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An updated insight into the natural attenuation of As concentrations in Reigous Creek (southern France)

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ABSTRACT

The removal of metals and metalloids occurring in acid mine drainage has been studied on different scales (years, days). Dissolved and particulate concentrations of Fe and As were monitored over a 4-a period along Reigous Creek, an acid mine drainage from a former Pb–Zn mine in southern France. Dissolved concentrations of Fe ($12\text{--}25\text{ mmol L}^{-1}$), As ($0.9\text{--}3.5\text{ mmol L}^{-1}$) and SO_4^{2-} ($10\text{--}70\text{ mmol L}^{-1}$) exhibited seasonal variations related to rainfall, with an increase during the driest months. About 30% of the As initially present in solution as As(III) was coprecipitated with Fe oxides in the first 40 m of Reigous Creek. The corresponding As removal rate was $3.58 \times 10^{-7}\text{ mol L}^{-1}\text{ s}^{-1}$. The mineralogy of resultant precipitates varied spatially and seasonally. Over the first 40 m, amorphous As(V)–Fe(III) phases and tooeleite, were formed. Sediments deposited in the bed of the creek close to the spring contained both types of solid phases. Laminated concretions, which consist of precipitates around bacterial structures, were mainly constituted of tooeleite. Further downstream, these Fe-oxide phases were replaced by schwertmannite and ferrihydrite. On a daily basis, concentrations of dissolved Fe and As have been shown to vary up to 10% during the day as a result of photoreduction of Fe-oxide phases.

1. Introduction

Arsenic is a highly toxic element that is released into water by natural processes as well as by human activity (Smedley and Kinniburgh, 2002). The biogeochemical processes controlling the fate of As in water have consequently been widely studied. These studies have shown that As mobility is limited by its ability to bind to solid oxide phases such as Fe oxides and to a lesser extent to Al hydroxides (Masue et al., 2007, and references therein).

In water, inorganic As may occur as arsenate (As(V)) and arsenite (As(III)). The adsorption of As onto Fe oxides depends on pH and on As speciation. Arsenate adsorbs strongly to Fe-oxide surfaces in acidic and near-neutral-pH water (Dzombak and Morel, 1990; Waychunas et al., 1993). Adsorption experiments by Raven et al. (1998) also indicated greater adsorption of arsenate than of arsenite at pH values below 6–7.5 with a relatively low initial As/Fe molar ratio (0.024–0.071). With a higher initial As/Fe ratio (1.18), arsenite adsorption is at a maximum at approximately pH 9 and greater than that of arsenate, which decreases continuously from pH 3 to 11. Other parameters such as concentrations of the

major ions and the nature of the Fe mineral phases also influence As sorption on Fe oxides (Raven et al., 1998; Jain et al., 1999; Pedersen, 2006; Banerjee et al., 2008).

Mining of some metal ores results in large quantities of sulfide-rich wastes that often contain high concentrations of As. The oxidation of these wastes by meteoric water can generate Fe and As-rich acid mine drainage (AMD), and subsequent precipitation of Fe oxyhydroxide phases as a function of pH. As pH rises the following sequence of minerals has been observed: jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, schwertmannite $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$, ferrihydrite $\text{Fe}_5(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, goethite $\alpha\text{-FeOOH}$, or lepidocrocite $\gamma\text{-FeOOH}$, as a function (Bigham et al., 1996a). These Fe oxides are efficient in scavenging As by adsorption (Fukushi et al., 2003, 2004; Jönsson and Sherman, 2008) or coprecipitation (Carlson et al., 2002; Morin et al., 2003; Pedersen et al., 2006). The reduction of the Fe-oxyhydroxides can subsequently release As into solution. In AMD surface water, conditions are generally oxidizing, however Fe photoreduction can take place causing diel variations in dissolved As concentrations (Fuller and Davis, 1989; Nimick et al., 2005; Karlsson et al., 1995; Tate et al., 1995).

In Reigous Creek, which drains the tailings impoundment of the Carnoulès mine, the precipitation of Fe oxides is linked to bacterial activity and As is removed through coprecipitation (Bruneel et al., 2003; Casiot et al., 2003; Duquesne et al., 2003). Depending on the

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location, precipitation of Fe(III)–As(III) (tooeite) nano-crystals and/or amorphous Fe(III)–As(V) was observed (Casiot et al., 2003; Morin et al., 2003). These data from 1-year monitoring studies of water composition provided evidence for seasonal variations in As removal by Fe oxides, with the highest removal being recorded in winter. However, these studies did not cover a complete hydrological cycle and uncertainty remains regarding the relationship between the hydrologic conditions and Fe and As removal. Hydrological conditions vary drastically from season to season and from year to year in a Mediterranean climate and further investigation was necessary to resolve the relationship between the hydrologic conditions and Fe and As removal.

The present study was undertaken to better characterize the variability of dissolved As concentrations in Reigous Creek over different time scales and to gain more insight than was previously possible into the processes that control As removal in Reigous Creek. To this end, the concentrations of As(III), As(V), total dissolved As (AsT), Fe(II) and total dissolved Fe (FeT) together with some selected physicochemical parameters (temperature, rainfall, redox potential, light intensity, dissolved O_2 , SO_4^{2-}) were determined over different time scales (diurnal, seasonal, interannual). The concentrations of particulate As and Fe and the mineralogy of solid phases were also determined.

2. Site description

The Carnoulès Pb–Zn mine is located in southern France in the drainage basin of the Gardon d'Anduze, a tributary of the Rhone River (Fig. 1). The mine, which was abandoned in 1963, produced 1.2 MT of spoil material containing quartz, sulfide minerals, metals (Pb, Zn, Tl) and As. The material was deposited behind a dam.

The hydrogeological and biogeochemical conditions of the Carnoulès spoil heaps that generate As-rich AMD have been characterized in several studies (Casiot et al., 2003; Koffi et al., 2003; Bruneel et al., 2005). AMD is generated at the base of the tailings stock where O_2 -rich water that drains from the surroundings penetrates during rainfall events. The groundwater of the tailings stock is characterized by exceptionally high As concentrations of up to 1 gL^{-1} (i.e. 13 mmol L^{-1}).

