

Geochemistry of Cu, Zn and Fe in the Tambo River, Australia II. Field investigation under low-flow conditions

Barry T. Hart^{A,B}, Tina Hines^A and Bruce A. W. Collier^A

^AWater Studies Centre and School of Chemistry, Monash University, Victoria 3800, Australia.

^BCorresponding author. Email: barry.hart@waterscience.com.au

Abstract. The behaviour of Fe, Cu and Zn, added to the upper Tambo River (Victoria, Australia) via a metal-enriched groundwater input, was studied during a period of very low river flow. Water samples were collected over a 1.3-km section of the river located immediately downstream of the spring input. Heavy metals were separated into three fractions (dissolved, colloidal and particulate) using tangential flow filtration. Within the 'input region', the pH was low (5.1–5.8) and sulfate (306–359 mg L⁻¹), total Fe (2.81 mg L⁻¹), total Cu (19.7 mg L⁻¹) and total Zn (24.1 mg L⁻¹) concentrations all increased significantly. Subsequently, the total metal concentrations reduced with distance downstream of the input, and approached values similar to those recorded upstream of the input region at the end of the study region. Most of the Fe was oxidised before it entered the river as a thick hydrous iron oxide floc that travelled downstream close to the riverbed. The remaining dissolved Fe (mainly Fe(II)) that entered the river largely controlled the behaviour of Cu and Zn in the 'active region' (75–400 m). This Fe(II) was rapidly oxidised to Fe(III), which then removed large amounts of the dissolved Cu (65%) and Zn (55%) into the colloidal fraction. Processes such as settling of particles, dilution by groundwater inputs and sorption of dissolved Cu and Zn onto sediments removed the remainder of the Cu and Zn.

Additional keywords: acid mine drainage, contamination, hydrous iron oxide, oxidation, surface precipitation, transport.

Introduction

In a previous publication (Hart *et al.* 1992), we reported contamination of the upper Tambo River, situated in the Australian highlands north-east of Melbourne (Fig. 1), by a natural metal-rich spring (Wilga Spring), the source of which is a Cu/Zn ore body located adjacent to the river. The downstream effects of the spring are both obvious in that the rocks and sediments are stained red with iron oxides (a red-brown floc also builds up in sections during low flows), and less obvious in that biological studies have shown the river is essentially devoid of animal life for a distance of around 1 km downstream of the spring input to Formfit Creek. There is then some recovery of the biota from here to the South Branch (a major tributary), a distance of ~7 km, and then a marked recovery below the South Branch junction.

The unique feature of this system is that although it is metal-enriched, particularly with Cu and Zn, the spring water is almost neutral when it enters the Tambo River. This provided an opportunity to study the *in situ* behaviour of elevated metal concentrations in a river with only slightly acidic pHs, rather than the more often reported studies of very acidic, metal-enriched water (e.g. acid mine drainage) entering a river (Johnson 1986; Filipek *et al.* 1987; Webster *et al.* 1998; Yu and Heo 2001; Lee *et al.* 2002; Younger *et al.* 2002).

In the previous study, Hart *et al.* (1992) suggested that under most flow conditions, the concentrations of dissolved Cu and Zn in the 'contaminated region' of the Tambo River are largely controlled by adsorption/surface precipitation onto

hydrous iron oxide (HIO) surfaces formed *in situ* by the oxidation of Fe(II) present in the spring water. Subsequently, the Cu and Zn concentrations in this region of the river appear to be controlled by the transport and sedimentation of this metal-enriched colloidal and particulate material.

We report a further study of the Tambo River under conditions when the river flow was extremely low, and the spring input made up an estimated 10% of the total flow. The study focused on the 1.3 km-region between Wilga Weir and Formfit Creek (Fig. 1), designated the 'contaminated region' of the river. The objectives of the present study were to: (i) identify better the location and amount of the spring inputs; (ii) measure changes in the size distribution of Fe, Cu and Zn with distance down the river; and (iii) provide further information on the geochemical processes controlling the behaviour of Cu and Zn in the river under low flow conditions. We have used the results from a companion paper (Hart and Hines 2008) to assist in interpreting the changes that occurred within the river – that study reports a laboratory experiment in which a sample of acidic (pH 5.8) river water, taken at the same time as the present study, was oxidised under controlled conditions over a period of 288 h.

Materials and methods

Study system

The location of the study site is shown in Fig. 1 with details of the river and its catchment provided by Hart *et al.* (1992).

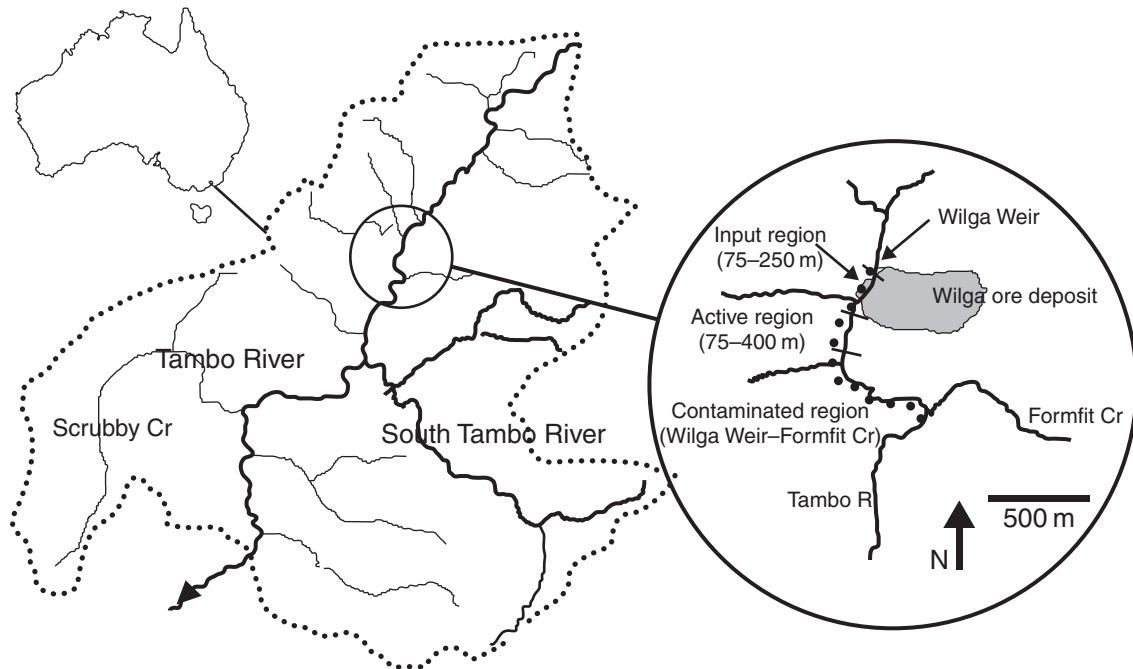


Fig. 1. Location map showing the sampling sites.

