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Variation of dissolved and particulate metal(loid) (As, Cd, Pb, Sb, Tl, Zn) concentrations under varying discharge during a Mediterranean flood in a former mining watershed, the Gardon River (France)

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ABSTRACT

The variation of dissolved and particulate metal(loid) concentrations was investigated during a Mediterranean flood in a former mining watershed, the Gardon River (SE France), using high-temporal resolution sampling.

Dissolved antimony originating from the Upper Gardon River watershed underwent dilution during flood. Conversely, dissolved As and particulate As, Pb, Zn, Cd and Tl concentrations exhibited increased values during rising flood compared to low and receding flow conditions, with a double-peak shape. As, Pb, Cd and Tl concentration data in suspended particulate matter from this double-peak were distributed along two different correlation lines, showing the successive mobilization of two groups of particles highly enriched with As and Cd or Pb and Tl, both inherited from ancient Pb/Zn mines.

Metal(loid) loads during the monitored 24 h-flood event were: 0.5 kg for Cd, 19.4 kg for Sb and 204 kg for As in the dissolved phase and 24 kg for Cd, 38 kg for Tl, 94 kg for Sb, 1915 kg for As, 2860 kg for Pb and 5214 kg for Zn in the particulate phase.

Altogether, these results highlighted the importance of floods in the mobilization of metals and metalloids from ancient mining sites in Mediterranean regions, showing the need for high-temporal resolution monitoring of flood events to accurately assess the long-term contribution of mining activity to metal(loid) loads of downstream watershed.

1. Introduction

River systems that drain former mining regions are generally contaminated with metals and metalloids even long after the mining activity has ceased (Coulthard and Macklin, 2003; MacKenzie and Pulford, 2002; Macklin et al., 1997; Young, 1997). This trend is due to the persistence of contamination sources which include untreated mining waters, mining wastes, tailings and smelting slags that remained on sites as well as contaminated sediments stored downstream in riverbeds, floodplains or reservoir lakes (Hudson-Edwards, 2003; Moore and Luoma, 1990). These mining-related pollutions affect the immediate vicinity of mines and also hydrosystem further downstream (Axtmann and Luoma, 1991; Miller et al., 2004, 2007; Moore and Luoma, 1990).

In Europe, metal(loid) inputs from former mining sites often represent an obstacle to achieve the good chemical and ecological status of surface waters aimed by the Water Framework Directive (2000/60/EC) (Foulds et al., 2014; Mayes et al., 2009; Mighanetara et al., 2009; Younger and Wolkersdorfer, 2004). Assessment of water quality downstream from these former mining sites is generally based on discrete measurements of metal(loid) concentrations during baseflow, on a monthly or weekly basis at best. However, little studies have focused on metal(loid) dynamic during flood events in former mining regions although floods are particularly effective agents of metal(loid) transport in rivers (Bradley, 1984; Coynel et al., 2007; Dennis et al., 2003; Foulds et al., 2014; Gozzard et al., 2011; Miller et al., 1999; Žák et al., 2009). This is especially relevant in Mediterranean rivers affected by short and intense floods during which the great part of suspended particulate matter (SPM) and contaminant flux occur (Cánovas et al., 2008, 2012; David et al., 2012; Meybeck, 2001; Pont et al., 2002).

Significant variations of metal(loid) concentrations have been recorded in mining-impacted rivers within a single flood event both in dissolved and particulate phases. Metal-contaminated particles enter the river through erosion of mine waste tips and contaminated soils caused by heavy rainfalls (Byrne et al., 2012; Dennis et al., 2003; Gao and Bradshaw, 1995; Gozzard et al., 2011; Hudson-Edwards, 2003; Macklin et al., 2006) and reworking of historically contaminated sediments containing both primary (e.g. sulfides) and secondary (e.g. Fe and/or Al (oxy)hydroxides) metal-bearing phases (Cánovas et al., 2012; Coulthard and Macklin, 2003; Coynel et al., 2007; Dennis et al., 2003; Foulds et al., 2014; Gozzard et al., 2011; Hudson-Edwards, 2003; Macklin and Klimek, 1992; Macklin et al., 1997, 2006; Žák et al., 2009). Therefore, increasing particulate metal(loid) concentrations in SPM have been reported in relation with increasing discharge in

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mining-impacted river (Coynel et al., 2007; Lehmann et al., 1999) while the usual trend for particulate metal(loid) concentrations during floods is decreasing due to dilution by less contaminated sediment, change in grain size and exhaustion of available contaminated particles (Bradley, 1984; Bradley and Lewin, 1982; Dawson and Macklin, 1998; Schäfer and Blanc, 2002).

Furthermore, an increase of dissolved metal(loid) concentrations downstream from old mines has been reported during rising floods and was assigned to flushing of metal-rich soluble secondary sulfates which accumulated at mining sites during summer (Byrne et al., 2013; Cánovas et al., 2008, 2010; Grimshaw et al., 1976; Hudson-Edwards et al., 1999; Keith et al., 2001), contribution of contaminated subsurface water or groundwater (Byrne et al., 2013; Cánovas et al., 2008) and metal(loid) release from mineral phases (Byrne et al., 2013).

Overall, these studies have highlighted the need to monitor floods with high-temporal resolution sampling in order to better understand metal(loid) behavior and fate downstream from mining site under flood conditions. However, flood monitoring studies are scarce and often focused on small watershed at the outlet of a single mining site, only little research was carried out on medium watersheds affected by several contamination sources (Cánovas et al., 2008, 2012; Coynel et al., 2007).

The aim of this study was to investigate temporal variability of dissolved and particulate metal(loid) concentrations during a Mediterranean flood in a former mining watershed of medium size, the Gardon River watershed (France). For this purpose, spatial surveys of metal(loid) concentrations were carried out during low and high flow. Moreover, high-temporal resolution sampling was performed during two consecutive floods at two stations of the Gardon River watershed and SPM, dissolved and particulate metal(loid) concentrations were determined.

2. Study area

2.1. Geological characteristics and mining legacy of the Upper Gardon River

The Gardon River is the most southern tributary of the Rhône River (SE France, Fig. 1). The Upper Gardon River is divided into two main sub-basins; the Gardon of Anduze watershed (~627 km^2) and the Gardon of Ales watershed (~448 km^2); from its headwaters in the Cevennes Mountains to the junction of the two subwatersheds at Ners, the Gardon River has a drainage area of 1100 km^2 (Fig. 1).

The Upper Gardon River drains granitic and metamorphic bedrocks belonging to the Paleozoic geological formations of the French Massif Central. The middle and lower parts are underlain by Jurassic (west) to Cretaceous (east) carbonated formations (BRGM, Infoterre website; Resongles et al., 2014).

Land occupation on the Upper Gardon River consists mainly in forest, being 76% for the Gardon of Ales subwatershed and 89% for the Gardon of Anduze subwatershed (Corine Land Cover 2006 data). There is also one mid-size town, Ales (~40,000 inhabitants) and a chemical industrial center at Salindres (Fig. 1). The Upper Gardon River drains many former mining sites exploited mainly for Pb, Zn, Sb, pyrite and coal. Modern exploitation occurred from the mid-19th century to the end of the 1960s and let large amounts of mining wastes on sites (Table 1). This ancient exploitation has durably enriched the Gardon River sediments with As, Cd, Hg, Pb, Sb, Tl and Zn (Resongles et al., 2014). This enrichment reaches a factor 24 for main stream sediments compared to the local geochemical background and a factor 1849 for mine-impacted tributaries (Aiguesmortes, Amous, Avène, Ourne, Grabieux, Ravin des Bernes, Richaldon) (Resongles et al., 2014).