The water emerges at the bottom of the dam forming the source of Reigous Creek (station S), at a flow rate of $0.8\text{--}1.7\text{ L s}^{-1}$. The

water is acidic (pH 2–3) and rich in dissolved Fe and As ($[Fe] = 0.5\text{--}1\text{ gL}^{-1}$ i.e. $9\text{--}18\text{ mmol L}^{-1}$; $[As] = 50\text{--}350\text{ mgL}^{-1}$ i.e. $0.7\text{--}4.7\text{ mmol L}^{-1}$) predominantly in the reduced forms, Fe(II) and As(III) (Casiot et al., 2003). Over the first 40 m of the creek, the addition of seepage water is negligible and large amounts of Fe precipitates forming laminated orange to yellow concretions that accumulate around bacterial structures and contain up to 20% wt. of As (Leblanc et al., 1996). At a distance of 150 m from its source (station Gal), the Reigous receives water from a small Fe-rich tributary, the Ru Gal. Before the confluence with the Amous River 1.5 km downstream from its source (station Reigous UC), Reigous Creek also receives inputs from quarries and mine galleries.

3. Materials and methods

The location of sampling stations in Reigous Creek is shown in Fig. 1. During the long term monitoring programme, water samples were taken monthly from November 2004 to 2008 at four stations located along Reigous Creek. Hourly variations in water physicochemistry over a diurnal cycle were monitored during a 36 h survey that was conducted at station G, on the 9th and 10th of May 2007.

The pH, temperature, conductivity and redox potential (Eh) were measured in the field with an Ultrameter™ model 6P (Myron L Company, Camlab, Cambridge). Dissolved O_2 (DO) was measured with CHEMets® tests (CHEMetrics, Calverton, USA) based on colorimetric detection after reaction of DO with indigo carmine for the $0\text{--}12\text{ ppg}^{-1}$ range and with rhodazine D for $0\text{--}1\text{ ppg}^{-1}$ range.

Water samples were filtered immediately after collection through $0.22\text{ }\mu\text{m}$ Millipore polycarbonate membranes fitted on Sartorius polycarbonate filter holders. One aliquot was immediately acidified to pH 1 with HNO_3 Merck Suprapur and stored at $4\text{ }^\circ\text{C}$ for the determination of total dissolved Fe (FeT). Another aliquot was taken for determination of Fe(II). It was buffered to pH 4.5 with an ammonium acetate/acetic acid buffer immediately after filtration and Fe(II) was complexed by adding 1 mL of a 0.5% (w/w) 1,10-phenanthroline chloride solution to 10 mL of sample (Rodier et al., 1996). Samples for As speciation were preserved with 5% EDTA 0.25 M, as recommended by Bednar et al. (2002), and deep frozen until analysis. The samples for the determination of SO_4^{2-} were also deep frozen.

Total Fe was determined by Flame Atomic Absorption Spectrometry (FAAS). Iron(II) concentrations were determined using spectrophotometry at 510 nm, and Fe(III) was calculated by the difference between total Fe and Fe(II). Total As was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, PQ 2+, VG-elemental, Fisons or X Series, Thermo). The elevated As concentrations required dilution. The dilution was done by introducing an aliquot of the initial sample into Milli-Q water (Millipore®) and which was then acidified (1/1000 v/v) with HNO_3 (Merck Suprapur). No interference due to ArCl was detected. ICP-MS was calibrated using peak intensity, acquired in peak jump mode, with standard solutions. Indium-115 was used as internal standard to correct for changes in peak intensities due to instrumental drift. Inorganic As speciation analyses were carried out using anion-exchange chromatography (25 cm \times 4.1 mm i.d. Hamilton PRP-X 100 column with Varian ProStar gradient solvent delivery system) coupled to Hydride Generation (HG) (VGS 200, Fisons, France) with Atomic Fluorescence Spectrometry (AFS) detector (Excalibur, PSAAnalytical, GB) (Casiot et al., 2005). The detection limit was $0.17\text{ }\mu\text{g L}^{-1}$ (i.e. 2.27 nmol L^{-1}) for As(III) and $0.46\text{ }\mu\text{g L}^{-1}$ (i.e. 6.13 nmol L^{-1}) for As(V) with a precision of $>5\%$. Sulfate concentrations were determined after precipitation with $BaCl_2$ and stabilisation with polyvinyl-pyrrolidone by nephelometry with a spectrophotometer at 650 nm (Rodier et al., 1996).

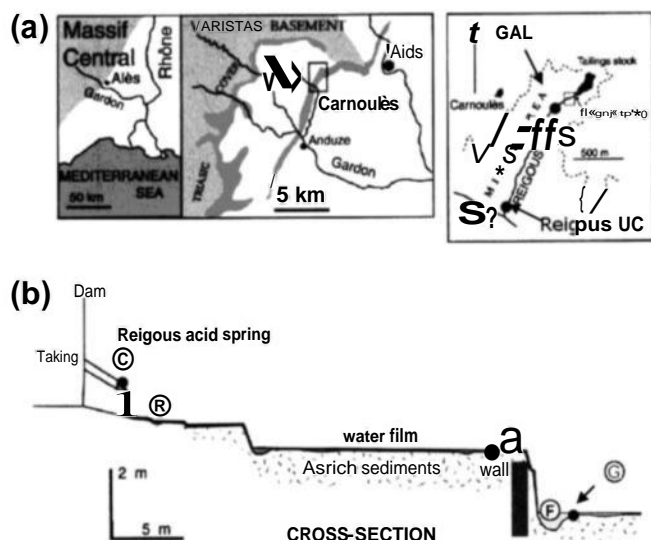


Fig. 1. Location of the study area and sampling stations along Reigous Creek. (a) General maps and (b) cross section of the first 40 m of Reigous Creek.

