Geochemistry of Cu, Zn and Fe in the Tambo River, Australia I. Oxidation of Fe(II)-rich water entering the river

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Abstract. The behaviour of Fe, Cu and Zn was studied during the laboratory oxidation of an acidic (pH 5.8) sample of naturally contaminated water from the Tambo River (Victoria, Australia). Changes in the concentrations of the dissolved, colloidal and particulate fractions of these metals were followed over 288 h. The initial concentrations of dissolved Cu ($18.5\,mg\,L^{-1}$) and Zn ($22.6\,mg\,L^{-1}$) were ~15-fold greater than that of the dissolved Fe ($1.13\,mg\,L^{-1}$). Dissolved Fe was completely removed from solution in 60 h, with removal following the well established first order oxidation kinetics for Fe(II). A relatively small amount of the dissolved Cu (18%) and dissolved Zn (14%) was removed from the solution, although the removal mechanisms appear to be different. A 'co-precipitation-surface precipitation' mechanism is proposed to explain the behaviour of the Cu and Zn, with Cu(II), Zn(II) and Fe(III) co-precipitating to form colloidal $Fe(OH)_3$-$Cu(OH)_2$-$Zn(OH)_2$ particles following the initial oxidation of Fe(II) to Fe(III).

Additional keywords: contamination, co-precipitation-surface precipitation, heavy metals, hydrous iron oxide, kinetics.

Introduction

The geochemistry of heavy metals in aquatic systems is complicated and difficult to predict. This is particularly so for rivers, where physical (hydrological), chemical and biological interactions must be coupled if the behaviour of the metals is to be understood and eventually predicted (Hart and Hines 1995). Despite the obvious variability and complexity of river systems, there exists a quite detailed understanding of many of the processes controlling heavy metal geochemistry, with much of this understanding coming from laboratory-based studies of trace metal speciation and the interactions of elements with a variety of substrates (e.g. natural organic matter, colloids, suspended particulate matter) (Hart and Hines 1995; Stumm and Morgan 1996; Hart *et al*. 1997; Harris 2001).

There have been relatively few field studies that have focused specifically on the changes in the (bio)geochemistry of reactive trace metals that can occur as a result of the wide range of natural variations characteristic of stream ecosystems, and those that have been undertaken have been dominated by investigations of the very obvious changes occurring when acid mine drainage (i.e. acidic, metal-enriched water) enters a river (Johnson 1986; Filipek *et al*. 1987; Hart *et al*. 1992; Kimball *et al*. 1994; Balistrieri *et al*. 1998; Webster *et al*. 1998; Lee *et al*. 2002; Younger *et al*. 2002). In these cases, the effects of metal precipitation, adsorption onto newly formed hydrous metal oxides (HIO) and biological uptake dominate. Of these processes, the role of HIO in controlling the behaviour of heavy metals has been most studied (Dzombak and Morel 1990; Grossl *et al*. 1994; Karthikeyan *et al*. 1997, 1999; Swedlund and Webster 2001; Tonkin *et al*. 2002; Waychunas *et al*. 2002).

A unique opportunity to study the *in situ* behaviour of elevated heavy metal concentrations in a river system close to neutral pH, was provided by the upper Tambo River, situated in the Australian highlands some 270 km north-east of Melbourne. A section of this river receives input from a naturally metal-rich spring (Wilga Spring), the source of which is a Cu/Zn ore body located adjacent to the river (Hart *et al*. 1992). The downstream effects of the spring are obvious in that the rocks and sediments are stained red with iron oxides (a red-brown floc also builds up in sections of the river during low flows). Biological studies have shown the river is essentially devoid of animal life for a distance of at least 1 km downstream of the spring input (Macquarie Resources Ltd 1989).

Previous work (Hart *et al*. 1992) has shown that under most flow conditions, the spring input has little effect on the river pH, which remains close to neutral. However, the spring was found to cause an average sixfold increase in the Cu and Zn concentrations in the region close to the spring input. It was suggested that the acidic waters from the ore body oxidation zone are largely neutralised either before entering the river by carbonate-rich groundwater, or rapidly upon entering the river. Under most flow conditions, the concentrations of dissolved Cu and Zn in the 'contaminated region' of this river (region between spring and 1.3 km downstream) appear to be controlled largely by adsorption onto HIO surfaces formed *in situ* by the oxidation of Fe(II) present in the spring water. The subsequent behaviour of the Cu and Zn in this region of the river is then controlled by the transport and sedimentation of this metal-enriched colloidal and particulate material (Hart *et al*. 1992).

Under extremely low flows, when the spring input can make up a significant proportion of the river flow, some reduction in the river pH is observed. For example, in a study conducted when the river flow was $\sim$0.2 ML day^{-1} (cf. long-term mean 22 ML day^{-1}), and the spring input made up $\sim$10% of the flow, the river water pH was reduced from 7.2 to 5.8 at the start of the 'input region' (75 m downstream of Wilga Weir) and was further reduced to pH 5.1 at the second input point (160 m downstream of the weir) (Hart *et al.* 2008). However, despite these low pHs, it still appeared that the oxidation of Fe(II) played a significant role in controlling the behaviour of Cu and Zn within the 'active region'.

We report a laboratory study designed to investigate the oxidation of Fe(II), and the associated loss of dissolved Cu and Zn, in these low pH waters. A Cu and Zn-enriched Tambo River water sample (pH 5.8) was oxidised in the laboratory under controlled conditions, and the changes in the dissolved ($<$0.003 μm), colloidal ($>$0.003 to $<$0.2 μm) and particulate ($>$0.2 μm) concentrations of Fe, Cu and Zn were followed over 288 h. Despite the relatively low pH, all of the dissolved Fe (assumed to be Fe(II)) was removed from solution in around 60 h, and there was a considerable reduction in the dissolved Cu and Zn concentrations (14–18%, c. 3 mg L^{-1}). The mechanisms responsible for these changes are discussed. A companion paper (Hart *et al.* 2008) reports a field study of the geochemistry of Fe, Cu and Zn in the Tambo River at the time of this low flow.

Materials and methods

System

Hart *et al.* (1992) defined two regions of the Tambo River in the vicinity of Wilga ore body: a 'contaminated region' between Wilga Weir and Formfit Creek, a distance of $\sim$1.3 km; and an 'input region' between $\sim$75 m and 250 m downstream of Wilga Weir. There appears to be two main locations where Wilga spring water enters the river, the main input point being at 75 m and the other at 160 m (Hart *et al.* 1992, 2008). During the present study, the river flow was only 0.2 ML day^{-1} with the main spring input making up an estimated 10% of this flow; the other input contributed $\sim$10% of the main input. Full details on the system at the time of this low flow period are provided by Hart *et al.* (2008).

