



Sorption and redox processes controlling arsenic fate and transport in a stream impacted by acid mine drainage

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Abstract

Reigous acid creek originating from the Carnoulès tailings impoundment supplies high concentrations of arsenic under soluble (up to ~4 mg/l) and particulate (up to 150 mgAs/g) phases to the Amous river, situated at the drainage basin of the Rhône river (Southern France). The metalloid is present as As(III) (>95%) in Reigous creek water while As(V) predominates (50–80%) in the solid phase, i.e. schwertmannite. At the confluence between acid (pH<5) creek and alkaline Amous river, As(III) concentrations decrease ten-fold through dilution and formation of As-rich ferrihydrite (As/Fe=0.02–0.1) containing 10–30% As(III). However, these attenuation processes are not efficient in the summer heatwave of 2003 since As concentrations in Amous river water (≥ 20 µg/l) and As/Fe ratios in particulate matter (≥ 0.07) are closed to those of Reigous creek (≤ 22 µg/l and ≤ 0.02 , respectively) or even higher. Downstream the confluence, processes involved in the transport of aqueous As along Amous river flowpath vary seasonally. Arsenic is transported conservatively in the aqueous phase away from the confluence in the cooler months; thus, dilution by unpolluted tributaries is the only process that decreases As concentrations. However, As(III) is rapidly oxidized and As(V) remains in solution. In contrast, during the warm season, desorption from As-rich sediment occurs which results in an increase of As(V) and As(III) concentrations along Amous river flow until they reach up to ~20 µg/l each. Therefore, Amous river seems not to be totally recovered from mine-related arsenic contamination after 3.5 km and may affect freshwater resources further downstream.

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1. Introduction

The concentrations of arsenic in acid mine drainage (AMD) can reach hundreds of mg/l, as a result of the oxidation of As-rich sulfides (Williams, 2001). Such

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As concentrations are potentially harmful for the aquatic ecosystem located downstream from mining sites and compromise a significant part of freshwater resources.

In AMD, aqueous arsenic occurs either as As(III) or As(V) (Williams, 2001). Although in rare cases the precipitation of tooeleite, an As(III)–Fe(III) mineral, has been observed (Morin et al., 2003), the As(III) form, which is believed to be the most toxic, is rather stable in solution, especially at low pH. On the contrary, As(V) presents a strong affinity for Fe(III). In AMD from the former Carnoulès mine (France), the formation of an amorphous As(V)–Fe(III)-oxyhydroxysulfate precipitate has been reported (Leblanc et al., 1996; Morin et al., 2003). More frequently, As(V) forms scorodite (Roussel et al., 1999) or adsorbs on schwertmannite and ferrihydrite as a function of pH (Carlson et al., 2002).

When transported downstream during floods, these minerals may dissolve upon water neutralization and release their As. The dissolution of As may be counteracted by the precipitation of Fe- or Al-oxyhydroxides which efficiently scavenge As(V) (Kimbal et al., 1995). Depending on local site conditions, the As concentration and partitioning between the solid phase and the solution may be further modified along the flowpath by pH and redox condition changes (Fuller and Davis, 1989).

A principal issue for the assessment of As mobility is the elucidation of the forms in which arsenic is transported or immobilized.

The aim of this study was to deepen the understanding of the processes which control the transport and fate of arsenic in mining environments. Therefore, we studied arsenic speciation and partitioning in the Amous river, which receives acid mine drainage from an abandoned Pb–Zn mine in Southern France.

2. Site description

The mine of Carnoulès (Fig. 1a) is located in Southern France in the drainage basin of the Rhône river. The mining activity, stopped in 1962, has left about 1.5 Mt of sulfidic wastes containing 0.7% Pb, 10% Fe and 0.2% As deposited over a segment of the Reigous Creek (Leblanc et al., 1996). The seepage water, which percolates through the wastes, emerges at the bases of the impoundment and forms the spring of the Reigous creek. The water is acidic (pH 3–4.5) and contains up to 250 mg.l⁻¹ of As in the As(III) form (Casiot et al., 2003). The As concentration decreases within the first 30 m of the creek in relation with the precipitation of amorphous As(V)–Fe(III) and As(III)–Fe(III) gels and tooeleite (Casiot et al., 2003; Morin et al., 2003). At 1.5 km from its source,