2.2. Hydrological characteristics of the Upper Gardon River

The Gardon River is characterized by a Mediterranean hydrological regime i.e. high seasonal variations (Fig. 2a). Its mean annual discharge maximum during the studied period (2011–2013) was 26.6 m^3/s at Ners, 15.4 m^3/s at Anduze and 6.9 m^3/s at Ales (Banque Hydro website). Summer flows are very low with mean monthly discharge generally below 3 m^3/s at Ners during July and August. In spring and autumn, the Gardon River watershed is affected by flash flood events, with instantaneous discharges which can reach more than 100 fold the mean annual discharge (Delrieu et al., 2005; Dezileau et al., 2014). These floods are caused by heavy rainfalls: precipitations greater than 200 mm can be recorded in a single day while the average annual precipitation ranges between 500 and 1100 mm (Dezileau et al., 2014).

During the studied period, three main flood events occurred in March 2011, November 2011 and March 2013 (Fig. 2a). The instantaneous peak discharge and average daily discharge at Ners reached

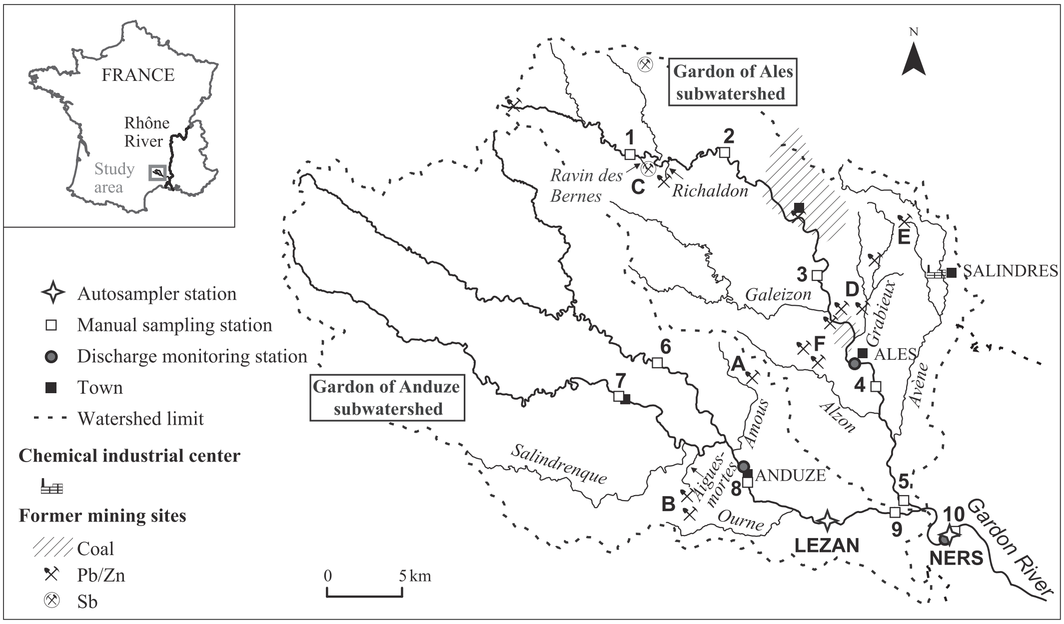

Fig. 1. Map of the studied area, showing the sampling station locations (details are given in Table 1 for mining districts indicated by letters A–F).

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Table 1
Largest mining districts, their metal production, remaining wastes and the rivers that drain sites (Alkaaby, 1986; BRGM, SIG Mines website).

Mining district	Metal production	Mining wastes	Impacted river	Location code (Fig. 1)
Carnoulès	Pb 30,000–65,000 t; Zn 3500 t; Ag 20 t	1.3 Mt	Amous	A
Pallières	Zn 80,000 t; Pb 20,000 t; Ag 22 t	0.27 Mt	Ourne and Aiguesmortes	B
La Felgerette	Sb 2750 t	38,000 t	Ravin des Bernes	C
Le Soulier	Pyrite 4 Mt; Pb; Zn	1 Mt	Gardon of Ales, Grabieux	D
Rousson	Zn 4300 t; pyrite	n.d.	Avène	E
Saint Jean du Pin	Zn 1000 t; pyrite 2000 t	n.d.	Alzon	F

716 m^3/s and 403 m^3/s, respectively, in March 2011, 1110 m^3/s and 670 m^3/s in November 2011, 820 m^3/s and 431 m^3/s in March 2013 (Banque Hydro website).

3. Materials and methods

3.1. Sampling

3.1.1. Spatial sampling

Three spatial sampling campaigns were carried out throughout the Upper Gardon River watershed in 2011 and 2012; sample locations are indicated in Fig. 1. One campaign in December 2012 was representative of winter low flow conditions (no significant rainfall in the previous 3 weeks). Campaigns in March 2011 and November 2011 were carried out during high flow periods, 1 and 4 days after the flood peak of two major floods, respectively (Fig. 2).

For the three campaigns, water samples for the analysis of dissolved metal(loid) concentrations were filtered in the field as described in Section 3.2.1. In November 2011, SPM and particulate metal(loid) concentrations were also determined. For this, 2 L of raw water were sampled in acid-cleaned HDPE bottles and filtered immediately back to the laboratory as described in Section 3.2.2.

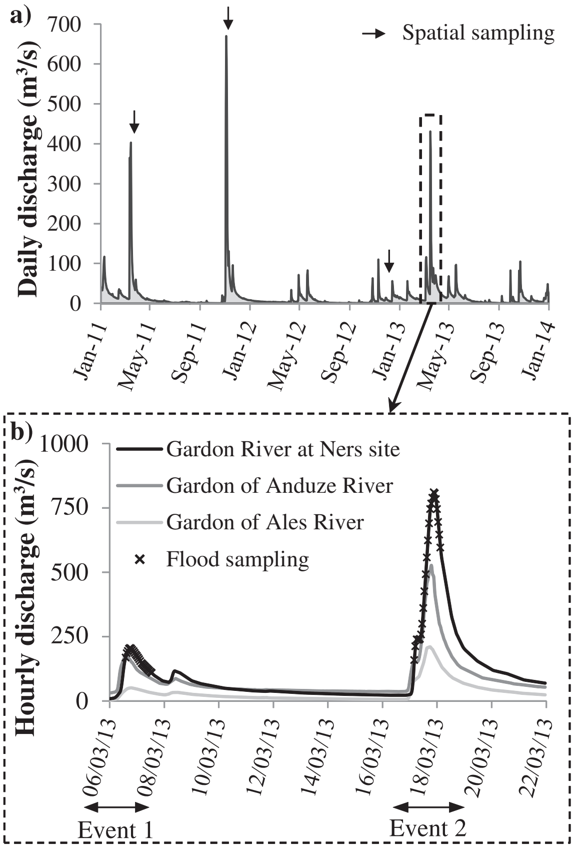

Fig. 2. a) Daily discharge (in m^3/s) measured at Ners from 2011 to 2013; arrows represent spatial sampling campaign dates. b) Hourly discharge in m^3/s measured at Ners and at Anduze and Ales towns during the two monitored floods of March 2013, crosses represent sample collection.

3.1.2. Flood monitoring

Two consecutive flood events (Event 1 on 6–7 March 2013 and Event 2 on 17–18 March 2013, Fig. 2b) were monitored with high resolution sampling during 24 h each at two sampling sites (1) at the station "Lezan" situated ~7 km upstream from the outlet of the Gardon of Anduze subwatershed and (2) at the station "Ners" (station 10) downstream from the confluence between the Gardon of Anduze and the Gardon of Ales Rivers (Fig. 1). Hourly discharge reached 171 m^3/s at Anduze station (~6 km upstream from the Lezan site) and 206 m^3/s at Ners station during Event 1; it reached 527 m^3/s and 811 m^3/s, respectively, during Event 2. This second flood event was characterized by a temporary steady flow pattern during the rising limb of the hydrograph (Fig. 2b).

