Redox processes in a eutrophic coal-mine lake

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ABSTRACT

The water column chemistry of lake St Eloy (St Eloy-les Mines, Allier, France) was monitored over a period of a year. This is a small stratified lake created by subsidence of an underground coal mine. The results show a permanent stratification and the development of two water bodies with contrasting chemistry. The superficial oxic layer (i.e. the upper 5 m) is of high water quality and the water, not affected by seasonal changes, is suitable as a source of drinking water. In contrast, the deeper layer is permanently anoxic and the waters have a conductivity which is six times greater than in the epilimnion. Due to density difference and the small size of the lake, no turn-over occurs and all elements that diffuse from bottom sediments are strongly concentrated in the hypolimnion. Arsenic concentrations are very low in the epilimnion, but they increase quickly with depth below the oxycline, to reach up to 7 µM below 8 m depth. Different solid phases could control the fate of arsenic in this lake such as gypsum for As(V) in the hypolimnion, mackinawite for As(V) and As(III) in the hypolimnion, and close to the oxycline, Fe(III) oxyhydroxides are possible hosts for both As(III) and As(V).

Introduction

ARSENIC is classified as a human carcinogenic compound, responsible for chronic poisoning in different parts of the world (Jekel, 1994; Hering and Elimelech, 1995) and the most common means by which arsenic is ingested is the consumption of contaminated drinking water. The toxicity and bioavailability of As in waters strongly depend on its speciation (Yamauchi *et al.*, 1992). The major inorganic species in raw waters are arsenite (As III) under anoxic conditions and arsenate (As V) in oxic waters. The transformation of As(V) to As(III), and As(III) to As(V), is controlled by Eh conditions, biological activity, adsorption phenomena and precipitation of authigenic phases (Hering *et al.*, 1997; Tournassat *et al.*, 2002).

In the Earth's crust, arsenic is associated primarily with igneous and sedimentary rocks in the form of inorganic compounds (Riedel and Eikman, 1986; Tanaka, 1988) where it is most frequently combined with sulphur, e.g. in arsenopyrite (FeAsS) and pyrite (FeS_2). Weathering of arsenic-containing rocks is considered to be the most important natural pathway that releases As to the environment (Azcue and Nriagu, 1994). The common occurrence of arsenopyrite and arsenic-rich pyrite in coal has resulted in significant release of As and sulphate to natural environments as a result of mining activities (Yudovich and Ketris, 2005). In mining-impacted regions, arsenic can greatly exceed background values and redox processes control significantly the arsenic release in groundwaters and mining lakes. Arsenic compounds are major contaminants of these systems, but heavy metals (such as Zn, Co, Cr) as well as organic compounds and ammonium, have also been reported (Sigg, 1992; Kuhn *et al.*, 1994; Manning and Hutcheon, 2004).

After the closure of mining activities in the Massif Central range, France, several lakes were formed as groundwater abstraction was stopped and the coal mines' substratum collapsed. At present, these lakes are used for recreational activities and they represent a potential source of

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drinking water. Evaluation of water quality and biogeochemical processes that control sediment-water interface fluxes become crucial because former mines, now located below these lakes, are a certified source of arsenic and other inorganic contaminants (Seyler and Martin, 1989; Paquette *et al.*, 2000; Manning and Hutcheon, 2004). This paper reports on the behaviour of arsenic in lake St-Eloy, also called 'La Poule d'Eau'. This small lake with a surface area of 12.5 ha and a maximum depth of 13 m is situated on the coal-field of St-Eloy (Allier, France). In this region, several mines were located along a 25 km long and 1.2 km wide coal-field area. At present, all mines are closed.

The objectives of this work were: (1) to asses the temporal variability in As over an annual time scale; (2) to study the geochemical controls governing the mobility and speciation of As in the lake; and (3) to evaluate the processes that affect water quality in order to predict the evolution of the lake. Based on this information, we attempted to determine the fate of pollutants and the implications for the lake water as a drinking water resource.

Methodology

Water samples from the water column were collected at six different dates within a period of one year (December 1999–November 2000), at the same location (2°52′38″E, 46°52′38″N). Conductivity, pH, pε, dissolved oxygen and water temperature were measured during sampling with a multi-parameter probe (YSI, 600 XLM) calibrated before and after sampling according to specifications. The probe measures temperature with an accuracy of 0.01ºC and the resolution of the electrical conductivity measured is better than 1 μS cm^{-1}. The accuracy of the dissolved oxygen measurement was <0.1 mg l^{-1} and of pH measurements, 0.1 units.

