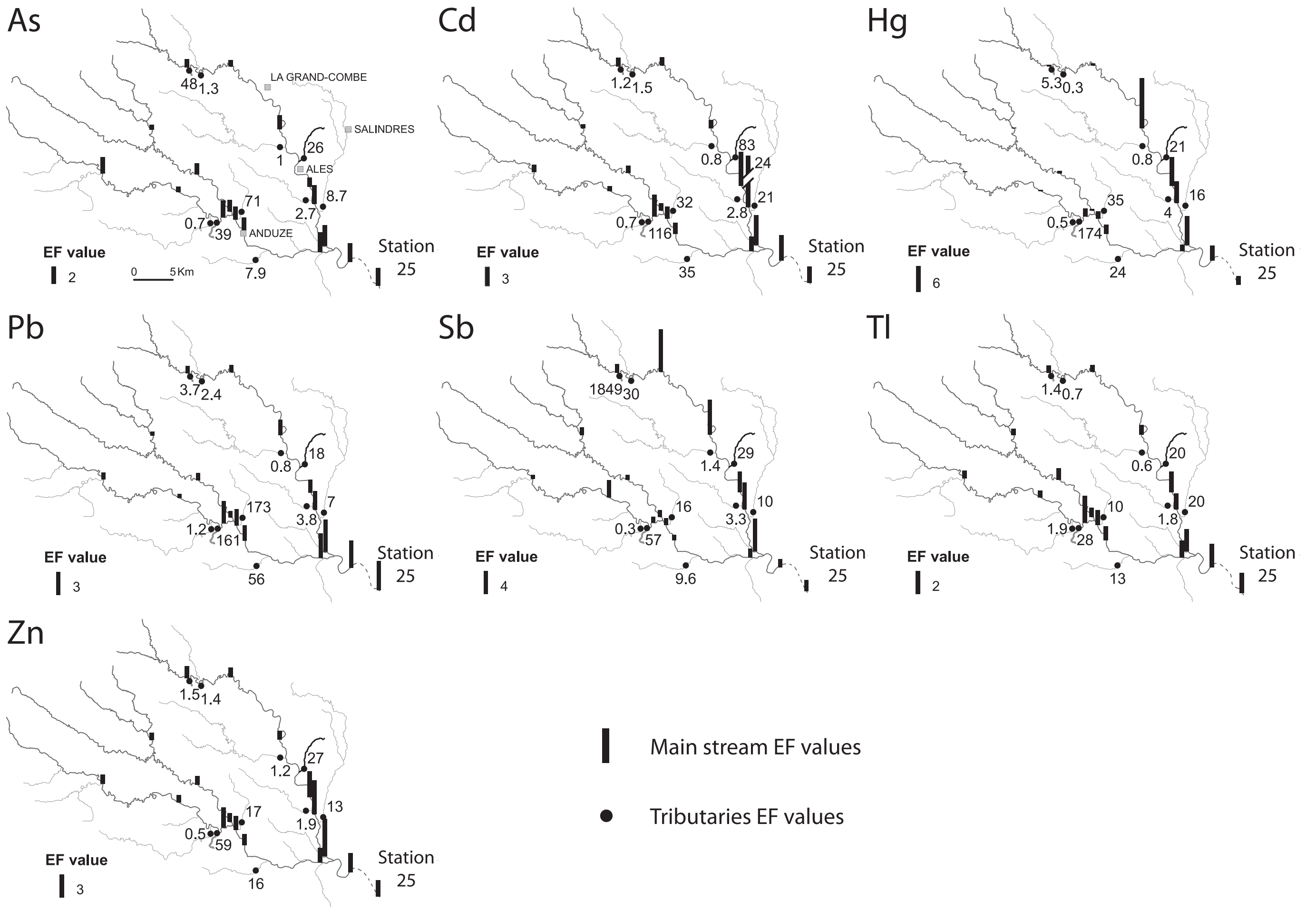

Fig. 4. Enrichment Factors (EFs) of As, Cd, Hg, Pb, Sb, Tl and Zn in sediments sampled during the most complete campaign (December 6–7, 2012). EFs are represented using bar charts for sediments of the main stream and a dot with EF value for sediments of the tributaries.