Flood samples were collected using two automatic samplers manually triggered (Sigma SD900 at the Lezan site and Isco 6712 at the Ners site). Water was pumped using a peristaltic pump and a ~10 m PTFE sampling tube. Its outlet was equipped with a polypropylene strainer and fixed on a bridge pier (Lezan station) or a water mill wall (Ners station) to prevent the sampling tube washout during floods. In such a way, water was pumped at 1 m from the riverbank and 0.5 m above the riverbed. Such a setting was shown to be adapted to automatic sampling in river systems (Coynel et al., 2004).

Automatic samplers were scheduled to collect a sample of 1 L every hour during a 24 h-period. An automatic purge allowed rinsing the sampling tube before each sampling to avoid sample cross-contamination. Water samples were stored in acid-cleaned 1 L polypropylene bottles. Finally, samples were retrieved at the end of the program (within 6 h) and were filtered back to the laboratory within less than 72 h after collection. For technical reasons, the record of the Event 1 started at the flood peak at Lezan and 4 h before the flood peak at Ners.

3.2. Sample treatment

3.2.1. Dissolved metal(loid) concentrations

Filtrations were performed using a syringe and a disposable 0.22 µm cellulose acetate syringe filter rinsed with river water before sample filtration. Filtrates were collected in acid-cleaned HDPE bottles, acidified to 1‰ with HNO_3 (14.5 M, suprapur) and stored at 4 °C until analysis. The filtrate will be referred to dissolved fraction, although colloidal particles may pass through 0.22 µm filters.

3.2.2. SPM concentrations

Determination of SPM concentrations was performed by filtration of a precise volume (from 150 mL to 900 mL) of homogenized water through acid-cleaned, dried and pre-weighed 0.22 µm PVDF filters (Millipore) fitted on polycarbonate filter holders (Sartorius). Then, filters were dried in a desiccator until constant weight. Three successive weighing were performed after the drying step to estimate weight reproducibility. The collected SPM mass ranged from 4.7 mg to 194 mg (43 mg of average). Weighing error (relative standard deviation) was better than 5% even for low masses. Filters were stored in a freezer for subsequent acid digestion and particulate metal(loid) concentration determination.

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3.2.3. Particulate metal(loid) concentrations

Filters with SPM were digested in closed Teflon reactors on hotplates at 100 °C for 24 h with 4 mL HNO_3 (14.5 M, suprapur) and 3 mL HF (22.6 M, suprapur). After cooling, filters were rinsed with double deionized water (Milli-Q) and removed. The remaining solutions were evaporated to dryness at 65 °C. Finally, samples were brought to 30 mL using 3 mL HNO_3 (14.5 M, suprapur) and 27 mL of double deionized water (Milli-Q). For each set of samples, method blanks and certified reference river sediments (NCS DC70317 from LGC Standards) were digested in the same way.

3.3. Analysis

3.3.1. Determination of dissolved and particulate metal(loid) concentrations

Dissolved and particulate metal (Cd, Pb, Tl, Zn) and metalloid (As, Sb) concentrations were measured using ICP-MS (X7 Series II and iCAP Q, equipped with a CCT — Collision Cell Technology chamber — Thermo Scientific). Concentrations were determined with external calibration using In and Bi as internal standards to correct potential sensitivity drifts. The quality of analysis was checked by analyzing international certified reference waters (CNRC SLRS-5, NIST SRM 1643e). Accuracy was better than 5% relative to the certified values and analytical error (relative standard deviation) was better than 5% for concentrations ten times higher than the detection limits.

For mineralized solid samples, accuracy was within 10% of the certified values for reference standards (NCS DC70317 from LGC Standards, n = 5). Finally, mineralization blanks represented less than 5% of particulate metal(loid) concentrations; except for Sb and Zn in a set of samples for which these elements were excluded from the results.

3.3.2. Assessment of the potential alteration of samples during storage in automatic sampler

To evaluate potential sample alteration during storage in the automatic sampler (e.g. eventual sorption of metal(loid) onto SPM or bottle walls), we compared dissolved concentrations in two samples from stations Lezan and Ners after immediate filtration in the field and after 72 h storage at 6–10 °C followed by filtration in the laboratory (Table 2).

Recovery averaged 100% for As, Cd and Sb in the dissolved fraction after 72 h storage in whatever hydrological conditions (high or low SPM concentration). Conversely, recovery was lower than 100% for Pb and Zn and higher than 100% for Tl, showing adsorption (Pb, Zn) or desorption (Tl) of these elements onto/from SPM during 72 h storage, in an extent which appeared to depend on SPM concentration (Table 2). Therefore, temporal variations of dissolved concentrations during the flood will be presented only for As, Cd and Sb.

However, particulate concentrations will be presented for all studied metals and metalloids (As, Cd, Pb, Sb, Tl and Zn) because the contribution of adsorption (Pb, Zn) or desorption (Tl) evidenced during storage (Table 2) and that modified significantly dissolved concentration values for Pb, Zn and Tl appeared to affect very slightly particulate concentrations. Indeed, concerning Tl in samples from the monitored flood, if we consider that all Tl present in the dissolved phase originates from desorption during storage (which is the worst case), particulate Tl concentrations during the flood would be underestimated by no more than 26% (Supplementary data, Fig. 1). Concerning Pb and Zn, previous unpublished dissolved concentration data obtained after filtration in the field in various hydrological conditions (high and low flow) at Lezan (n = 5) and Ners (n = 4) indicated low values, less than 0.82 µg/L for Pb and less than 6.3 µg/L for Zn (Supplementary data, Fig. 2), showing that dissolved Pb and Zn concentrations were low in whatever hydrological conditions. Dissolved concentrations represented 18% (Zn) and 5% (Pb) of total (dissolved + particulate) Zn and Pb concentrations in our November 2011 survey (Section 4.1.2), in agreement with the predominant association of these elements to the particulate phase in river systems at near neutral pH (Gaillardet et al., 2003; Masson et al., 2006; Ollivier et al., 2011). Thus, Pb and Zn present in the dissolved phase in our flood samples would reasonably not contribute to significantly increase the particulate concentration values during storage.

3.3.3. Metal(loid) load assessment

Dissolved loads of As and Sb during the second monitored 24 h-flood at Ners were calculated using hourly discharge (Q_h) (Banque Hydro website) and hourly dissolved concentrations (C_d) (Eq. (1)). Particulate loads of metal(loid)s were estimated using hourly discharge, hourly SPM concentration (C_{SPM}) and hourly particulate metal(loid) concentrations (C_p) (Eq. (2)).

$$\text{Dissolved load}: L_D = \sum (Q_h \times C_d). \qquad (1)$$

$$\text{Particulate load}: L_P = \sum (Q_h \times C_{SPM} \times C_p). \qquad (2)$$

4. Results

4.1. Spatial distribution of dissolved and particulate metal(loid) concentrations at high and low flow

4.1.1. Dissolved metal and metalloid concentrations

Dissolved concentrations of the studied elements along the Gardon River watershed exceeded world river averages up to 3- (Pb), 13- (As), 19- (Zn), 52- (Tl) and 161-fold (Sb), with the exception of Cd (Fig. 3) (Gaillardet et al., 2003). The highest concentrations were obtained at low flow for Cd, Sb, Tl and Zn (stations 4 and 5 for Cd, Tl and Zn; stations 2 to 5 for Sb, Fig. 3) and at high flow for Pb (stations 2 to 4 and 8 to 10) while As concentration did not vary significantly between high flow and low flow during these spatial surveys, showing different dynamics of the studied elements relatively to hydrological conditions. The concentrations of Cd, Sb, Tl and Zn were higher along the Gardon of Ales subwatershed (Fig. 3b, d, e, f, zone 1) than along the Gardon of Anduze subwatershed (Fig. 3b, d, e, f, zone 2), while the reverse was observed for As (Fig. 3a); no clear trend was evidenced for Pb in the dissolved phase (Fig. 3c). For Sb, a general decrease of dissolved concentrations was observed from upstream to downstream stations along the Gardon of Ales subwatershed (Fig. 3d, zone 1). This dilution pattern suggests that the predominant Sb sources were localized at the uppermost course of the subwatershed, where ancient Sb mines are present. Conversely, Cd, Tl and Zn concentrations increased from upstream (1, 2, 3) to downstream (4, 5) stations along the Gardon of Ales subwatershed, showing significant inputs downstream station 3, where several Pb/Zn mines and the urban area of Ales are localized (Fig. 1).