The samples were collected at 1 m depth intervals in a Niskin bottle and, were immediately filtered on-site using syringe filter-tip units holding 0.45 μm cellulose nitrate membranes. Each sample was split into two subsamples: a HNO$_3$-acidified sample for dissolved metals analysis, and another sample preserved at 4ºC for determination of dissolved anions and alkalinity. Arsenic speciation was carried out on site using an anion exchange resin, according to the procedure described by Wilkie and Hering (1998). Total ICP As concentrations (Detection

limit equal to 0.13 μM) were used to control As (III+V) speciation.

To preserve Fe from oxidation, samples for Fe(II) determination were immediately mixed with O-phenantroline and pH 3.5 buffer solutions. The total ferrous iron (Fe(II)) and sulphide (S(II)) concentrations were measured in the field with a portable spectrophotometer according to the procedures of Vogel (1989) and Lindsay and Baedecker (1986), respectively.

Total major cation (Ca, K, Na, Mg, Fe) and trace element (P, As, Mn, Cd, Co, Cr, Pb, Ni, Zn) concentrations were determined by inductively coupled plasma emission (ICP-AES/OPTIMA 3300 DV) on pre-acidified solutions. Calibration standards were prepared immediately prior to each analysis by dilution of stocks obtained commercially (Merck, FLUKA, 1.00 g/l). Higher-concentration samples were diluted into the operating range and reanalysed. Typical analytical uncertainty for all analyses was <5%, with a mean uncertainty of 3%.

Anions (Cl$^-$, SO$_4^{2-}$, NO$_3^-$) were analysed using a water capillary Ion Analyser Millipore on raw filtered waters. The detection limit for these anions is 6 μM for Cl$^-$, 4 μM for SO$_4^{2-}$ and 4 μM for NO$_3^-$.

Alkalinity measurements were performed by a spectroscopic method (detection limit of 16 μM) on filtered waters using a mixture of bromophenol blue and formic acid (Sarazin *et al.*, 1999).

A composite sample of bottom lake sediments was taken with an Ekman dredge from the most superficial layer (0–20 cm), sealed in 0.125 mm polyethylene bag and maintained at 3ºC for transport to the laboratory where it was stored at −15ºC for analytical determinations. Major and trace element concentrations in sediments were measured after digestion with HF and HClO$_4$ by ICP-AES.

The geochemical speciation model *PHREEQC*-2 (Parkhurst and Appelo, 1999) was used to calculate the distribution of different aqueous species, as well as the Saturation Index (SI) of these waters with respect to various solid phases (i.e. the ion activity product to solubility product) (see Appelo and Postma, 2005).

Results and discussion

Lake structure

In spite of the significant temperature changes observed in the superficial water body, the lake shows a lack of turn over and a permanent
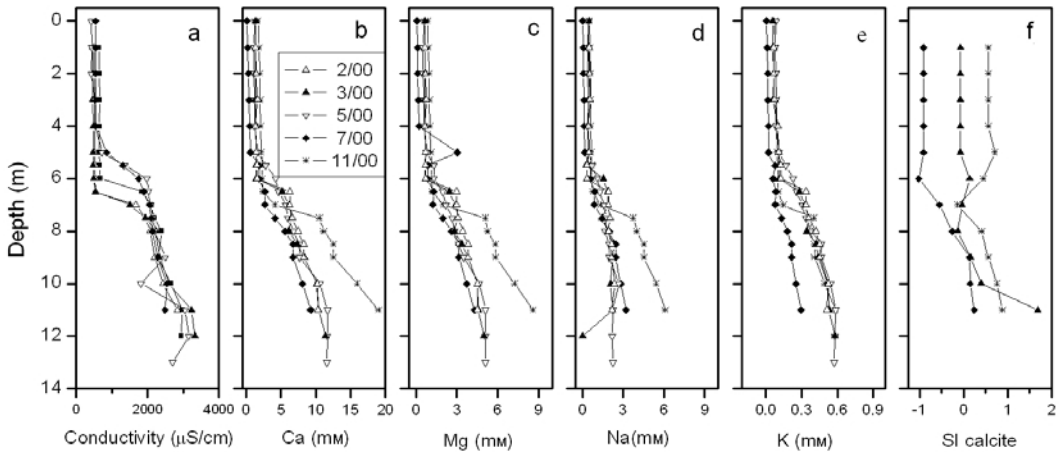
FIG. 1. Vertical profiles of physico-chemical parameters in the water column of lake St-Eloy for different sampling dates. Missing data for probe parameters are due to operational problems during sampling.