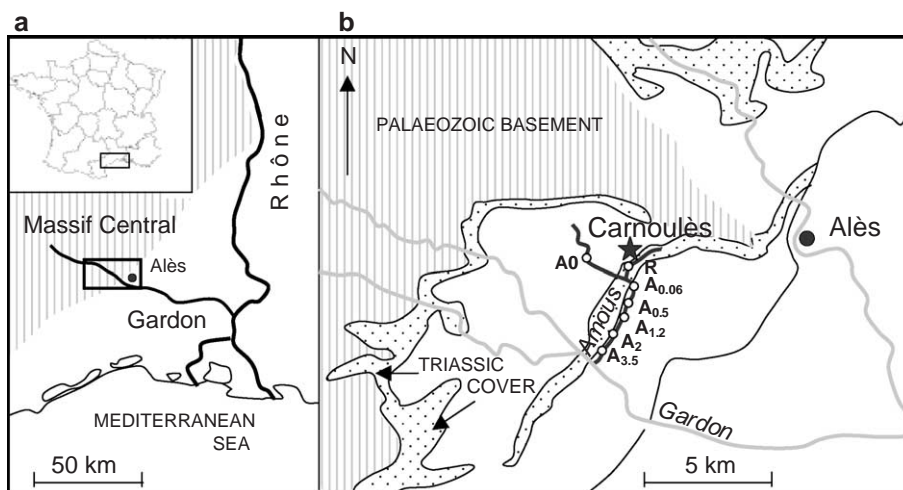


Fig. 1. Site localisation (a) and sampling stations (b). The station in Reigous creek (R) is situated 3 m upstream from the confluence; in Amous river, stations are situated 1.5 km upstream from the confluence (A₀) and 0.06 km (A_{0.06}), 0.5 km (A_{0.5}), 1.2 km (A_{1.2}), 2 km (A₂) and 3.5 km (A_{3.5}) downstream from the confluence.

the Reigous creek meets the relatively pristine Amous river. After the junction, the water becomes yellowish and the fishes disappear at a few hundred meters.

The mean annual rainfall at the site is 1100 mm, with a seasonal distribution typical of the Mediterranean climate including long drought periods and intense precipitation events especially in spring and autumn. The 21-month period investigated was marked by a dramatic flooding in September 2002 and extreme heatwave during summer 2003. The flow rate of the Reigous creek, measured continuously during the year 2003, varied between 0.2 and 20 l/s, with highest values in spring and winter. For the Amous river, the highest values (150 l/s) are generally reached in autumn while the flow rate averages 100 l/s in spring and 50 l/s in summer. Both rivers have a thin (<30 cm) water layer and are well oxygenated (DO \geq 5 mg/l).

3. Materials and methods

3.1. Sampling and analyses

Water samples were collected during 10 surveys carried out over one year from spring 2002 to autumn 2003. The sampling stations are shown in Fig. 1b. The pH and conductivity were measured in the field with an Ultrameter™ Model 6P (Myron L Company, Camlab, Cambridge). Water samples were filtered immediately through 0.22 μ m Millipore membranes fitted on Sartorius polycarbonate filterholders. Samples for major cations (Ca^{2+} , Na^+ , Mg^{2+}) determination were acidified to pH=1 with HNO_3 (14.5 M) and stored at 4 °C in polyethylene bottles until analysis. The samples for anions (Cl^- , SO_4^{2-}) determination and As speciation were frozen to avoid chemical species conversion. Unfiltered samples were used for carbonate determination. Suspended particulate matter (SPM) corresponding to size fraction >0.22 μ m was mineralised on a hot plate in concentrated HNO_3 (80 °C, 24 h). Suspended sediments settled on gravels and cobbles were collected in Reigous creek and Amous river in October 2002 and February, March and May 2003 for solid phase characterization and arsenic speciation.