Precipitates were sampled over a period of 18 months between May 2006 and February 2008. Three different types of precipitates were collected: sediments (fine particles deposited at the bottom of the stream), laminated concretions made of sediments precipitated around bacterial structures, and sediments that undergo periods of drying when they are temporarily out of the water during low flow periods. The precipitates were dried under vacuum. They were then dissolved in a microwave oven using 10 mL of HN_3 (Merck Suprapur) for 50 mg sample following the 3051 EPA protocol with slight modifications. The microwave oven programme consisted of two steps: increasing the temperature for 15 min from ambient to 500 °C followed by 15 min at 500 °C. Total As and Fe concentrations were determined by ICP-MS as described for the aqueous phase. The mineralogical composition of the solid samples was determined by X-ray powder diffraction (XRD) using $\text{Co K}\alpha$ radiation. Data were recorded over a 2θ range of 5–85° with

a step size of 0.03°. Samples were analyzed in continuous mode using a Panalytical X'Pert Pro MPD diffractometer equipped with an X'Celerator detector, counting 2 h per sample.

4. Results

4.1. Monthly variations in water chemistry

The variations in the main physicochemical parameters (rainfall, pH, DO, temperature (T), and SO_4^{2-}) along Reigous Creek are presented in Fig. 2. The mean annual rainfall in the Reigous basin during the study period was 660 mm. The distribution of monthly rainfall was typical of the Mediterranean climate, including long drought periods in summer and intense rainfall events especially in autumn (September to November) and to a lesser extent in

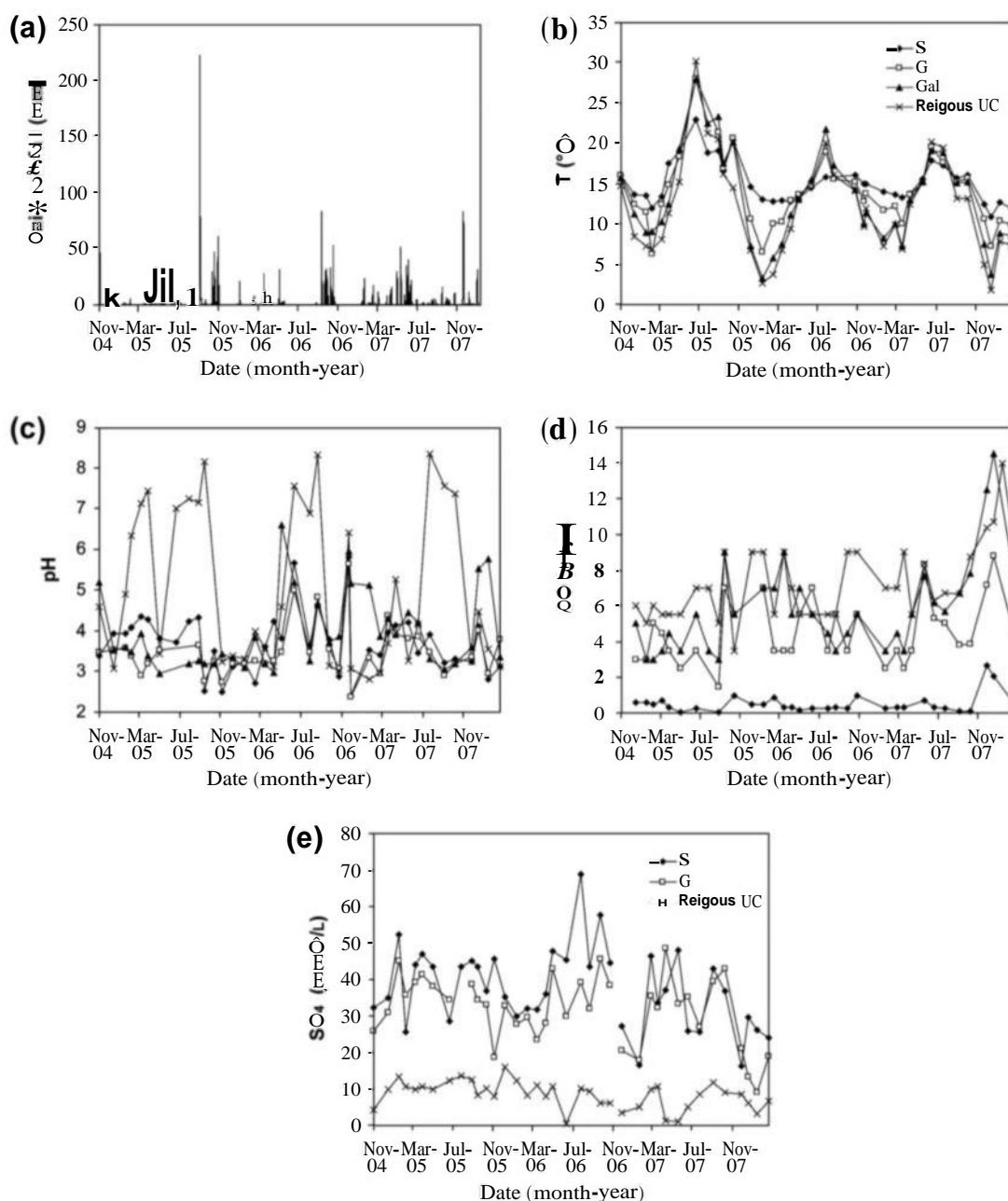


Fig. 2. Monthly variations in the main physicochemical parameters during the period of this study. (a) Daily rainfall over the tailings stock, (b) temperature of Reigous water (T), (c) pH, (d) dissolved O_2 (DO), and (e) concentrations of dissolved SO_4^{2-} .

spring (May). The temperature of the water at the source of the Reigous varied slightly ($15.1 \pm 2.6^\circ\text{C}$). In Reigous Creek, the water temperature is affected by the air temperature resulting in a larger range of values. Except at the Reigous UC station, the Reigous water was generally acidic with pH values between 2.39 (station G) and pH 6.60 (station Gal). The variance of pH values was less than 25%. At Reigous UC station, greater pH variations were observed, with pH values ranging from 2.82 to 8.35, the highest values being encountered during the driest months. This pattern of pH variations attests to the negligible contribution of AMD during the dry period due to evaporation between the source and the Reigous UC station. It also indicates that the input of water is not contaminated by AMD. Dissolved O_2 concentrations in the water at the Reigous source ranged from below detection limit (0.1 mg L^{-1}) to 2.7 mg L^{-1} , the highest values being observed after rainfall events. Dissolved O_2 increased sharply between stations S and G, indicating rapid oxygenation occurs in this creek segment.

