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# Fate of Sb(v) and Sb(III) species along a gradient of pH and oxygen concentration in the Carnoulès mine waters (Southern France)

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The speciation and behaviour of antimony were investigated in surface waters downstream from the abandoned Pb–Zn Carnoulès mine (Gard, France). These waters exhibit a permanent gradient of oxygen concentration and pH, ranging from acid suboxic in Reigous Creek at the outlet of sulfide tailings impoundment, to near neutral oxygenated at downstream sites along the rivers Amous and Gardon. The concentration of total dissolved (<0.22 µm) antimony, acquired through a seven-year monitoring, decreased from 7.7–409.9 µg L<sup>-1</sup> at the source of Reigous Creek to 0.22–0.45 µg L<sup>-1</sup> in the Gardon River, showing natural Sb attenuation. Speciation analysis carried out during three surveys indicated that Sb(III) represented up to 70% of the total dissolved Sb concentration at the source of Reigous Creek, while Sb(v) represented less than 50%. Field characterization showed that Sb(III) and Sb(v) species were attenuated through dilution and were also removed from the dissolved phase during downstream transport. Speciation analysis in suspended particulate matter extracts gave a distribution of particulate Sb into 70 to 100% of Sb(III) and less than 30% of Sb(v). The removal of Sb(III) and Sb(v) species from the dissolved phase was concordant with the oversaturation of Reigous Creek water relative to Sb(III)- and Sb(v)-oxides and Sb(III)- and Sb(v)-Fe oxides. Sb(III) was more efficiently removed than Sb(v) or As(III) and was no more detectable in the dissolved phase at downstream sites in the rivers Amous and Gardon. Conversely, the concentration of Sb(v) in the rivers Amous and Gardon still denoted contamination arising from the Carnoulès mine. The range of log K<sub>d</sub> values, from 2.4 L kg<sup>-1</sup> to 4.9 L kg<sup>-1</sup>, indicated that Sb was mainly transported in the dissolved phase downstream the Reigous Creek input. Altogether, these results give a better understanding of the fate of Sb downstream from sulfide-rich mining wastes.

## Environmental impact

Mining of metallic sulfide ores is an important source of Sb to the aquatic system. The fate of Sb downstream from mining sites depends on its oxidation state which controls its reactions with the mineral phases. However, few studies have investigated the speciation and behavior of Sb in mine waters. The fate of Sb was studied along a river continuum formed by the Reigous Creek, the Amous river and the Gardon river, the headwaters of which drained an abandoned tailings pile generating acid mine drainage. The suboxic and acidic conditions at the source of Reigous Creek offered a unique opportunity to study the distribution of Sb(III) and Sb(v) species along a gradient of pH and redox potential from upstream to downstream sites along the river continuum.

## 1 Introduction

Antimony and its compounds are considered as pollutants of priority interest by the Environmental Protection Agency of the United States<sup>1</sup> and the European Union.<sup>2</sup> Anthropogenic

emissions of atmospheric Sb have increased dramatically since the beginning of the Industrial Revolution as evidenced by increased concentrations of Sb in Alpine ice and peat bogs from Europe and polar ice from the Canadian Arctic.<sup>3–5</sup> Antimony has many industrial applications; it is added to plastics as a flame retardant, used as a catalyst during the synthesis of plastics and in alloys for ammunition.<sup>6</sup> Even so, there have been remarkably few studies dealing with the fate of antimony in the environment, compared to other potentially toxic metals such as Hg, Pb, Cd or As.<sup>7–9</sup> In natural waters, the concentration of Sb is generally lower than 1 µg L<sup>-1</sup>. Mining of sulfide ores is also an important source of Sb to the aquatic system. Antimony

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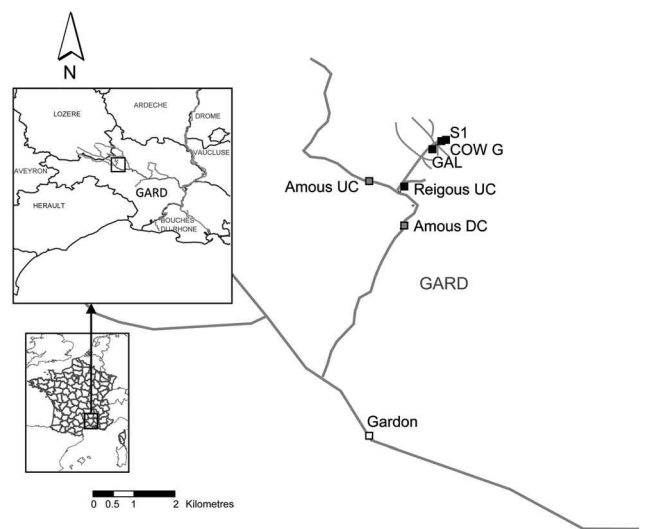
concentrations ranging from  $3.5 \mu\text{g L}^{-1}$  to  $55 \text{mg L}^{-1}$  were reached in waters draining Sb mines.<sup>10–13</sup> Because mine drainage phenomena may last hundred years after mine closure, the question of Sb fate in the aquatic environment downstream from mining sites is an important issue. One essential point to be considered is the redox speciation of Sb, which controls its reactions with the mineral phases, thus conditioning its dissemination into the aquatic environment. In this respect, adsorption of Sb(v) to pure Fe hydroxides appeared to be strong;<sup>9</sup> however, Sb(v) sorbed less well than Sb(III) to Fe and Mn (hydr)oxide surfaces.<sup>14</sup> Sb(v) forms oxides ( $\text{Sb}_2\text{O}_5$ ) that are more soluble than oxides of Sb(III) ( $\text{Sb}_2\text{O}_3$ ).<sup>15</sup> Until now, few studies have investigated the speciation of Sb and its behavior in mine waters. In mine tailings, Sb(III) released from the oxidation of primary Sb sulfide minerals is precipitated in the form of secondary Sb(III) oxides and Sb(III) sulfates in the supergene zone.<sup>12</sup> Secondary Sb(III)– and Sb(v)–Fe oxides were also evidenced in stibnite deposits and might limit the solubility and mobility of Sb in oxidizing mining environments.<sup>12,16,17</sup> In mine waters, a large predominance of Sb(v)<sup>11,13,18–20</sup> in the form of  $\text{Sb}(\text{OH})_6^-$  (ref. 13) was generally observed under oxic conditions, and only trace levels of Sb(III).<sup>13</sup> Natural attenuation of Sb occurs in mine drainage as a result of sorption onto ochre precipitates, particularly schwertmannite<sup>21</sup> and onto amorphous iron and manganese oxides.<sup>11,12,20,22,23</sup>

In the present study, we investigated the fate of Sb along a river continuum formed by the Reigous Creek, the Amous river and the Gardon river. The headwaters of Reigous Creek drain an abandoned tailings pile containing sulfides that generates acid mine drainage. The suboxic and acidic conditions at the source of Reigous Creek offered a unique opportunity to study the distribution of Sb(III) and Sb(v) species along a gradient of pH and oxygen concentration from upstream to downstream sites along the Reigous–Amous–Gardon continuum. In order to better identify the processes that control the behaviour of Sb, long-term monitoring of Sb concentrations in the dissolved and particulate phases was carried out at six sampling sites along this gradient. Measurements of redox Sb species were performed in the total dissolved fractions ( $<0.22 \mu\text{m}$ ), truly dissolved fraction ( $<10 \text{kDa}$ ), and in the suspended particulate matter ( $>0.22 \mu\text{m}$ ).