chemical stratification with a pronounced thermo and oxycline at 6−7 m depth (Fig. 1a,e). The permanent stratification throughout the year in a cold-climate area results from the high total dissolved solids and thus a high-density contrast between bottom waters, with conductivity as high as 3000 μS/cm, and surface waters, characterized by a conductivity six times less (Fig. 2a).

Acid-base conditions are stable with a pH value of 6.9±0.2 in the hypolimnion throughout the year. The pH fluctuates more in the surface waters where pH increases to 9 in Spring as a result of algal bloom and photosynthesis (Fig. 1b). The

low ionic strength of epilimnetic waters is maintained by the continuous input of fresh waters from a small stream and by the output, via a temporal spring. Other input waters to the lake include meteoric waters, surface runoff and under-lacustrine spring waters. Impounded in 1978, the reservoir has a basin volume of 1.1×10^6 m^3 and the hypolimnion is ~40% the total lake volume. The reservoir outflow is regulated by inputs and varies on a monthly basis according to rain records. The annual mean precipitation is 334 mm (85% of rain recorded occurs between December and May) and the
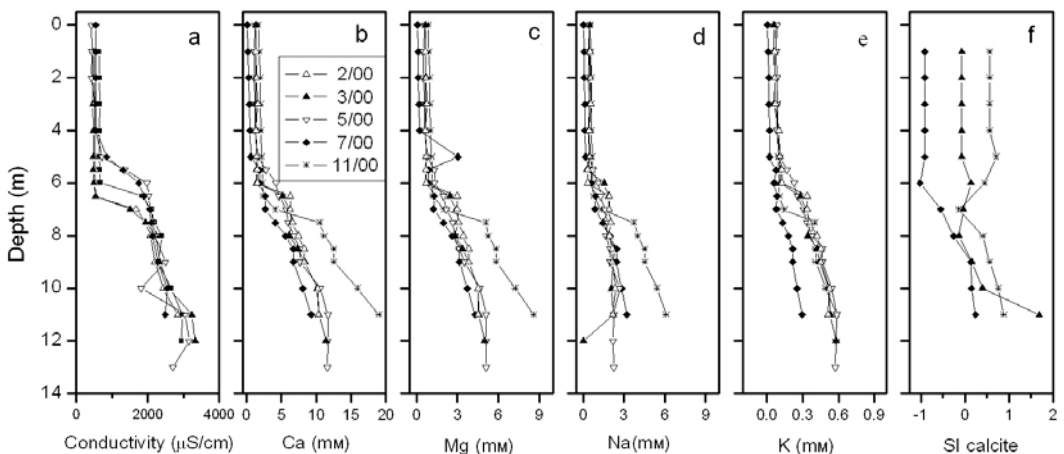

FIG. 2. Evolution of alkaline earth elements in the water column. These elements were determined for five sampling dates (ICP detection limits equal to 0.25 μM for Ca, 0.41 μM for Mg, 0.43 μM for Na and 0.25 μM for K). The calcite saturation index, included in Fig. 2f, indicates contrasted values for Spring (▲), Summer (◆) and Winter (*).

annual mean outflow is estimated to be 1.46×10^6 m³/y, so that the average residence time in the lake is 9 months. If we assume that epilimnetic waters do not mix at all with the hypolimnion, residence time in the epilimnion is only 3 months. An even shorter residence time is observed for $\geqslant 8$ m deep waters as inferred from the chloride profile (Fig. 1*d*). De-icing salt was added in December−January following application of de-icing salt to the road running alongside the lake. In March, low chloride concentrations were observed in the epilimnion and high concentrations were detected in the hypolimnion but only on the February profile. One month later, the Cl^- concentration was back to 1 mM throughout the profile. Thus, the residence time of water in deep waters (i.e. $\geqslant 8$ m) was short, $\leqslant 1$ month. A tentative explanation is as follows. In December or January, chloride-rich road drainage waters were introduced to the frozen lake. Due to density, these comparatively warm waters were introduced by a typical interflow mechanism directly into the hypolimnion, where the chloride concentration in February (1.5−3 mM) is typical of small water bodies affected by road de-icing activities. Afterwards, the same interflow mechanism with fresh run-off waters led to concentrations similar to that observed later on (i.e. ~1 mM). Thus, the water residence time in the hypolimnion is short during winter, i.e. when the surface of the lake is frozen.