Sampling

A 20-L sample of river water was obtained from the 'input region', at a point about 150 m downstream of Wilga Weir, during the period of very low flow. The sample was pumped from the river into a 25-L acid-washed polyethylene container using a battery-operated peristaltic pump. The pH of this water was 5.8, the sulfate concentration was 320 mg L^{-1} and the chloride concentration 17 mg L^{-1}.

Oxidation experiment

The sample contained in the polyethylene container was continuously aerated by bubbling air through the water column using a battery-operated air pump. One-litre samples were then taken from the container 10 min after the initial sample was collected from the river, and then at 12, 18, 36, 60, 96, 144 and 288 h. The container was shaken vigorously before each sub-sample was taken through a tap at the bottom into an acid-washed polyethylene bottle. Each sample was separated into three fractions using

the tangential flow filtration (TFF) system as outlined below. The first sample ($t = 0$ h) was filtered on-site at the river.

The container was then taken back to the Macquarie Resources offices, $\sim$1 h drive, where the second and third samples were processed. After this the container was transported back to the Water Studies Centre laboratory in Melbourne (7.5 h travel time) where the remainder of the experiment was carried out. The pH of the mixture, measured at the time each sub-sample was taken, remained constant over the course of the experiment (Hines 1995). The pH meter (Activon A211, Biolab, Clayton, Vic) was calibrated before each measurement using pH 7.0 and 4.0 standard buffer solutions. Temperature was maintained close to the original temperature ($15 \pm 2^\circ$C) throughout the experiment.

Fractionation

Two 100-mL duplicate samples were taken from each of the 1-L sub-samples, concentrated HNO$_3$ added (to pH 2) and the solutions analysed for total (T) Fe, Cu and Zn. The remainder of each sub-sample was then separated into three fractions using the Minitan TFF system described below and each fraction analysed for Fe, Cu and Zn. Manganese was also determined in all samples. However, the Mn concentration was always around two orders of magnitude lower than the corresponding Fe concentration (Hines 1995), and for this reason Mn is not considered further.

Filtration of water samples was carried out using TFF (Millipore Minitan System, Millipore Corp, Billerica, MA, USA). This allowed samples to be fractionated into three fractions: particulate (MeP: $>$0.2 μm); colloidal (MeC: 0.2–0.003 μm); and dissolved (MeD: $<$0.003 μm). This filtration unit used a set of horizontally stacked Minitan plates, with 60 cm^2 each of filter area, each separated by a silicone retentate separator. Once assembled, the Minitan plates and the retentate separators were sandwiched between two perspex plates. A stainless steel plate, four washers and nuts were placed on the top perspex plate and pressure was applied uniformly (torque wrench) to ensure adequate sealing. A pump head (Cole Palmer Model 7518, Cole Palmer, Vernon Hills, IL, USA) was fitted to the Minitan system using food grade silicone tubing. The pump head was attached to a masterflex L/S DC-powered pump drive, which required an external 12 V DC, 3 A power source. The power source for the operation of the peristaltic pump was a 12 V acid-lead battery.

Water was pumped into the Minitan holder at $\sim$1 L min^{-1} using the peristaltic pump. Two different filter sizes were used: 0.2 μm and 0.003 μm (10 000 Da). In the first stage of the fractionation procedure, the filtrate ($<$0.2 μm) was collected in a 1-L acid-washed polyethylene bottle from which a sub-sample was taken and analysed for Cu, Zn and Fe. The system was washed after each filtration step with two aliquots of ultrapure (Milli-Q, Millipore Corp, Billerica, MA, USA) water, followed by one aliquot of 0.1 M nitric acid and then finally again with one aliquot of ultrapure water. A duplicate sample was then filtered through the 0.2-μm filter plates.

After this, the 0.2-μm filter plates were replaced with 0.003-μm filter plates for the second sequential filtration step. Approximately 900 mL of the $<$0.2-μm filtrate was run through the TFF system until around 100 mL had passed through the $<$0.003-μm

filter, resulting in a concentration factor of around 9. Larsson *et al*. (2002) have shown that retention of colloidal particles in TFF systems is sensitive to the concentration factor, and using the results of these researchers, we estimate that the concentrations of the MeC fractions were probably within $\pm 20\%$ of the true concentration. A duplicate sample was also filtered through the 0.003-μm filter plates.

The final filtrates were analysed for Cu, Zn and Fe using the techniques outlined below. The metal concentrations in the duplicate samples were typically within 5–10% of each other, a not surprising result given the high metal concentrations in the present study.

After each filtration step, the filter plates and the retentate separator were further cleaned by washing them in an acid-washed plastic container filled with ultrapure water, then transferring them to a different container that was filled with 0.1 M nitric acid and finally to another container containing ultrapure water. A blank was carried out after each filtration step and these showed that no contamination of Cu, Zn or Fe was present.

The three fractions (total, $<0.2\,\mu$m and $<0.003\,\mu$m) were acidified with 0.5 mL Suprapur nitric acid. Copper, Zn and Fe were determined using flame Atomic Absorption Spectrometer (AAS): detection limits were Fe: $10\,\mu g\,L^{-1}$, Cu: $10\,\mu g\,L^{-1}$ and Zn: $4\,\mu g\,L^{-1}$. In those cases where the concentrations were less than these detection limits, the samples were analysed using graphite furnace AAS; detection limits were $1\,\mu g\,L^{-1}$, $0.5\,\mu g\,L^{-1}$ and $0.5\,\mu g\,L^{-1}$ for Fe, Cu and Zn respectively. USEPA standard reference water samples were also analysed with satisfactory results (e.g. low level standard: Fe: analysed $820\,\mu g\,L^{-1}$ cf. reference value $780\,\mu g\,L^{-1}$, Cu: $372\,\mu g\,L^{-1}$ cf. $339\,\mu g\,L^{-1}$, Zn: $442\,\mu g\,L^{-1}$ cf. $418\,\mu g\,L^{-1}$; high level standard: Fe: $2040\,\mu g\,L^{-1}$ cf. $2000\,\mu g\,L^{-1}$, Cu: $1970\,\mu g\,L^{-1}$ cf. $2000\,\mu g\,L^{-1}$, Zn: $503\,\mu g\,L^{-1}$ cf. $500\,\mu g\,L^{-1}$).