Sulfate concentrations ranged from 10 to 70 mmol L^{-1} in the water at the source. Concentrations decreased gradually along

Reigous Creek. At the Reigous UC station, they ranged between 1 and 16 mmol L^{-1} . Seasonal variations were also observed with an increase in concentrations during the driest months. The variations in dissolved Fe and As in Reigous Creek are shown in Fig. 3. The variations in the concentrations of the two elements confirm those reported by Casiot et al. (2003). Dissolved Fe concentrations ranged from 12 to 25 mmol L^{-1} in water at the source. Concentrations decreased from the source to the Reigous UC station where Fe concentrations were always below 0.84 mmol L^{-1} . Iron concentrations generally increased during the driest months and decreased as a result of intense rainfall events except at the Reigous UC station where the reverse pattern was observed (i.e. lower values during the driest months) due to resurgences of unpolluted water from the Amous River in the Reigous Creek just before the confluence. In the water at the source, the concentrations of dissolved As ranged from 0.9 to 3.5 mmol L^{-1} . Arsenic concentrations decreased with distance from the source to values below 25 pmol L^{-1} at the Reigous UC station. Generally higher concentrations were observed during the driest months except at Reigous UC station, which displayed higher concentrations during the wet season. Over the year, the proportion of As removed from water was almost constant around 30%, whatever the flow rate or the concentrations of Fe or As in the dissolved phase. The proportion of Fe(III) was generally negligible in Reigous Creek except at the Reigous UC station where it was 30% (Fig. 4). In the first 150 m of the creek, the mean proportion of As(V) reached 40%. Further downstream the proportion of As(V) increased to reach 80% at the Reigous UC station.

4.2. Solid phase mineralogy and chemistry

Results of XRD analyses are presented in Fig. 5. At stations S and G, they indicate the presence of generally amorphous precipitates probably made of Fe(III)–As(V) phases as previously found by Morin et al. (2003) except in July at station S where very small quantities of tooeleite were encountered. The structure of this Fe(III)–As(III) mineral has been described by Morin et al. (2007). At station E, the data revealed the presence of significant proportions of tooeleite throughout the year. At the same stations, dry sediments were generally more crystalline than fresh sediments suggesting that ageing and/or dehydration of precipitates favor the formation of tooeleite. At the Gal and Reigous UC stations, the presence of schwertmannite was observed, in agreement with the results of Casiot et al. (2005).

The mean chemical composition of precipitates is given in Table 1. The mean proportion of As ranged between 2% and 20%, and that of Fe between 13% and 35%. Arsenic/Fe molar ratios at upstream stations (S, G and E) varied from 0.20 to 0.94 with an average of 0.61. The data did not indicate any influence of phase crystallinity

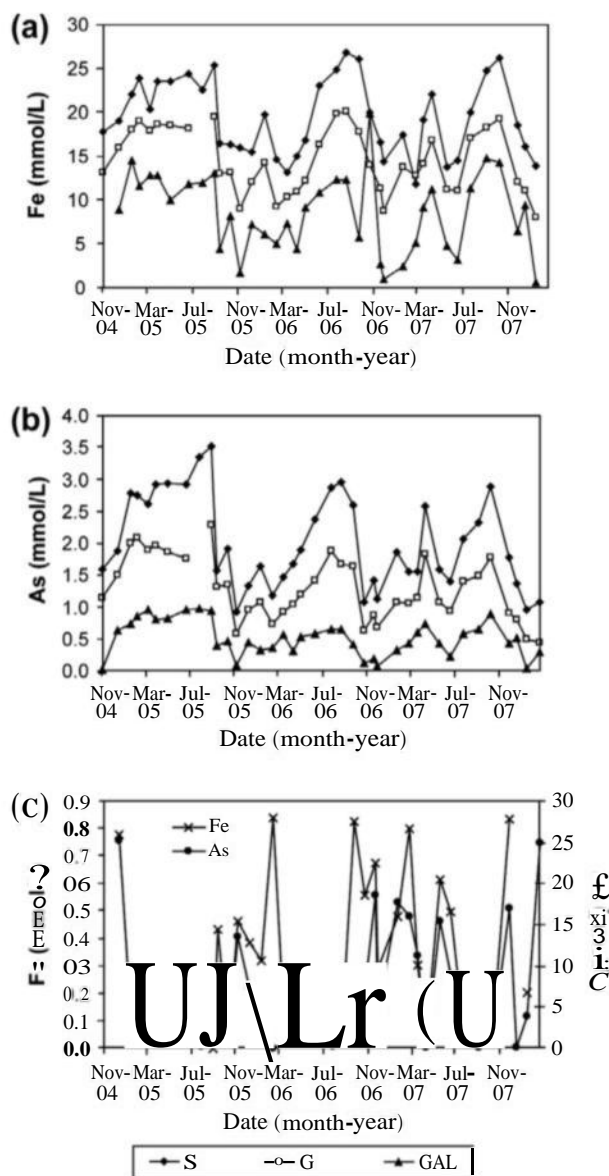


Fig. 3. Monthly variations in As and Fe concentrations in Reigous Creek (a) total dissolved Fe, (b) total concentrations of dissolved As, (c) total concentrations of dissolved Fe and As at Reigous UC station.