Table 2
Comparison of dissolved concentrations in the filtrates when filtration was performed at t = 0 h and t = 72 h.

	Filtration delay	SPM	As	Cd	Pb	Sb	Tl	Zn
		mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Ners station	t = 0	<5	5.45 ± 0.06	0.009 ± 0.002	0.234 ± 0.003	0.99 ± 0.01	0.086 ± 0.002	1.31 ± 0.09
	t = 72 h		5.1 ± 0.1	0.008 ± 0.003	0.171 ± 0.001	1.00 ± 0.02	0.094 ± 0.002	1.36 ± 0.06
Lezan station	t = 0	71	5.7 ± 0.1	0.010 ± 0.002	0.82 ± 0.01	0.57 ± 0.02	0.071 ± 0.001	3.18 ± 0.01
	t = 72 h		5.6 ± 0.2	0.010 ± 0.002	0.136 ± 0.001	0.60 ± 0.02	0.116 ± 0.001	0.28 ± 0.02

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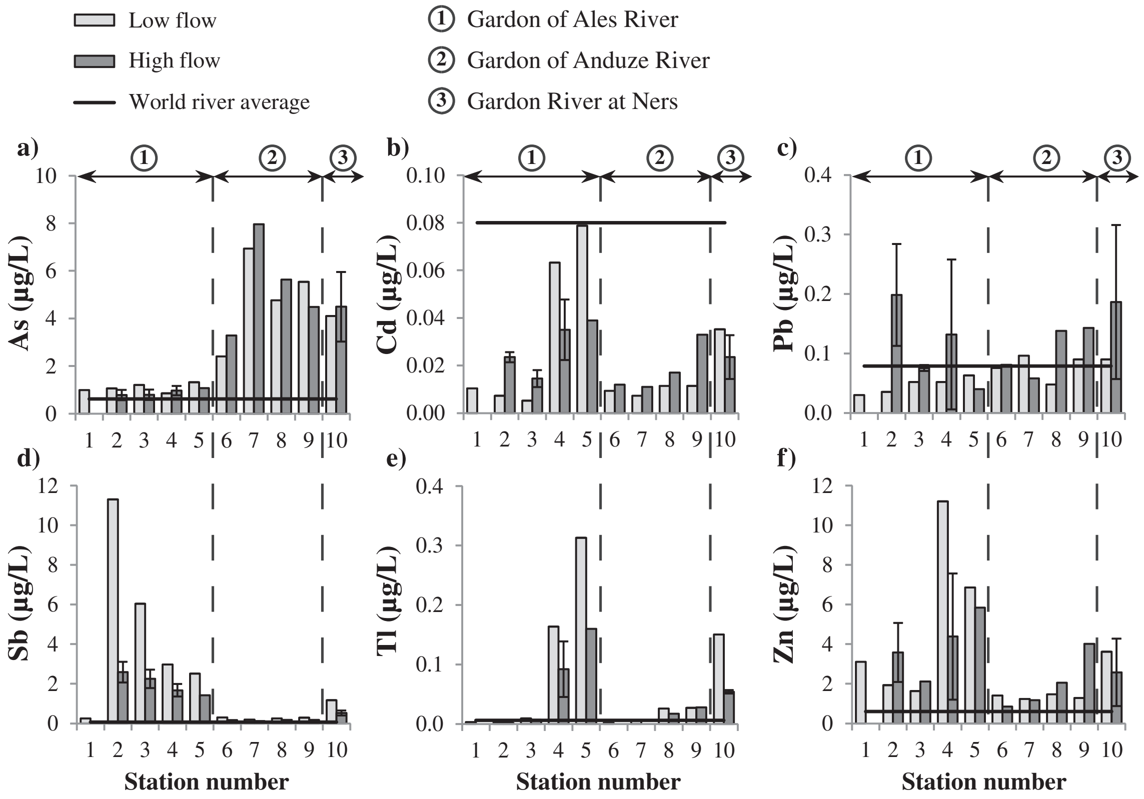

Fig. 3. Spatial evolution of dissolved As, Cd, Pb, Sb, Tl and Zn concentrations from upstream to downstream sites along the Gardon Ales River (zone 1), the Gardon Anduze River (zone 2) and downstream from the confluence of these two rivers, at the Ners site (zone 3) under low flow and high flow conditions. World river average values of dissolved concentrations from Gaillardet et al. (2003).

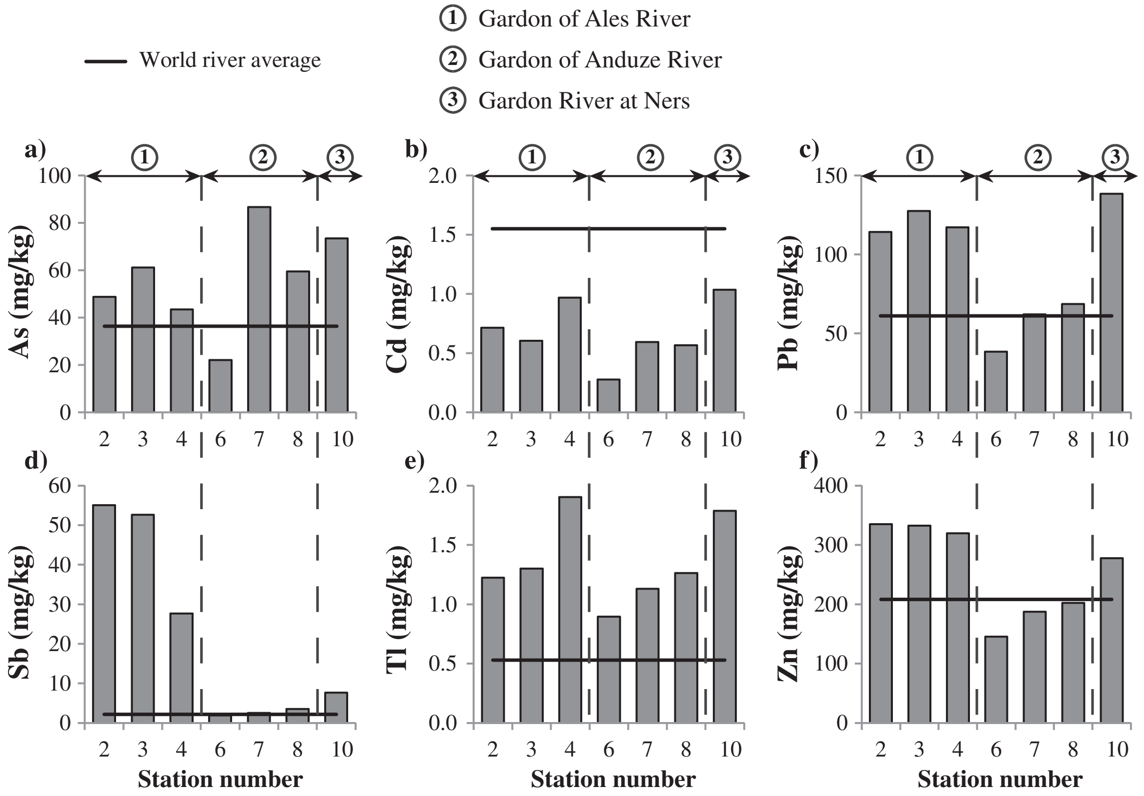

Fig. 4. Spatial evolution of particulate As, Cd, Pb, Sb, Tl and Zn concentrations from upstream to downstream sites along the Gardon Ales River (zone 1), the Gardon Anduze River (zone 2) and downstream from the confluence of these two rivers, at the Ners site (zone 3) in SPM recovered during high flow in November 2011. World river average values in SPM from Viers et al. (2009).