Analyses of major cations and anions were carried out by capillary electrophoresis (Waters Capillary Ion

Analyzer, Waters, France). HCO_3^- and CO_3^{2-} were determined by titration with HCl 0.05 M. Analyses of inorganic (As(III) and As(V)) arsenic species were carried out using anion-exchange chromatography (25 cm \times 4.1 mm i.d. Hamilton PRP-X100 column with ProStar gradient solvent delivery system (Varian Analytical Instruments, France) coupled to Hydride Generation (HG) (VGS 200, FISONs, France) with Atomic Fluorescence Spectrometry (AFS) detector (Excalibur, PSAAnalytical, GB). The method, described by Bohari et al. (2001), has a detection limit of 0.17 μ g/l for As(III) and 0.46 μ g/l for As(V) and a precision better than 5%. Total Fe (dissolved and colloidal) was determined by Flame or Graphite Furnace Atomic Absorption Spectrometry (Thermo Electron Corporation, France). Tl and Mn concentrations were determined using ICP-MS ("Option S" PQ2+, VG-Elemental, Fisons).

3.2. Solid samples characterization

Crystalline phases were identified using X-ray powder diffraction (XRD). XRD data were collected with a PHILIPS PW1710 diffractometer using Co-K α radiation operating at 40 kV, 30 mA in step scan mode, between 3 and -90° 2θ with a 0.03° 2θ step and a counting time of 8–20 s per step. Samples were loaded on hollowed aluminum plates.

3.3. XANES spectroscopy

Oxidation state of arsenic in field samples was studied using X-ray Absorption Near-Edge Structure (XANES) spectroscopy. Data were recorded at the As K-edge at room temperature in transmission mode on the D44 bending-magnet beamline at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France) or at a temperature of 10 K on the BM30 beamline at the European Synchrotron for Radiation Facility (ESRF, Grenoble, France). The oxidation state of arsenic was determined in natural samples by linear-least squares fitting of their XANES spectra using a set of experimental XANES spectra of relevant model compounds. Those include cpp5 (Fe–As(V) coprecipitate), Shc5 and Sha5 (respectively, As(V) coprecipitated with schwertmannite and sorbed onto schwertmannite), Fh5 (As(V) sorbed onto ferrihydrite), cpp3 (Fe–As(III) coprecipitate), Shc3

and Sha3 (respectively, As(III) coprecipitated with schwertmannite and sorbed onto schwertmannite) and Fh3 (As(III) sorbed onto ferrihydrite). Absolute accuracy on the As(III)/ΣAs ratio was ±2%, as determined by fitting of synthetic mixtures of reference compounds (Morin et al., 2003).

4. Results

4.1. Main physico-chemical characteristics

The main physico-chemical characteristics of the water from Reigous and Amous rivers are presented in Table 1. The Reigous creek water is characterized by low pH (≤4.9) except during summer 2003 where it reached near-neutral values as a result of increased contribution of unpolluted tributaries at lowest water level. Conductivity is higher than 1100 μS/cm, with water chemistry dominated by sulphate (767±8 mg/l), Ca (220±72 mg/l), Mg (62±18 mg/l) and Fe (31±23 mg/l). Extremely high As concentrations (up to 3.9 mg/l) were recorded in relation with the oxydation of As-rich pyrite within the tailings impoundment (Casiot et al., 2003). Both As and Fe concentrations were drastically lower during summer 2003 while sulphate did not decrease throughout this period, showing increased precipitation of Fe and As in Reigous creek, which might be related to higher pH values.

The Amous river water is slightly alkaline (≥7.3) with a composition dominated by Ca (82±17 mg/l) and hydrogenocarbonate (285±7 mg/l). Downstream the confluence with the Reigous creek, the pH decreases by up to 1.6 pH units at station A_{0,06} in spite of carbonate buffering and then increases until it reaches 8.0±0.1 after station A_{1,2} (data not shown). The conductivity increases by 24±6% on average in relation with increasing Ca, Mg and sulphate concentrations. The increase was even higher (2- to 3-fold) during summer 2003. Fe concentrations remained lower than 0.07 mg/l downstream the confluence, showing rapid precipitation of Fe as AMD is neutralized.

