

Kinetic Controls on Iron and Arsenic Precipitation in Acid Mine Drainage (Carnoulès, France)

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Abstract

Reigous Creek, located in the Rhône river basin (SW France), is affected by acid mine drainage. Mining has generated 1.5 million tons of waste (10% sulphides) stored at the springs where the creek originates. As a result of pyrite oxidation, the creek water displays low pH (down to 2.5) and high levels of sulphate (about 40 mmol/L), Fe (12-25 mmol/L), and As (1-3.5 mmol/L). The water chemistry, which has been monitored monthly for 4 years, varies seasonally. At the spring of the Reigous Creek, iron (mainly Fe(II)), exhibits concentrations decreasing from 25 mmol/L in summer to 12 mmol/L after rain events. Arsenic varies from 3.5 to 1 mmol/L and is mainly (50 to 95%) in the reduced form, As(III). Natural attenuation of As concentrations occurs as a result of microbiologically mediated As-Fe coprecipitation. From 10 to 47% of the Fe and 17 to 46% of the As are removed from the aqueous phase within the first 30 m of the stream. The efficiency of this attenuation varies seasonally. The solid that precipitates in the stream has a mean As/Fe ratio of 0.15 with seasonal variations. Suspended sediments consist of an As-rich amorphous phase of schwertmannite; most laminated concretions contain tooeleite. Laboratory experiments demonstrated that As-rich schwertmannite is formed during rapid Fe oxidation while a slow oxidation rate rather favours the formation of tooeleite. Short-term variation (24 h) of As and Fe concentrations were evidenced in Reigous Creek due to photoreduction of iron-bearing phases, which results in fluctuations of about 10% in Fe and As concentrations over a 24 h-period.

Key words: Iron, arsenic, seasonal variation, acid mine drainage, precipitation, tooeleite, photoreduction

Introduction

Many processes control the fate of metals and metalloids in aqueous environments. In acid mine drainage (AMD), these processes are often linked to iron chemistry: (1) dissolution and precipitation of hydrous iron oxides, (2) microbial oxidation of ferrous iron, and (3) photoreduction of dissolved ferric iron (McKnight et al., 2001). The mineralogical composition of Fe(III) phases in AMD depends on pH but also on the ambient concentration of metal ions and metalloids. Among them, arsenic seems to play a major role. Schwertmannite can incorporate up to 70 mg/g As but higher As concentrations inhibit its crystallization (Carlson et al., 2002). When arsenite (As (III)) is the predominant As species in solution, the formation of tooeleite, a rare As(III)-Fe(III) mineral ($\text{Fe}_5(\text{AsO}_3)_3\text{SO}_4(\text{OH})_4\cdot 4\text{H}_2\text{O}$), may occur (Cesbron and Williams, 1992; Morin et al., 2003). The aim of this study was to evaluate the processes that control diurnal- and seasonal variations of dissolved Fe and As concentrations and the mineralogy of precipitating solids in a stream impacted by AMD.

Site description

Reigous Creek is located in the Rhône river basin (SE France), in the Southern part of the Massif Central Mountains, named the Cevennes. The Mediterranean climate of the region is characterised by long drought periods and sudden and intense rains in autumn and spring. Mining has generated 1.5 million tons of wastes, containing 0.7% Pb, 10% Fe, and 0.2% As, which were dumped at the springs where the creek originates. As a consequence of pyrite oxidation, the water emerging from the tailings pile has a low pH (down to 2.5) and high concentrations of sulphates (about 40 mmol/L), Fe (12-25 mmol/L) and As (1-3.5 mmol/L). Before its confluence with an unpolluted stream (Amous River), 1.5 km downstream, Reigous creek receives seepage from quarries, especially after rainy events; these strongly influence acidity and metallic content. Since November 2004, 4 stations have been monitored on a monthly basis: Source (Reigous spring), COW G (30 m downstream), GAL (150 m from the source), and RaC (just before the confluence with the unpolluted Amous river).