## 2 Site description

The abandoned Pb–Zn Carnoulès mining site is located in the drainage basin of the Rhone River in Southern France (Fig. 1).

The mining activity stopped in 1962 and has left 1.5 Mt of sulfide tailings material retained behind a dam. These wastes contain 0.7% Pb, 10% Fe, 0.2% As, and about  $60 \mu\text{g Sb g}^{-1}$ . The Sb minerals identified in the tailings are tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) and pyrrargyrite ( $\text{Ag}_3\text{SbS}_3$ ).<sup>24</sup> These wastes are deposited over the headwaters of the Reigous Creek. Thus, the water emerging at the base of the tailings dam constitutes the actual source of the Reigous Creek. As a result of the oxidation of pyrite within the tailing impoundment,<sup>25–27</sup> the water is acid ( $\text{pH} \sim 3\text{--}4.5$ ) and contains Fe ( $\sim 2 \text{g L}^{-1}$ ), sulfate ( $\sim 4 \text{g L}^{-1}$ ), and arsenic ( $250 \text{mg L}^{-1}$ ). Heavy metals, such as Pb and Zn, are also



**Fig. 1** Sketch map of the study area with location of the sampling points along the Reigous–Amous–Gardon continuum.

present. The oxidation of Fe(II) in the Reigous Creek leads to the precipitation of a succession of amorphous Fe–As phases, tooeite ( $\text{Fe}_6(\text{AsO}_3)_4\text{SO}_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ ) and As–schwertmannite from upstream to downstream sites,<sup>28,29</sup> and the subsequent decrease of Fe and As concentrations in water. The Reigous Creek collects acidic seepage waters from the surrounding quarries. It joins the Amous River 1.5 km downstream from its source. At the confluence with the Amous River (Fig. 1), the Reigous discharge ranges between 0.6 and  $20 \text{L s}^{-1}$ . The Amous discharge ranges between 50 and  $150 \text{L s}^{-1}$ . Upstream from the confluence, the Amous River is not affected by Acid Mine Drainage (AMD), and the concentrations of dissolved metals, arsenic and sulfate, which are generally several orders of magnitude lower than in the Reigous Creek, provide no evidence of contamination but simply reflect the natural regional background.<sup>30</sup> Downstream from the confluence, the Reigous is neutralized on mixing with the Amous; this causes the precipitation of Fe- and Al-oxyhydroxides. This Suspended Particulate Matter (SPM) removes most metals from the dissolved phase<sup>30</sup> with the exception of thallium.<sup>31</sup> Seven kilometers downstream from the Reigous–Amous confluence, the Amous river joins the Anduze Gardon River (Fig. 1) the median flow rate of which in the city of Anduze is  $15 \text{m}^3 \text{s}^{-1}$  (<http://www.hydro.eaufrance.fr>).

## 3 Materials and methods

### 3.1 Sampling and storage

The location of sampling stations along the 9 km transect from the source of the Reigous Creek (station S1) to the Anduze Gardon River (station Gardon) is shown in Fig. 1.

The Amous UC station located on the Amous River 1500 m upstream from the confluence with the Reigous Creek is not affected by former mining activities. From June 2002 to November 2003, nine surveys were carried out; they were focused on the Amous River and the Anduze Gardon River

**Table 1** Concentration of the main chemical constituents of the water at stations along the Reigous–Amous–Gardon continuum in April 2012. Data used in the CHESS simulation

Parameter	Unit	S1	COW G	GAL	Reigous UC	Amous DC	Gardon
pH		2.9	3.09	5.2	3.44	8.06	8.21
Cl <sup>-</sup>	mg L <sup>-1</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>	15.8	5.4	4.4
NO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>	14.3	11.5	2.6
SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	3969	3342	1389	549.2	79.3	20.1
Ca <sup>2+</sup>	mg L <sup>-1</sup>	278.5	290.2	191.9	95.1	82.4	20.6
Mg <sup>2+</sup>	mg L <sup>-1</sup>	87.5	83.5	51.7	20.7	16.9	6.3
Na <sup>+</sup>	mg L <sup>-1</sup>	3.9	4.0	4.5	5.1	3.4	4.2
K <sup>+</sup>	mg L <sup>-1</sup>	16.1	13.2	5.5	2.1	1.1	0.9
HCO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	<DL <sup>a</sup>	<DL <sup>a</sup>	<DL <sup>a</sup>	<DL <sup>a</sup>	244	74
Fe(II)	mg L <sup>-1</sup>	1404	1040	268.4	10.1	<DL <sup>a</sup>	<DL <sup>a</sup>
Fe(III)	mg L <sup>-1</sup>	<DL <sup>a</sup>	<DL <sup>a</sup>	<DL <sup>a</sup>	15.1	<DL <sup>a</sup>	<DL <sup>a</sup>
As(III)	µg L <sup>-1</sup>	124 400	95 360	15 820	265.9	11.9	1.3
As(V)	µg L <sup>-1</sup>	32 090	31 000	8467	263.9	3.4	4.2
Al	µg L <sup>-1</sup>	44 060	34 710	6587	11 570	69.2	9.8
Mn	µg L <sup>-1</sup>	7454	6161	3406	2780	209.7	5.3
Zn	µg L <sup>-1</sup>	22 800	17 950	6348	8412	285	3.5
Pb	µg L <sup>-1</sup>	1717	1108	39.2	418.7	0.2	0.1
Sb(V)	µg L <sup>-1</sup>	14.5	7.7	1.25	0.36	0.34	0.26
Sb(III)	µg L <sup>-1</sup>	17	4.9	<1	<0.1	<0.1	<0.1

<sup>a</sup> n.d.: not determined; concentration was too low relative to sulphate (not possible to quantify). DL: detection limit.

downstream from the confluence with the Amous River. During this period, only one station (Reigous UC) located on the Reigous Creek a few meters upstream from the confluence with the Amous River was monitored. The aim of these campaigns was to

establish the levels of Sb concentrations along the watershed. From November 2004 to February 2011, 71 surveys were carried out; during this period, sampling was focused on the Reigous Creek, at the source (S1) and at 40 m (station COW G) and 150 m (station GAL) downstream from the source, to better assess the behavior of Sb in the acid water. During these surveys, only one station (Amous DC) on the Amous River was monitored; this station was located 1.2 km downstream from the confluence with the Reigous Creek. Water samples for redox Sb speciation in water were collected in January 2011, March 2012 and April 2012. Filters with suspended particulate matter (SPM) for redox Sb speciation in the solid phase were collected in triplicate at each station in April 2012.