The concentrations of the three fractions were obtained as follows:

$$\text{Dissolved MeD} = [\text{Me}(<0.003\,\mu\text{m})]$$

$$\text{Colloidal MeC} = [\text{Me}(<0.2\,\mu\text{m})] - [\text{Me}(<0.003\,\mu\text{m})]$$

$$\text{Particulate MeP} = [\text{MeT}] - [\text{Me}(<0.2\,\mu\text{m})]$$

Results

General

The river water sample used in this experiment was taken 150 m downstream of Wilga Weir and $\sim$75 m downstream of the first spring input. The pH of the sample was 5.8 and it contained elevated concentrations of sulfate ($320\,\text{mg}\,L^{-1}$). The sample was representative of much of the water in the 'input region' during the low flow period (Hart *et al*. 2008), although the pH was considerably lower and the concentrations of Fe, Cu and Zn were very much higher than those experienced in this region during more typical flow conditions in the Tambo River (Hart *et al*. 1992).

The initial speciation of the Fe, Cu and Zn suggests that some geochemical transformations had already occurred in this sample (Table 1). For example, initially only $\sim$51% of the Fe was in dissolved forms, although dissolved forms dominated the speciation of Cu (86%) and Zn (94%).

During the oxidation experiment, the pH and the total concentrations of Fe, Cu and Zn of the sample remained constant, suggesting that no loss of metals occurred during the experiment (Table 1). The initial CuD/ZnD molar ratio was $\sim$0.75 and this decreased to $\sim$0.70 over the duration of the experiment, indicating that more Cu than Zn was lost from the dissolved phase.

It is well known that both Cu(II) and Zn(II) are readily complexed by natural organic matter (Morel 1983; Stumm and Morgan 1996). However, in this case the very high concentrations of these metals ($\text{mg}\,L^{-1}$), when combined with the typical dissolved organic carbon concentrations (5–$10\,\text{mg}\,L^{-1}$) in this upland river, would mean that the amount of each metal complexed by organic matter would be trivial ($\mu g\,L^{-1}$).

Iron

The behaviour of the three forms of Fe with time is shown in Figs 1*a* and 2*a*. The initial FeT concentration was $2.21\,\text{mg}\,L^{-1}$, with 51% in dissolved forms, 43% in particulate forms and only 6% in colloidal forms. The change in Fe speciation with time was quite clear. The FeD decreased to a negligible concentration after around 60 h, whereas the concentration of both FeC and FeP increased with time up to around 60 h and then remained essentially constant for the duration of the experiment (Fig. 2*a*). At the end of the experiment, 80% of the particle-bound Fe was distributed in the particulate fraction and 20% in the colloidal fraction (initially 88% particulate, 12% colloidal).

Copper

The behaviour of the three forms of Cu is shown in Figs 1*b* and 2*b*. During the experiment, the CuD concentration was reduced from $15.8\,\text{mg}\,L^{-1}$ to $12.5\,\text{mg}\,L^{-1}$ (a reduction of $3.3\,\text{mg}\,L^{-1}$ or 18%), this being mostly (72%) distributed into the colloidal fraction. Initially, the Cu was distributed 85% CuD, 5% CuC and 10% CuP, whereas at the completion of the experiment, the distribution was 67% CuD, 18% CuC and 15% CuP. Dissolved Cu was continually lost from solution over the duration of the experiment, and not just during the first 60 h of the experiment when FeD was removed. The amount lost over the first 60 h ($1.8\,\text{mg}\,L^{-1}$) was approximately the same as that lost over the remaining 228 h ($1.5\,\text{mg}\,L^{-1}$). Most of the CuD removed from solution became associated with the colloidal fraction, with only a small amount associated with the particulate fraction (Fig. 2*b*).

It is possible that there was a short time lag before the CuD decrease commenced. However, if this did occur it was before the first sample was taken at 12 h. The CuC/FeC molar ratio was very high ($\sim$6.0), suggesting that simple adsorption onto HIO surfaces was not the mechanism responsible for the removal of Cu from solution.

Zinc

The changes in the Zn speciation are shown in Figs 1*c* and 2*c*. The ZnD concentration was reduced from $21.3\,\text{mg}\,L^{-1}$ to $18.4\,\text{mg}\,L^{-1}$ ($2.9\,\text{mg}\,L^{-1}$, 14%) over the period of the experiment, and this was almost all transferred into the colloidal fraction. The major changes in the ZnD concentration occurred in the period up to 60–75 h, and after this the concentration changed little (Fig. 2*c*). Initially, the Zn was distributed 94% as ZnD, 5% as ZnC and 1% as ZnP, and at the completion of the experiment,

Table 1. Metal concentrations (mg L^{-1}) for the oxidation experiments
MeD: dissolved metal; MeC: colloidal metal; MeP: particulate metal; MeT: total metal

Time (h)	FeT	FeD	FeC	FeP	CuT	CuD	CuC	CuP	ZnT	ZnD	ZnC	ZnP
0	2.21	1.13	0.13	0.95	18.5	15.8	0.89	1.78	22.6	21.3	1.13	0.16
12	2.23	0.66	0.20	1.37	18.5	15.5	1.01	2.02	22.6	21.2	1.11	0.25
18	2.27	0.47	0.20	1.60	18.5	15.0	1.22	2.22	22.6	20.9	1.66	0.02
36	2.24	0.11	0.28	1.85	18.5	14.7	1.53	2.25	22.6	19.3	3.27	0.01
60	2.27	0.00	0.38	1.89	18.5	14.0	2.17	2.33	22.6	19.0	3.67	0.01
72	2.24	0.00	0.36	1.88	18.5	13.4	2.50	2.62	22.7	18.8	3.85	0.01
96	2.24	0.00	0.36	1.88	18.5	13.3	2.59	2.63	23.0	18.6	4.10	0.30
144	2.21	0.00	0.37	1.84	18.5	12.9	2.93	2.66	22.8	18.6	3.94	0.23
288	2.21	0.00	0.36	1.85	18.5	12.5	3.29	2.70	22.6	18.4	4.19	0.00

the distribution was 81% ZnD and 19% ZnC. The particulate fraction appeared to play little part in the changes in the Zn speciation in this experiment.