Above Wilga Weir (Fig. 1) the Tambo River is essentially pristine, with low conductivity (mean $95 \mu\text{S cm}^{-1}$), is slightly alkaline (mean pH 7.5), dominated by calcium and bicarbonate ions and contains very low concentrations of heavy metals (Hart 1993). The input of metal-enriched groundwater just downstream of Wilga Weir, causes a significant increase in the concentrations of Cu and Zn concentrations (155-fold increase in mean concentrations between Wilga Weir and 250 m downstream), a measurable increase in the sulfate concentration (14-fold), but no significant decrease in pH (e.g. at 250 m downstream mean pH was 7.5 (range 4.4–8.1)) in the region between Wilga Weir and Formfit Creek a distance of ~ 1.3 km.

The annual flow pattern in the Tambo River is quite regular, with low flows generally experienced during the period January to June and high flow in the period between July and November. The mean long-term (September 1988 to February 1993) annual river flow is 22 ML day^{-1} (Hart 1993). The period before the present study was characterised by low rainfall and corresponding low river flow. For example, in the month before the present study, only 19 mm of rain fell in the region and the mean daily flow at Wilga Weir was only 1.0 ML day^{-1} . Even over the more extended period, between January and April 1992, the total rainfall was 224 mm and the mean daily flow was 3.2 ML day^{-1} . The daily mean river flow measured at Wilga Weir on the sampling day was very low at 0.2 ML day^{-1} , with the estimated travel time of the river water in the region between 75 m and 400 m being around 50 h^{-1} .

The study site was divided into three regions (Fig. 1):

- *Contaminated region* – the full study region between Wilga Weir and Formfit Creek, a distance of 1.3 km.
- *Input region* – between the first surface expression of Wilga Spring (75 m) and 250 m downstream of the weir.
- *Active region* – between 75 m and 400 m downstream of the weir. In a previous paper (Hart *et al.* 1992), we called the region between 150 m and Formfit Creek the ‘active region’. However, we now believe that a more restrictive area that includes the ‘input region’ and down to 400 m below the weir better describes the region where most of the major chemical changes occur, at least under the low flow condition described here.

Field samples

Water samples were taken over a 1.3-km stretch of the Tambo River from Wilga Weir to the confluence with Formfit Creek (Fig. 1). The most intensive sampling occurred in the region between 75 m and 250 m downstream of Wilga Weir, where it has been shown that most of the spring input occurs. Two 125-mL samples were taken at each sampling site, one in an Extran-washed polyethylene bottle for sulfate and chloride analysis, and the other in an acid-washed polyethylene bottle for heavy metal (Fe, Cu, Zn) analysis. All sampling and fractionation equipment was acid washed and rinsed in ultrapure water (Milli-Q, Millipore Corp, Billerica, MA, USA) before use.

On-site filtration of water samples was carried out at selected sites using a tangential flow filtration (Millipore Minitan System, Millipore Corp, Billerica, MA, USA). This allowed samples to be fractionated into three fractions: P, particulate ($>0.2 \mu\text{m}$); C, colloidal (<0.2 to $>0.003 \mu\text{m}$); and D, dissolved ($<0.003 \mu\text{m}$). All of the metal fractions were acidified on-site with 0.5 mL Suprapur nitric acid, and analysed using either flame Atomic Absorption Spectrometer (AAS) or graphite furnace AAS. Hart and Hines (2008) provide full details on the filtration process, and the analytical methods and the QC/QA protocols used.

Table 1. Analytical results for the floc samples

Distance (m)	Fe (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Cu:Fe (mol mol ⁻¹)	Zn:Fe (mol mol ⁻¹)
75	262 000	7080	1040	0.025	0.004
100	247 000	6980	960	0.026	0.003
125	260 000	6500	1050	0.023	0.004
150	288 000	7690	1260	0.024	0.004
160	325 000	7890	1360	0.022	0.004
175	298 000	6980	1180	0.021	0.004
200	231 000	5690	950	0.022	0.004
Mean	273 000	6970	1110	0.023	0.004

Sulfate and chloride concentrations were determined by flow injection analysis using the method of Madsen and Riley (1983); in both cases the detection limit was 0.2 mg L⁻¹. The pH of the water at each sampling location was measured using a portable Activon A105 pH (Activon, Clayton, Vic, Australia) meter that was calibrated before each measurement with pH 4.0 and 7.0 standard buffer solutions.

The red-brown floc material that covered much of the river bottom in the region between 75 m and 200 m was sampled at seven locations (Table 1). The floc was collected using a plastic scoop into a 500-mL acid-washed polyethylene bottle, washed several times with Milli-Q water and dried overnight at 105°C. Approximately 0.2 g (dry weight) of floc was digested with concentrated HNO₃ and then made up to 125 mL. One digestion blank and one duplicate each from three of the different floc samples were also taken through the digestion procedure. The digested samples were analysed for Cu, Zn and Fe using flame AAS.

Results

pH and sulfate

There was an obvious influence of the spring input on the pH and sulfate concentration, which commenced at around 75 m below Wilga Weir (Fig. 2). For example, the pH decreased from 7.2 at Wilga Weir to 5.8 at 75 m, and then to 5.1 at around 160 m. pH then remained at around 5.4–5.5 between 165 m and 250 m, and then increasing steadily to pH 7.2 at Formfit Creek (Fig. 2). The mean pH (5.4) in the input region was considerably lower than the mean pH of 7.5 reported for this region by Hart (1993) over a 4-year period (1988 to 1993).