Mixing ratios (χ_{Reigous}) based on the relative contribution that Reigous creek makes to the total mass of individual constituents downstream of its confluence with Amous river have been calculated according to the following equation: χ_{Reigous}=(C_{A0.06}-

Table 1
Main physico-chemical characteristics of the water from Reigous creek (R) and Amous river upstream (A₀) and downstream (A_{0,06}) the confluence

	March-02		June-02		September-02		October-02		February-03		March-03		May-03		June-03		August-03		November-03		Mean values (SD)															
	R	A ₀	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}	R	A _{0,06}														
pH	3.23	7.44	6.43	3.11	8.12	6.55	8.31	8.09	3.34	8.41	7.62	3.72	8.61	7.63	3.71	7.30	7.30	4.92	8.26	7.36	6.82	8.09	7.36	7.08	8.12	7.92	3.29	8.00	7.30	4	(2)	8.1	(0.4)	7.4	(0.5)	
Cond. μS/cm	1606	491	625.6	1600	470	610	487	587	1357	507	593.9	1301	488	639	1634	480	858	1787	561	1347	1867	489	1489	1106	521	600	1547	(245)	498	(26)	797	(339)				
Ca ²⁺ mg/l	161	73	85	179	78	93	77	87	178	88	93	153	74	87	242	88	124	331	99	297	324	60	244	150	120	130	220	(72)	82	(17)	135	(74)				
Na ⁺ mg/l	6	3	4	6	3	3	2	3	<DL	3	3	6	2	2	11	5	4	5	3	5	9	5	12	10	3	13	5	4	6	(3)	3	(1)	6	(4)		
Mg ²⁺ mg/l	47	22	26	47	23	27	20	21	48	24	28	62	23	45	70	26	32	74	24	36	88	41	78	81	29	64	38	32	62	(18)	26	(6)	39	(18)		
Cl ⁻ mg/l	6	4	3	5	4	2	2	2	<DL	3	<LD	19	6	6	5	3	4	<DL	5	1	<DL	4	2	15	5	8	6	(7)	4	(1)	3	(2)				
SO ₄ ²⁻ mg/l	1118	15	135	821	21	131	16	112	662	15	83	529	20	116	681	11	97	751	17	266	894	22	569	898	13	624	550	11	152	767	(188)	16	(4)	229	(201)	
HCO ₃ ⁻ mg/l	-	-	-	286	231	-	-	-	284	243	-	276	193	-	295	204	-	280	209	-	288	191	-	-	-	-	-	-	-	-	285	(7)	212	(21)		
CO ₃ ²⁻ mg/l	-	-	-	<DL	<DL	-	-	-	<DL	<DL	-	15.8	<DL	-	59.6	-	3.3	<DL	-	0.657	0.001	<LD	3.8	-	-	-	-	-	-	-	10	(9)	<DL			
Fe tot mg/l	61.6	0.03	0.07	25.5	0.001	<DL	-	0.003	0.007	19.9	0.003	0.003	43.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	31	(23)	0.01	0.02			
Mn tot mg/l	4.01	0.001	0.569	5.6	0.004	0.734	-	0.002	0.488	3.5	0.002	0.702	5.1	0.002	0.722	5.0	0.003	1.096	7.75	0.004	3.032	6.5	0.005	2.788	1.5	0.0006	0.403	5	(2)	0.003	1	(1)				
As (III) μg/l	1607	2.5	99	44	0.6	10.8	-	<DL	18.9	681	<DL	52.9	2900	<DL	189.0	1789	<DL	86.5	18	<DL	5.8	22	1.3	18.4	12.4	<DL	153.7	1974	<DL	50.8	1005	(1088)	1	(1)	69	(63)
As (V) μg/l	82	23.1	<DL	64	1.6	0.95	-	3.6	1.9	<DL	<DL	1009	<DL	<DL	<DL	<DL	<DL	1.7	<DL	0.4	3.5	1.8	<DL	1.1	19.3	74.9	<DL	3.5	205	(396)	5	(8)	5	(8)		
Σ As μg/l	1689	25.6	99	108	2.2	11.8	-	3.6	20.8	681	<DL	52.9	3900	<DL	189.0	1789	<DL	86.5	18	1.7	5.8	22.4	4.8	20.2	12.4	1.1	173	2049	<DL	54.3	1141	(1333)	6	(9)	71	(66)
Tl μg/l	24.1	<DL	4.1	15.3	<DL	2.3	-	-	13.2	<DL	1.7	19.1	<DL	3.7	23.6	<DL	3.2	8.6	<DL	2.3	7.3	<DL	4.8	6.7	<DL	5.44	20.7	<DL	5.26	15	(7)	<DL	4	(1)		

DL=detection limit; <->not determined.