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Finally, dissolved concentrations downstream from the junction between the two subwatersheds (station 10) clearly reflected the predominant flow contribution of the Gardon of Anduze River upon the Gardon of Ales River (average discharge ratio 2:1, Banque Hydro data), with As concentration at station 10 similar to station 9 while significant dilution was evidenced for Cd, Sb, Tl and Zn from station 5 to station 10.

4.1.2. Particulate metal and metalloid concentrations

Particulate As, Cd, Pb, Sb, Tl and Zn concentrations in SPM recovered at high flow in November 2011 exceeded world river averages up to 2 (As, Pb, Zn), 4 (Tl) and 25 fold (Sb) with the exception of Cd (Fig. 4).

The particulate phase represented on average 36% (Sb), 43% (As), 57% (Cd), 82% (Tl, Zn) and 95% (Pb) of total (dissolved + particulate) concentrations, showing significant contribution of particulate over dissolved load to metal transport during high (receding) flow.

Spatial distribution showed extremely higher concentrations of Sb in SPM along the Gardon of Ales subwatershed compared to the Gardon of Anduze subwatershed (Fig. 4d), as already observed for dissolved Sb, and subsequent dilution in particles at the junction between the two subwatersheds (station 10), confirming the predominance of Sb source on the upper course of the Gardon of Ales subwatershed. For other metal(loid), particulate concentrations did not show clear trend from upstream to downstream stations in both subwatersheds indicating that there were more than one predominant source for these metal(loid)s.

4.2. Flood monitoring

4.2.1. Dissolved As, Cd and Sb concentrations

The pattern of dissolved As concentrations during the two consecutive flood events (Fig. 5a, d) differed from that of Sb (Fig. 5b, e) and Cd (Fig. 5c, f). Arsenic concentration increased with the discharge during Event 2, with a few hour shift between the two consecutive upstream (Lezan) and downstream (Ners) stations (Fig. 5a, d). Concentration reached 10.2 μg/L at Lezan (17/03/2013 at 06:00) and 7.3 μg/L at Ners (17/03/2013 at 09:00), which exceeded the values obtained during the winter low flow conditions. This first peak coincided with a stationary flow phase occurring during the rising limb of the hydrograph (Event 2′, Fig. 5a, d) in response to a temporary rainfall decrease (data not shown). A second peak occurred (Event 2″, Fig. 5a, d), with As concentration reaching 5.7 μg/L, both at Lezan (17/03/2013 at 16:00) and Ners (17/03/2013 at 17:00). A concentration peak was also visible during Event 1 at Ners (Fig. 5d) but it was missed at Lezan (Fig. 5a), due to the time shift. Conversely, Sb concentration decreased with increasing discharge during Event 2 at Ners (Fig. 5e) and increased at receding flow during Event 1, ranging between the high and low flow values recorded at this station (10) during the spatial surveys. At Lezan, dissolved Sb concentration remained low and relatively stable during the flood (Fig. 5b), with a value of 0.17 ± 0.01 μg/L which is lower than the concentration measured during winter low flow. For Cd, dissolved concentrations also decreased with increasing discharge during Event 2 at Lezan and during Event 1 at Ners. At Lezan, the concentrations recorded during the flood were higher than the winter low flow values, indicating that a concentration peak was probably missed at the early stage of the floods while at the Ners station, Cd presented a dilution pattern compared to winter low flow level (Fig. 5c, f).

4.2.2. SPM and particulate metal and metalloid concentrations

SPM concentration increased with the discharge during Events 1 and 2; it reached higher values during Event 2 (334 mg/L at Lezan and 647 mg/L at Ners) than during Event 1 (73 mg/L at Lezan and 141 mg/L at Ners), in relation with a higher discharge (Fig. 6). During Event 2, a first SPM peak coincided with the stationary flow phase occurring during the rising limb of the hydrograph (Fig. 6).

The pattern of particulate metal(loid) concentrations during the floods was similar to that of dissolved As concentrations; two consecutive peaks were recorded during the rising limb of Event 2 for As, Cd, Pb, Sb, Tl and Zn at Lezan (Fig. 7a,b) and for As, Pb and Zn at Ners (Fig. 7c), with lower concentration values at downstream station Ners located at the junction between the two subwatersheds compared to upstream station Lezan, located at the lowermost course of the Gardon of Anduze River. These concentrations during flood Event 2 were higher than those recorded at high (receding) flow during the spatial survey, by a factor 1 to 3 for Sb, 2 to 6 for Zn and Tl, 2 to 11 for Pb, 3 to 14 for Cd, and 5 to 20 for As. This may suggest the contribution of a common source highly

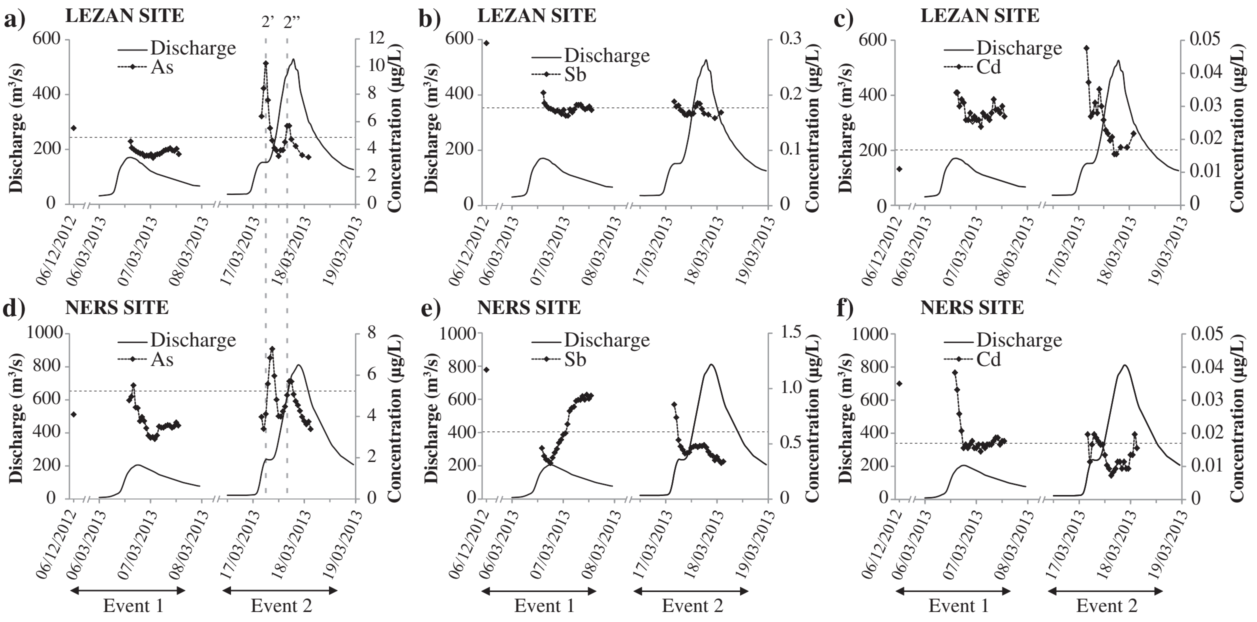

Fig. 5. Temporal variations of dissolved As, Cd and Sb concentrations (in μg/L) and hourly discharge (in m^3/s) at Lezan (discharge measured at Anduze ~6 km upstream from Lezan site) and Ners during the monitored floods of March 2013. The first point represents the dissolved concentrations measured during winter low flow in December 2012. Horizontal dashed lines represent the concentration measured at station 8 (a, b and c) and station 10 (d, e, f) during the receding flow of November 2011.