This dilution effect in February and March is not true for all ions, as displayed by conductivity values which, like alkalinity values (measured only after March 2000), gradually increase from the oxycline to the lake bottom, displaying a pronounced contrast between oxic and anoxic layers (Figs 1*c*, 2*a*).

In these waters, alkalinity may be attributed to both bicarbonate and, to a lesser extent, ammonium ions, as high concentrations of ammonium ions are often reported in coal-mine waters (typically up to 7 mM (Manning and Hutcheon, 2004)). However, since the hypolimnion water pH is buffered at pH 7, i.e. to a pH equal to the *pKa* of ammonium, only half of this unmeasured inorganic N(III) concentration would participate in the alkalinity. Therefore, we consider that bicarbonate is the major component of alkalinity in the hypolimnion. The high bicarbonate concentrations observed in hypolimnetic water (Fig. 1*c*) are directly correlated with the pε of these anoxic waters (correlation factor *r* of 0.99, 0.98, 0.92 and 0.95 in March, May, July

and November, respectively). Indicated by pH values, photosynthesis activity is at its peak in May (Fig. 1*b*). Subsequent biomass mineralization in the epilimnion leads to the production of bicarbonate, following a series of redox reactions discussed in the next section. This algal bloom had little impact on P concentration which remains constant in the epilimnion throughout the year at a level of ~1.6 μM, which is low and similar to that measured in the input stream (1.2 μM). Note that we measured total dissolved P with a detection limit of 0.9 μM. In contrast, P concentration increases by three orders of magnitude with depth (Fig. 3*a*) to reach 92 μM in the bottom hypolimnion waters, which are oversaturated with respect to hydroxylapatite (Fig. 3*b*). Phosphorous and alkaline earth elements (AEE) concentration profiles indicate that these elements diffuse upward from the sediments, where reductive dissolution of P-rich Fe oxyhydroxides may release P into the waters from the underlying impounded mine galleries. Phosphorus is confined to hypolimnetic anoxic zone due to sorption of P during the oxidative precipitation of Fe(III) oxyhydroxides at the oxycline. This confinement is a common feature of anoxic hypolimnetic waters (Mortimer, 1941,
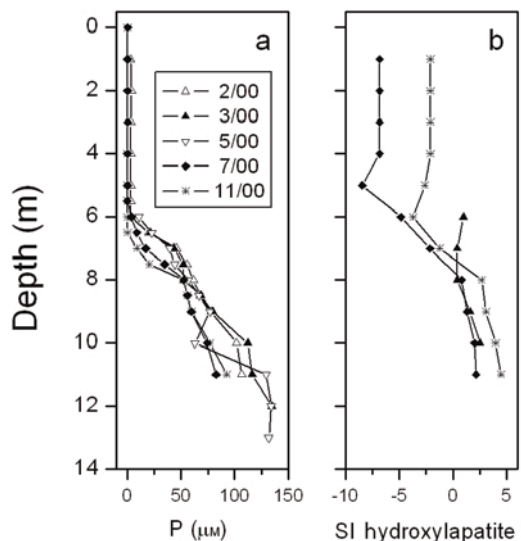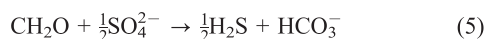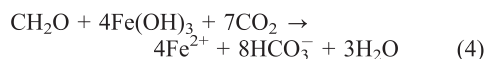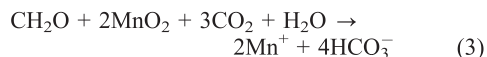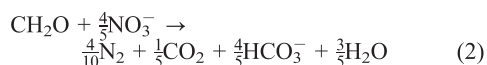

FIG. 3. Vertical distribution of (*a*) phosphorous concentration, (*b*) saturation index (expressed as log (*Q/K*) for hydroxylapatite. Solubility constant taken from the *PHREEQC-2* database (Pankhurst and Appelo, 1999). Data for Spring (▲), Summer (◆) and Winter (*) are shown.

1942; Bostrom *et al.*, 1988; Caraco *et al.*, 1990). The extremely low P concentration registered in superficial waters is due to the combined effect of low P supply by runoff waters, permanent stratification and biological activity.