3.4. Chemical partitioning of metals and metalloids

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

Chemical partitioning of Cd, Zn, Pb, Tl, As and Sb in current stream sediments from the Gardon River was similar to that of the sedimentary archive (Table 5). Cd and Zn exhibited the highest proportion in exchangeable/carbonates fraction F1, ranging from 25% to 62% for Cd and from 6% to 37% for Zn, with the most reactive fractions (F1 + F2 + F3) accounting respectively for 71 ± 12% and 40 ± 16% (Table 5). For Pb, the reactive fractions represented 44 ± 12% and were dominated

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

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

*** p-value < 0.0001.

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

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

* p-value < 0.05.
** p-value < 0.001.

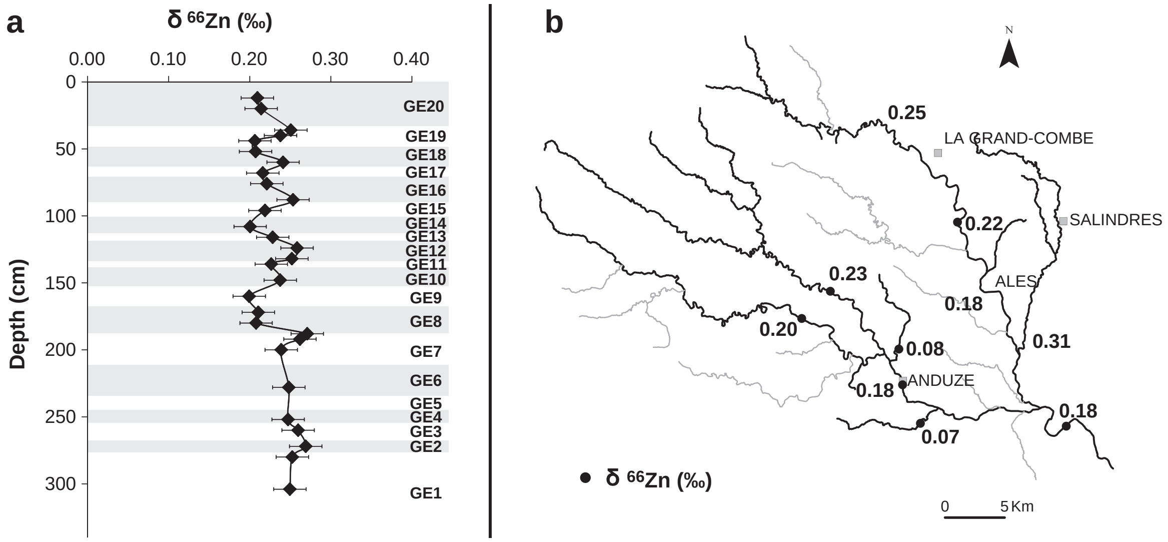

Fig. 5. a) δ^{66}Zn (‰) variations in the sedimentary archive and b) δ^{66}Zn (‰) in current stream sediments of the campaign of November 2011.

by the Fe/Mn oxyhydroxides fraction (F2 = 30 ± 8%). Tl and As were largely bound to the residual fraction (F4 > 56% and 75% respectively) with Fe/Mn oxyhydroxides fraction accounting for the majority of the remaining content. Sb was essentially contained in the residual fraction (F4 > 94%).

For Cd, Zn, Pb and to a lesser extent for Tl and As, the proportion of the most reactive fractions (F1 + F2 + F3) in main stream sediments tended to increase from upstream to downstream sites along the watershed in relation with increased EF value. F1 + F2 + F3 represented on average 62% for Cd, 27% for Zn, 40% for Pb, 6% for Tl and 12% for As in sediments of the upstream Gardon River (stations 1, 3, 13 and 15) and reached 84% for Cd, 54% for Zn, 45% for Pb, 21% for Tl and 22% for As in sediments of downstream watershed at station 24 downstream from the junction between the Gardon of Anduze and the Gardon of Ales Rivers.