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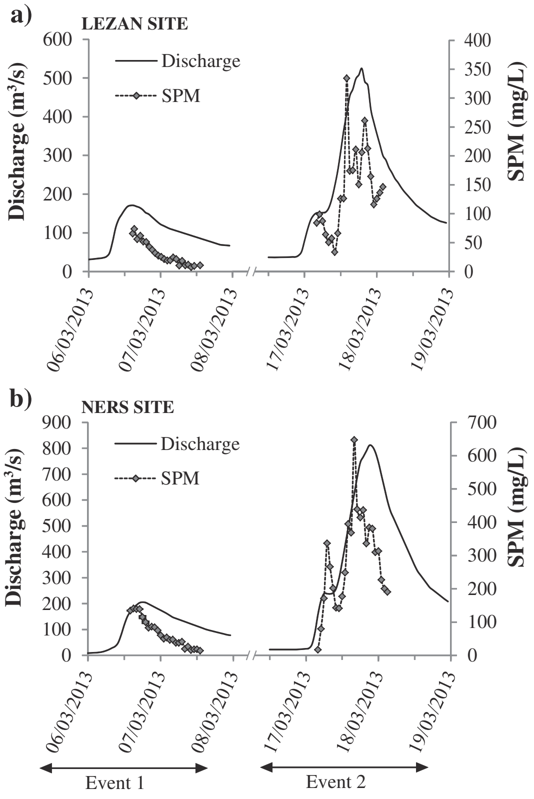

Fig. 6. Temporal variations of suspended particulate matter (SPM) concentration (in mg/L) and hourly discharge (in m^3/s) at Lezan (discharge measured at Anduze ~6 km upstream from Lezan site) and at Ners.

enriched with these metal(loid)s in the particulate phase during flood Event 2 on the Gardon of Anduze subwatershed.

By plotting Pb versus As and Tl versus Cd concentration data from Event 2 at Lezan, a distribution along two different correlation lines was observed, corresponding to Event 2′ and 2" (Fig. 8a, b). SPM from Event 2′ were more enriched with As and Cd compared to SPM from Event 2" which were more enriched with Pb and Tl. Correlation line from Event 2′ fitted with Pb–As data from Amous River SPM and surface bed deposit (Fig. 8c); this river is located downstream from the Carnoulès Pb–Zn mine, where exceptionally high As concentrations were recorded in the drainage waters and associated secondary precipitates (Leblanc et al., 1996; Casiot et al., 2003, 2009; Héry et al., 2014). Correlation line from Event 2" fitted both with Pb–As and Tl–Cd Amous River bulk sediment data and also with the Ourne and Aiguesmortes Rivers sediment data (Fig. 8c, d); these two latest rivers are located downstream from the ancient mining district of Pallières which is close to Carnoulès mining district. Correlation line from Event 2" also fitted with data from sulfide-rich tailings of the Carnoulès mine and with data from a sediment layer in a flooding terrace recovered at 45 km downstream from Lezan; this contaminated layer was attributed to the failure of a tailing dam at the Carnoulès mine (Dezileau et al., 2014; Resongles et al., 2014).

5. Discussion

The Gardon River is a typical Mediterranean mid-size river that has been durably impacted by metal contamination from ancient mining activity (Resongles et al., 2014). Levels of As, Pb, Sb, Tl and Zn in the dissolved and particulate phases recorded in the present study showed enrichments relatively to average river values, in agreement with the contamination status of sediments and the high geochemical background established in a previous study (Resongles et al., 2014). For As,

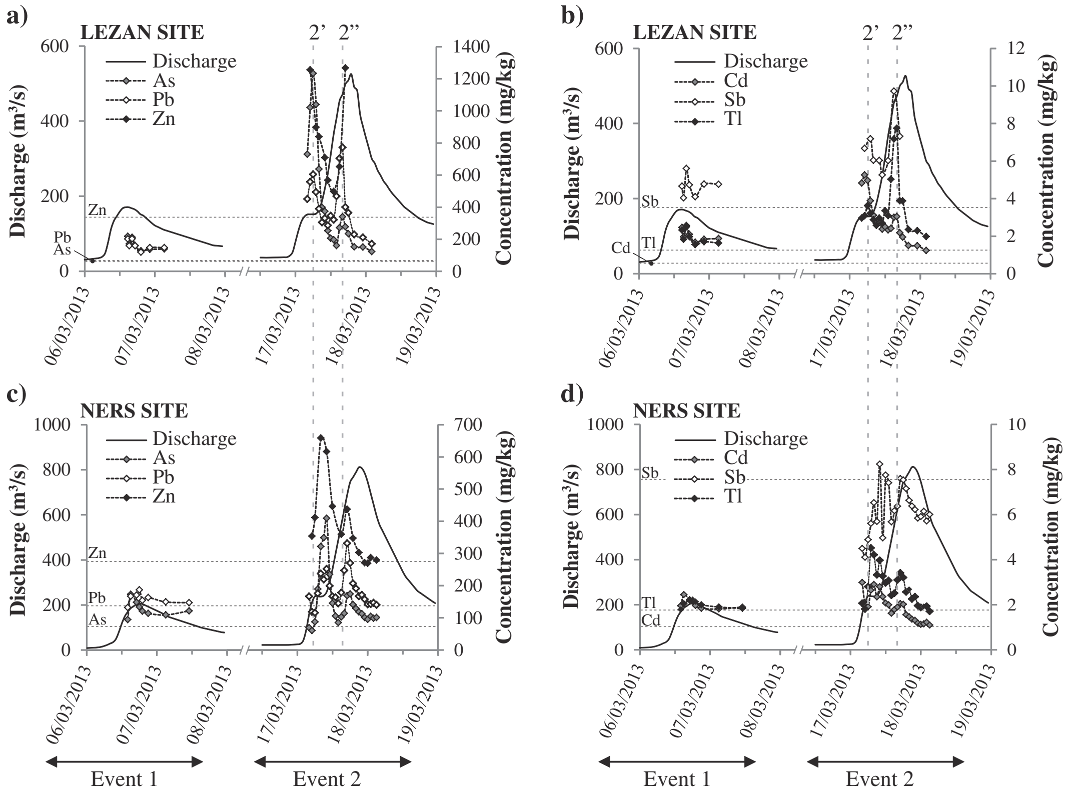

Fig. 7. Temporal variations of particulate metal (Cd, Pb, Tl, Zn) and metalloid (As, Sb) concentrations (in mg/kg) and hourly discharge (in m^3/s) at Lezan (discharge measured at Anduze ~6 km upstream from Lezan site) and Ners during the monitored floods of March 2013. Horizontal dashed lines represent the concentration measured at station 8 (a, b) and station 10 (c, d) during the receding flow of November 2011.