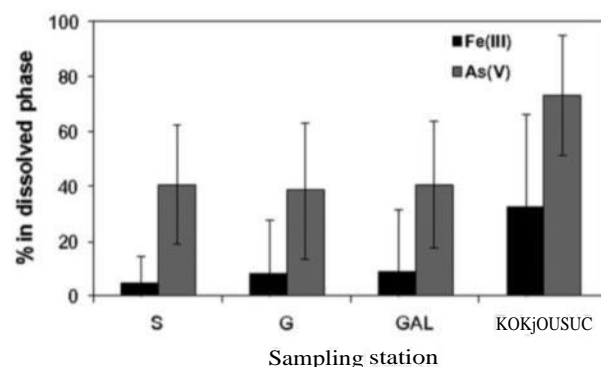


Fig. 4. Mean values and standard deviations of monthly variations in the proportion of (a) Fe(III) and (b) As(V) in Reigous Creek.

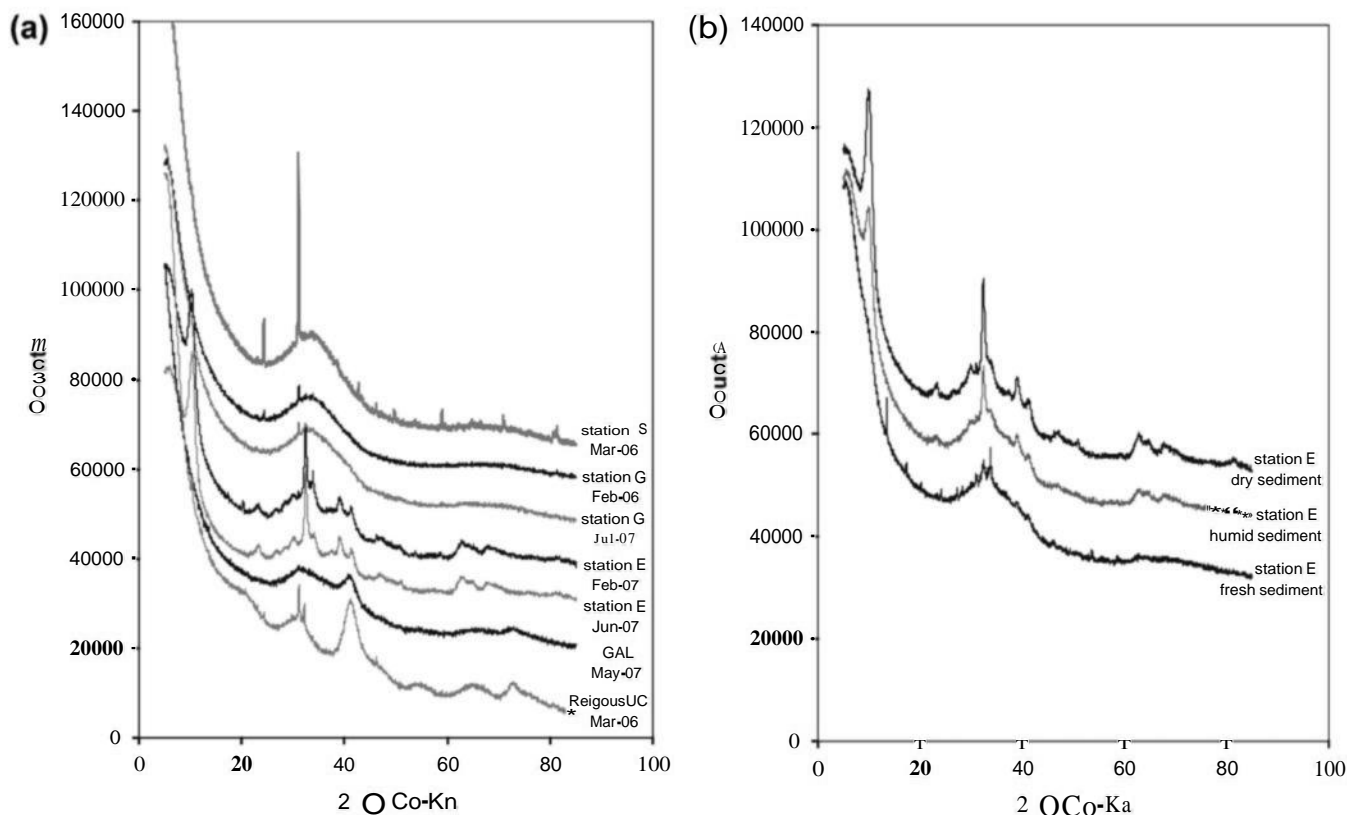


Fig. 5. XRD spectrum of Reigous Creek precipitates.

Table 1

Mean chemical composition and mineralogy (Am As(III)-Fe(III) = amorphous As(III)-Fe(III) phase, Am As(V)-Fe(III) = amorphous As(V)-Fe(III) phase, Too = tooelite, Schw = schwertmannite, Fh = ferrihydrite) of different precipitates recovered in the bed of the Reigous Creek.

Sampling stations	Facies	%As			%Fe			As/Fe			Mineralogy
		Mean	Min	Max	Mean	mm	Max	Mean	mm	Max	
S	Fresh sediments	15	12	19	23	20	30	0.58	0.54	0.69	Am As(III)-Fe(III)/Am As(V)-Fe(III)
	Laminated concretions	16	12	19	28	24	33	0.62	0.49	0.71	
	Dry sediments	6	4	7	12.6			0.25	0.20	0.34	Too
E	Fresh sediments	15	13	17	26	21	32	0.57	0.39	0.71	Too
	Laminated concretions	15	11	23	27	24	33	0.56	0.43	0.82	Too
	Dry sediments	17	11	22	22	16	29	0.74	0.45	0.90	Too
G	Fresh sediments	15	11	21	21	13	29	0.74	0.60	0.92	Am As(V)-Fe(III)
	Dry sediments	20	14	23	23	18	27	0.83	0.70	0.94	Too
GAL	Fresh sediments	12	7	18	31	20	37	0.35	0.18	0.39	Schw
Reigous UC	Fresh sediments	2	0	3	35	24	43	0.05	0.02	0.10	Schw/Fh

and/or the speciation of As on the As/Fe ratio. Between stations S and G, the precipitates displayed higher As/Fe ratios than the As/Fe ratio calculated using the quantities of As and Fe that disappeared from the aqueous phase, which were between 0.045 and 0.14 (Table 1). One explanation for this discrepancy could be related to granulometric sorting of phases with different As/Fe ratios during sedimentation. At the Gal and Reigous UC stations, the As/Fe ratios were generally lower than those upstream.