The behaviour of sulfate and chloride (not shown) was similar over the study region, although the sulfate concentrations were 10–20 times higher than chloride. The sulfate concentration increased from 1.0 mg L⁻¹ at Wilga Weir to 306–359 mg L⁻¹ in the input region between 75 m and 250 m. The concentration then decreased to 206 mg L⁻¹ at 400 m and then finally to 20.8 mg L⁻¹ at Formfit Creek (Fig. 2). The chloride concentration increased 11-fold between Wilga Weir (1.6 mg L⁻¹) and the input region (mean 18 mg L⁻¹), and then decreased rapidly between 250 m and Formfit Creek to a final value of 2.0 mg L⁻¹.

The sulfate data indicate that a major input of contaminated groundwater occurred at 75 m (estimated at 10% of the river flow), with another smaller input at around 160 m. This latter input was estimated to be only 10% as large as the first input. These inputs are also reflected in the data for Cu and Zn (Fig. 3).

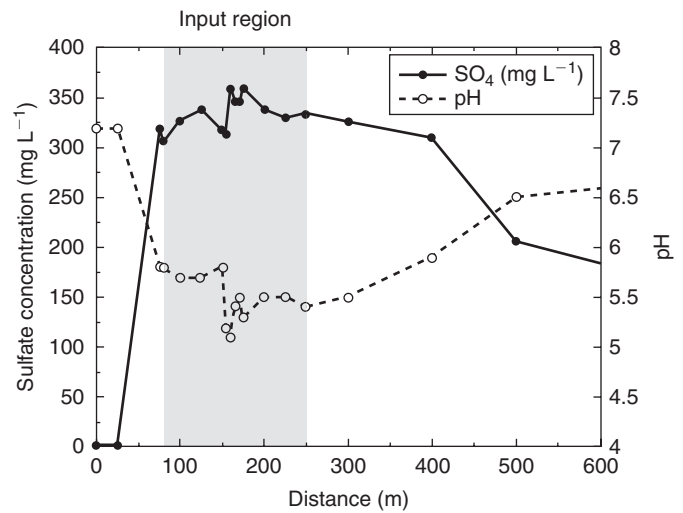


Fig. 2. Variations in the pH and sulfate concentration with distance over the 'active region' in the Tambo River.

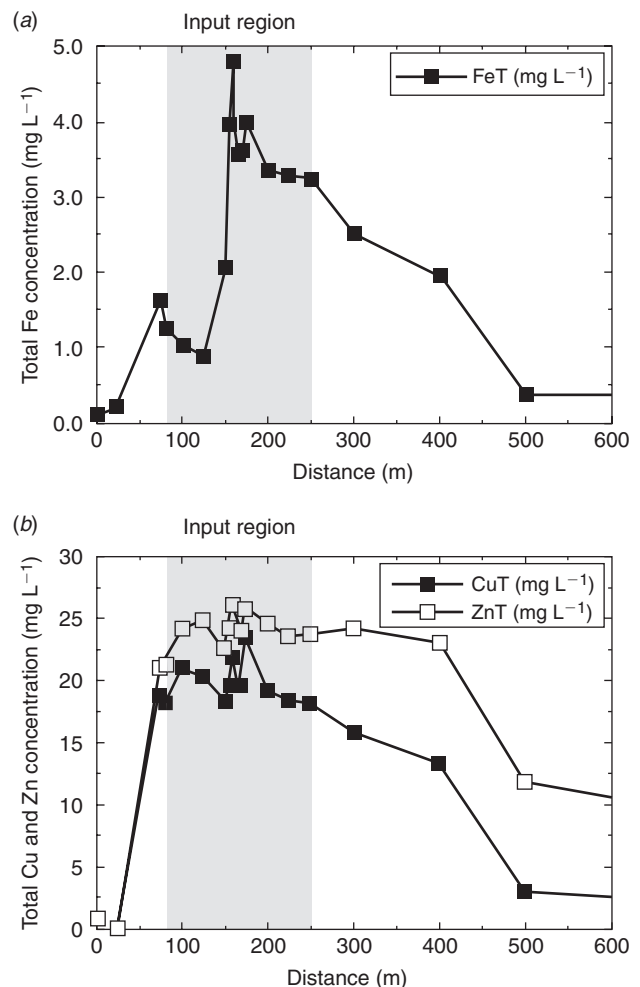


Fig. 3. Variations in total metal concentrations with distance over the 'active region' in the Tambo River. (a) FeT, (b) CuT and (c) ZnT.

Heavy metals

General

The total concentrations of all three metals (CuT, ZnT and FeT) were elevated in the input region during the present study period (mean \pm standard error (s.e.): CuT – $19.7 \pm 1.5 \text{ mg L}^{-1}$; ZnT – $24.7 \pm 1.5 \text{ mg L}^{-1}$; FeT – $2.8 \pm 1.3 \text{ mg L}^{-1}$) (Fig. 3). For CuT and ZnT, these concentrations are ~ 74 -fold and 46 -fold, respectively, higher than the mean concentrations recorded by Hart (1993) during a 5-year study of this river. Interestingly, the mean FeT concentration in the input region on the sampling day was only 2.5 times higher than the mean FeT concentration reported by Hart (1993), and over 150 times smaller than the concentration ($\sim 431 \text{ mg L}^{-1}$) thought to be present in the oxidation zone. The reason for the relatively small increase in the FeT concentration compared with CuT and ZnT is almost certainly because much of the Fe was oxidised and deposited in the groundwater system *before* entering the river.

Iron

The behaviour of FeT in the Tambo River was quite different to that of Cu and Zn (Fig. 3a). An obvious input of Fe occurred at around 75 m, with a further input between 150 m and 160 m. Rather surprisingly, this latter input introduced ~ 2.5 times more Fe to the river than did the first input, a situation quite different to that for Cu and Zn where $\sim 90\%$ of the total entered at the first input region. There was also a significant reduction in the FeT concentration following each of these inputs, the reductions being approximately exponential with distance.