Redox equilibria and kinetics

The evolution with time and depth of the different redox-sensitive species is illustrated in Fig. 4. The profiles depict the classical sequence of electron acceptor reactions with organic matter occurring during the course of its sedimentation, in agreement with thermodynamics (Stumm and Morgan, 1981).

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{1}$$

$$CH_2O + \tfrac{4}{5}NO_3^- \rightarrow \\ \tfrac{4}{10}N_2 + \tfrac{1}{5}CO_2 + \tfrac{4}{5}HCO_3^- + \tfrac{3}{5}H_2O \tag{2}$$

$$CH_2O + 2MnO_2 + 3CO_2 + H_2O \rightarrow \\ 2Mn^+ + 4HCO_3^- \tag{3}$$

$$CH_2O + 4Fe(OH)_3 + 7CO_2 \rightarrow \\ 4Fe^{2+} + 8HCO_3^- + 3H_2O \tag{4}$$

$$CH_2O + \tfrac{1}{2}SO_4^{2-} \rightarrow \tfrac{1}{2}H_2S + HCO_3^- \tag{5}$$

$$CH_2O \rightarrow \tfrac{1}{2}CO_2 + \tfrac{1}{2}CH_4 \tag{6}$$

At the redoxcline, oxygen and nitrate disappear simultaneously and abruptly at 6 m depth (Fig. 1e), as indicated by equation 2. By the end of Spring (e.g. during the algal bloom in May), O_2 starts to be depleted even in the epilimnion, which indicates limited mixing of surface waters at the beginning of the dry season. Nitrate concentration could only be detected above detection limit (4 μM) in the hypolimnion in February and March, when nitrogen is introduced in the lake by surface runoff after agricultural soil applications (Fig. 4a). In summer, biological activity depletes epilimnetic waters of N, and in Winter, N is very low throughout the water column due to little input and limited biological activity from March to July in these cold-climate remote areas.

In agreement with theoretical predictions (equation 3), Mn oxide reductive dissolution occurs just after nitrate reduction. As the surface becomes O_2-depleted, an aqueous Mn peak develops just below the oxycline, at 6 m depth in March and at 5 m in May–July (Fig. 4b). At a greater depth, i.e. below 8 m, the Mn^{2+} profile concentration is constant throughout the year and waters are at equilibrium with respect to rhodochrosite precipitation (Fig. 5b) and undersaturated with respect to siderite. However, at the same time, i.e. after March, an HS^- concentration peak is developed below 7 m depth (Fig. 4c) and water becomes supersaturated with respect to $FeS_{(s)}$, e.g. mackinawite (solubility data from Wolthers *et al.*, under revision), but not with respect to $MnS(s)$ (Fig. 5c). $MnS(s)$ is known to be more soluble than $FeS_{(s)}$ and to precipitate with much slower kinetics (Davison, 1993). As particles settle in the anoxic environment,
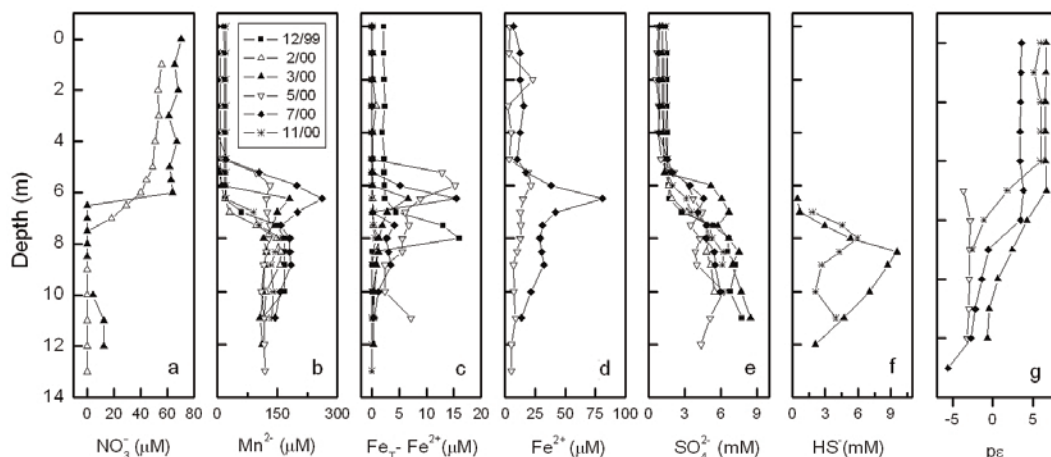