4.3. Diel variations in the main physicochemical parameters and As and Fe concentrations

The variations in the main physicochemical characteristics of water over a 36-h period and their relationship with light intensity

were studied in Reigous Creek. Water-quality parameters such as pH, redox potential (Eh), conductivity (σ), dissolved O₂ (DO), light intensity (Li) and temperature (T) were measured in the field. Dissolved O₂, T and Li data are reported in Fig. 6a. Diel variations in As and Fe concentrations were also evidenced in Reigous Creek, with an increase in Fe and As concentrations during the day (maximum at 12 am) and a decrease during the evening and the night (Fig. 6b). The cyclical trend reflects the influence of the daily light cycle. Variations in Fe and As concentrations are positively correlated with light intensity. The maximum difference in the dissolved concentrations of both elements between 12 am and 12 pm was around 10% (1.1 mmol L⁻¹ and 0.16 mmol L⁻¹ for Fe and As, respectively). Given that Fe is mainly in the reduced form, fluctuations in the Fe(II)/Fe_{tot} ratio values are not significant and it can be

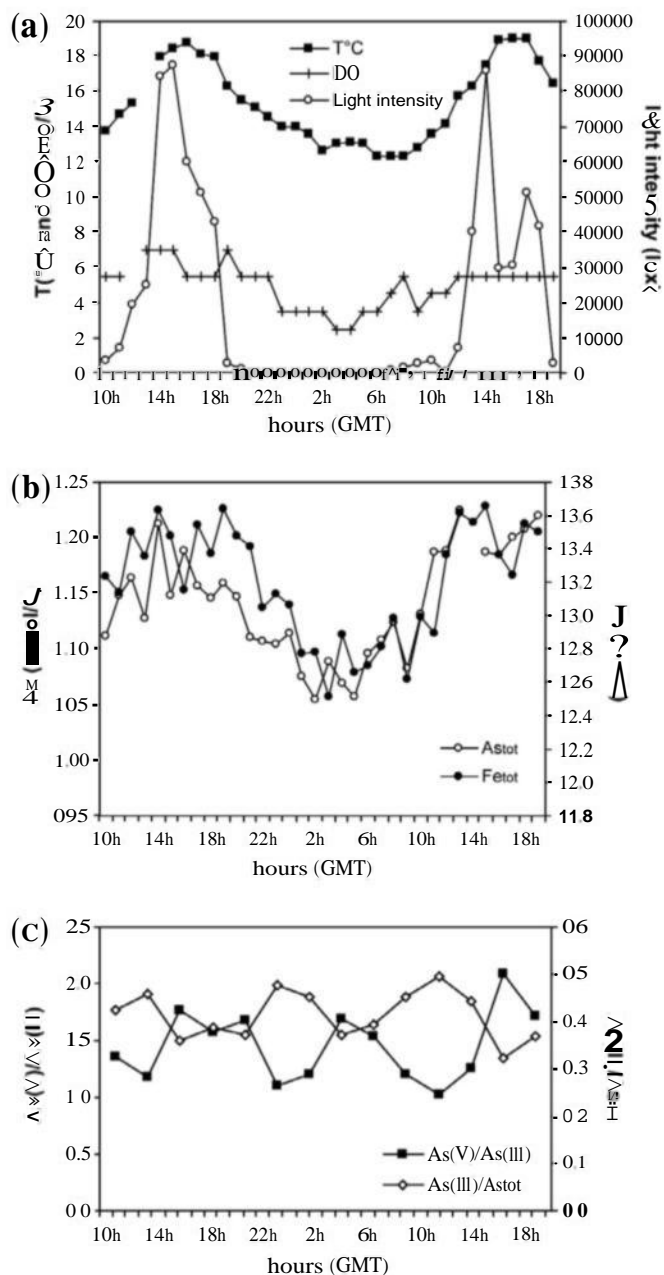


Fig. 6. Diel variations at station G (May 9–10, 2007) in (a) light intensity (Li), dissolved O₂ (IX) and temperature (T); (b) dissolved Fe and As; (c) As(III)/As(I) and As(V)/As(III).

assumed that variations in total Fe concentrations reflect Fe(II) variations. Between 30% and 50% of As is in the reduced form, and As(III) is negatively correlated with total Fe, while total As concentrations vary between 370 and 590 pmol L⁻¹ which represents 35% of variations. Interestingly, maximum As(III)/As_{tot} ratios were observed between 2 pm and 4 pm (Fig. 6c).

5. Discussion

5.1. Coprecipitation of Fe and As

In the first 40 m of the creek, monitoring confirmed previous results obtained during a shorter observation period, which showed intense decrease in the concentrations of dissolved As and Fe with increasing distance from the source. In this section of the creek,

which receives negligible quantities of water from other sources, this decrease is due to Fe oxidation and removal of As by coprecipitation with Fe oxides. However unlike previous observations, results of the present study showed that the percentage of As removed from solution was constant at around 30% and independent of the initial concentration of dissolved As or Fe.

The saturation indices reported as a function of pH are shown in Fig. 7. These saturation indices have been calculated using the chemical composition of water emerging at the Reigous spring according to the following formula:

$$SI = \log(IAP) - \log(K) \quad (1)$$

where SI corresponds to saturation indices, IAP is the ionic activity product and K is the equilibrium constant of the mineral phase.