The pH, redox potential and dissolved oxygen (DO) concentrations were measured in the field with an HQ40d Portable Multi-Parameter Meter (HACH Company) equipped with a refillable pH electrode (pHC301), gel filled ORP/Redox electrode (MTC101) and Luminescent DO probe (LDO101) or an Ultrameter™ model 6P (Myron L Company, Camlab, Cambridge) and CHEMets® colorimetric DO tests (CHEMetrics, Calverton, USA).

Water samples for the analysis of the total dissolved fraction were filtered in the field through 0.22 µm Millipore™ membranes fitted on Sartorius polycarbonate filter holders. Subsamples for the analysis of Sb and trace elements (Al, Zn, Pb, Fe, and Mn) were taken in acid-cleaned polyethylene bottles. They were acidified to pH = 1 with HNO<sub>3</sub> Merck Suprapur (14.5 M) and stored at 4 °C until analysis. Another 100 mL of filtered subsample was brought in a cool box back to the laboratory and processed within 4 hours of collection for redox Sb speciation analysis. During the survey carried out in January

**Table 2** Dissolved (<0.22 µm) and particulate (>0.22 µm) Sb concentrations (in µg L<sup>-1</sup>) in the water samples collected during a long-term monitoring study (nine surveys from June 2002 to November 2003 and 71 surveys from November 2004 to February 2011) at the Carnoulès mining site. The solid-solution partitioning of Sb was quantified using the distribution coefficient, *K<sub>d</sub>*, representing the ratio of the concentration of Sb in the particulate phase (in µg kg<sup>-1</sup>) to the concentration of Sb in the dissolved phase (in µg L<sup>-1</sup>)

Station		S1	COW G	GAL	Reigous UC	Amous UC	Amous DC	Gardon
Distance from the tailings pile (km)		0	0.03	0.15	1.48	-1.5	2.7	8.5
Dissolved	Average	74	34	20	3	0.14	0.8	0.4
	SD <sup>a</sup>	70	41	34	3	0.04	0.5	0.1
	Min	7.7	3.2	0.49	<DL <sup>a</sup>	0.09	0.34	0.22
	Max	409.9	229.7	136.4	13.2	0.23	2.93	0.45
	Median	54.9	16.7	5.1	1.3	0.13	0.66	0.38
	<i>n</i> <sup>a</sup>	61	61	58	63	12	64	4
Particulate	Average	14.5	n.d. <sup>a</sup>	n.d. <sup>a</sup>	1.3	n.d. <sup>a</sup>	0.1	0.014
	SD <sup>a</sup>		n.d. <sup>a</sup>	n.d. <sup>a</sup>	0.5	n.d. <sup>a</sup>	0.2	0.003
	Min		n.d. <sup>a</sup>	n.d. <sup>a</sup>	0.9	n.d. <sup>a</sup>	0.001	0.01
	Max		n.d. <sup>a</sup>	n.d. <sup>a</sup>	1.6	n.d. <sup>a</sup>	0.47	0.02
	Median		n.d. <sup>a</sup>	n.d. <sup>a</sup>	1.3	n.d. <sup>a</sup>	0.019	0.01
	<i>n</i> <sup>a</sup>	1	n.d. <sup>a</sup>	n.d. <sup>a</sup>	2	n.d. <sup>a</sup>	11	4
log <i>K<sub>d</sub></i>	Average	4.5	n.d. <sup>a</sup>	n.d. <sup>a</sup>	4.9	n.d. <sup>a</sup>	3.6	4.1
	SD <sup>a</sup>		n.d. <sup>a</sup>	n.d. <sup>a</sup>	0.2	n.d. <sup>a</sup>	0.6	0.7
	Min		n.d. <sup>a</sup>	n.d. <sup>a</sup>	4.8	n.d. <sup>a</sup>	2.4	3.4
	Max		n.d. <sup>a</sup>	n.d. <sup>a</sup>	5	n.d. <sup>a</sup>	4.6	4.9
	Median		n.d. <sup>a</sup>	n.d. <sup>a</sup>	4.9	n.d. <sup>a</sup>	3.7	4.1
	<i>n</i> <sup>a</sup>	1	n.d. <sup>a</sup>	n.d. <sup>a</sup>	2	n.d. <sup>a</sup>	11	4

<sup>a</sup> SD: standard deviation; *n*: number of samples; n.d.: not determined; DL: detection limit.

2011, an aliquot of the filtered sample from station S1 was stored at 4 °C and analyzed for Sb species after 3, 7 and 16 days of storage; this experiment allowed investigation of the fate of Sb species during sample storage.

SPM recovered from the filtration of 500 mL of water sample through a 0.22 µm filter was dried in an oven at 105 °C until constant weight for subsequent mineralization.

The samples for the determination of major anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) were preserved and analyzed according to the routine procedures described by Casiot *et al.*<sup>30</sup>

For As speciation, 100 µL of a 8.7 M acetic acid solution and 100 µL of 50 g L<sup>-1</sup> EDTA solution were added in the field to 9.8 mL of the filtered sample.<sup>32</sup> Samples were stored in the dark and analyzed within a few days after collection.

For Fe(II) determination, a 10 µL to 8.5 mL aliquot of filtered sample water was added to a mixture of 0.5 mL acetate buffer (pH 4.5) and 1 mL of 1,10-phenanthroline chloride solution;<sup>33</sup> the vials were made up to 10 mL with deionized water and absorbance was measured at 510 nm.

### 3.2 Sample processing

The SPM was mineralized on a hot plate using a three step procedure employing 30% H<sub>2</sub>O<sub>2</sub>, then 65% HNO<sub>3</sub>, and finally 40% HF which was validated for Sb extraction on a standard reference sediment PACS-2 from the NRCC (Ottawa, Ontario, Canada).