4. Discussion

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

The Gardon River watershed is a typical example of an ancient mining basin with multiple sources of metal contamination. The assessment of anthropogenic metal levels in this watershed and the deciphering of the origin of these contaminants is complex for several reasons: (1) the geology of the watershed, which includes several metal-mineralized areas, contributes to high metal levels in the transported sediments, thus confounding metals from anthropogenic origin, (2) the temporal variability of the hydrological regime, typical of the Mediterranean climate, with flash flood events responsible for most of the transport and deposition of polluted sediments in the riverbed and floodplain away from their contamination sources, making it difficult to acquire representative samples. Therefore, the use of a sedimentary archive, which integrates both anthropogenic metal emissions and geochemical background related to local geology of the whole upstream watershed, combined with current stream sediment analysis, can make sense for a rigorous estimation of the contamination status of the watershed. Sedimentary archives have recently been used to reconstruct watershed contamination histories in several European river basins (Audry et al., 2004b; Ayrault et al., 2012; Ferrand et al., 2012; Gocht et al., 2001; Grosbois et al., 2012; Grousset et al., 1999; Le Cloarec et al., 2011; Monna et al., 2000; Müller et al., 2000; Winkels et al., 1998); these archives are generally floodplain cores (Ayrault et al., 2012; Gocht et al., 2001; Grosbois et al., 2012; Le Cloarec et al., 2011) or reservoir cores (Audry et al., 2004b; Müller et al., 2000). On the Gardon River watershed, there is no reservoir downstream from mining sites and it is very difficult to find intact continuous record in the floodplain mainly due to possible remobilization of sediments during flash floods which affect the watershed (Dezileau et al. accepted for publication; Delrieu et al., 2005). For these reasons, the sedimentary archive used was a high-standing flooding terrace which recorded only extreme flood events with a minimum discharge of 2100 m^3/s (Dezileau et al., 2013, accepted for publication); the recording is thus discontinuous and provides a low temporal resolution. Nevertheless, the archive has recorded (i) pre-industrial floods allowing to determine the geochemical background of the watershed and (ii) 12 floods from the late 19th century to 2002 allowing to study the evolution of contamination level throughout the industrial era. Pre-industrial levels of Pb, Zn, Cd, Tl, Hg, As, and Sb in the archive allowed to characterize the local geochemical background of the Gardon River watershed, which was highly enriched for As, Sb and to a lesser extent for Cd, Pb, Zn and Tl relatively to the Upper Continental Crust, while being slightly depleted in Hg. These results point out the importance to assess the local reference level in mine-impacted watersheds for estimation of anthropogenic status as also highlighted elsewhere (Audry et al., 2004b; Dolgopolova et al., 2006; Lapworth et al., 2012). This high geochemical background for As, Sb, Cd, Pb, Zn and Tl in the Gardon watershed was related to the presence of several mineralized areas containing pyrite, galena, sphalerite and stibnite (BRGM, SIG Mines website; Alkaaby, 1986; European Commission, 1988) on the Gardon of Ales and the Gardon of Anduze subwatersheds.

Since the late 19th century, 12 floods have been recorded by the sedimentary archive (layer GE9 to layer GE20), revealing a global enrichment of metals (Pb, Zn, Cd, Tl, Hg) and metalloids (As, Sb) in sediments of the Gardon River over time, until 1969, together with a contamination peak related to tailing dam failure in 1976 and a latest record in 2002 that presented levels similar to those of 1969 except for enrichment in Hg and Sb which was lower in 2002 than in 1969. This latest sedimentary record in 2002 might reflect remobilization of ancient floodplain sediments, acting as secondary contamination source during exceptional flooding events (Hudson-Edwards, 2003). However, the similarity of EF values in the 2002 sedimentary record and in current stream sediments (station 25), characterized by respectively high (maximum discharge of 7200 m^3/s in 2002, Dezileau et al., 2013, accepted for publication) and moderate (1140 m^3/s in 2011, Banque Hydro website) intensity floods rather points out limited improvement of sediment quality over recent years. This historical pattern contrasted with that of large French Rivers such as the Loire River (Grosbois et al., 2012), the Seine River (Le Cloarec et al., 2011) or the Rhône River