To make a more equitable comparison, the saturation indices for all Fe-containing minerals have been adjusted to one Fe atom per formula unit (Gammons et al., 2008). For the calculations, it was hypothesized that available Fe(III) for precipitation within the first 40 m corresponded to total Fe precipitated along this distance. Based on the equilibrium constants given by different authors (Bigham et al., 1996a; Regenspurg, 2002; Yu et al., 2002; Majzlan et al., 2004; Parmentier, 2006), Reigous Creek is supersaturated with respect to all Fe hydroxides precipitates regardless of the schwertmannite solubility constant used (Bigham et al., 1996a; Yu et al., 1999, 2002; Majzlan et al., 2004). According to these calculations, jarosite precipitation would be expected to occur below pH 4 whereas schwertmannite should form at pH > 4 as generally observed in AMD (Bigham et al., 1996a; Regenspurg et al., 2004; Sanchez-España et al., 2007). However, the field observations did not conform to these calculations. In agreement with the previous observations of Morin et al. (2003), the study showed the precipitation of amorphous As(V)–Fe(III) or As(III)–Fe(III) solid phases and tooeleite in the first 40 m downstream from the source of Reigous Creek. This may be explained by the fact that thermodynamic predictions do not take into account kinetic factors (such as Fe(II) oxidation and subsequent of Fe(III) precipitation) and by the presence of high quantities of As, which prevent the formation of classical crystalline phases, as suggested by Langmuir et al. (2006) and Carlson et al. (2002) for schwertmannite. Concerning schwertmannite, its precipitation should occur when As concentra-

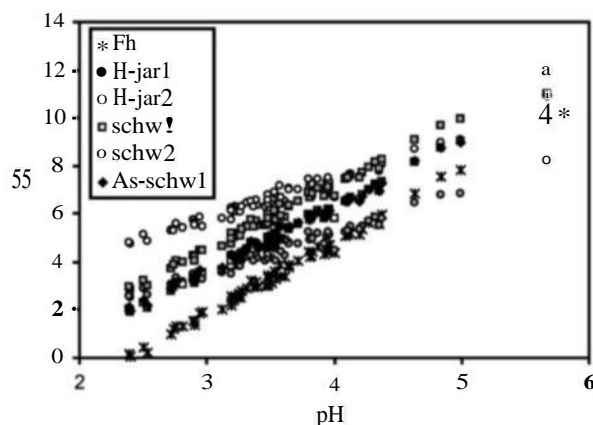


Fig. 7. Saturation indices of the main Fe-minerals as a function of pH in the water at the source of Reigous Creek. The saturation indices for all Fe-containing minerals were adjusted to one Fe atom per formula unit (Gammons et al., 2008). The following stability constants were used: H-jarosite 1, $\log K = -5.39$ (Sarmiento, 2007); H-jarosite 2, $\log K = 12.1$ (Sarmiento, 2007); ferrihydrite, $\log K = 4.89$ (Bigham et al., 1996a); schwertmannite 1, $\log K = 18$ (Bigham et al., 1996b); schwertmannite 2, $\log K = 10.5$ (Yu et al., 1999); arsenical schwertmannite, $\log K = 13.5$ (Regenspurg, 2002).

tion is low compared to Fe(III) and this is not the case in Reigous Creek close to the spring. Moreover, although thermodynamic data for amorphous phases and tooeite are not available, both field observations and laboratory experiments have shown that the formation of this mineral is clearly linked to bacterial activity and kinetic aspects. It is favoured by slow reactions and flow rates (Morin et al., 2007; Egal et al., 2009). Its crystallinity is improved by ageing and subsequent dehydration of a primary mineral phase that seems to be an amorphous As(III)–Fe(III) oxide. Indeed, bacteria that mediate redox reactions involving As and Fe in the system could also play a major role in determining the nature of the solid phase, as demonstrated by Duquesne et al. (2003), however, preliminary results on bacterial strain evolution throughout the year in Reigous Creek did not allow an explanation of mineralogical variations observed in the field.

After 40 m, Reigous Creek receives water from seepage and small tributaries, which are not influenced by AMD. This process results in the dilution of As. In contrast to the findings obtained in the first 40 m of the creek, the formation of more common As–Fe phases such as As-rich schwertmannite and ferrihydrite was observed in this reach. This is consistent with the low concentrations of As that do not prevent formation of crystalline mineralogical phases as described above. The succession of Fe oxides (schwertmannite and ferrihydrite) is consistent with the increase in pH values along the stream from spring to confluence.

5.2. Iron oxide photoreduction and release of arsenic

At station G, concomitant diel variations in As and Fe in solution were observed. An increase in concentrations characterized by a maximum at 12 am was observed and is likely due to photoreduction of Fe-oxide phases which releases Fe(II) as reported elsewhere for acidic waters (Collienne, 1983; Sullivan et al., 1998; McKnight et al., 2001; Butler and Seitz, 2006; Gammons et al., 2008). Iron photochemical reduction is a chemical process whereby photons, generally in the wavelength range of 360–450 nm (ultraviolet radiation) or slightly longer in very acidic waters (Diez Ercilla et al., 2009), are absorbed by dissolved Fe(III) species or freshly precipitated Fe(III) oxyhydroxide surfaces. At night the decrease in Fe and As concentrations is explained by oxidation of Fe(II) into Fe(III) and subsequent precipitation of Fe oxides combined with adsorption or coprecipitation of As. During the day, the photoreduction competes with oxidation and leads to the dissolution of Fe precipitates and the release of the sorbed As.