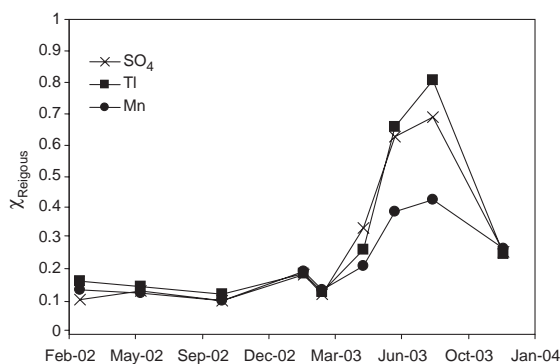


Fig. 2. Evolution of mixing ratios (χ_{Reigous}) at the confluence between Reigous and Amous rivers calculated from SO_4 , Tl and Mn concentrations, according to Gault et al. (2003) : $\chi_{\text{Reigous}} = (C_{\text{A}0.06} - C_{\text{A}0}) / (C_{\text{R}} - C_{\text{A}0})$, where $C_{\text{A}0}$ and $C_{\text{A}0.06}$ are the constituent concentrations in Amous river upstream and downstream the confluence, respectively, and C_{R} is the concentration in Reigous creek.

$C_{\text{A}0}) / (C_{\text{R}} - C_{\text{A}0})$ (Gault et al., 2003), where $C_{\text{A}0}$ and $C_{\text{A}0.06}$ are the constituent concentrations in Amous river upstream and downstream the confluence (station $\text{A}_{0.06}$), respectively, and C_{R} is the concentration in Reigous creek. Mixing ratios were similar when calculated from sulphate and Tl concentrations while Mn gave a lower contribution of Reigous creek in summer 2003 (Fig. 2). Such difference suggests a conservative mixing for Tl and SO_4 while Mn is partially removed from the aqueous phase at the confluence (Gault et al., 2003). This conservative behaviour of Tl was confirmed during mixing experiments with various proportions of Reigous and Amous river water (data not shown), which allowed to use this element as a tracer of dilution at the confluence and for downstream sites below the confluence.

According to mixing ratios from Fig. 2, the contribution of the Reigous creek to the Amous river flow ranges between 10% and 80%, with a maximum in summer 2003, in agreement with extremely high increase in conductivity.

4.2. Arsenic in the aqueous phase

In Reigous creek water, the As concentrations are comprised between 12 and 3900 $\mu\text{g/l}$ (Table 1). They decrease by one order of magnitude after mixing with Amous river (station $\text{A}_{0.06}$), except during summer 2003 (especially August) when they are surprisingly higher in Amous river than in Reigous creek (Table

1). The corresponding As/Tl ratio varies drastically during the flow from Reigous creek (R) to Amous river ($\text{A}_{0.06}$) (Fig. 3), implying that dilution is not the only process controlling As concentrations in the mixing zone. As/Tl is generally lower in the mixing zone ($\text{A}_{0.06}$) than in Reigous creek, which implies that As is removed from the aqueous phase; however, the reverse is observed during summer 2003 which indicates As release from the suspended particles or sediment to the aqueous phase (Fig. 3). Little variation of As/Tl ratio occurs further downstream in the cooler months (March 2002 and February and March 2003), showing little exchange between aqueous and solid phases. Conversely, the As/Tl ratio still increases downstream the mixing zone during the warm period, implying desorption from the sediment along the flowpath. However, there was no correlation between the evolution of As/Tl ratio downstream station $\text{A}_{0.06}$ and the slight pH increase measured between $\text{A}_{0.06}$ and $\text{A}_{1.2}$.