Methods

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

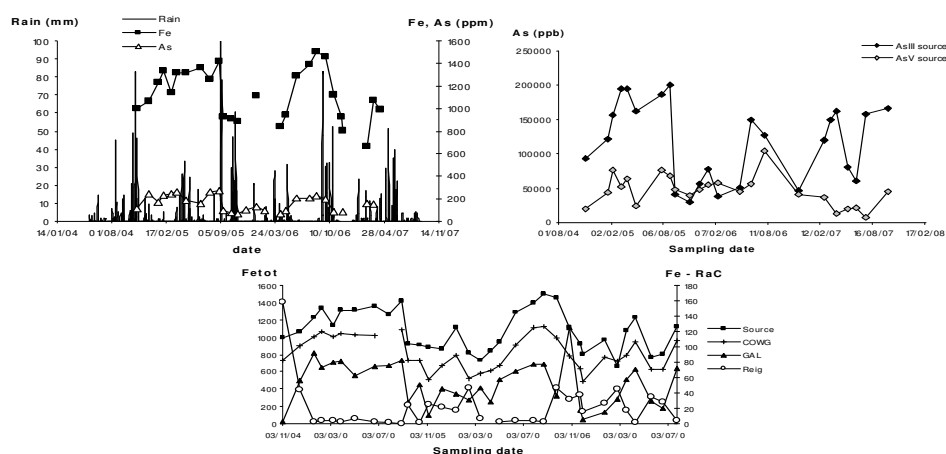
Water samples were collected and immediately filtered through 0.22 μm Millipore membranes fitted on Sartorius polycarbonate filter holders. Samples for total iron were acidified to pH=1 with HNO₃ Merck Suprapur (14.5 M) and stored at 4°C in polyethylene bottles until analysis. EDTA was added to samples for As speciation to prevent Fe and As precipitation; samples were then frozen until analysis. The samples for SO₄²⁻ determination were frozen until analysed using nephelometry. Total Fe was quantified using Flame Atomic Absorption Spectrometry (FAAS). Fe(II) concentrations were determined using spectrophotometry at 510 nm (ferrozine method) and Fe(III) was calculated by difference between total Fe and Fe(II). As analysis was carried out by HPLC coupled to Hydride Generation (HG) with Atomic Fluorescence Spectrometry (AFS) detector (Casiot et al., 2005). Mineralogical composition of solid samples was determined by powder X-ray diffraction (XRD) and bacterial growth was determined by counting using Thoma cells. Laboratory experiments were conducted to study the processes leading to the formation of different As-rich iron minerals in Reigous creek. For this, we used different strains of *Acidithiobacillus ferrooxidans* inoculated in variable proportions in sterilized Reigous spring water.

Results and Discussion

Seasonal variations in As and Fe concentrations in the Reigous creek

The water chemistry shows seasonal variations. At the spring of Reigous Creek, Fe exhibits concentrations decreasing from 25 mmol/L in summer to 12 mmol/L after rainy events. It is mainly in the reduced form, Fe(II), throughout the first 30 m. At downstream station COW G, dissolved Fe(III) concentrations increase, ranging up to 20% at station RaC. Arsenic shows the same trend, with concentrations in source water varying from 3.5 to 1.0 mmol/L (Fig.1b).

Figure 1 Variations of rain, dissolved Fe, and As (ppb) (a) and As speciation in spring water (b) and variations of dissolved Fe in the Reigous creek (c)



The observed seasonality can be explained by rain events in autumn and spring that dilutes dissolved Fe and As concentrations (fig.1a and 1c). At station RaC, located just before the confluence with the unpolluted Amous river, an increase of aqueous Fe and As content can be noted after rainfall events (fig. 1c). This can be attributed to an important discharge of metal-rich waters from the quarries located upstream from this station. Arsenic speciation also displays seasonal variations (fig. 1b) with proportions of As(III) ranging between 50 and 95% of total As during the dry period whereas both As(III) and As(V) are present in comparable proportions after rainy events.

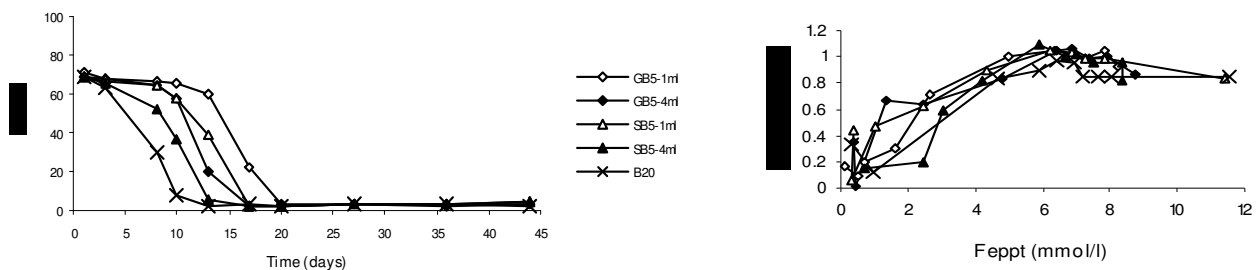
Natural attenuation of As concentrations occurs as a result of microbiologically mediated As-Fe coprecipitation. From 10 to 47% of Fe and 17 to 46% of As are removed from the aqueous phase

within the first 30 m of the stream and the efficiency of this attenuation varies seasonally. The rate of Fe and As removal from the dissolved phase is greater during the driest months. The mineral phase that precipitates displays an As/Fe molar ratio in the solid phase ranging from 0.08 to 0.35 with an average of 0.15 ± 0.06 ; this seasonality influences the mineralogy (nature and crystallinity) of precipitates. Suspended sediments, consisting of an As-rich amorphous phase within the first 30 m, are mainly As(III)-Fe(III) solids in winter and As(V)-Fe(III) in summer. As-rich schwertmannite, which precipitates downstream, is more (in winter) or less (in summer) crystallized. Most laminated concretions that form within the first 30 m from the source contain tooeleite throughout the year.