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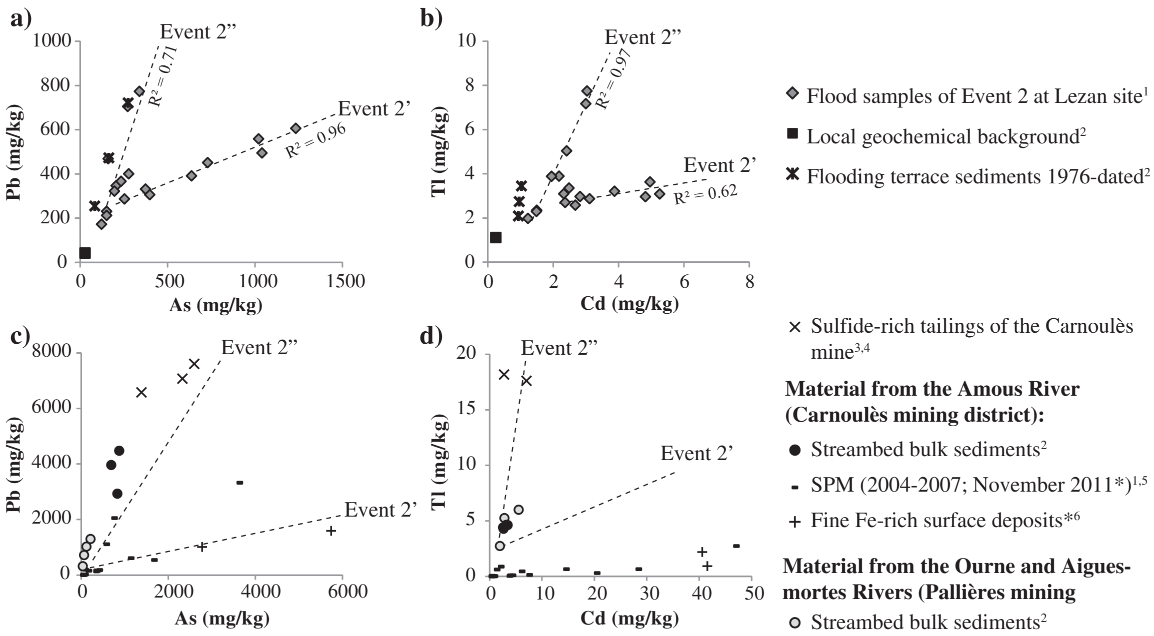

Fig. 8. Relationship between a) Pb and As concentrations and b) Tl and Cd concentrations in SPM collected during the flood Event 2 at Lezan. The geochemical background value of the Gardon River watershed and sediments from flooding layers dated at 1976 are also shown. Relationship between c) Pb and As concentrations and d) Tl and Cd concentrations in various contaminated materials collected on the two main mining districts of the Gardon of Anduze River subwatershed (Carnoulès and Pallières mining districts, Fig. 1 and Table 1). The lines in panels c) and d) are extrapolations of regression lines shown in panels a) and b). *Concentrations are divided by 2 to fit into the scale. References: [1]this study, [2]Resongles et al., 2014, [3]unpublished data, [4]Leblanc et al., 1996 (graph c only), [5]Casiot et al., 2009, [6]Héry et al., 2014.

Cd, Pb, Tl and Zn, the dissolved and particulate concentration values were within the range of other mid-size rivers impacted by ancient mines (Table 3). For Sb, the present data showed higher values than those recorded for the Isle and Lot Rivers impacted by ancient mines from the western border of the French Massif Central (Coynel et al., 2007; Grosbois et al., 2009).

The spatial distribution of metal(loid) contamination in the dissolved and particulate phases corroborated previous sediment characterization along the Gardon River watershed (Resongles et al., 2014). In this previous study, Cd, Sb, and Zn appeared to be enriched in the sediments along the Gardon of Ales subwatershed relatively to the Gardon of Anduze subwatershed, with predominant sources localized at the uppermost course of the river (Sb) and around Ales urban and Pb/Zn mining area (Cd, Zn). For other elements (As, Pb, Tl), the concentrations in the sediments upstream from the junction between the two subwatersheds were similar (Resongles et al., 2014), these elements being associated to ancient Pb/Zn mines present on both subwatersheds.

In the present study, the level of contamination and the contribution of the different sources were shown to vary with hydrological conditions. For Sb, a decrease of dissolved concentrations was observed at high flow on the Gardon of Ales subwatershed compared to low flow conditions and a dilution pattern was also evidenced after the junction between the two subwatersheds during the flood events. This was attributed to a dilution effect generally observed with increasing river discharge (Grimshaw et al., 1976; Cánovas et al., 2008, 2012; Grosbois et al., 2009; Ollivier et al., 2011). For As, dissolved concentrations

Table 3
Dissolved and particulate metal(loid) concentrations from several European mining-impacted rivers.

River	Watershed area (km²)	Sample type	As	Cd	Pb	Sb	Zn	Reference
Gardon River (France)	1100	Dissolved phase (μg/L)	0.7–8.0[a]	0.005–0.08[a]	0.03–0.20[a]	0.12–11[a]	0.85–11[a]	This study
			2.9–10[b]	0.007–0.05[b]	–	0.2–0.9[b]	–	
		SPM (mg/kg)	22–87[a]	0.28–1.0[a]	38–138[a]	1.9–55[a]	145–335[a]	
			61–1233[b]	1.1–5.3[b]	116–772[b]	4.0–9.7[b]	270–1267[b]	
Lot River (France)	11,840	Dissolved phase (μg/L)	–	0.01–0.27	0.05–0.32	–	3.1–17	Audry (2003) & Coynel et al. (2007)
		SPM (mg/kg)	51–95	0.26–38	14–272	2.7–18	52–2656	for As and Sb
Isle River (France)	6600	Dissolved phase (μg/L)	0.1–35	<0.002–0.22	0.01–2.8	0.4–1.1	0.53–27	Grosbois et al. (2009) & Masson
		SPM (mg/kg)	18–109	0.79–12	32–338	–	180–2270	et al. (2006, 2007)
Odra River (Czech Republic)	136,528	Dissolved phase (μg/L)	0.1–8.8	0.002–1.1	<d.l.—11	–	1.3–202	Helios Rybicka et al. (2005)
		SPM (mg/kg)	2.0–302	0.9–40	9.4–1614	–	111–31,369	
Tees River (UK)	1906	Dissolved phase (μg/L)	–	0.02–0.10	0.05–0.82	–	0.7–14	Laslett (1995)
		SPM (mg/kg)	–	0.6–5.4	110–320	–	190–1100	
Tamar River (UK)	1700	Dissolved phase (μg/L)	2.1–9.9	<d.l.	<0.46	–	3.1–28	Mighanetara et al. (2009)
Avoca River (Ireland)	652	Dissolved phase (μg/L)	0–0.03	0–0.61	–	–	170–640	Gray (1998)
Litavka River (Czech Republic)	630	SPM (mg/kg)	–	6.1–47	102–2070	–	603–3800	Žák et al. (2009)
Rhône River (France)	98,800	Dissolved phase (μg/L)	1.2–4.7	–	0.02–0.43	0.16–0.65	0.70–8.4	Ollivier et al. (2011)
		SPM (mg/kg)	–	0.28–1.1	22–109	0.82–5.0	107–336	

<d.l.: Lower than detection limit.

[a] Range of values obtained from spatial surveys.

[b] Range of values obtained during flood monitoring at Lezan and Ners stations.