FIG. 4. Distribution of redox-sensitive species against depth for different sampling dates. Nitrate, Fe^{2+} and sulphide concentrations above the detection limits (4 μM, 1 μM and 0.01 mM, respectively) are presented. ICP detection limits were equal to 0.18 μM for Mn and Fe_T.
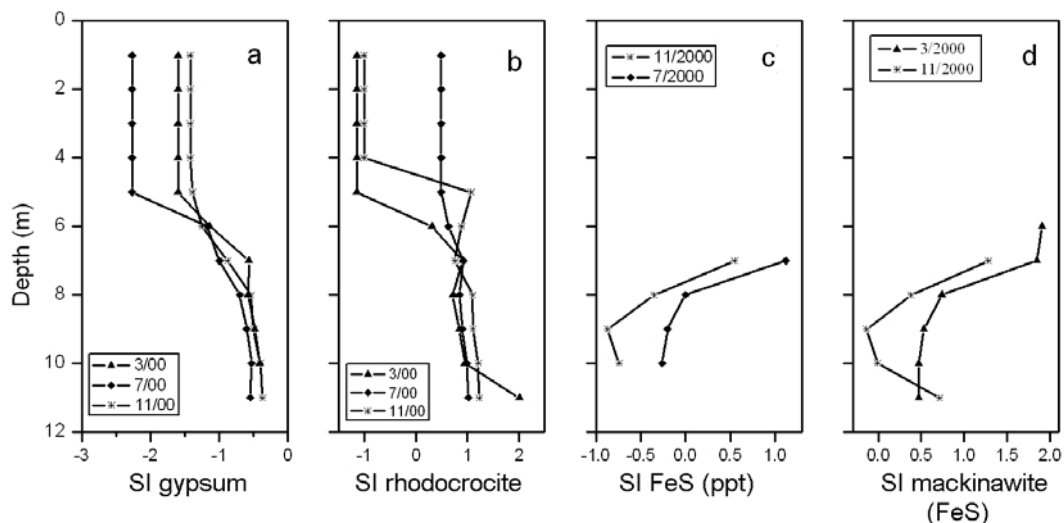
FIG. 5. Saturation index for various minerals *vs.* depth: (*a*) gypsum; (*b*) rhodocrocite; (*c*) FeS; and (*d*) mackinawite.

$MnCO_{3(s)}$ and $FeS_{(s)}$ will not dissolve and will be buried in the sediment where Mn is found to be present at high concentrations (1807 mg/kg).

The next electron acceptor at pH 7 in the redox sequence (equation 4) is $Fe(OH)_3(s)$. It is dissolved nearly at the same depth as MnO_2, although at pH 7, this reaction should occur at a significantly lower pε than MnO_2 reductive dissolution. However, in these Fe^{2+}-rich waters, Fe^{2+} diffusing upwards will reductively dissolve $MnO_{2(s)}$ and thus blur the 'classical' electron cascade (Appelo and Postma, 1999).

During Spring, the Fe(III) concentration, methodologically defined as Fe_T-$[Fe^{2+}]$, is maximal at the oxycline and decreases noticeably in Winter (Fig. 4*c*). The Fe(III) concentration peak depth increases from Spring to Winter (−6 m in May, −6.5 m in July, −8 m in December). Waters at the oxycline are over-saturated with respect to a variety of Fe(III)(oxy)hydroxides (SI equal to 8.5 for goethite, 17 for hematite and 2.6 for $Fe(OH)_{3(s)}$). While these solid phases are likely to trap both As(III) and As(V) (Dixit and Hering, 2003), their survival in such a reducing environment is questionable.

As a result of Fe oxyhydroxide reductive dissolution, waters from the hypolimnion are slightly enriched for various metal ions in comparison with epilimnetic waters. Besides the case of P already mentioned, heavy metals, though present in significant amounts in the sediments (339 mg/kg Zn, 94 mg/kg Cr and 94

mg/kg Ni) have concentrations in the hypolimnion which are, except for the Cr, below European standards for drinking water (0.2 μM Zn, 2.51 μM Cr, 0.9 μM Ni and 0.09 μM Cd; the drinking water standard for Cr is 0.96 μM, (WHO, 2002)). This is true all year around, due to the permanent stratification of the lake. In the epilimnion, heavy metal concentrations were always less than ICP detection limits (0.17 μM Ni, 0.19 μM Cr, 0.08 μM Cd and 0.153 μM Zn).