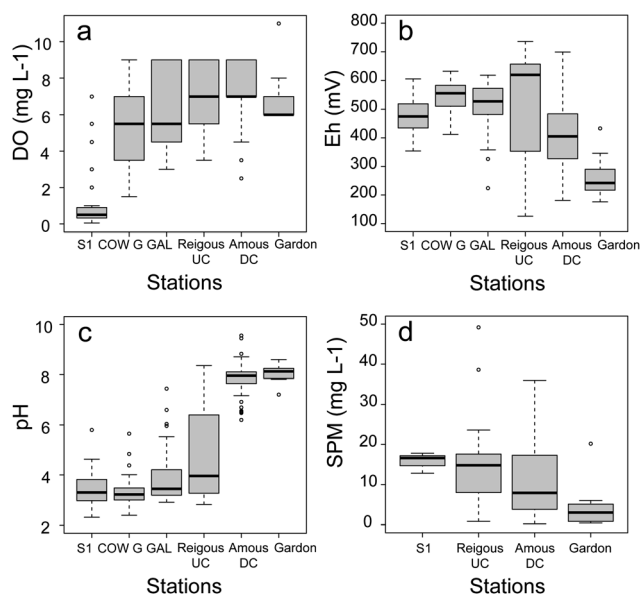
To determine the particulate Sb(III) and Sb(V) concentrations, we used the procedure described by Potin-Gautier *et al.*<sup>34</sup> Briefly, the filter with air-dried SPM was extracted with 30 mL of a solution containing 100 mmol L<sup>-1</sup> citric acid in 1% (w/v) ascorbic acid, in an ultrasonic bath. This procedure allowed the total dissolution of the SPM after 60 min sonication. The extracts were centrifuged (3000 RPM, 30 minutes), filtered through 0.22 µm pore size membranes and analyzed immediately for Sb speciation. Because Sb(III) oxidation is possible,<sup>34</sup> the Sb(III) concentration determined using this procedure represents a minimum value for Sb(III) concentration in SPM.

The colloidal Sb(III) and Sb(V) concentrations were determined by the difference between the total dissolved (<0.22 µm) concentrations and the truly dissolved (<10 kDa) concentrations, the latter being determined after ultracentrifugation of the sample. For this, an aliquot of 15 mL of water sample previously filtered on a 0.22 µm membrane was transferred into centrifugal tubes (Vivaspin 15R, Vivascience, Sartorius group) equipped with a permeable membrane of 10 kDa (with 1 Da = 1 g mol<sup>-1</sup>). The colloidal Sb fraction is retained by the ultrafiltration membrane, while free ions and small Sb complexes pass into the ultrafiltrate, defined as the truly dissolved Sb fraction. Each centrifugal filter device was washed and rinsed with 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and Milli-Q water before use. Centrifugation (3000g for 30 min at room temperature) was performed with a Rotofix 32 (Hettich) centrifuge equipped with a swinging bucket. Analyses of redox Sb species in the ultrafiltrate were carried out within 4 h of sample collection.

### 3.3 Analysis

The total dissolved Sb concentrations and the particulate Sb concentrations were determined using ICP-MS (X Series II – Thermo Electron Corporation, France). The instrument settings were checked daily for Sb sensitivity and optimised when necessary. All samples and standards were acidified with 2.5% HNO<sub>3</sub>. A solution of indium (30 µg L<sup>-1</sup>) in 2.5% HNO<sub>3</sub> was pumped continuously as an internal standard. External calibration was used, with certified standard solution (SCP Science). Both isotopes <sup>121</sup>Sb and <sup>123</sup>Sb were monitored. The quality of analysis was checked by analyzing the certified international reference material SLRS-4 (NRCC, Ottawa, Ontario, Canada) for the concentration of total Sb in river water. The accuracy was within 5% of the certified values and the analytical error (relative standard deviation) generally better than 5% for concentrations 10 times higher than the detection limit.

Determination of Sb(III) and Sb(V) concentrations in the total dissolved phase, in the truly dissolved phase and SPM extracts was carried out by High Performance Liquid Chromatography coupled to Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS).<sup>35</sup> Chromatographic separation was performed using an anion-exchange Hamilton PRP-X100 column (15 cm × 4.6 mm i.d.) and a precolumn (2 cm × 4.6 mm i.d.) with a SpectraSystem P4000 (ThermoScientific) coupled to an ICP-MS at a flow rate of 1 mL min<sup>-1</sup>. The mobile phase contained 5 mmol L<sup>-1</sup> ethylenediamine tetraacetic acid disodium salt (J. T. Baker) and 2 mmol L<sup>-1</sup> potassium hydrogen-phthalate (SigmaUltra; 99.95%; Sigma-Aldrich) (pH 4.5). Sb(V) and Sb(III) standard solutions (1 g L<sup>-1</sup>) were prepared by dissolving an appropriate



**Fig. 2** Boxplots representing variation of the main physico-chemical parameters (DO, Eh, and pH) and concentrations of suspended particulate matter (SPM) from upstream to downstream sites along the Reigous–Amous–Gardon continuum. Data were obtained from a long-term monitoring study at the Carnoulès mining site: between June 2002 and November 2003 (nine surveys), between November 2004 and October 2008 (57 surveys) (some of these data being published by Egal *et al.*,<sup>29</sup> Casiot *et al.*<sup>30</sup> and Casiot *et al.*<sup>31</sup>), and between January 2009 and February 2011 (14 surveys).

amount of potassium hexahydroxoantimonate(v) and potassium antimony(III) oxide tartrate hemihydrates, both from Merck, in deionized water. Detection was carried out with an ICP-MS at  $m/z = ^{121}\text{Sb}$ . The detection limits were  $0.01 \mu\text{g L}^{-1}$  for Sb(v) and  $0.03 \mu\text{g L}^{-1}$  for Sb(III) and the precision was better than 3% for Sb(v) and 5% for Sb(III). Water samples from rivers Amous and Gardon were analyzed without dilution. Samples from the Reigous Creek and SPM extracts were diluted respectively ten times and hundred times with deionized water before injection in HPLC-ICP-MS; such dilution allowed to cope with the complex matrix that may alter the chromatographic separation.<sup>34</sup> For samples in which both Sb(v) and Sb(III) species were detected, the sum of Sb(III) and Sb(v) concentrations in the total dissolved phase ( $<0.22 \mu\text{m}$ ) measured by HPLC-ICP-MS matched the total dissolved Sb concentration measured by ICP-MS within 2 to 18%, except for one sample (S1, April 2012), for which it was degraded to 28%. Such a discrepancy might be ascribed to a slight loss of Sb(III) species during transport. Indeed, a 29% decrease of Sb(III) concentration in filtered samples (from January 2011 survey) was observed after 2 days preservation at  $4^\circ\text{C}$  while the Sb(v) concentration remained constant.

