Impact of Iron Duke Pyrite Mine on water chemistry and aquatic life – Mazowe Valley, Zimbabwe

S Ravengai[1]*, D Love[1,2], I Love[3,4], B Gratwicke[5], O Mandingaisa[1] and RJS Owen[6]
[1] *Department of Geology, University of Zimbabwe, Box MP167, Mount Pleasant, Harare, Zimbabwe*
[2] *WaterNet, Box MP600, Mount Pleasant, Harare, Zimbabwe*
[3] *Department of Chemistry and Chemical Technology, National University of Lesotho, Roma 180, Lesotho*
[4] *Department of Chemistry, University of Zimbabwe, Box MP167, Mount Pleasant, Harare, Zimbabwe*
[5] *National Fish and Wildlife Foundation, 1120 Connecticut Ave. N.W. Suite 900, Washington D.C. 20036 USA*
[6] *Mineral Resources Centre, University of Zimbabwe, Box MP167, Mount Pleasant, Harare, Zimbabwe*

Abstract

Iron Duke Mine is the only active pyrite mine in Zimbabwe, and has been in operation since the 1940s. Its location in the multiple-use upper catchment of the Mazowe Valley is strategic in terms of water resource management. The mine disposes of its highly acidic wastewater into two evaporation ponds on the north-eastern side of the mine. This has led to acidification of the groundwater to a pH of about 2 near the evaporation ponds as well as contamination with Fe, Ni, Cu, Co, Pb, Zn and SO_4^{2-}. The pH gradually increases in a north-westerly direction, but much faster towards the west and south-west. Water samples taken from the Yellow Jacket River, which runs through the mine premises, indicated that the upper part of the river was not contaminated with Fe, Ni, Cu, Co, Pb, Zn or SO_4^{2-} and had a neutral pH. However, where the river cuts through gossans and passes adjacent to the mine waste dump and the seepage zone from the evaporation ponds, the water quality deteriorates. The symptoms are a reduction in pH of river water from 7 to about 4 and the precipitation of complex iron hydroxy-sulphates known as "yellow boy" on the streambed. Fe, Ni, Cu, Co, Pb, and Zn concentrations are also elevated here. This poor water quality persisted downstream until the confluence with the Mazowe River where the acidic waters were diluted, and the pH returned to 7. The poor water quality in the Yellow Jacket River is related to an overall reduction in the diversity of aquatic macro-invertebrates and fish downstream of the mine until the confluence with the Mazowe River.

Keywords: water chemistry, water pollution, acid mine drainage, aquatic ecosystems

Introduction

Mining and acid mine drainage

The majority of materials and metals extracted from the Earth by mining occur naturally as sulphide ores or are associated with sulphide minerals. During the extraction process, those sulphides which are not part of the ore material are dumped in waste rock dumps with other rocks. Sulphides containing valuable material (either metals, or in the case of a pyrite mine, sulphide itself) are processed, and the residue dumped in slimes (tailings) dams. The tailings contain large amounts of sulphide, which are either unwanted or were not extracted (Lupankwa et al., 2004a). This results in more of the sulphides being exposed to the surface environment, where they are unstable. Thus spontaneous chemical weathering takes place, releasing acid, metals and sulphate into surface water and groundwater (Bigham and Nordstrom, 2000). This process, whereby sulphide minerals break down in the presence or oxygen and catalysing bacteria, is known as acid mine drainage (AMD).

Pyrite (iron sulphide) is the most abundant sulphide and the major sulphide at the mine studied in this paper. It breaks down in the presence of oxygen and water to form iron (II) sulphate and sulphuric acid (Eq. (1)) and ultimately iron (III) sulphate (Eq. (2)):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (2)$$

Certain chemolithotrophic bacteria, notably *Thiobacillus thiooxidans*, *Thiomicrospira* sp. (Knickerbocker et al., 2000), but also *Thiobacillus ferrooxidans* to a limited extent (Benner et al., 2000), use pyrite as an energy source for CO_2 fixation and cellular metabolism, and thus can catalyse sulphide oxidation (Eq. (1)). Such bacteria are common in sulphide tailings.