The dominant As species in Reigous creek is generally As(III) (>95%) although As(V) may be present occasionally (60% of total As in June 2002 and 26% in February 2003) (Table 1). When As(V) is present in significant proportion in Reigous creek ($\text{As(V)/As(III)} > 0.1$), it is efficiently removed from the aqueous phase in the mixing zone compared to As(III) according to the drastic decrease of the As(V)/As(III) ratio between stations R (Reigous) and $\text{A}_{0.06}$ (Amous) (Fig. 4a). As a consequence, As(III) is the dominant species ($\geq 90\%$) at station $\text{A}_{0.06}$. Downstream station $\text{A}_{0.06}$, there is a general increase of As(V)/As(III) ratio

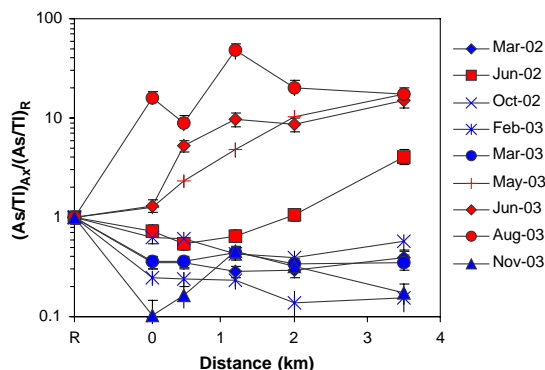


Fig. 3. Variation of the aqueous As/Tl ratio at each sampling site in Amous river downstream the confluence (As/Tl_{Ax}) normalized to the ratio in Reigous creek (As/Tl_{R}).

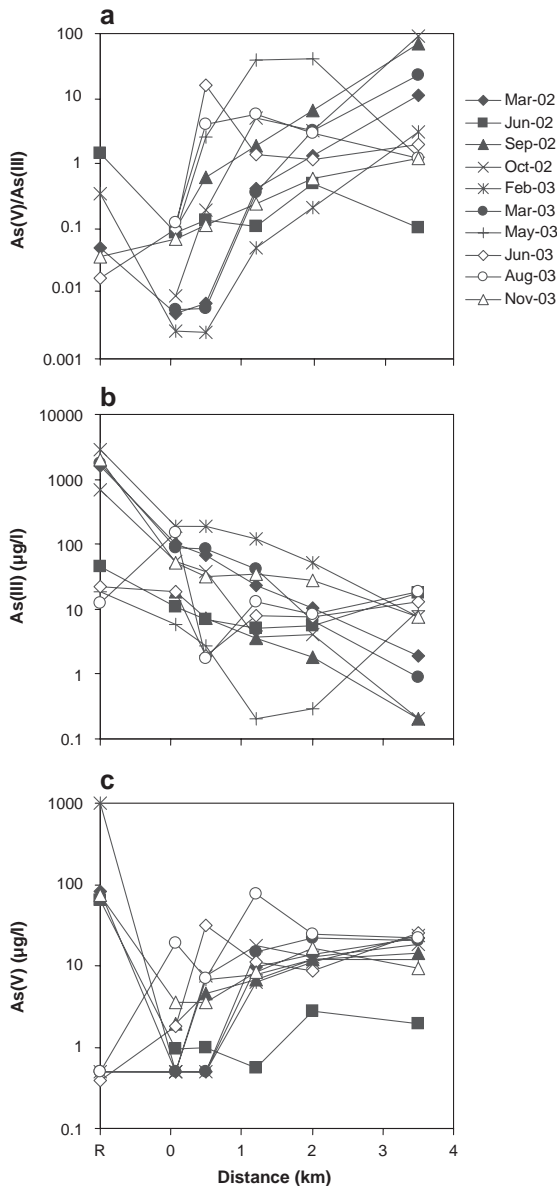


Fig. 4. Evolution of aqueous As(V)/As(III) ratios (a), As(III) (b) and As(V) concentrations (c) for sampling stations in Reigous creek (R) and in Amous river downstream the confluence.

away from the confluence (Fig. 4a) in relation with a decrease of As(III) concentration (Fig. 4b) and a concomitant increase of As(V) (Fig. 4c) which becomes predominant after a few kilometers. Nevertheless, a slight As(III) increase was recorded downstream station A₂ during the warm period (Fig. 4b).