Laboratory experiments

Differences in kinetics clearly appear in Fe(II) oxidation and subsequent precipitation of Fe according to the size of inocula introduced in batch reactors (Fig. 2a). Moreover, whatever the strain involved, iron precipitation occurs in two steps: Fe and As precipitated jointly until the As remaining in solution was about 0.3 mmol/L (which corresponds to 1 mmol/L of As incorporated in the solid phase), then iron continues precipitating so that 50-60% of Fe has been removed from the aqueous phase at the end of the experiment (Fig. 2b).

Figure 2 Evolution of Fe(II) oxidation (a) and As precipitated versus Fe precipitated (b) according to the bacterial strain involved in batch experiments

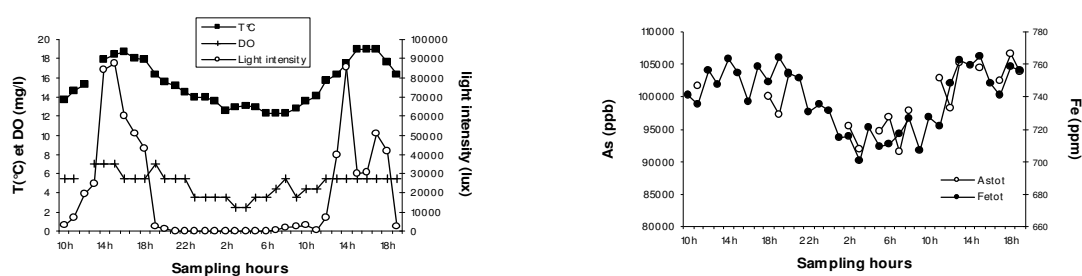


Laboratory experiments demonstrated that kinetics, more than the bacterial strains involved, seem to better constrain the mineral phase that forms after the Fe(II) oxidation and subsequent precipitation of iron. Indeed, the same strain inoculated with different amounts of bacterial cells have shown that As-rich schwertmannite is formed during rapid Fe oxidation (GB5-4 ml and SB5-4 ml) while a slow oxidation rate rather favours the formation of tooeleite (GB5-1 ml and SB5-1 ml). The formation of tooeleite is followed by schwertmannite precipitation. Both tooeleite and schwertmannite incorporate large amount of arsenic. Whatever the strain involved and the mineral phase that previously precipitated, jarosite is the only mineral phase that formed during the second step of oxidation. This confirms that jarosite is not an effective scavenger for arsenic, as shown by Savage et al. (2005) and Wang et al. (2006). The occurrence of jarosite coincides with a slight increase of As in the aqueous phase. As suggested by Fukushi et al. (2003) and Pedersen et al. (2006), this could indicate that the jarosite is formed by transformation of a pre-existing mineral phase.

Dial variations of As and Fe concentrations in Reigous creek

Short-term (24 h) variation of As and Fe concentrations and physicochemical parameters were evidenced in Reigous Creek (Fig. 3). The Fe and As concentrations increase during daylight hours and decrease during the night (fig.2b). Such cycling has already been observed by Gammons et al. (2007) and Butler and Seitz (2006). Variations are likely due to photoreduction of iron-bearing phases and result in fluctuations of about 10% in Fe and As concentrations throughout a 24 h-period. Indeed, photochemical reduction of iron oxides releases Fe(II) into the aqueous phase and the As incorporated into the iron-bearing minerals. Thus, the cycling of Fe and As concentrations is explained by photoreduction competing against oxidation of Fe(II) during the day, leading to an equilibration between the two processes and to almost constant concentrations of dissolved Fe(II).

Figure 3 Variations of temperature, dissolved oxygen (DO), light intensity (a), and total Fe and total



As (b) over a 34 h-period sampling

At night (from 10pm to 6am), when light intensity decreases below 7 W/m^2 , the only process involved is oxidation of dissolved Fe(II) (Butler and Seitz, 2006), and subsequent precipitation of Fe(III) (oxy)hydroxides, which produces a decrease in Fe and As concentrations in the dissolved phase.

Conclusions

The rate of Fe and As precipitation varies seasonally and is dependent on parameters such as rainfall but also on light intensity on a short scale. Moreover, kinetics of Fe(II) oxidation, more than the nature of bacterial strain, strongly influence the mineral phase that precipitates in Carnoulès AMD.

Acknowledgements

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