Figure 1*c* shows the detailed changes in concentration of the three forms of Zn with time. There appeared to be a definite time lag of around 12 h before the ZnD concentration commenced to decrease, after which time there was a very rapid reduction in concentration. The rate of association of Zn with the colloidal fraction was obviously more rapid than for Cu (Fig. 2*b*, *c*). The ZnC/FeC molar ratio was very high (~8.0), suggesting as with Cu that simple adsorption onto HIO surfaces was not the mechanism responsible for the removal of Zn from solution.

Discussion

General

As noted above, the very low flow experienced in the Tambo River during the present study provided an opportunity to study the geochemistry of Fe, Cu and Zn added to the river by a natural metal-rich spring (Wilga Spring), the source of which is a Cu/Zn ore body located adjacent to the river. Under most flow conditions, the river downstream of the spring input has elevated metal concentrations, and a near neutral pH (Hart *et al.* 1992). However, under low flow conditions, the spring input does lower the pH and also results in elevated metal concentrations in the river.

A large amount of research has been undertaken on both the oxidation of Fe(II) (Liang *et al.* 1993; King *et al.* 1995; Emmenegger *et al.* 1998; Rose and Waite 2002, 2003*a*, 2003*b*; Duesterberg and Waite 2006), and the metal adsorption properties of the HIO formed through these oxidation reactions (Farley *et al.* 1985; Dzombak and Morel 1990; Grossl *et al.* 1994; Karthikeyan *et al.* 1997, 1999; Tonkin *et al.* 2002; Waychunas *et al.* 2002).

However, the work reported here differs in three significant ways from the bulk of these oxidation and adsorption studies. First, most Fe(II) oxidation experiments are conducted in solutions that contain a much greater concentration of Fe than Cu and Zn. However, in our experiment, the initial CuD and ZnD concentrations (18.5 mg L^{-1} and 22.6 mg L^{-1} respectively) were ~15 times higher than the FeD concentrations (1.13 mg L^{-1}). Second, and related, most adsorption experiments are run under conditions where the concentration of HIO is significantly greater than

the concentrations of the adsorbing cations. Under these conditions, an excess of surface binding sites would exist, but this was not the case here. Third, the bulk of the adsorption experiments present already formed HIO to the aqueous solution, rather than simulating the situation here where Cu(II) and Zn(II) ions were present during the time Fe(II) was being oxidised. Some recent studies, however, have investigated the co-precipitation of Fe and heavy metals such as Cu, Zn, Cd, Ni and Pb (Karthikeyan *et al.* 1997; Webster *et al.* 1998; Ford *et al.* 1999; Lee *et al.* 2002).

Iron

The loss of FeD at pH 5.8 was complete in 60 h, with the FeD being distributed ~15% into the colloidal fraction and ~85% into the particulate fraction (Figs 1*a* and 2*a*). The final split between colloidal and particulate fractions was essentially the same as at the start of the experiment.

The most obvious mechanism to explain the removal of Fe from this solution is oxidation of Fe(II) to Fe(III). The redox cycling of iron in natural waters has been extensively studied over several decades (Stumm and Morgan 1996). The mechanism proposed by King *et al.* (1995) (the Haber–Weiss mechanism) is now widely accepted (Emmenegger *et al.* 1998; Rose and Waite 2002, 2003*a*, 2003*b*). For many situations in freshwaters at least, the rate determining step for the oxidation of Fe(II) to Fe(III) is (Liang *et al.* 1993):

$$Fe^{II}OH^+ + O_2OH^- \rightarrow Fe^{III}(OH)_2^+ + {}^{\bullet}O_2^- \quad (1)$$

where O_2OH^- is a hydroxylated oxygen molecule and ${}^{\bullet}O_2^-$ a superoxide radical. This leads to the homogeneous first order rate equation for oxidation of Fe(II):

$$\frac{d[Fe(II)]}{dt} = -k_1[Fe(II)] = -k[O_{2 \bullet aq}][OH^-]^2[Fe(II)] \quad (2)$$

The presence of other inorganic and organic ions in the natural water can influence the overall rate of oxidation by reducing the amount of free ionic Fe(II) and/or scavenging the superoxide and hydroxyl radicals produced (Liang *et al.* 1993; Rose and Waite 2002). In some situations (e.g. poorly oxygenated groundwaters), natural organic material can significantly increase the oxidation rate has been found to have little effect on the rate of oxidation at high oxygen concentrations (Liang *et al.* 1993).
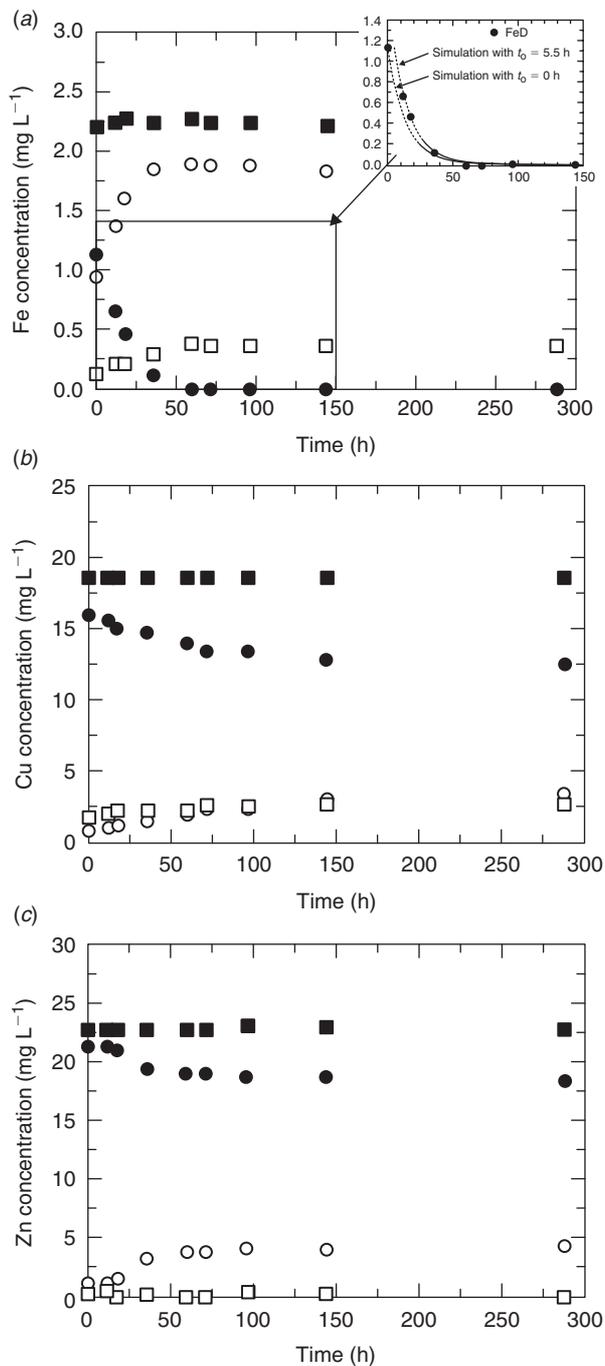
Fig. 1. Variation in the concentrations of (*a*) Fe, (*b*) Cu and (*c*) Zn with time in Tambo River water (pH 5.8). Each diagram shows the total (■), dissolved (●), colloidal (○) and particulate (□) metal concentrations. Figure 1*a* inset shows the results of two simulations, one with the oxidation commencing at zero time ($t = 0$ h) and the other with oxidation commencing at 5.5 h ($t = 5.5$ h).