Size distribution data for Fe in the vicinity of the second input showed that most of the Fe was in dissolved forms (55–71%), with 20–39% in particulate forms and a smaller amount (6–15%) in colloidal forms (Fig. 4a). The FeD was present largely as ferrous iron (Fe(II)). Downstream of the input region, there was a significant change in the Fe size distribution, in addition to the reduction in concentration noted earlier. For example, at 400 m the proportion of the total in dissolved forms had reduced to 31% and the proportion in particulate forms increased to 61%; there was still only a very small amount in colloidal forms. At Formfit Creek, the small concentration of FeT (0.36 mg L^{-1}) was divided equally between particulate and colloidal forms. There was no FeD at this site.

Copper

Most of the copper entered the river at the first input region around 75 m, with other smaller inputs at around 150–160 m and 175 m (Fig. 3b). The CuT concentration appeared to decrease slightly over the input region, although this was masked somewhat by the additional inputs that also occurred in this region. There was a further decrease in the CuT concentration between 250 m and 400 m from 18.3 mg L^{-1} to 13.4 mg L^{-1} , and then a rapid decrease between 400 m and 500 m, and a further decrease from there to Formfit Creek (Fig. 3b). Overall, between the input region and Formfit Creek there was a 17-fold decrease in CuT concentration. However, even with this significant decrease, the Cu concentration at Formfit Creek was still almost two orders of magnitude greater than that upstream of the metal inputs.

Within the input region, most (79–88%) of the Cu was present in dissolved forms, with only minor amounts in colloidal

(4–13%) and particulate (5–14%) forms (Fig. 4b). However, downstream of the input region, there appeared to be a significant change in the Cu size distribution, in addition to a reduction in the CuT concentration noted earlier. For example, at 400 m the

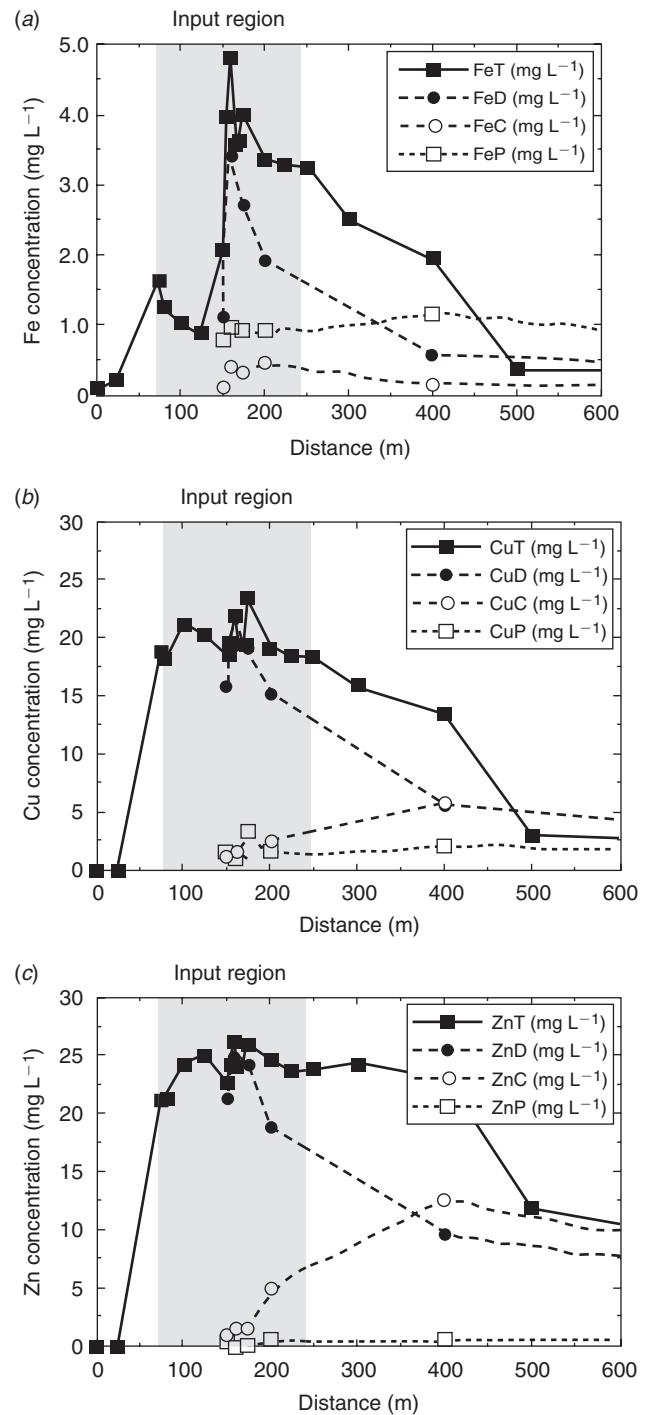


Fig. 4. Variation in the dissolved, colloidal and particulate metal concentrations with distance in the Tambo River. (a) Fe. (b) Cu. (c) Zn. (Note: at 1.3 km (i.e. confluence with Formfit Creek) the concentrations were (mg L^{-1}): FeD – 1.0, FeC – 180, FeP – 180; CuD – 20, CuC – 40, CuP – 56; ZnD – 210, ZnC – 60, ZnP – 60.)

proportion of the total in dissolved forms had reduced to 41% and the proportion in colloidal forms had increased to 43%; there was still only a small amount in particulate forms. It is possible that the large decrease in CuD occurred within the latter part of the input region (i.e. between 200 m and 250 m); unfortunately, size distribution data were not collected for this region. At Formfit Creek, the CuT concentration (0.12 mg L^{-1}) was distributed with 17% in dissolved forms, 34% in colloidal forms and 48% in particulate forms.

Zinc

Most of the zinc was also input through the base of the river around 75 m downstream of Wilga Weir, with only a small additional amount added around 150–160 m (Fig. 3b). The total Zn appeared to be behaving differently to the total Cu with very little reduction in concentration between the input region and 400 m (Fig. 3b). Subsequently, there was a major reduction in the ZnT concentration between 400 m and 500 m, and again between 500 m and Formfit Creek.