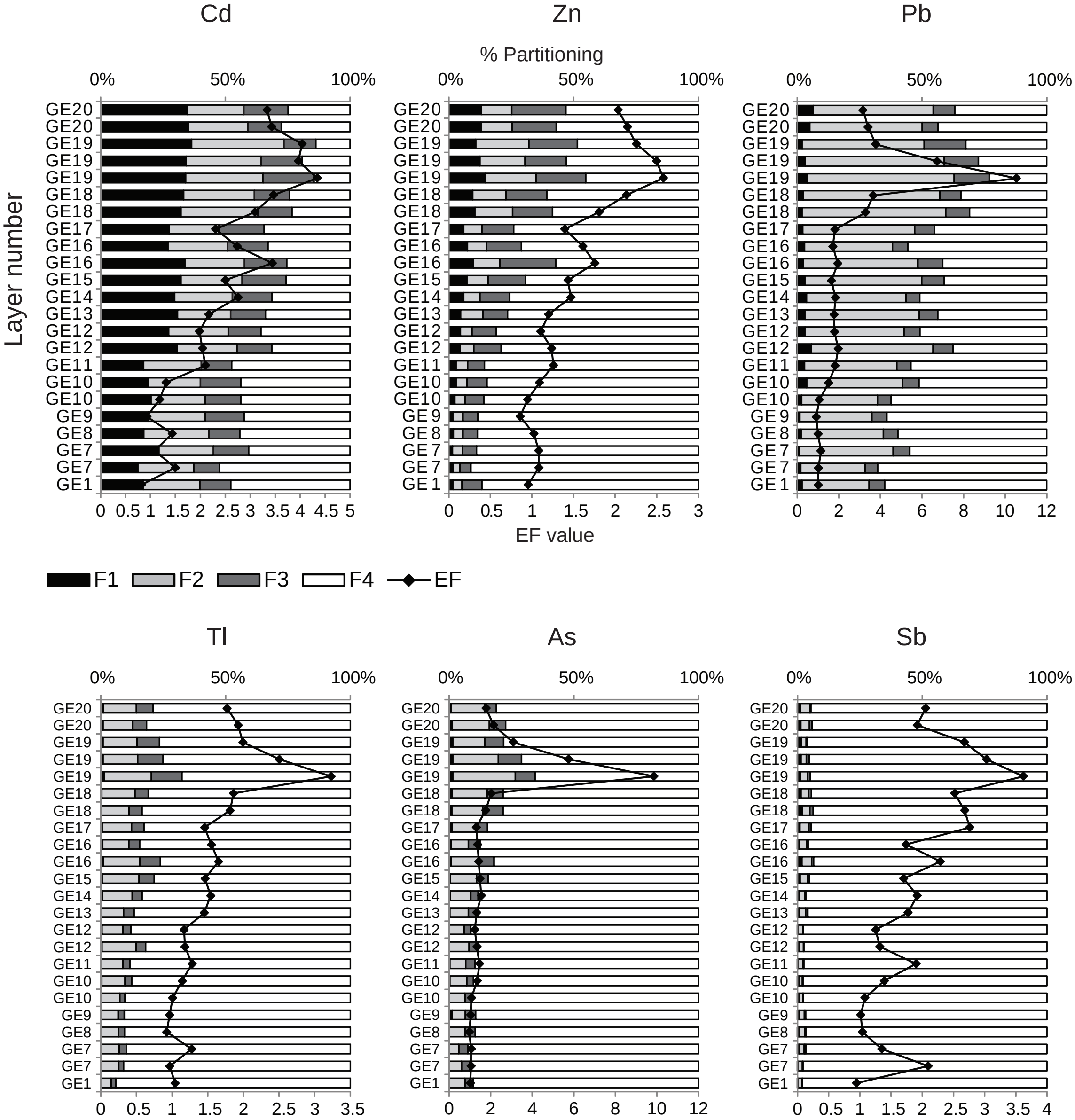

Fig. 6. Chemical partitioning of Cd, Zn, Pb, Tl, As and Sb in sediments of the archive between operationally defined fractions F1, F2, F3 and F4, expressed as percentage of total metal content and enrichment factor EF values. F1: exchangeable and bound to carbonates, F2: bound to Fe/Mn oxyhydroxides,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

(Ferrand et al., 2012) where a gradual decrease was observed for most contaminants in sediments after 1980. This general decontamination has been explained by improvement of waste water treatment, de-industrialization and industrial processes changes and generally by more stringent environmental regulations (Ferrand et al., 2012; Grosbois et al., 2012; Le Cloarec et al., 2011; Meybeck, 2013).

4.2. Current sediment contamination

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

In the sediments of the Gardon of Ales River, Hg and Sb were significantly (5 < EF < 20) to moderately (2 < EF < 5) enriched. In both the Gardon of Anduze and the Gardon of Ales Rivers, Pb, Zn, As and Cd were moderately enriched (2 < EF < 5) downstream from polluted tributaries (AF4, AF6, AF8, AF9, AF10) while EF values for Tl reflected no or minimal pollution signal in sediments. Variation of EF values along the Gardon of Ales and the Gardon of Anduze Rivers downstream from the uppermost affected tributaries differed for the following two groups of elements. For Pb, Zn, Cd, As and Tl, EF values remained almost constant, suggesting a continuous input of these elements by several polluted tributaries along the main stream (AF8, AF9 and AF10 on the Gardon of Anduze River and AF4 and AF6 on the Gardon of Ales River). For Sb and Hg, the decrease of EF values along the flowpath may reflect the prevailing contribution of sources located on the upstream watershed and then the dilution by less contaminated

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

Station number	Gardon of Ales River				Gardon of Anduze River				Gardon River
	1	3	9	11	13	15	22	23	24
Cadmium									
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
Zinc									
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
Lead									
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
Thallium									
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
Arsenic									
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
Antimony									
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

sediments, hydraulic sorting or storage in reservoir and floodplain (Byrne et 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_2), in sulfosalts (proustite Ag_3AsS_3) and in galena (PbS), antimony in sulfosalts (pyrargyrite Ag_3SbS_3) 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%) contents. 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 38,000 T 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.