Fig. 2. Variation in the normalised concentration of (*a*) Fe, (*b*) Cu and (*c*) Zn with time in Tambo River water (pH 5.8). Each diagram shows the dissolved (●), colloidal (○) and particulate (□) metal concentrations. Concentrations were normalised to better show the relative differences in each metal species with time.

Additionally, it is well known that Fe(II) oxidation is autocatalytic, where the rate is enhanced by the formation of Fe(III) hydroxides (Stumm and Morgan 1996).

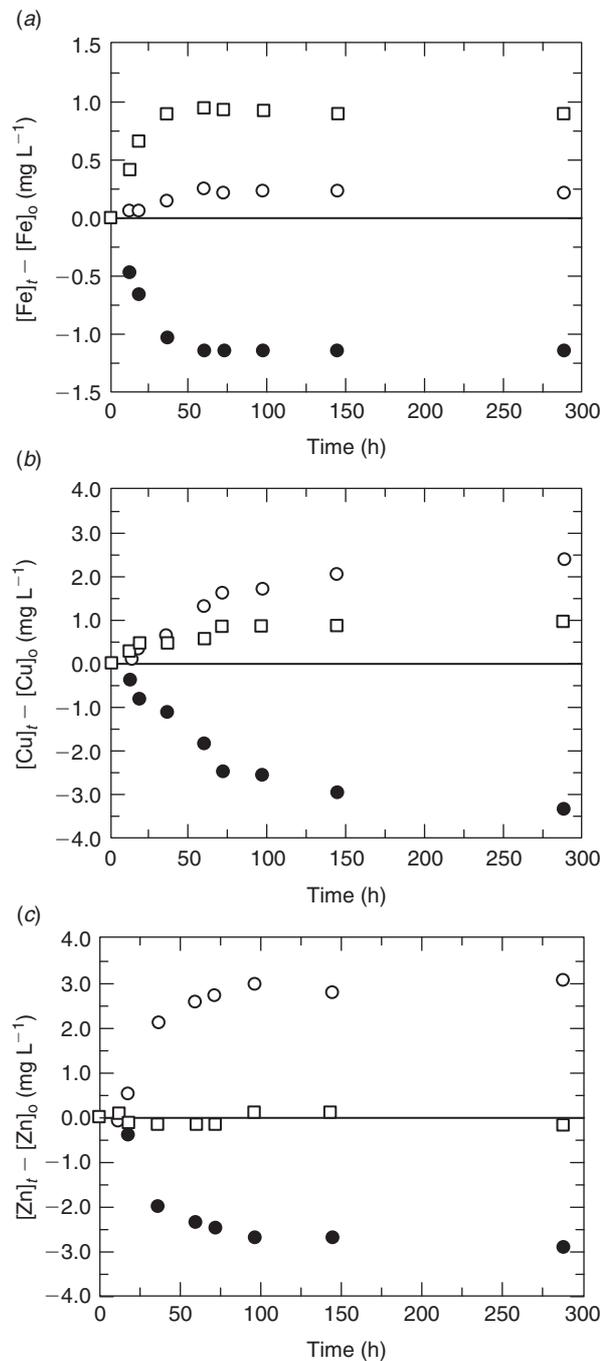However, for the experiment reported here, we expect the simple rate equation (Eqn 2) to hold. Potentially interfering anions are not present in high enough concentrations, and the autocatalytic mechanism is unlikely to be relevant because the relatively large concentrations of Cu(II) and Zn(II) would out-compete Fe(II) ions for available HIO surfaces sites.

Assuming first order Fe(II) oxidation kinetics (rate constant $k = 1.2 \times 10^{17}\,M^{-3}\,min^{-1}$ (Morel 1983, p. 373),

$(O_2) = 8\,mg\,L^{-1}$, $(OH^-) = 10^{-8.2}\,M$) and the commencement of oxidation at $t = 0\,h$, we were able to simulate the experimental data reasonably well (Fig. 1a). The computer package STELLA was used for the simulations (Cronk *et al*. 1990). However, a more detailed analysis of the FeD data suggests that there may have been a slight delay of around 5–6 h before oxidation commenced (Fig. 1a inset). A second simulation, with a 5.5 h time lag produced a very good fit to the experimental data (Fig. 1a). Interestingly, there appears to be a delay of $\sim$5–12 h before the dissolved Cu and Zn concentrations started to reduce (Fig. 2b, c). For this simulation, the rate constant (k_1) was $0.07\,h^{-1}$ and the half time for reaction was around 9 h.

The apparent delay of 5–6 h before the oxidation of the Fe(II) commenced is difficult to explain. The most plausible explanation is that the aeration system was less effective during the initial stages of the experiment, which is certainly a possibility, given the rather primitive conditions that existed in the Macquarie Resources office at that time.

In most situations, the oxidation of Fe(II) to Fe(III) is followed by rapid hydrolysis to form insoluble HIOs (Stumm and Morgan 1996). In a study of 28 acid mine drainage sites, Bigham *et al*. (1996) found the dominant form of the HIO to depend on the pH at which the precipitate formed. Ferrihydrite (FeOOH) dominated in solutions of pH 6.5 and greater, schwertmannite (formula $Fe_8O_8(OH)_6SO_4$) dominated in solutions with pHs in the range 2.8–4.5, and mixtures of these two HIO forms were produced from solutions with intermediate pH. Hence, if HIO colloids did form in the Tambo River sample, it is likely they would be a mixture of ferrihydrite and schwertmannite.

Interestingly, most (85%) of the FeD was distributed into the particulate fraction and only 15% to the colloidal fraction. This was almost the reverse of the CuD and ZnD behaviour, as these were both largely distributed to the colloidal fraction.