Inorganic arsenic species ( $\text{As(III)}$  and  $\text{As(V)}$ ) were analyzed using anion-exchange chromatography (25 cm  $\times$  4.1 mm i.d. Hamilton PRP-X100 column and SpectraSystem P4000 ThermoScientific pump) in isocratic elution mode with 30 mM phosphate buffer, coupled to ICP-MS.

Analysis of major cations and anions, trace elements (Mn, Al, Zn, Pb, and Fe) were carried out using, respectively, ion chromatography (Dionex ICS-1000) and ICP-MS (Thermo X7 Series), as described by Casiot *et al.*<sup>30</sup>

### 3.4 Geochemical modelling

Speciation calculations were carried out using the computer program CHESS<sup>36</sup> with the CHESS thermodynamic database. The set of equilibrium constants for Sb from Filella and May<sup>37</sup> was implemented in the database. Equilibrium constants for the formation of Sb(III)- and Sb(V)-Fe oxides recently determined by Leverett *et al.*<sup>17</sup> were added to this set of constants. Sorption of Sb(III) and Sb(V) onto Fe-As minerals that form in the Reigous Creek could not be considered in the simulation because of the lack of sorption constants for these uncommon minerals. The composition of the water collected along the Reigous-Amous-Gardon continuum in April 2012 was used in the simulation (Table 1). This involved pH, concentrations of major cations and anions, concentrations of trace metals that are particularly enriched in this water such as Zn, Pb, Al, and Mn. Eh was not introduced into the simulation and the function redox state was disabled because of redox disequilibria; instead, measured species concentrations of redox sensitive elements Fe, As and Sb were used. The electrical balance was done on sulfate.

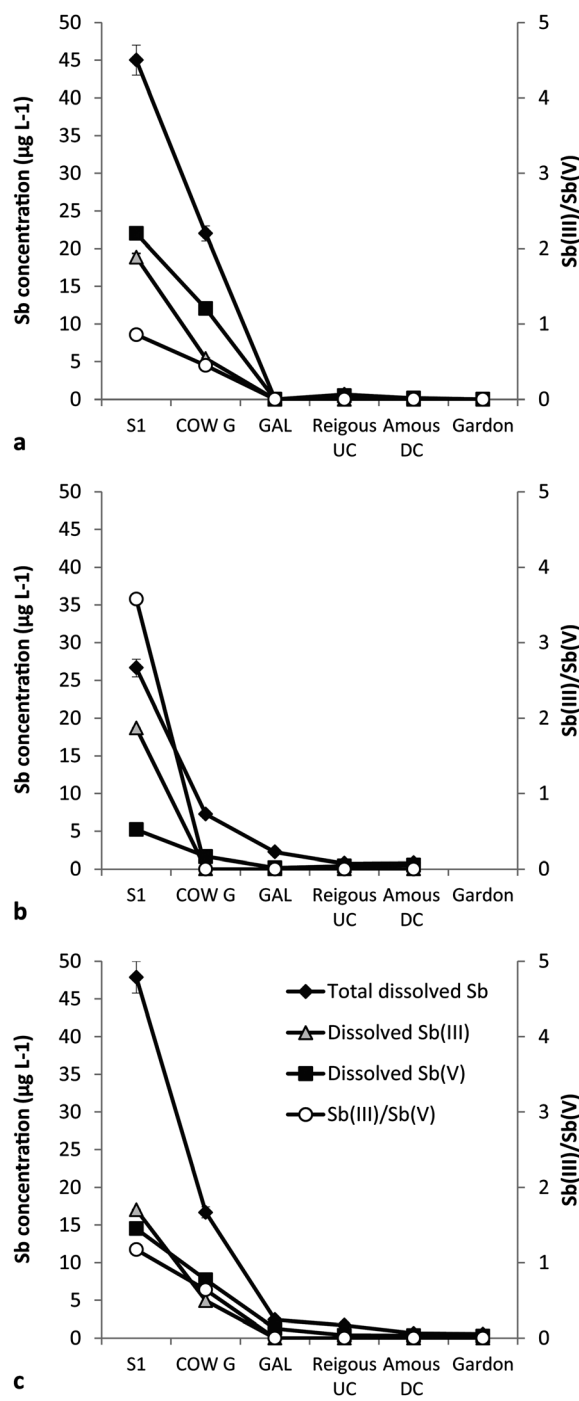
## 4 Results

### 4.1 Main physico-chemical parameters

Boxplots representing variations of the main physico-chemical parameters (DO, Eh, and pH) and concentrations of suspended

particulate matter (SPM) from upstream to downstream sites along the Reigous-Amous-Gardon continuum are presented in Fig. 2.

At the source of the Reigous Creek, the oxygen content ranged from 0.05 to  $7 \text{ mg L}^{-1}$ , with a median value of  $0.5 \text{ mg L}^{-1}$  over 56 samples, which denoted generally suboxic conditions at this station. The oxygen concentration increased drastically from the source of the Reigous Creek to the station COW G (Fig. 2a).



**Fig. 3** Spatial variation of the total dissolved ( $<0.22 \mu\text{m}$ ) Sb concentration, dissolved Sb(v) concentration, dissolved Sb(III) concentration and the corresponding Sb(III)/Sb(v) ratio along the Reigous-Amous-Gardon continuum in January 2011 (a), March 2012 (b) and April 2012 (c).