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along the Gardon of Anduze River were similar at low and high (receding) flows. Nevertheless, these relatively stable dissolved As levels have been exceeded two-fold during flood Event 2 at Lezan, showing that unusual As levels may be reached during such peculiar hydrological events. Indeed, surface leaching processes occurring during rising floods may upgrade the usual As levels; these processes involve flushing of surface tailings and contaminated soils, desorption from As-rich particles from riverbed in mine-impacted tributaries; such flushing events were often observed during floods in mining areas (Grimshaw et al., 1976; Cánovas et al., 2008; Byrne et al., 2013). As an example, Masson et al. (2007) observed maximum dissolved As concentrations in the Garonne River during a major flood event due to heavy rainfalls in the upper Lot River watershed which is known for important potential As point sources such as mining wastes, tailings and contaminated reservoir sediments. The concentration of the other studied elements (Cd, Pb, Zn, Tl) in the particulate phase was also significantly increased during flood Event 2 at Lezan and also at Ners, relatively to receding flow of November 2011, making the Gardon of Anduze subwatershed the predominant contributor to downstream particulate As, Pb, Zn, Cd and Tl load during this peculiar flood event. Increasing metal(loid) concentration in SPM during floods can be due to several processes such as remobilization of contaminated sediments from the riverbed or the riverbank and erosion of soil and waste deposits at mining sites caused by surface runoff. Here, the two successive contamination peaks and associated distinct Pb–As and Tl–Cd correlations evidenced during the rising flood of Event 2 at Lezan clearly highlighted that two different predominant sources or transport mechanisms were involved during this flood. The mobilization of particles highly enriched with As and Cd and in a lesser extent with Pb (Event 2′) was followed by the mobilization of particles highly enriched with Pb and Tl and in a lesser extent with As and Cd (Event 2"). The corresponding activated sources or mechanisms are difficult to discriminate since floods are complex events. Source contribution depends on the spatial and temporal repartition of rainfalls and the distance between the source and the sampling station (Coynel et al., 2007). In the present study, the main potential sources of As and Pb on the Gardon of Anduze subwatershed are the mining districts of Carnoulès and Pallières (Fig. 1, Table 1). During Event 2, these mining districts were roughly equally affected by rainfalls; they recorded about 140 mm of precipitations in 36 h (data from Meteo-France). Moreover, the two mines are nearly equidistant from the flood monitoring station of Lezan, thus both mining sites may have contributed to increase metal(loid) levels in SPM during flood Event 2. Thus, the two correlation lines may rather reflect the composition of different kinds of particles, being more or less easily flushed as the flow rate increased. SPM of Event 2′ exhibited Pb/As and Tl/Cd ratios of 0.5 and 0.7 and the corresponding correlation line fitted with some of the Amous River SPM highly enriched with arsenic (Pb/As and Tl/Cd ratios of 0.5 and 0.2 on average, Fig. 8c). This correlation also fitted with few data from fine Fe-rich superficial Amous River bed deposits (Pb/As and Tl/Cd ratios of 0.3 and 0.04 on average); these deposits were orange loosely packed and watery, they were deposited onto the top of Amous river bed (Héry et al., 2014). Their consistency makes these deposits prone to flushing as soon as the flow rate increases. SPM corresponding to Event 2" presented higher Pb/As and Tl/Cd ratios of 2.3 and 2.5 and the correlation line fitted with data from sulfide-rich tailings from the Carnoulès mine (Pb/As and Tl/Cd ratios of 3.6 and 4.5 on average), also with sediment data from rivers draining the ancient mining districts of Carnoulès and Pallières (Pb/As and Tl/Cd ratios of 6.4 and 1.5 on average, Fig. 8c, d) (Resongles et al., 2014). Moreover, this correlation line also fitted with data from a sedimentary archive layer located at a downstream station in the Gardon River; this layer corresponded to sulfide-rich sands originating from the failure of a tailings dam at Carnoulès in 1976 (Pb/As and Tl/Cd ratios of 2.8 on average). Therefore, the geochemical signature of SPM transported during Event 2′ may be related to the remobilization of easily flushed secondary precipitates temporarily stored in the streambed in the vicinity of Carnoulès mine while SPM transported during Event 2" may reflect the contribution of primary sulfides originating from tailings or from downstream diffuse sources (remobilization of these primary sulfides stored temporally in riverbed or riverbank) which may have a similar composition in As, Pb, Tl and Cd throughout the whole Carnoulès–Pallières mining area. Such sulfide-rich gray sands were observed after storm events at the outlet of the drain that crossed the tailings pile at Carnoulès and in the streambed of the small Reigous Creek that flows into the Amous River.

Altogether, these results highlight the importance of flood events in the mobilization of metal(loid)s in the Gardon River. Exceptionally high particulate concentrations of As were reached during flood Event 2 in the present study, compared to other mining-impacted rivers; the values reached 1233 mg/kg at Lezan and greatly exceeded European guidelines for sediment quality (Macklin et al., 2006). Considering the dissolved and particulate loads downstream from the junction between the two subwatersheds (Ners station), our calculations indicated dissolved As, Cd and Sb loads reaching 204 kg, 0.5 kg and 19.4 kg, respectively and particulate load reaching 1915 kg for As, 24 kg for Cd, 94 kg for Sb, 38 kg for Tl, 2860 kg for Pb and 5214 kg for Zn within 24 h during Event 2. Although these particulate metal(loid) loads are significant, they are relatively low compared to those exported from the Lot River watershed that also drained ancient mines from the western border of the French Massif Central, besides receiving inputs from an ancient Zn smelter. The particulate load of the Lot River during a 5-day major flood was about 14 times (As), 18 times (Pb), 47 times (Sb), 164 times (Zn) and 349 times (Cd) higher than the particulate load of the Gardon River during the flood Event 2, in relation with a 30 times higher SPM load (Coynel et al., 2007) and a higher level of Cd and Zn (Table 3).

The geochemical signature of the Gardon River, characterized by relatively high dissolved As and Sb concentrations, was evidenced during three important flood events recorded on the Rhône River in 2002 and 2003 (Ollivier et al., 2006). During these floods, dissolved As (1–5 μg/L) and Sb (0.2–0.7 μg/L) concentrations in the Rhône River at Arles, downstream from the junction with the Gardon River, were close to those recorded in the present study (3–7 μg/L for As and 0.3–0.9 μg/L for Sb) during the floods at Ners; this was related to the unusual contribution of Cevenol tributaries to the whole Rhône flow during the 2002 and 2003 flood events. In particular, Cevenol tributaries accounted for 90% of the Rhône flow at Arles during the September 2002 flood event (Ollivier et al., 2006, 2011).

6. Conclusion

In this study, high-temporal flood monitoring allowed to evidence that significant temporal variations of dissolved and particulate metal (Cd, Pb, Tl, Zn) and metalloid (As, Sb) concentrations occurred during Mediterranean floods in the former mining watershed of the Gardon River. Dissolved Sb concentration was affected by usual dilution processes often observed with increasing discharge. Conversely, dissolved As and particulate As, Cd, Pb, Tl and Zn concentrations exhibited two successive contamination peaks during the rising flood with higher concentrations than those recorded during low or receding flow conditions showing that mine-related sources were activated during the flood.

The correlation between particulate As, Pb, Tl and Cd concentrations showed two different signatures associated with the two contamination peaks, suggesting that two different kinds of contaminated particles were successively transported during the studied flood in the Gardon River system. Based on the location of the potential contamination sources and the geochemical signature of associated contaminated particles, we could infer that the first group of particles might be ascribed to the flushing of secondary precipitates which are commonly found in mining streams affected by acid mine drainage. The second group might correspond to primary sulfides originating from tailings or from downstream secondary sources. However, further work is necessary to distinguish between point sources and diffuse downstream sources of such particles.

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Finally, this study highlighted the importance of floods in the mobilization of metals and metalloids from ancient mining sites in Mediterranean regions, showing the need for monitoring flood events to understand metal and metalloid transport in such river systems and accurately assess the long-term contribution of mining activity to metal(loid) loads of downstream watershed. Further research is needed to estimate the contribution of this kind of flood event to annual metal(loid) flux.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2015.07.010.

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