Sulphate depicts a classical diffusion-like profile, in contrast to nitrate and iron. This is clear evidence for sulphate input coming from the bottom of the lake, i.e. from the sediment and/or from the underlying mine network, while nitrate and the organic matter may be introduced from the top of the lake as detrital materials *via* input of surface waters. The epilimnion waters are slightly undersaturated with respect to gypsum (Fig. 5*a*), while hypolimnion waters are at quasi-equilibrium with respect to gypsum, although this mineral is not present in the coal-ore deposits (Paquette *et al.*, 2000). Pyrite oxidation is expected to be the source of sulphate in the lake. Fires in the coal galleries were reported just before their closure (Piboulle, pers. comm.). As a result, a friable weatherable crust of gypsum may have been formed, and may continue to be formed, as oxygenated waters percolate the watershed substratum. In many mines, the reaction:

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (7)$$
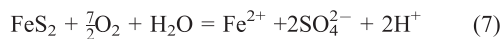
is linked to acid drainage. In the present case, the lake bottom waters have high enough alkalinity to neutralize the protons produced by reaction 7 and to buffer pH at pH 7.

Hypolimnetic waters are also supersaturated with respect to calcite throughout the profile and throughout the year, except in the epilimnion, at the end of the algal bloom (Fig. 2*f*), thus reinforcing the hypolimnion buffer capacity.

The presence of sulphide in bottom water (Fig. 4*f*) indicates that sulphide is produced from sulphate ions at roughly 8 m depth. Theoretical på values for the S(VI)/S(-II) redox couple are between -3 and -4 and are close to those measured *in situ* in February at 6 m depth, in November at 7 m depth and in July at 12 m depth (Fig. 4*g*). Sulphide ions produced by reaction 5 lead waters from below 8 m depth to be slightly supersaturated with respect to mackinawite and slightly undersaturated with respect to FeS as discussed previously (Fig. 5*c,d*).

The source of oxygen in reaction 7 is two fold: whereas it has often been assumed to be introduced together with infiltration water, there is historical evidence of fires occurring in these mines shortly before the coal-mining operation ceased. Thus, pyrite present along the mine gallery walls may have then been fully oxidized to sulphate and ferric hydroxides at that time.

Arsenic chemistry in the lake

The seasonal cycle of aqueous As(III) and As(V) in the lake water column is illustrated in Fig. 6. Arsenic(V) concentrations are very small in the epilimnion, but increase quickly below the oxycline to reach concentrations up to 7 μM below 8 m depth, whatever the season. Clearly,

the sediments (where As is present at 187 mg/kg concentration level) and/or the underlying mine galleries are the source of As(V). With respect to water quality, only the surface water is of appropriate quality for human consumption (European As drinking standards = 0.13 μM; prior to 2003 this standard was 0.60 μM As). These waters are regularly monitored by the St-Eloy-les Mines City Council.

In spite of anoxic conditions in the hypolimnion, As(V) remains the predominant species throughout the profile; As(III) is found only at very small concentrations in deep waters. During spring and summer (dry season), As(III) concentration increases in the hypolimnion, simultaneously with Fe(II) and S(-II), but As(V) remains the dominant species. During the wet season when oxygenated waters are introduced to the hypolimnion, As(III) concentrations become very small. The rather constant As(V) concentration indicates a solubility control, e.g. by gypsum where only one sulphate ion in thousands may be substituted by $HAsO_4^{2-}$. The structure and solubility of such solid solutions are presently under study in our laboratory (Fernandez-Martinez *et al.*, submitted).