4.3. Arsenic in the particulate phase

SPM from Reigous creek and Amous river both contain Fe as the main component (up to 56 wt.%) (Table 2); however, the phases progressively transform from schwertmannite (Sch) in the Reigous creek to ferrihydrite (Fh) in the Amous River (from the top to the bottom of Fig. 5), corresponding to the pH stability field of these minerals (pH 3–4 for schwertmannite and >5 for ferrihydrite) derived from AMD (Yu et al., 1999). Seasonal fluctuations of the As content of SPM in Amous river follow those of Reigous creek (Table 2); highest values are recorded during the cold period and lowest values during the warm period, in relation with the variations of As concentrations in the aqueous phase (Table 1). However, the corresponding As/Fe molar ratios in SPM from Amous river reached higher values in summer 2003 (up to 0.9 at station A_{3,5}, data not shown) compared to other periods (As/Fe=0.01–0.05), in relation with a lower Fe content (Table 2). XANES data indicates that As(V) is predominant in freshly settled sediment, both in Reigous creek (As(V)≥51%) and in Amous river (As(V)≥69%), unlike species distribution in the aqueous phase.

5. Discussion

Reigous acid creek supplies high amounts of As(III) to the Amous river. However, this supply varies seasonally; the lowest concentrations were measured during the warm season and the highest during the cold period whereas sulphate, which is a tracer of As-rich pyrite dissolution, is relatively stable. This suggests that natural attenuation processes lower the concentrations of As(III) in the warm period. The formation of As(V)-bearing compounds through bacteria-catalysed As(III) oxidation is promoted in the warm period in the upper course of Reigous creek (Casiot et al., 2003; Morin et al., 2003). Furthermore, increased pH values as a result of dilution by unpolluted tributaries also contribute to increase As and Fe precipitation at lowest water level. However, the solid phase formed upstream from the confluence, schwertmannite, differs from As(V)–Fe(III) oxyhydroxides formed in the upper part of Reigous creek (Morin et al., 2003). Besides the higher pH in the

Table 2

As and Fe content in SPM of Reigous creek and Amous river and the corresponding As/Fe molar ratio and As speciation

	Reigous				Amous			
	As (mg/g)	Fe (mg/g)	As/Fe (mol/mol)	As(III)/As total (%) [†]	As [#] (mg/g)	Fe [#] (mg/g)	As/Fe [#] (mol/mol)	As(III)/As total (%) [†]
Mar-02	149	391	0.28		12±2	270±26	0.034±0.003	
Jun-02					1±1	82±95	0.012±0.004	
Sep-02					4±1	127±25	0.023±0.002	
Oct-02	31	565	0.04	19	6±3	221±118	0.022±0.004	8*
Feb-03	56	298	0.14	31	19±6	295±144	0.05±0.02	31**
Mar-03	28	561	0.04	49	15±4	237±84	0.05±0.01	24*, 29**
May-03	1	170	0.004	25	3±1	69±70	0.1±0.1	25**
Jun-03	2	308	0.005		3±1	55±89	0.3±0.4	
Aug-03	5	230	0.02		4±2	44±16	0.07±0.05	
Nov-03	46	219	0.16		10±1	217±70	0.04±0.01	

* From sample collected at station A_{0,06}.** From sample collected at station A_{1,2}.

† The oxidation state of As in freshly settled sediments is given by the percentage of As(III) in comparison with total As. The remaining part of arsenic is As(V).

Mean and SD values calculated from samples A_{0,06}, A_{0,5}, A_{1,2}, A₂ and A_{3,5}.

lower course of the creek, the lower As/Fe ratios in the solid (0.004–0.14) could make the formation of schwertmannite possible whereas it is degraded at As/Fe ratio > 0.15 (Carlson et al., 2002). This phase

appears to trap both As(III) (20–50%) and As(V). This capability had been demonstrated for As(V) in both natural and synthetic schwertmannite (Carlson et al., 2002) while As(III) adsorption on this mineral occurred as a result of bacterial-mediated Fe precipitation (Duquesne et al., 2003). Despite these natural attenuation processes, As(III) is still present at high concentrations in the aqueous phase of Reigous creek upstream from the confluence with Amous river.