Eh values ranged from 354 to 605 mV (Fig. 2b) and reflect the redox chemistry of the Fe(II)/Fe(III) couple, as usually observed for AMD.<sup>38</sup> The pH of the source ranged between 2.3 and 5.8 (Fig. 2c). Average Eh and pH values did not change drastically from station S1 to station COW G in the Reigous Creek; conversely, Eh and pH values respectively decreased and increased significantly from the Reigous Creek to the rivers Amous and Gardon (Fig. 2b and c), as a result of AMD neutralization and subsequent Fe(II) oxidation and precipitation. The relatively high SPM content (up to 49.2 mg L<sup>-1</sup>) along the Reigous–Amous–Gardon continuum (Fig. 2d) was due to the precipitation of Fe–As solid phases and schwertmannite in the Reigous Creek,<sup>28,29,39</sup> together with Fe- and Al-oxyhydroxides in the Amous river.<sup>30</sup>

#### 4.2 Dissolved and particulate Sb concentrations

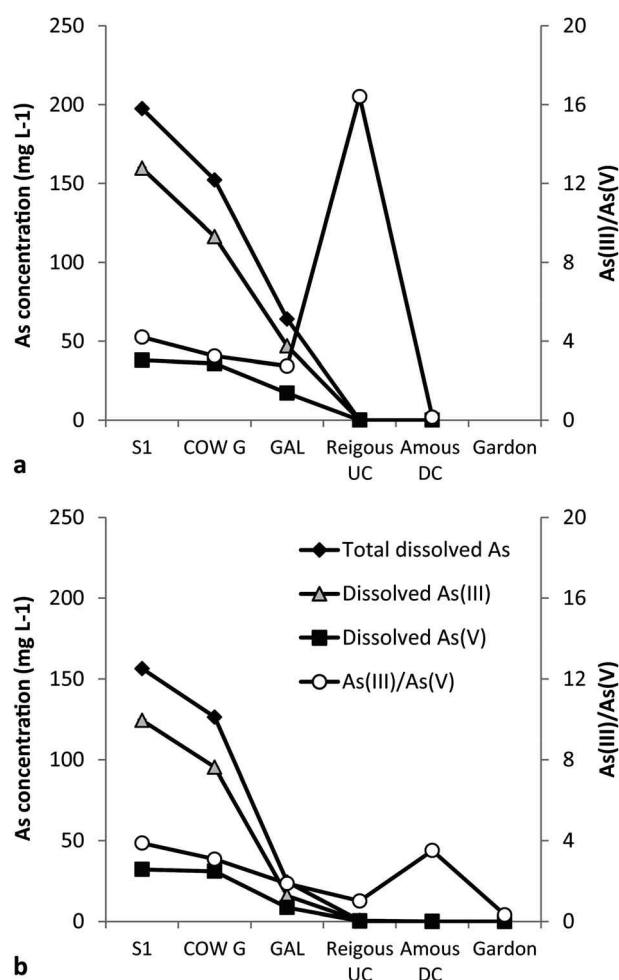
At the source of the Reigous Creek (S1), total dissolved Sb concentrations ranged between 7.7 and 409.9 µg L<sup>-1</sup> (Table 2). They decreased to less than 13.2 µg L<sup>-1</sup> at the Reigous UC station, located 1.5 km downstream from the source. This decrease was at least in part due to dilution by small tributaries (Fig. 1). In the Amous River upstream from the confluence with the Reigous Creek (Amous UC), total dissolved Sb concentrations did not exceed 0.23 µg L<sup>-1</sup> (Table 2).

Downstream from the confluence (Amous DC), total dissolved Sb concentrations increased within the range 0.34 µg L<sup>-1</sup> to 2.93 µg L<sup>-1</sup>. In the Gardon River downstream from the junction with the Amous River, total dissolved Sb concentrations ranged between 0.22 and 0.45 µg L<sup>-1</sup>, which still exceeded the values measured at station Amous UC located upstream from the confluence with the Reigous Creek. Concentrations of Sb in SPM were lower than total dissolved values with the corresponding solid-solution partitioning coefficient log K<sub>d</sub> varying in a wide range, from 2.4 L kg<sup>-1</sup> to 4.9 L kg<sup>-1</sup>, and indicating that Sb was mainly transported in the dissolved phase along the Reigous–Amous–Gardon continuum.

#### 4.3 Sb speciation in water

At the source of the Reigous Creek, both Sb(V) and Sb(III) were present in the total dissolved fraction (<0.22 µm); Sb(III)

represented 36% to 70% of the total dissolved Sb concentration at station S1 and 25–30% at station COW G (Fig. 3). Geochemical modeling indicates that dissolved Sb(V) was in the form of Sb(OH)<sub>6</sub><sup>-</sup> and Sb(OH)<sub>5</sub>(aq.) in various proportions, while



**Fig. 4** Spatial variation of the total dissolved (<0.22 µm) As concentration, dissolved As(V) concentration, dissolved As(III) concentration and the corresponding As(III)/As(V) ratio along the Reigous–Amous–Gardon continuum in March 2012 (a) and April 2012 (b).

**Table 3** Concentration (in µg Sb L<sup>-1</sup>) of the different inorganic Sb species along the Reigous–Amous–Gardon continuum obtained from geochemical modeling using the set of equilibrium constants published by Filella and May.<sup>37</sup> Input data used in the simulation corresponded to the composition of the waters collected along the Reigous–Amous–Gardon continuum on April 12, 2012 (Table 1)

Station	S1	COW G	GAL	Reigous UC	Amous DC	Gardon
Distance from the tailings pile (km)	0	0.03	0.15	1.48	2.7	8.5
Sb(OH) <sub>6</sub> <sup>-</sup>	8.8	5.4	1.2	3.0 × 10 <sup>-1</sup>	3.4 × 10 <sup>-1</sup>	2.6 × 10 <sup>-1</sup>
Sb(OH) <sub>5</sub> (aq.)	5.7	2.3	4.4 × 10 <sup>-3</sup>	6.3 × 10 <sup>-2</sup>	1.8 × 10 <sup>-6</sup>	1.0 × 10 <sup>-6</sup>
Sb(OH) <sub>3</sub> (aq.)	17	4.9	<1 × 10 <sup>-15</sup>	<1 × 10 <sup>-15</sup>	<1 × 10 <sup>-15</sup>	<1 × 10 <sup>-15</sup>
SI <sup>a</sup> FeSb <sub>2</sub> O <sub>4</sub>	170	169	138	133	<-3	<-3
SI <sup>a</sup> FeSbO <sub>4</sub>	135	135	118	116	<-3	<-3
SI <sup>a</sup> Sb <sub>2</sub> O <sub>3</sub> (rhombic)	3.2	2.6	<-3	<-3	<-3	<-3
SI <sup>a</sup> Sb <sub>2</sub> O <sub>4</sub>	2.7	1.6	<-3	<-3	<-3	<-3