The Fe rate data (Figs 1a and 2a) shows that the formation of FeP closely followed the first order loss of FeD. However, the rate of formation of FeC appeared to be linear and not first order. This suggests that the association of Fe with the particulate fraction was primarily dependent upon the oxidation of Fe(II), but just how this Fe(III) was associated with the particulate fraction is not known. The linear formation of FeC over the first 60 h ($r^2 = 0.996$) suggests the rate-determining step is slower than the production of Fe(III) and constant with time. The formation of CuC ($r^2 = 0.991$) and ZnC ($r^2 = 0.950$) was also linear, although more rapid than Fe (Fig. 2). This strongly suggests precipitation (or co-precipitation) is the rate-determining step in the formation of the colloidal fraction (Neilsen 1964; Stumm and Morgan 1996).

As discussed below, this Fe(II) oxidation had a major influence on the behaviour of the dissolved Cu and Zn. Briefly, two related mechanisms are proposed (Fig. 3), these being: (i) the formation of HIO colloids that then form nuclei for the adsorption and surface precipitation of Cu and Zn; and (ii) the co-precipitation of Fe(III), Cu and Zn could form colloidal particles of $Fe(OH)_3$, $Cu(OH)_2$ and $Zn(OH)_2$.

Copper

Approximately 18% ($3.3\,mg\,L^{-1}$) of the CuD was lost from solution during the oxidation experiment, with most (72%)
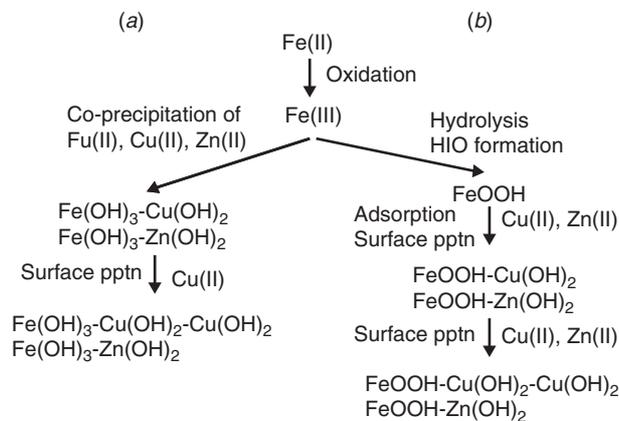

Fig. 3. Possible mechanisms for the association of Cu(II) and Zn(II) with the colloidal fraction. (*a*) Initial co-precipitation of $Fe(OH)_3$, $Cu(OH)_2$ and $Zn(OH)_2$ followed by surface precipitation of $Cu(OH)_2$ and $Zn(OH)_2$. (*b*) Initial formation of hydrous iron oxides (HIO) colloids followed by adsorption and surface precipitation of $Cu(OH)_2$ and $Zn(OH)_2$.

partitioned into the colloidal fraction (Fig. 2b). Possible reasons for the speciation are discussed below. There is evidence that the loss of CuD from solution may have commenced after a short lag time; the evidence for ZnD is even stronger (Fig. 2c). A lag of 5–6 h was also apparent in the loss of FeD and was ascribed to a fault in the aeration system during the initial stages of the experiment.

The removal of CuD from solution appeared to occur in two steps, an initial rapid reduction of around 50% over the first 60 h, followed by a slower removal of the remaining 50% over a further 222 h (Figs 1b and 2b). A plot of CuC *v*. time over the first 60 h was first order ($r^2 = 0.985$, $k = 0.015\,h^{-1}$) and was very similar to that measured for the formation of FeC ($0.017\,h^{-1}$). The rate of formation of CuC over the period 72–288 h was also first order ($r^2 = 0.931$), but with a significantly lower rate constant ($k = 0.0013\,h^{-1}$).

The CuD removal mechanism at pH 5.8 appears to be linked with the formation of FeC. The initial rapid removal of both FeD and CuD suggests that the oxidation of Fe(II) to Fe(III) provide the trigger for the loss of CuD from solution. We propose a 'co-precipitation-surface precipitation' mechanism to explain this behaviour (Fig. 3) (Dzombak and Morel 1990; Fendorf and Gronsky 1992; Zhu 2002). Initially, $Cu(OH)_2$ co-precipitation with the $Fe(OH)_3$ that would have formed by the hydrolysis of Fe(III). Following this, further $Cu(OH)_2(s)$ precipitated on the surface of the new particles. The change in the rate of production of CuC after FeD oxidation had been completed (60 h) suggests that (surface) precipitation of Cu(II) ions after this time took place onto a somewhat different colloidal surface, perhaps a surface largely dominated by $Cu(OH)_2(s)$ and $Zn(OH)_2(s)$.

Further evidence for the co-precipitation-surface precipitation mechanism (Fig. 3) is provided by the observation that most of the Cu (and Zn) lost from the dissolved fraction became associated with the colloidal fraction. Several studies have shown that the addition of foreign ions can inhibit aggregate growth. For example, Karthikeyan *et al*. (1997) found that the addition of Cu ions to precipitating HIO hindered aggregate growth and

resulted in a greater proportion of smaller particles. Waychanus *et al.* (1993) also found that arsenate ions caused the same effect on HIO particles.

Homogeneous precipitation of $Cu(OH)_2(s)$ is another mechanism that could explain the loss of CuD from this solution. However, calculations using the computer program CHEMEQL (Muller 2000) showed that this solution was undersaturated with respect to $Cu(OH)_2(s)$, and that precipitation would not have commenced until a pH in excess of $\sim$6.4 was reached.

The other possible mechanism to explain the behaviour of CuD in these experiments is sorption of Cu(II) to HIO produced through the oxidation of Fe(II). Two lines of evidence make it unlikely that an adsorption mechanism is important. First, very high Cu/Fe molar ratios were measured in both the colloidal (ratio 4.5–8.1) and particulate (ratio 1.1–1.6) fractions. When compared with the maximum adsorption density for Cu onto HIO ($0.25\,mol\,mol^{-1}$) reported by Karthikeyan *et al.* (1997), it is obvious that these values are much too high for adsorption to be the principal mechanism responsible for the association of CuD with the colloidal and particulate fractions. Second, CuD was still being removed from solution after all the FeD had been lost from solution, an unlikely situation if sorption to HIO surfaces was controlling the behaviour of CuD.