Reduction of As(V) by S(-II) seems a possible pathway to the formation of As(III). According to the SI calculated for various As(III) and S(-II) solid phases in the hypolimnion, orpiment (SI = 20) could be the solid phase controlling the solubility of As in the presence of sulphide. However, As(III) at pH 7 and As(V) below pH 8.5 easily adsorb on FeS (Walthers *et al.*, under revision) and this sorption process may be a geochemical controlling mechanism in this lake. The oxidation of As(III) to As(V) by oxygen is a rather slow process (Kuhn *et al.*, 1994) but Mn
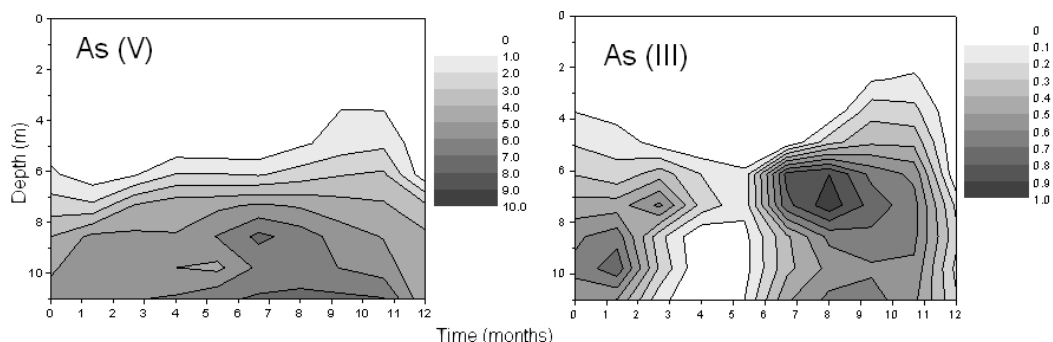

FIG. 6. Spatio-temporal evolution of As(V) and As(III) concentrations (in μM). Time reference: 1: January, 2: February, 3: March, etc.

oxides were shown to be effective oxidants of As(III) (Tournassat *et al.*, 2002). A good correlation between As(V) and Mn(II) concentrations ($r = 0.85$ during the wet season and $r = 0.98$ during the dry season) support the Mn oxide oxidation of As(III) hypothesis. This would account for the As(III) depletion in summer and if As(V) concentration were to increase further (they presently remain unsaturated), the most likely precipitated solid phase would be a Mn arsenate. The discrepancies observed in the estimation of pε values from the redox couples As(V)/As(III) and Fe(III)/Fe(II) clearly indicate, in any case, a lack of equilibrium conditions. This is a general trend that As(III) increases as the measured redox potential decreases. However, the use of Eh in predicting arsenic species has some limitations. These facts make it more difficult to interpret the Eh values measured and those calculated from redox species. A more detailed study of the sediment solid phase is being carried out to determine the various solid phases which control the fate of arsenic in this lake.

Conclusions

Biogeochemical cycles, mainly controlled by N and P availability do not have a great influence on the lake St-Eloy chemistry where weathering and redox processes, occurring to a large extent in the underlying mine, appear to be the most significant factor controlling the chemical composition of these coal-mine lake waters. The geochemical evolution of the anoxic permanent layer is dominated by the mineralization of sinking organic matter particles according to thermodynamics and by the release of elements diffusing out of the sediments.

The differential behaviour between Fe and Mn is caused by the slower oxidation of Mn(II) compared to Fe(II). Consequently, Mn(II) is spread more diffusely throughout the water body than Fe(II). During the May event, the Mn concentration reaches its lowest value. This coincides with large inputs of oxygenated groundwaters which, in turn, lead to high concentrations of Fe(III), to an absence of S, and to high concentrations of reduced Mn(II), Fe(II) and As(III) species. The As cycle in the lake is therefore controlled to a large extent by Mn and Fe hydroxides.

The old impounded mines are the main source of arsenic in this lake. The As(V) and As(III) are not at equilibrium and this can be attributed to

slow reaction kinetics, a common feature reported for anoxic lake waters. The control of arsenic concentrations in these anoxic waters may result from competition of various solid phases for arsenic: gypsum (present in the underlying mines) can accommodate significant amounts of As(V) in its unit cell (Fernández-Martínez *et al.*, submitted); when it is reductively dissolved in the presence of Fe(II), mackinawite may be the new trap controlling solid phases for both As(III) and As(V) (Wolthers *et al.*, submitted). Close to the oxycline, Fe(III) oxyhydroxides are possible hosts for both As(III) and As(V) (Smedley and Kinninburg, 2002). More detailed studies with sediment traps and anoxic sampling of the sediments may in future determine which is the main mineral controlling aqueous arsenic concentration.

In spite of good quality epilimnetic water, the possibility of using the reservoir as a drinking water resource appears limited; if pumping were to introduce hypolimnetic water into the epilimnion, arsenic inputs into surface waters would substantially degrade the water quality, which may even make it unfit for recreational purposes.

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