The maximum As(V)/As(III) ratio (Fig. 6c) observed during the decreasing phase of As concentrations between 2 and 4 pm suggests that As(III) has more rapid recombination (coprecipitation or adsorption) kinetics with Fe oxides than As(V). This corroborates the results of Raven et al. (1998) who showed more rapid adsorption of As(III) on ferrihydrite in acidic (pH 4.6) water with a high (As/Fe molar ratio 1.18) initial addition of As. Moreover, the concomitant increase of As(III)/As_{tot} ratio and decrease of As(V)/As(III) ratio (Fig. 6c) in the dissolved phase during the increase in light intensity may be related to As(III) release from the solid phase due to the reduction of As(V) released into solution consequent to desorption from Fe hydroxides. Indeed, reduction of arsenate to arsenite may occur after Fe(III) reduction (Islam et al., 2004; Pedersen, 2006). The decrease in As(III)/As_{tot} molar ratio simultaneously with light intensity may be explained by both a decrease in photoreduction intensity and As(V) reduction. During the first hours of night, As(III)/As_{tot} molar ratio shows an increase simultaneously with a decrease in As concentrations that may be related to greater precipitation or adsorption of As(V). Then a balance with oxidation of As and subsequent decrease in As(III) concentrations related to precipitation of As-rich Fe oxides is evidenced in the dissolved concentrations. Mineralogical analyses have previously

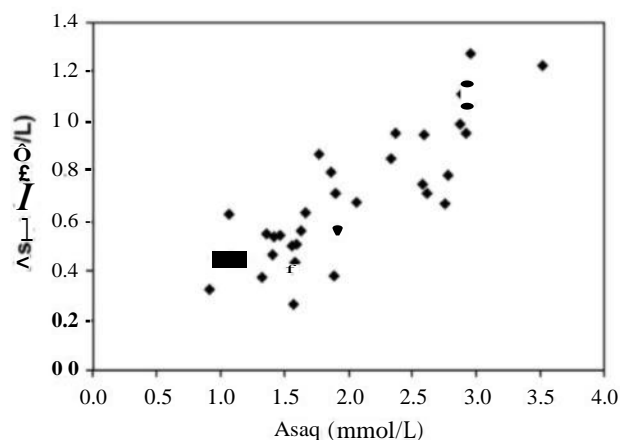


Fig. 8. Quantity of As removed from solution between stations S and G (ASpp) as a function of the total concentration of dissolved As at station S (Asaq).

demonstrated that Fe precipitates at the station G are mainly constituted of an As(V)–Fe(III) amorphous phase (Morin et al., 2003) which is consistent with As(V) precipitation and release. Moreover, As/Fe ratios are about 0.086 ± 0.003 and cyclical variations of this ratio emerge with slightly lower values during the night and an increase during daytime. Such an increase in As/Fe ratio means that more As is released into solution than Fe.

5.3. Global removal of iron and arsenic

Despite diel variations leading to the release of Fe and As into solution, a consequence of photoreduction, natural removal of pollutants occurs in Reigous Creek, on a greater scale. The quantity of As removed per liter of water in the first 40 m of Reigous Creek was calculated by the difference between the As concentrations at stations S and G. This quantity is proportional to the As concentration in spring water (Fig. 8). The corresponding percentage of As removed from solution is constant (around 30%) over the year. This result, which was based on a longer observation period, does not corroborate the results obtained from a 1-year monitoring study carried out in 2001 (Casiot et al., 2003), where a greater proportion of As was removed in the first 40 m of Reigous creek in winter than in summer.

The mean rate of Fe(II) oxidation in the first 40 m between stations S and G was estimated from the following equation:

$$rox = A[Fe(II)]/At = ([Fe(II)]_S - [Fe(II)]_G)/t \quad (2)$$

where rox is the oxidation rate and t is the travel time of the water (1080 s) between the two stations. The values found for rox ($3.8 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ on July 2008) are in good agreement with the value ($8 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$) reported by Sanchez-Espana et al. (2007) in a similar environment.

The precipitation rate of Fe(III) was identical to the Fe(II) oxidation rate since there was no build-up of Fe(III) in solution. Using a mean discharge at the source of 0.6 L s^{-1} the corresponding quantity of Fe precipitated was 4 kg a^{-1} . The mean rate of As removal between the two stations calculated in the same manner was $0.55 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ yielding the quantity of As removed, 0.8 kg a^{-1} .

Between the Gal and Reigous UC stations, dilution processes added to coprecipitation contribute to a further decrease in the dissolved concentrations of As. At Reigous UC station, the dissolved As concentration was between 0.4% and 2.3% of that measured at the source of Reigous Creek.

6. Conclusions

Monthly monitoring of both As and Fe concentrations and the main physicochemical parameters in Reigous Creek was done over 4 years. Reigous creek drains the tailings stock of the former Pb–Zn mine of Carnoulès. The monitoring found an increase in As concentration in the AMD source occurred during the dry season.

Over the first 40 m of the creek, monitoring confirmed previous results obtained during a shorter observation period, which showed intense removal of As by coprecipitation with Fe oxides. However unlike previous observations, the results of the present study showed that the percentage of As removed from solution was constant at around 30%. The corresponding rate of As removal was $3.58 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$.

The As–Fe rich precipitates that are deposited in the bed of this section of Reigous Creek consist of tooeleite, As(III)–Fe(III) and/or amorphous As(V)–Fe(III) phases. Seasonal variations in sediments were observed with the appearance of tooeleite during the coldest months. Laminated concretions were mainly made up of this tooeleite whatever the period of the year.

Diel cycles of dissolved As and Fe concentrations were linked to photoreduction of Fe oxides. Fluctuations in dissolved As concentrations between midday and night were about 10%.

After 40 m, the combination of both dilution and adsorption/coprecipitation processes led to a further decrease in As concentrations. The formation of more conventional Fe-oxide phases such as schwertmannite and ferrihydrite was observed. Upstream from the confluence with the Amous River the concentrations were between 0.4% and 2.4% of those observed at the source of Reigous Creek.

This study confirmed previous studies and showed that As undergoes significant natural attenuation in AMD impacted water. Nevertheless a significant quantity of highly contaminated sediment was produced and transported downstream during floods.

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