Within the input region, most (69–94%) of the ZnT was present in dissolved forms, with minor (5–29%) amounts in colloidal forms and very small quantities (<2%) in particulate forms (Fig. 3b). Despite the fact that the ZnT concentration changed little between 100 m and 400 m, there were some significant changes in Zn size distribution. For example, in the region to 175 m over 93% of the Zn was in dissolved forms. However, between this point and 400 m, the proportion of the total in dissolved forms was reduced to 42% and the proportion in colloidal forms increased to 55%. At 400 m, there was still only a small amount in particulate forms. As noted for Cu, it is possible that the large decrease in ZnD observed between 200 m and 400 m may have occurred within the latter part of the input region (i.e. between 200 m and 250 m), but again it is not possible to confirm this since size distribution data were not collected for this region.

By the time the water had reached Formfit Creek, the ZnT concentration was reduced to 1.3% of the concentration in the input region, although this concentration (0.32 mg L^{-1}) was still two orders of magnitude higher than that above Wilga Weir. This smaller Zn concentration at Formfit Creek was distributed with 62% in dissolved forms, 18% in colloidal forms and 20% in particulate forms.

Floc material

The presence of Fe in the river was obvious at the time of the present study, with a fine red-brown floc covering the bottom sediments from around 75 m to 250 m. The Fe, Cu and Zn content of the floc material collected over the input region is given in Table 1. As expected, this material consisted predominantly of iron (~27%, which would account for 56% of the floc material if present as $\text{Fe}(\text{OH})_3$), with smaller amounts of Cu and Zn. The mean molar Cu:Fe ratio was 0.023 and the mean Zn:Fe ratio was 0.004. These were noticeably less than the metal:Fe ratios found in the water column in this input region. For example, in the colloidal fraction both the Cu:Fe and Zn:Fe molar ratios were very large (3:6 and 3:9 respectively), and even in the particulate fraction, although the values were less than in the colloidal fraction, they were still considerably higher (Cu:Fe 0.9:3.0; Zn:Fe 0.1:0.5)

than in the floc. The floc contained considerably more Cu than Zn (Zn:Cu molar ratio = 0.16, standard deviation (s.d.) = 0.01, $n = 6$).

Discussion

The present study of a metal-contaminated section of the Tambo River, under very low flow conditions, has provided an opportunity to identify in detail the inputs of Wilga Spring to the river, and to contribute further information on the flow-related processes controlling the behaviour of Fe, Cu and Zn in this river.

Wilga Spring

Hart *et al.* (1992) first provided information showing that Wilga Spring enters the Tambo River through the riverbed over a 175–200 m length of the river immediately downstream of Wilga Weir (Fig. 1). Further detailed information on this input region (which extends from 75 m to 250 m downstream of the weir) is provided by the present study. There were two obvious input zones, one at 75 m and the other at 150–160 m (Fig. 2), with most (~90%) of the sulfate, Cu and Zn entering the river through the first input zone. Interestingly, only 34% of the Fe (measured in the water column) appeared to enter the river at this point, with most (~66%) entering at 150–160 m downstream of Wilga Weir. A more detailed investigation of the input region would possibly show that there were more than two input zones. For example, the sulfate and Fe data suggests that small inputs may also occur at 100 m and at 175 m (Figs 2 and 3a), and our previous work suggested an additional input of Cu at around 700 m downstream of Wilga Weir (Hart *et al.* 1992).

On the basis of the sulfate concentrations, it was estimated that the groundwater input contributed ~10% of the river flow on the sampling day. This calculation assumed that the spring water entering the river was identical in composition to the adit water reported by Hart *et al.* (1992), which in turn was assumed to reflect closely the acidic water from the oxidised zone associated with the Wilga orebody. This calculation may underestimate the input, since some changes appear to have occurred within the groundwater system before the groundwater enters the river (e.g. groundwater pH 5.1–5.8 compared with adit water pH 2.9–4.7 (Hart *et al.* 1992)), and these could have resulted in some loss of sulfate.

In the region between 400 m and 500 m, the concentrations of all measured variables were observed to decrease rapidly, sulfate by 1.5 times, Fe and Cu by four to five times, and Zn by two times. The most likely reason for the reduction in the sulfate concentration is dilution by an additional groundwater source entering the river in the region between 400 m and 500 m. Dilution could also explain part of the observed decrease in the FeT, CuT and ZnT concentrations. However, the situation for these metals is more complicated and is further discussed below. To achieve the observed reductions in concentration, the groundwater inflow in this region would need to be around 1.5 times greater than the river flow (i.e. around 0.3 ML day^{-1}), assuming the groundwater had the same chloride concentration as the river water at Wilga Weir.

A further large reduction in the concentrations of sulfate, Cu and Zn (but not Fe) occurred between 500 m and Formfit

Creek. The reduction in the CuT and ZnT concentrations was 26–36-fold, whereas that for sulfate was around 10-fold. The reduction in the sulfate concentration can only be explained by further dilution by groundwater, since there are no tributaries entering the Tambo River between Wilga Weir and Formfit Creek. The additional reduction in the CuT and ZnT concentrations in this region over that shown by the sulfate suggests that other loss mechanisms (e.g. sorption, sedimentation) affect the behaviour of these heavy metals. This is further discussed below.

Iron

Under the very low river flow condition existing at the time of the present study, a considerable proportion (55–71%) of the FeT in the input region was in soluble forms (i.e. $<0.003 \mu\text{m}$ in size). From the oxidation experiment reported by Hart and Hines (2008), it is clear that this FeD is in the form of ferrous iron (Fe(II)), which when discharged to the river would be rapidly oxidised to hydrous iron oxides (HIO) even at the acidic pHs existing over much of the input region; the estimated half life for Fe(II) at pH 5.8 is around 9 h. Hart and Hines (2008) also showed that although the HIO formed was deposited in the colloidal and particulate fractions in roughly the same proportions as that which existed initially, it was the colloidal fraction that contained most of the Cu and Zn. They postulated that a 'co-precipitation-surface precipitation' mechanism was responsible for the loss of dissolved Cu and Zn at these low pH values, with the Fe(III) formed by oxidation of the FeD, co-precipitating with Cu(II) and Zn(II) to form (mainly) colloidal particles consisting of HIO (probably a mixture of ferrihydrite and schwertmannite (Bigham *et al.* 1996)), $\text{Cu}(\text{OH})_2(\text{s})$ and $\text{Zn}(\text{OH})_2(\text{s})$.