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

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

To our knowledge, the δ^{66}Zn data presented in this study are the first for riverbed sediments from AMD-impacted streams. They showed an isotopic composition at δ^{66}Zn ~ 0.07‰, thus within the range of 0.02 to 0.46‰ measured for the water compartment in a variety of streams draining historical mining district in United States and Europe (Borrok et al., 2008). This lower value for AMD-impacted sediments compared to the local Zn-ore (δ^{66}Zn = 0.18‰) was unexpected considering the low isotopic fractionation during Zn sulfide dissolution (Fernandez and Borrok, 2009) and the preferential uptake of heavier Zn isotopes during adsorption on ferrihydrite, which precipitates in AMD-impacted rivers (Aranda et al., 2012; Balistrieri et al., 2008; Borrok et al., 2008). However, it probably reflects the complex processes leading to enrichment either in the heavier or in the lighter isotopes depending on the mineral phase onto which Zn is sorbed (Pokrovsky et al., 2005). Moreover, Borrok et al. (2008) highlighted that lighter isotopes are enriched in the solid reservoir during important diel fluctuations of dissolved Zn concentrations. Considering the variety of processes involved in the cycle of Zn in AMD-impacted streams, further research would be required to elucidate those controlling Zn isotopic composition in our mine-impacted streambed sediments.

4.4. Environmental significance of metal partitioning in sediments

Considering the relatively high enrichment factors for the studied metals and metalloids in the sediments of the Gardon River watershed, it is important to evaluate the potential mobility of these elements in the sediments that can act as a chemical sink or a potential source of pollutants to the overlying water. The three first fractions (F1, F2 and F3) define as exchangeable, reducible and oxidizable fractions are supposed to contain metals that may be mobilized toward the aqueous phase by changing redox conditions i.e. from reducing to oxidizing (floods, dredging), and conversely from oxidizing to reducing (early diagenesis) or pH conditions (Byrne et al., 2012). Subsequently to their release, metals may be transported downstream in the dissolved phase or they might re-distribute to another solid phase in the sediment (Audry et al., 2010; Byrne et al., 2012). Considering the percentage of metals and metalloids extracted in the fractions F1 + F2 + F3, the order of potential mobility in the sedimentary archive and in current stream sediments was Sb (1–7%) < Tl (3–34%) = As (4–35%) < Zn (9–65%) < Pb (25–77%) < Cd (48–88%). Comparison with other studies is limited due to the diversity of the extraction protocols used (Byrne et al., 2012; Filgueiras et al., 2002). Nevertheless, other authors using BCR procedure or a similar one also reported an important potential mobility for Cd, Zn and Pb in mine affected rivers. For As and Sb, geochemical associations and subsequent estimation of their potential mobility in mine-affected stream sediments differed widely through studies. Galán et al. (2003) showed that As was mainly bound to the relatively mobile pool in poorly crystallized Fe and Mn oxyhydroxides (fraction F2) in acidic Odiel and Tinto Rivers (Spain) affected by AMD while other studies reported low mobility for As in other mining impacted environments (Bird et al., 2003; Grosbois et al., 2001; Rapant et al., 2006). Association of Sb to the residual fraction evidenced in other mine-impacted watersheds (Grosbois et al., 2001; Kraus and Wiegand, 2006; Rapant et al., 2006) was ascribed to its presence in stibnite which is an insoluble sulfide phase (Kraus and Wiegand, 2006).

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

5. Conclusion

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

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

Altogether, these results showed that about fifty years after the closure of mines, the former mining sites remained the prevailing sources of Pb, Zn, Cd, Tl, Hg, As and Sb in sediments of the Gardon River, some of these contaminants initially trapped in the sediment being potentially mobilizable toward the aqueous medium by changing environmental conditions. Further studies are necessary to quantify the contribution of specific mining sites to global metal and metalloid enrichment in sediments of the Gardon River and to determine if these sediments may actually become a source of contaminant to the overlying water.

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Conflict of interest

All authors claim that they do not have any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

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