Karthikeyan *et al.* (1997) found that co-precipitation with HIO was more effective in removing Cu from solution than adsorption. In experiments with an initial Cu and Fe concentration of 7×10^{-5} M and 3.7×10^{-4} M, respectively (Cu:Fe $=$ 0.2 cf. Tambo River sample Cu:Fe $=$ 12.5), they found co-precipitation removed around 50% of the Cu at pH 6 ($\sim$30% removal by adsorption) and this increased to 97% removal at pH 7 ($\sim$80% for adsorption).

Zinc

Considerable ZnD (14% or $2.9\,mg\,L^{-1}$) was also removed from solution during the oxidation, with almost all of this appearing in the colloidal fraction (Fig. 2*c*). The formation of ZnC appeared to be linearly related to the FeC (colloidal HIO) production ($r^2 = 0.91$). The behaviour of ZnD appeared to differ from CuD in three ways. First, there was a more noticeable time lag ($\sim$12 h) before the reduction of ZnD commenced (Fig. 2*c*). Second, after the lag period, the ZnD became associated with the colloidal fraction at a considerably faster rate than did the CuD (Fig. 2*c*); for example, in the initial period, ZnC was formed around 2.5 times faster than CuC (first order rate constants: $0.04\,h^{-1}$ compared with $0.015\,h^{-1}$). And third, little additional Zn became associated with the colloidal phase after around 60 h when all of the Fe had oxidised.

The time lag before the start of the ZnD removal, and the relatively small amount of ZnD associated with the colloidal phase after 60–75 h ($\sim$20%; Fig. 1*c*), suggests that like CuD, the loss of ZnD was linked to the oxidation of FeD and formation of colloidal HIO particles.

We postulate that the same 'co-precipitation-surface precipitation' mechanism used to explain the behaviour of Cu, also holds for Zn (Fig. 3) but with one major difference to explain why little ZnD was lost after FeD oxidation was completed. Initially, Zn(II) and Fe(III) would co-precipitate to form a solid solution of $Fe(OH)_3$-$Zn(OH)_2$. The high Zn:Fe molar ratio of these

colloidal particles ($\sim$5.7–12) suggest that further $Zn(OH)_2(s)$ precipitated on the surface of the new particles, at least until all of the FeD had been oxidised. Harvey and Linton (1984) found that surface precipitation of $Zn(OH)_2(s)$ occurred on HIO when sorption densities were high and pHs were in excess of 6.5.

However, it is clear that the (surface) precipitation of $Zn(OH)_2(s)$ did not continue after FeD oxidation ceased. Perhaps at this point the solution became under-saturated with respect to surface precipitation of $Zn(OH)_2(s)$. Certainly homogeneous precipitation of $Zn(OH)_2(s)$ would not have occurred. Calculations using CHEMEQL (Muller 2000) show that the initial solution was well under-saturated with respect to $Zn(OH)_2(s)$. This may also have been the situation after 60 h. At this point, the CuD and ZnD concentrations were almost the same ($14\,mg\,L^{-1}$ (or 2.2×10^{-4} M) cf. $19\,mg\,L^{-1}$ (or 2.9×10^{-4} M)) whereas the surface precipitation constants for Zn onto HIO ($\log K_s = -10.2$) are almost two orders less that Cu ($\log K_s = -8.3$) (Zhu 2002).

Acknowledgements

References

Balistrieri, L. S., Bookstrom, A. A., Box, S. E., and Ikramuddin, M. (1998). 'The geochemistry of water draining from the adits and tailings piles in the Coeur d'Alene mining district.' Open file report 98–127, US Geological Survey, Washington DC.

Bigham, J. M., Schwertmann, U., Traina, S. J., Winland, R. L., and Wolf, M. (1996). Schwertmannite and the chemical modelling of iron in acid sulfate waters. *Geochimica et Cosmochimica Acta* **60**, 2111–2121. doi:10.1016/0016-7037(96)00091-9

Cronk, J. K., Mitsch, W. J., and Sykes, R. M. (1990). Effective modelling of a major inland oil spill on the Ohio River. *Ecological Modelling* **51**, 161–192. doi:10.1016/0304-3800(90)90063-M

Duesterberg, C. K., and Waite, T. D. (2006). Process optimization of Fenton oxidation using kinetic modelling. *Environmental Science & Technology* **40**, 4189–4195. doi:10.1021/ES060311V

Dzombak, D. A., and Morel, F. M. M. (1990). 'Surface Complexation Modelling.' (John Wiley: New York.)

Emmenegger, L., King, D. W., Sigg, L., and Sulzberger, B. (1998). Oxidation of Fe(II) in a eutrophic Swiss lake. *Environmental Science & Technology* **32**, 2990–2996. doi:10.1021/ES980207G

Farley, K. J., Dzombak, D. A., and Morel, F. M. M. (1985). A surface precipitation model for the sorption of cations on metal oxides. *Journal of Colloid and Interfacial Science* **106**, 226–242. doi:10.1016/0021-9797(85)90400-X

Fendorf, S. E., and Gronsky, R. (1992). Surface precipitation reactions on oxide surfaces. *Journal of Colloid and Interfacial Science* **148**, 295–298. doi:10.1016/0021-9797(92)90141-8

Filipek, L. H., Nordstrom, D. K., and Ficklin, W. H. (1987). Interaction of acid mine drainage with waters and sediments of West Squaw Creek in the West Shasta Mining District, California. *Environmental Science & Technology* **21**, 388–396. doi:10.1021/ES00158A009

Ford, R. G., Kemner, K. M., and Bertsch, P. M. (1999). Influence of sorbate-sorbent interactions on the crystallization kinetics of nickel- and

lead-ferrihydrite coprecipitates. *Geochimica et Cosmochimica Acta* **63**, 39–48. doi:10.1016/S0016-7037(99)00010-1

Grossl, P. R., Sparks, D. L., and Ainsworth, C. C. (1994). Rapid kinetics of Cu(II) adsorpton/desorption on goethite. *Environmental Science & Technology* **28**, 1422–1429. doi:10.1021/ES00057A008**[AQ13]**

Harris, G. P. (2001). Biogeochemistry of nitrogen and phosphorus in Australian catchments, rivers and estuaries: Effects of land use and flow regulation and comparisons with global patterns. *Marine and Freshwater Research* **52**, 139–149. doi:10.1071/MF00031

Hart, B. T., and Hines, T. (1995). Trace elements in rivers. In 'Trace Elements in Natural Water'. (Eds B. Salbu and E. Steines.) pp. 203–221. (CRC Press: London.)