The water column data suggests that the major input of Fe occurred in the region 150–160 m (Fig. 2). This observation is at odds with that for sulfate, Cu and Zn data, where the major inputs occurred at 75 m. A plausible reason for this apparent anomalous result is that a considerable amount of the Fe entering at 75 m was rapidly oxidised within the sediments (in this region a small amount of gravel generally exists over the bedrock), and forms the red-brown HIO floc that was observed in this region.

The difference in the behaviour of Fe between the first and second input regions can then be explained in terms of the pH differences in each zone where the spring water first mixes with the river water. At the first input, the spring water (pH ~ 5) would mix with river water with a pH ~ 7.2 , whereas at the second input zone, the spring water would mix with river water of significantly lower pH (~ 5.4 – 5.8). This hypothesis is supported by the river water pH values observed at the time of the present study, these being pH 5.8 at 75 m and pH 5.1 at 160 m. A consequence of these pH differences would be that the rate of Fe(II) oxidation would be greatest in the vicinity of the first input region, since pH has a dramatic influence on the oxidation of Fe(II), with the rate increasing 100-fold (or half life decreasing 100-fold) for every 1 pH unit increase (Stumm and Morgan 1996). Thus, the lower Fe concentration in the vicinity of the first input region can be explained by the rapid oxidation of Fe(II) within, or close to, the sediments, leaving less to enter the water column.

We estimate that at least 97% of the Fe input in the first zone was oxidised within the sediments, with less than 3% entering

the water column as Fe(II); these estimates were based on the relative Fe concentrations in the adit water (Hart *et al.* 1992) and that entering the river on the sampling day.

Further evidence for this rapid oxidation of Fe(II) to Fe(III) is provided by the observation that a red-brown floc was present over the sediments in the region between 75 m and 200 m. This material contained around 56% HIO on a dry weight basis. We assume that the floc was formed in the sediments, mainly in the region of 75 m, and was then slowly transported downstream by the very slow moving river water.

The FeT concentration was observed to decrease with distance in the regions 75–125 m and 160–200 m (Fig. 3a). In both regions, the decrease in the FeT concentration was approximately first order with distance, but with the decrease more rapidly over the first region (75–125 m, $k = 0.007 \text{m}^{-1}$ ($r^2 = 0.961$, $n = 3$); 160–200 m, $k = 0.003 \text{m}^{-1}$ ($r^2 = 0.944$, $n = 8$)). The relative order of these rates is as expected, given that the pH in the first region was slightly higher than in the second region; the oxidation kinetics are expected to be faster at the higher pH. The change in the concentration of FeD in the region 160–200 m was also found to be approximately first order with distance ($k = 0.007 \text{m}^{-1}$ ($r^2 = 0.975$, $n = 4$)), and almost twice as fast as for the FeT. Unfortunately, FeD concentrations were not measured in the 75–125 m region.

Downstream of the input region, the FeT concentration continued to decrease, and between 400 m and 500 m there was a very rapid fivefold decrease in concentration. Part of this decrease, perhaps a 1.5-fold decrease, can be explained by dilution owing to ingress of groundwater in this region (see above for discussion). However, the rest of the decrease is again probably a result of sedimentation of FeP. Additionally, it is possible that agglomeration of some of the FeC (and associated Cu and Zn) to FeP could have occurred as a result of the relatively high conductivity in this region. The amount of FeP that settles out would be influenced by the flow in the river with the highest sedimentation rate expected to occur at the lowest river flows. Hart *et al.* (1992) provided some evidence that most of the Fe (and associated Cu and Zn) that settles to the bottom during low flow periods, is resuspended and transported further downstream at higher flows.

In summary, the above information can be combined with that provided by Hart and Hines (2008) to define the main processes controlling the observed reduction in total Fe with distance as (Fig. 5):

- (i) oxidation of Fe(II) to Fe(III);
- (ii) formation of Cu and Zn-enriched colloidal particles via the co-precipitation-surface precipitation mechanism proposed, with these colloidal particles largely remaining in suspension and being transported downstream;
- (iii) coating of HIO onto the existing particulate fraction, and possibly agglomeration of some of the colloidal fraction, and settling of at least part of this particulate fraction from the water column owing to the very low water velocity in the river;
- (iv) dilution owing to ingress of groundwater, particularly in the region between 400 m and 500 m, and between this region and Formfit Creek.

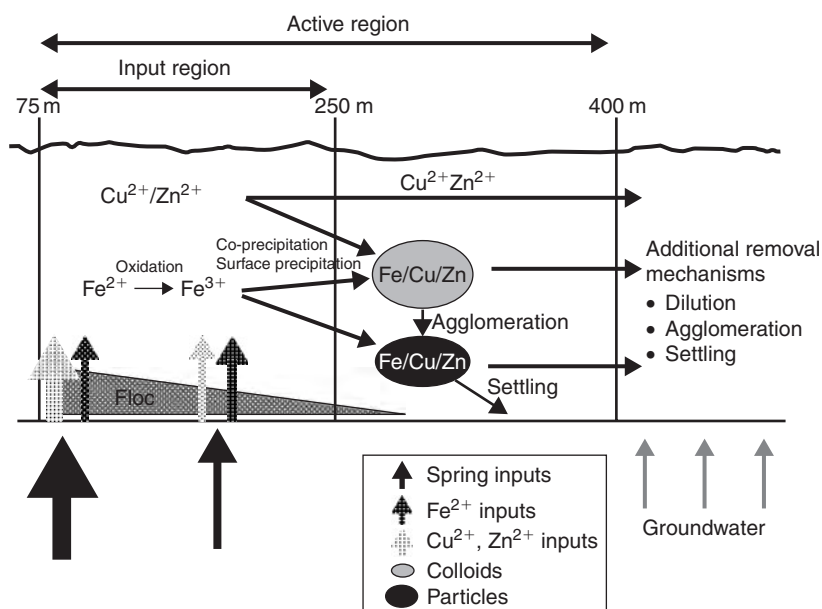


Fig. 5. Schematic diagram summarising the mechanisms controlling the concentrations of Fe, Cu and Zn in the Tambo River between Wilga Weir and Formfit Creek under low flow conditions.