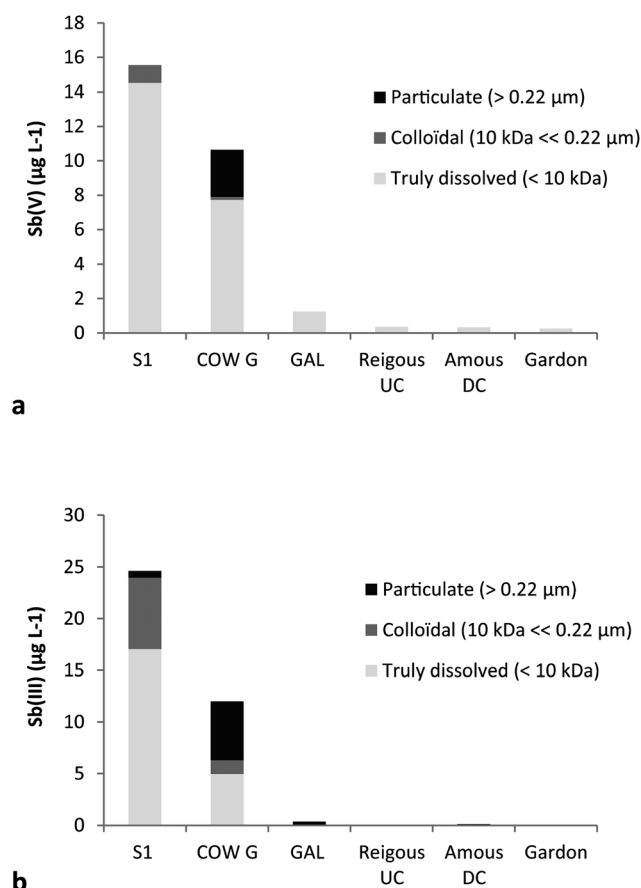
<sup>a</sup> SI: Saturation Index.

dissolved Sb(III) was in the form of  $\text{Sb(OH)}_3(\text{aq.})$  (Table 3). The waters from the stations S1 and COW G were supersaturated relative to Sb(III)- and Sb(V)-Fe oxides, respectively,  $\text{FeSb}_2\text{O}_4$  and  $\text{FeSbO}_4$ , and to Sb oxides,  $\text{Sb}_2\text{O}_3(\text{s})$  (rhombic) (valentinite) and  $\text{Sb}_2\text{O}_4(\text{s})$  (cervantite) (Table 3). This indicates that these solids may potentially precipitate in the Reigous Creek.

Both total dissolved Sb(III) and Sb(V) concentrations decreased during the flow from the source of the Reigous Creek to downstream sites in the rivers Amous and Gardon, and the Sb(III)/Sb(V) ratio decreased (Fig. 3). This indicates that attenuation was more efficient for Sb(III) than for Sb(V). Downstream station COW G, the Sb(III) concentration was below the detection limit.

Comparatively, the concentrations of As(III) and As(V) species also decreased along the flowpath and the As(III)/As(V) ratio decreased from station S1 to station GAL (Fig. 4); these attenuation processes were described previously for As in the Reigous Creek<sup>28,39</sup> and attributed to As(III) oxidation and the precipitation of As(III)-Fe(III) and As(V)-Fe(III) solid phases.

The speciation of Sb in the truly dissolved, colloidal and particulate phases in samples from April 2012 is presented in



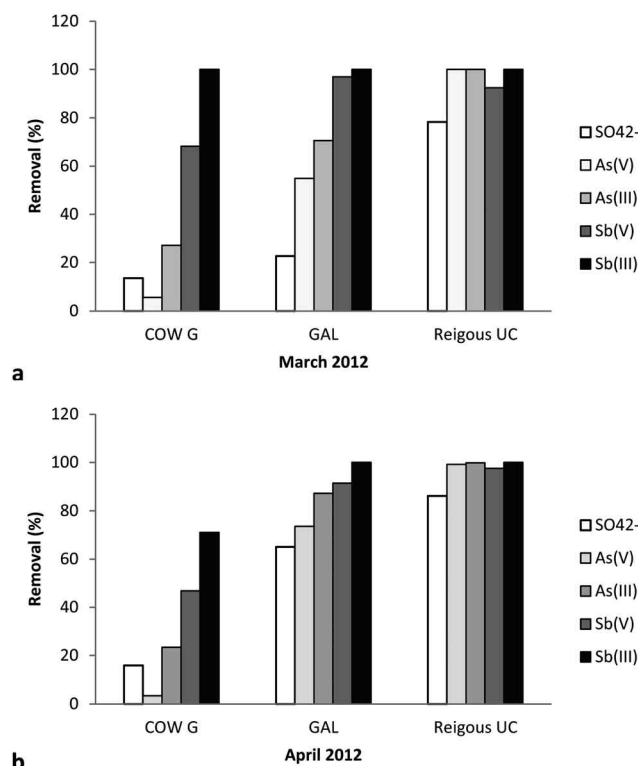
**Fig. 5** Distribution of Sb(V) (a) and Sb(III) (b) species between truly dissolved, colloidal and particulate phases at sampling stations along the Reigous-Amous-Gardon continuum on April 12, 2012. Speciation in the truly dissolved fraction and in the particulate phase was determined from direct measurement of Sb species in the ultrafiltrate and SPM extracts respectively; speciation in the colloidal phase was obtained by the difference between species concentration in the total dissolved phase (<0.22  $\mu\text{m}$ ) and their concentration in the truly dissolved phase (<10 kDa).

Fig. 5. It revealed the presence of Sb(III) and Sb(V) species both in the colloidal and in the particulate phases at stations S1, COW G and GAL. The sum of colloidal + particulate Sb(III) concentration represented 30 to 100% of total (truly dissolved + colloidal + particulate) Sb(III); for Sb(V), it represented less than 30%.

## 5 Discussion

The concentrations of Sb recorded from the long-term monitoring of the Reigous Creek hydrochemistry were of the same order of magnitude (tens to hundreds of  $\mu\text{g L}^{-1}$ ) as other drainage from Pb-Zn mines.<sup>12,40</sup> Although these concentrations denoted a significant contamination of the Reigous Creek with Sb, the concentration levels downstream from the Reigous Creek input in the rivers Amous and Gardon did not reach as much as  $\sim 3 \mu\text{g L}^{-1}$  and  $0.45 \mu\text{g L}^{-1}$ , respectively, the latter representing typical values for dissolved antimony in non-polluted waters. This denoted significant attenuation of Sb concentrations along the Reigous-Amous-Gardon continuum.