In the mixing zone, Fe is completely removed from the aqueous phase due to rapid oxidation of Fe(II) at near-neutral pH. This results in the formation of ferrihydrite, which is a common mineral in mine-impacted rivers (Carlson et al., 2002). With the exception of summer 2003, arsenic concentrations are lowered by one order of magnitude in the mixing zone as a result of 5- to 10-fold dilution with Amous river and trapping of As(III) and As(V) on ferrihydrite. Indeed, ferrihydrite has a strong affinity for both As(III) and As(V) at neutral pH (Raven et al., 1998; Pierce and Moore, 1980) which results in relatively high As/Fe ratios (0.02–0.05) in SPM of Amous river. However, As(V) was predominant in freshly settled sediment (≥69% of total As) compared to the corresponding aqueous phase (As(V) < 11%). This implies partial As(III) oxidation, either in the aqueous phase at the mixing zone or during ageing of the sediment after settling. This As(III) oxidation could be due to Fenton reaction which is known to occur in

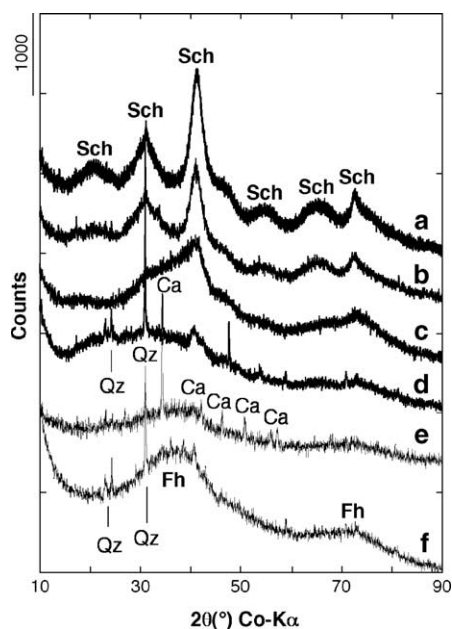


Fig. 5. XRD patterns of freshly settled sediment from Reigous Creek (a, b), Amous River 3 m after the confluence (c, d) and 1200 m after the confluence (station A_{1,2}) (e, f) in May 2003 (a, c, e) and February 2003 (b, d, f). (e) was multiplied by 1.5. Sch: schwertmannite, Fh: ferrihydrite, Qz: quartz, Ca: calcite.

oxygenated neutral waters containing Fe(II, III) (Hug and Leupin, 2003).

Downstream the mixing zone, the transport of arsenic is affected seasonally. During the cooler months (March 2002 and February and March 2003), arsenic is transported nearly conservatively along Amous river flowpath according to relatively stable As/Tl ratios. Furthermore, there is an increase of As(V)/As(III) ratio, which suggests As(III) oxidation in solution. This process is generally slow in natural waters (Cherry et al., 1979) and it is unlikely to occur through light-induced As(III) oxidation (Hug et al., 2001) since this process requires the presence of dissolved Fe, which is scarce in Amous river downstream station A_{0.06}. However, As(III) oxidation can be enhanced in AMD environments through Mn-oxides surface-catalyzed reactions (Oscarson et al., 1980) or bacterial catalysis (Oremland and Stolz, 2003). Thus, there is an increase of aqueous As(V) concentration along the flowpath. Therefore, it appears that As(V) from AMD may be transported over long distances, as demonstrated for arsenic from geothermal waters (Nimick et al., 1998). In contrast, during the warm season, there is an increase of As/Tl ratio away from the confluence together with increasing As(III) concentrations downstream station A₂. This suggests desorption of As(III) from the solid phase. This phenomenon is enhanced in extremely dry conditions of summer 2003, which might be attributed to the equilibrium of As concentrations between river water and As-rich solids. Increased As leaching from the sediment was observed at low flow conditions in mine-impacted river (Mok and Wai, 1990) and attributed to longer sediment–water contact time. Furthermore, As(III) was the almost exclusive species released under aerobic conditions in laboratory experiments (Mok and Wai, 1990). Such As(III) release has been attributed to the reduction of Fe-oxyhydroxides in the hyporheic zone of a contaminated stream and the transfer of sediment-bound As to the aqueous phase as As(III), which does not immediately reoxidize (Nagorski and Moore, 1999). Although the extreme character of summer 2003 may overestimate the general capability of As to be transferred from sediment to river water, it points out that river sediments are not an efficient trap for As; on the contrary they may act as a major source of As to the aquatic system during summer months.

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