Copper and zinc

Most of the Cu and Zn entered the Tambo River through the first input region at 75 m (Fig. 4b), apparently mostly (~90%) in dissolved forms (e.g. as Cu(II) and Zn(II)). Size distribution data are not available for this first input region, but it seems reasonable to assume that dissolved forms dominated, given that most of these two metals entered here and the size distribution after the second input region was still dominated by dissolved forms of both Cu (79–88%) and Zn (69–94%).

In the region between 160 m and 400 m, Cu and Zn appeared to behave quite differently (Fig. 3b), with the CuT concentration being reduced by around 33%, whereas the ZnT concentration was little changed. However, a more detailed investigation of the data shows that the concentrations of both CuD and ZnD changed quite significantly over this region, with CuD and ZnD being reduced by 70% and 60% respectively. Almost all of the ZnD was transferred to the colloidal fraction, whereas the CuD appeared to have been more evenly distributed between colloidal and particulate matter, with part of the particulate matter settling out of the water column and reducing the CuT concentration remaining.

Between 400 m and 500 m, the CuT concentration was further reduced by over fourfold, whereas the ZnT concentration was reduced by less than twofold. Earlier we postulated, on the basis of the sulfate data, that up to a twofold decrease in concentration could be explained by dilution from a possible groundwater input in this region. This could explain the reduction in the ZnT concentration, particularly if most of the Zn was present in dissolved and colloidal forms as is indicated by the data in Fig. 4b. The additional reduction in the CuT concentration may be explained by further loss of CuP, which made up almost 16% of the CuT at 400 m (Table 1).

In the region between 500 m and Formfit Creek, the CuT and ZnT concentrations were further reduced by ~26–36-fold.

As noted above, part of these changes (perhaps a 10-fold change) could be a result of dilution by groundwater. However, the additional losses over this probably occur by sedimentation of particulate and colloidal matter containing these metals. For this mechanism to be consistent with the earlier suggested mechanism, most of the colloidal Cu and Zn would need to be converted to particulate forms (probably by agglomeration and coagulation processes) (Fig. 5).

Despite the relatively small changes in the CuT and ZnT concentrations within the region between 75 m and 400 m at the time of the present study (Fig. 3b), several changes in the size distribution of these two metals occurred, which may provide new insights into the behaviour of high concentrations of Cu and Zn in natural waters (Fig. 4b, c). In particular, it appears that over one half of the ZnD added to the river became associated with the colloidal fraction within this region, whereas almost two-thirds of the CuD (~13.5 mg L⁻¹) became associated with both colloidal and particulate matter. Sedimentation of some of the particulate matter together with its associated Cu, would explain why the CuT concentration decreased by around one-third in this region.

The results of the oxidation experiment reported by Hart and Hines (2008) have been used to identify the processes controlling the association of CuD and ZnD with the colloidal (and particulate) matter within the active region from 75 m to 400 m. They investigated the behaviour over time and under controlled laboratory conditions of the Fe, Cu and Zn in a metal-enriched river water sample taken at 150 m at the same time as the present study. This sample had a pH of 5.8 and an initial FeD concentration of 1.13 mg L⁻¹.

Hart and Hines (2008) found that the FeD (assumed to be Fe(II)) was completely removed from solution in 60 h, with the rate of removal following the well established first order oxidation kinetics for Fe(II). A relatively small amount of the CuD (18%) was removed from solution, with this loss occurring in

two steps: an initial rapid loss of around half the amount over the first 60 h, followed by a slower removal of the other half over the remainder of the experiment. Most of the CuD lost became associated with the colloidal fraction. A small amount of the ZnD (14%) was also lost during the experiment, again mostly to the colloidal fraction. However, this loss of ZnD differed from that of CuD in that most (90%) was lost during the first 60 h. It was apparent that these losses of CuD and ZnD were closely linked with the oxidation of Fe(II).

Hart and Hines (2008) postulated a 'co-precipitation-surface precipitation' mechanism to explain how CuD and ZnD was lost to the colloidal fraction. They argued that after oxidation of Fe(II), the Fe(III) produced would co-precipitate with Cu(II) and Zn(II) to form a solid solution of $\text{Fe}(\text{OH})_3\text{-Cu}(\text{OH})_2\text{-Zn}(\text{OH})_2$. After all the FeD had been removed from solution, the behaviour of Cu and Zn differed. $\text{Cu}(\text{OH})_2(\text{s})$ continued to precipitate out, but at a significantly slower rate, whereas little further $\text{Zn}(\text{OH})_2(\text{s})$ precipitation occurred, possibly because the solution had become unsaturated with respect to $\text{Zn}(\text{OH})_2(\text{s})$, but not $\text{Cu}(\text{OH})_2(\text{s})$, at this point in time.

The results of the work by Hart and Hines (2008) are relevant to understanding the behaviour of Fe, Cu and Zn within the active region of the Tambo River. Given that the time for a 'parcel' of water to travel the distance between 75 m and 400 m would be 6–7 h (river flow rate was around 50 m h^{-1} at the time of the present study), and the pH in this region was between 5.1 and 5.9, we predict that FeD entering the active region would undergo oxidation to HIO over the whole distance, and that CuD and ZnD would interact with the colloidal (and particulate) fractions formed, again over the full distance (Fig. 5). These predictions are confirmed by the data in Fig. 4, which shows that between the active region and 400 m, the FeD concentration was reduced, the concentrations of both CuD and ZnD decreased and the concentrations of both CuC and ZnC increased.