The decrease of Sb species concentrations at each station in the Reigous Creek relative to their concentrations at station S1 could be compared to the decrease of sulfate in March 2012 and April 2012, because this constituent is usually considered as the most conservative species in AMD (Fig. 6). Sb removal reached 45–68% for Sb(V) and 71–100% for Sb(III) at station COW G and respectively 91–97% and 100% at station GAL. Comparatively, sulfate removal reached less than 20% at station COW G and



**Fig. 6** Percent of Sb(V), Sb(III), As(V) and As(III) species removed from the aqueous phase during the course of the Reigous Creek from station S1 to stations COW G, GAL and Reigous UC, compared to percent removal of sulphate; surveys were carried out in March (a) and April (b) 2012. The lower As(V) removal at COW G reflects As(V) production through As(III) oxidation evidenced in a previous study.<sup>39</sup>



23–65% at station GAL (Fig. 6). Thus, dilution is not the only process affecting Sb concentration in the Reigous Creek; the trapping of Sb species on SPM or sediments occurs along the flowpath. Furthermore, attenuation at stations COW G and GAL appeared to be more efficient for Sb species than for As species (Fig. 6). For As(v), the removal was even less efficient than for sulfate, due to the production of As(v) resulting from As(III) oxidation evidenced in previous studies.<sup>39</sup>

Speciation analyses revealed the coexistence of both reduced Sb(III) and oxidized Sb(V) species in the Reigous Creek while Sb(V) largely predominated further downstream. Sb(III) was rarely observed in mine waters.<sup>11,13,18</sup> The high proportion of Sb(III) recorded at the source of the Reigous Creek was related to the generally suboxic conditions that characterized station S1, which was a transition zone between oxygen-depleted groundwater draining the tailings pile and the Creek water itself, opened to the atmosphere. Thus, Reigous Creek water at station S1 had not reached thermodynamic equilibrium, as evidenced by the predominance of the reduced state for other redox sensitive elements such as As and Fe (Table 1 and Fig. 4). Under such conditions, the persistence of Sb(III) species in the Reigous Creek depends on Sb(III) oxidation kinetics and on the rate of Sb(III) removal from solution through sorption or precipitation. A number of studies have investigated Sb(III) oxidation rates in waters<sup>41–45</sup> but few were dedicated specifically to mine waters.<sup>46</sup> The rate of Sb(III) oxidation by O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> was shown to be very slow in aqueous solutions.<sup>43</sup> It may be increased in the presence of Fe(III) or Mn(IV) (hydr)oxides,<sup>41,44</sup> and also in the presence of humic acids,<sup>42,45</sup> with pseudo-first-order rate constants of respectively  $k = 0.887$  per day<sup>41</sup> and  $k = 3.033 \text{ h}^{-1}$ .<sup>45</sup> In acid mine waters, Asta *et al.*<sup>46</sup> measured a rate of Sb(III) oxidation of  $0.01\text{--}0.02 \mu\text{mol L}^{-1} \text{ h}^{-1}$  and suggested that Fe(III) formed from microbial oxidation may abiotically oxidize Sb(III). Comparatively, the Sb(III) removal measured in our study was much faster, with a removal rate of  $0.40 \pm 0.08 \mu\text{mol Sb(III) L}^{-1} \text{ h}^{-1}$  and a removal rate constant  $k = 6 \pm 3 \text{ h}^{-1}$ , when considering a travel time of 18 minutes from station S1 to station COW G and first order kinetics.<sup>29</sup> This suggested that Sb(III) attenuation in the Reigous Creek was most probably not mainly ascribed to the oxidation of dissolved Sb(III). The contrasted behavior of As(III), the removal of which at station COW G coincided with the production of As(V) (Fig. 6a and b) corroborated this hypothesis.

The presence of Sb(III) in the colloidal and particulate phases in the Reigous Creek demonstrates that Sb(III) was readily trapped on the solid phase during transport in Reigous Creek water. The Sb(III)-bearing phases were not strictly identified, however oversaturation relative to Sb(III) oxides and Sb(III)–Fe oxides identified in other Sb-containing AMD<sup>12</sup> suggests that these phases might form in Reigous Creek water. Sb(V) appeared to be less efficiently removed from the aqueous phase than Sb(III) since the proportion of colloidal and particulate fractions relative to the dissolved fraction was lower for Sb(V) (Fig. 5) and the dissolved Sb(III)/Sb(V) ratio decreased from upstream to downstream sites (Fig. 3). Geochemical modeling revealed oversaturation relative to Sb(V)–Fe oxide FeSbO<sub>4</sub>, which was shown to form at other mining sites.<sup>12,47</sup> Sb(V) and Sb(III) were also probably sorbed onto mixed As(III)/As(V)–Fe(III)

oxy-hydroxides<sup>28</sup> and schwertmannite<sup>29</sup> that precipitate successively along the flowpath in the Reigous Creek. Additional Sb(V) and Sb(III) sorption may also occur at the confluence between the Reigous Creek and the Amous river where Fe- and Al-rich SPM containing notably ferrihydrite precipitate upon AMD neutralization.<sup>30,48</sup> Sorption onto amorphous iron oxides<sup>12,49</sup> or schwertmannite<sup>21</sup> was shown to be involved in the natural attenuation of Sb in mine waters and Sb(III) appeared to sorb more strongly onto surfaces of Fe(III) (hydr)oxides than Sb(V).<sup>14</sup> This statement was in agreement with undetectable Sb(III) concentrations in the rivers Amous and Gardon while Sb(V) remained present. Here, the presence of a significant proportion of uncharged Sb(OH)<sub>5</sub> (up to 20% of total dissolved Sb(V)) in the Reigous Creek, related to the acid character of the water, may limit the sorption of Sb(V) to Fe precipitates, thus allowing substantial leak of Sb(V) to downstream watershed.

The efficiency of Sb(III) and Sb(V) removal through sorption on neoformed minerals or precipitation of secondary Sb solids along the Reigous–Amous–Gardon continuum appeared to change throughout time, according to the wide range of log  $K_d$  values. This probably reflects the important seasonal changes in the SPM concentration (from below 0.8 to 36 mg L<sup>-1</sup>, this study) and its Fe content (from 4 to 29% (ref. 48)) and Fe/Al ratio (from ~1 to 20 (ref. 30)), potentially able to influence Sb retention on particles.

## 6 Conclusion

The pH and oxygen concentration gradient that characterizes the Carnoulès mine waters offered a unique opportunity to investigate the redox speciation of antimony in such systems. The study revealed that Sb(III) can subsist during periods of hours in acid Reigous Creek waters, causing a distribution between Sb(V) and Sb(III) species that were at variance with thermodynamic predictions. Trapping of Sb(III) and Sb(V) on neoformed Fe minerals and precipitation of secondary Sb(III) and Sb(V) phases were the most probable causes of Sb attenuation along the Reigous–Amous–Gardon continuum, besides dilution. Further work is needed to unequivocally identify Sb-bearing secondary solid phases in SPM and sediments. Altogether, these results gave a better understanding of Sb behavior in mine waters and downstream watershed.

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