Hart, B. T., Sdraulig, S., and Jones, M. J. (1992). Behaviour of copper and zinc added to the Tambo River, Australia by a metal-enriched spring. *Australian Journal of Marine and Freshwater Research* **43**, 457–489. doi:10.1071/MF9920457

Hart, B. T., Beckett, R., Murphy, D., and Ranville, J. (1997). Role of colloids in cycling contaminants in rivers, In 'Biogeochemistry of Trace Metals'. (Eds D. C. Adriano, Z. S. Chen, S. S. Yang and I. K. Iskandar.) pp. 193–216. (Applied Science Publishers: Norwood, UK.)

Hart, B. T., Hines, T., and Coller, B. A. W. (2008). Geochemistry of Cu, Zn and Fe in the Tambo River, Australia, II. Field study under very low flow conditions. *Marine and Freshwater Research* **59**, 80–88.

Harvey, D. T., and Linton, R. W. (1984). X-ray photoelectron spectroscopy (XPS) of adsorbed zinc on amorphous hydrous ferric oxide. *Colloids and Surfaces* **11**, 81–96. doi:10.1016/0166-6622(84)80052-9

Hines, T. (1995). The fate of Cu and Zn in the Tambo River. M.Sc. Thesis, School of Chemistry, Monash University, Clayton.

Johnson, C. A. (1986). The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage: The adsorption of Cu and Zn on amorphous Fe oxyhydroxides. *Geochimica et Cosmochimica Acta* **50**, 2433–2438. doi:10.1016/0016-7037(86)90026-8

Karthikeyan, K. G., Elliott, H. A., and Cannon, F. S. (1997). Adsorption and coprecipitation of copper with the hydrous oxides of iron and aluminium. *Environmental Science & Technology* **31**, 2721–2725. doi:10.1021/ES9609009

Karthikeyan, K. G., Elliott, H. A., and Chorover, J. (1999). Role of surface precipitation in copper sorption by the hydrous oxides of iron and aluminium. *Journal of Colloid and Interfacial Science* **209**, 72–78. doi:10.1006/JCIS.1998.5893

Kimball, B. E., Broshears, R. E., Bencala, K. E., and McKnight, D. M. (1994). Coupling of hydrologic transport and chemical reactions in a stream affected by acid mine drainage. *Environmental Science and Technology* **28**, 2065–2073.

King, D. W., Lounsbury, H. A., and Millero, F. J. (1995). Rates and mechanism of Fe(II) oxidation at nanomolar total iron concentrations. *Environmental Science & Technology* **29**, 818–824. doi:10.1021/ES00003A033

Larsson, J., Gustafsson, O., and Ingri, J. (2002). Evaluation and optimization of two complementary cross-flow ultrafiltration systems towards isolation of coastal surface water colloids. *Environmental Science & Technology* **36**, 2236–2241. doi:10.1021/ES010325V

Lee, G., Bigham, J. M., and Faure, G. (2002). Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Applied Geochemistry* **17**, 569–581. doi:10.1016/S0883-2927(01)00125-1

Liang, L., McNabb, J. A., Paulk, J. M., Gu, B., and McCarthy, J. F. (1993). Kinetics of Fe(II) oxidation at low partial pressure of oxygen in the presence of natural organic matter. *Environmental Science & Technology* **27**, 1864–1870. doi:10.1021/ES00046A014

Macquarie Resources Ltd (1989). 'Benambra Project Water Quality and Hydrological Investigations.' Report by Centre for Stream Ecology, Chisholm Institute of Technology and Centre for Environmental Applied Hydrology, Melbourne University, Melbourne.

Morel, F. M. M. (1983). 'Principles of Aquatic Chemistry.' (John Wiley: New York.)

Muller, B. (2000). 'ChemEQL, V2.0.' (Limnological Research Institute, EAWAG, Kastanienbaum: Switzerland.) (http://www.eawag.ch/research/surf/forschung/chemeql.html.)

Neilsen, A. E. (1964). 'Kinetics of Precipitation.' (MacMillan Publishing: New York.)

Rose, A. L., and Waite, T. D. (2002). Kinetic model for Fe(II) oxidation in seawater in the absence and presence of natural organic matter. *Environmental Science & Technology* **36**, 433–444. doi:10.1021/ES0109242

Rose, A. L., and Waite, D. T. (2003*a*). Kinetics of hydrolysis and precipitation of ferric iron in seawater. *Environmental Science & Technology* **37**, 3897–3903. doi:10.1021/ES034102B

Rose, A. L., and Waite, T. D. (2003*b*). Effect of dissolved natural organic matter on the kinetics of ferrous iron oxygenation in seawater. *Environmental Science & Technology* **37**, 4877–4886. doi:10.1021/ES034152G

Stumm, W., and Morgan, J. J. (1996). 'Aquatic Chemistry.' 3rd edn. (John Wiley and Sons: New York.)

Swedlund, P. J., and Webster, J. G. (2001). Cu and Zn ternary surface complex formation with SO$_4$ on ferrihydrite and schwertmannite. *Applied Geochemistry* **16**, 503–511. doi:10.1016/S0883-2927(00)00044-5

Tonkin, J. W., Balistrieri, L. S., and Murray, J. W. (2002). Modeling metal removal onto natural particles formed during mixing of acid rock drainage with ambient surface water. *Environmental Science & Technology* **36**, 484–492. doi:10.1021/ES0109085

Waychunas, G. A., Rea, B. A., Fuller, C. C., and Davis, J. A. (1993). Surface chemistry of ferrihydrite, I. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochimica et Cosmochimica Acta* **57**, 2251–2269.

Waychunas, G. A., Fuller, C. C., and Davis, J. A. (2002). Surface complexation and precipitate geometry for aqueous Zn(II) sorption of ferrihydrite I: X-ray adsorption extended fine structure spectroscopy analysis. *Geochimica et Cosmochimica Acta* **66**, 1119–1137. doi:10.1016/S0016-7037(01)00853-5

Webster, J. G., Swedlund, P. J., and Webster, K. S. (1998). Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulphate. *Environmental Science & Technology* **32**, 1361. doi:10.1021/ES9704390

Younger, P. L., Banwart, S. A., and Hedin, R. S. (2002). 'Mine Water: Hydrology, Pollution and Remediation.' (Kluwer Academic Publishing: Berlin.)

Zhu, C. (2002). Estimation of surface precipitation constants for sorption of divalent metals onto hydrous ferric oxide and calcite. *Chemical Geology* **188**, 23–32. doi:10.1016/S0009-2541(02)00060-8