Additionally, large metal:Fe molar ratios were observed for the colloidal (and particulate) matter within the input region of the Tambo River under low flow conditions, making it most likely that surface precipitation also occurred in this region. The Cu:Fe molar ratio was 3:6 for the colloidal fraction and 0.9:3.0 for the particulate fraction, and the Zn:Fe molar ratio was equally high (3:9) in the colloidal fraction, but slightly less in the particulate fraction (0.1:0.3).

Although it is most unlikely that a simple sorption mechanism can explain the association of CuD and ZnD with the colloidal fraction, such a mechanism may explain the association of these metals with the HIO floc. The mean Cu:Fe molar ratio in the floc was 0.023 and the mean Zn:Fe molar ratio was 0.004 (Table 1), which are much closer to the metal:Fe molar ratios reported in the literature for adsorption of Cu(II) and Zn(II) onto HIO (Dzombak and Morel 1990; Karthikeyan *et al.* 1997, 1999; Swedlund and Webster 2001; Waychunas *et al.* 2002; Zhu 2002). A possible reason for the lower metal:Fe ratios in the floc is that there was a much greater ratio of Fe to Cu and Zn at the time the Fe(II) was being oxidized in the sediments, resulting in a greater number of HIO surface sites relative to the CuD and ZnD concentrations compared with the situation in the water column.

To explain the larger than expected amount of CuD and ZnD associated with the colloidal fraction in their oxidation experiment, Hart and Hines (2008) suggested that surface precipitation

of Cu and Zn hydroxides occurred on the newly formed colloidal particles, produced from the oxidation of Fe(II) to Fe(III) followed by co-precipitation of $\text{Fe}(\text{OH})_3\text{-Cu}(\text{OH})_2\text{-Zn}(\text{OH})_2$. This 'co-precipitation-surface precipitation' model is based on that formulated for the sorption of cations on metal oxides by Farley *et al.* (1985) and Dzombak and Morel (1990), which allows for a continuum between surface reactions and precipitation, with equilibrium sorption controlled by monolayer sorption at low metal concentrations and by the formation of a surface phase as the sorbate concentration is increased. At high concentrations of metal ions, the likely conditions existing in the active region of the Tambo River during the present study, the formation of a solid solution will control the sorption kinetics, which will be slower than the uptake rate when low metal ion concentrations exist and sorption controls the uptake (Farley *et al.* 1985).

It is not clear why the colloidal fraction in the active region contains more Zn than Cu (Zn:Cu molar ratio = 1.5 ± 0.4 , $n = 4$). Hart and Hines (2008) also reported a similar Zn:Cu molar ratio for the colloidal matter produced in their oxidation experiment. This high Zn:Cu ratio was very different to that in the floc and particulate matter sampled from the input region. Both these contained considerably more Cu than Zn (Zn:Cu molar ratio: floc 0.16 ± 0.01 (s.d.) ($n = 6$); particulate matter 0.18 ± 0.16 ($n = 4$)).

In summary, a plausible mechanism has been developed to explain the observed behaviour of Cu and Zn in the contaminated region of the Tambo River under low flow conditions, when the spring made up around 10% of the flow. This is shown schematically in Fig. 5, and consists of the following components:

- (i) Association of CuD and ZnD with colloidal matter (and particulate matter in the case of Cu) in the region between 75 m and 400 m, with the CuC and ZnC formed by co-precipitation of Cu(II), Zn(II) with Fe(III), followed by surface precipitation of $\text{Cu}(\text{OH})_2(\text{s})$ and $\text{Zn}(\text{OH})_2(\text{s})$.
- (ii) Sedimentation of the larger particulate matter, containing mainly Fe and Cu, mainly within the active region, between 75 m and 400 m.
- (iii) Downstream transport of the colloidal and dissolved fractions.
- (iv) Dilution owing to ingress of groundwater, with the first significant groundwater input occurring between 400 m and 500 m downstream of the spring inputs. The importance of groundwater ingress is expected to be relatively more important at times of very low river flow.
- (v) Other processes for which we have no detailed information, but that could feasibly explain the further reduction of Cu and Zn downstream of the input region, include:
 - sorption of CuD and ZnD onto bed sediments;
 - agglomeration of colloidal matter to form larger particulates that subsequently settle out of the water column.

Acknowledgements

Macquarie Resources Ltd. funded the present study and also provided a scholarship for T.H. We are grateful to Jovo Basic, Paul Dowd, Craig Jeffs and Hugh Stein of Macquarie Resources Ltd. for their support and assistance, and to Steven Hines for his assistance with the field work. B.T.H.

thanks the University of Western Australia for awarding him a Senior Gled-den Fellowship and to the Centre for Water Research at UWA for providing him facilities during which time this paper was completed.

References

- 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
- Dzombak, D. A., and Morel, F. M. M. (1990). 'Surface Complexation Modelling.' (John Wiley: New York.)
- 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
- 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
- Hart, B. T. (1993). 'Benambra Project: Water Quality Investigations.' Progress Report No. 5, Macquarie Resources Pty Ltd: Melbourne.
- Hart, B. T. and Hines, T. (2008). Geochemistry of Cu, Zn and Fe in the Tambo River, Australia, I. Oxidation of Fe(II)-rich groundwater entering the river. *Marine and Freshwater Research* **59**, 72–79.
- 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
- 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
- Karhikeyan, 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
- Karhikeyan, 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
- 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
- Madsen, P. P., Drabaek, I., and Sorensen, J. (1983). The determination of copper and lead in sediments by potentiometric stripping analysis. *Analytica Chimica Acta* **151**, 479–481.
- 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 SO₄ on ferrihydrite and schwertmannite. *Applied Geochemistry* **16**, 503–511. doi:10.1016/S0883-2927(00)00044-5
- 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.)
- Yu, J.-Y., and Heo, B. (2001). Dilution and removal of dissolved metals from acid mine drainage along Imgok Creek, Korea. *Applied Geochemistry* **16**, 1041–1053. doi:10.1016/S0883-2927(01)00017-8
- Zhu, C. (2002). Estimation of surface precipitation constants for sorption of divalent metals onto hydrous ferric oxide and calcite. *Chemical Geology* **188**, 23–32.

Manuscript received 15 March 2007, accepted 7 September 2007