However, the major role of bacteria such as *T. ferrooxidans* and *Leptosprillum ferrooxidans*, is in catalysing the oxidation of iron (II) to iron (III) (Benner et al., 2000; Kelly, 1988):

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{bacterial\_catalysis} 4Fe^{3+} + 2H_2O \quad (3)$$

T. ferrooxidans and similar bacteria have been found in water draining from various mine waste deposits, in soil and in the vadose zone below the same deposits (Benner et al., 2000; Loos *et al.*, 1990), as well as in streams draining mine dumps (Kelly, 1988). The bacteria can also function underground in a flooded mine (Bond et al., 2000). Such bacteria thrive in low pH environments - indeed the *Thermoplasmales* have been shown to grow at pH<0.5 (Edwards et al., 2000a).

According to comparisons of abiotic laboratory tests with field studies of sites with known *Thiobacillus* presence (Kirby

---

* To whom all correspondence should be addressed.
☎+26391 419 277; fax: +2634 336 740;
e-mail: ravengai@science.uz.ac.zw

Received 14 September 2004; accepted in revised form 6 January 2005.

and Elder Brady, 1998), the bacteria can increase oxidation rates by five to eight orders of magnitude. This is because iron (III) ions, produced by the bacterially-mediated oxidation, attack pyrite (Jambor et al., 2000). Dissolved iron (III) and pyrite react rapidly:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

At low pH, this reaction provides the most significant pathway because oxidation of pyrite by oxygen (Eq. (1)) proceeds very slowly, and iron (III) ions interact much more rapidly with the reactive sites on the surface of pyrite grains than oxygen (Edwards et al., 2000b). The bacterially-mediated oxidation of iron (II) (Eq. (3)) therefore becomes the rate-determining step at the low pH levels typical of AMD. The system is auto-catalytic: the product of Eq. (3) is a reactant for Eq. (4) and the products of Eq. (4) are reactants for Eq. (2) and Eq. (3).

Once pH rises slightly, a series of iron (III) hydroxide and oxyhydroxide complexes are precipitated from the AMD process, including ferrihydrite, goethite and leidocrocite (Jambor et al., 2000). The simplest of these is iron (III) hydroxide:

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 4Fe(OH)_3 + 3H_2SO_4 \quad (5)$$

This gives the water an orange colour. These are referred to frequently as “ochres” or “yellow boy”. The hydroxides and oxyhydroxides are precipitated at moderately low pH (5 to 6), but once the pH drops below 4.3 they are soluble. This often means that iron (III) stays in solution near the source of contamination, but precipitates downstream, where the pH has risen above 4.3, due to neutralisation or dilution. Dissolved metals (in addition to iron) may coprecipitate when the iron (III) hydroxide flocs form (Kelly, 1988). The accumulation of nickel, manganese and aluminium in these flocs or in colloids has been demonstrated (Rose and Ghazi, 1998), and they have the capacity to carry metals and metalloids - such as arsenic species - for some distance beyond the site (Zänker et al., 2002).

During dry conditions, the evaporation of water from ponds and pools leads to the precipitation of secondary sulphate and hydroxy-sulphate minerals (Musiwa et al., 2004). These minerals dissolve during later storm episodes, loading the runoff with metals and acidity (Bortnikova et al., 2001).

Acid mine drainage occurs where there is insufficient rock material capable of buffering the released acid. The buffering could be provided by the host rock, waste rock, and or soils (Bigham and Nordstrom, 2000). For example, where a significant proportion of waste rock is dominated by carbonate minerals, the released acid is readily buffered by reaction with these carbonates, and the resultant drainage is neutralised (Lupankwa et al., 2004b).

As has been seen, the main products of acid mine drainage on water are increased levels of acidity, dissolved sulphates and metals - iron in the case of pyrite. The reduction of pH is associated with the destruction of the bicarbonate buffering system in natural rivers, and increases in the concentrations of soluble and particulate metals. The other products of AMD lead to salinisation, metal toxicity and sedimentation processes in natural water systems (Nordstrom and Alpers, 1999). In surface water systems, these effects tend to be localised, with pH increasing and total dissolved solid levels decreasing downstream (Kim and Chon, 2001).

Extensive AMD can lead to elevated acidity and the accumulation of metals, metalloids (including highly toxic elements such as arsenic) and sulphate in the vadose zone below mine dumps (Rösner et al., 2000). Many of the metals that accumulate in the vadose zone are mobile and bio-available (Mabvira-Meck et al., 2004; Rösner et al., 2000). Ultimately groundwater contamination plumes develop of the same pollutants (Love and Hallbauer, 1998; Lupankwa et al., 2004a; Rösner et al., 2000) - which can subsequently contaminate surface water via baseflow (Keith et al., 2001). However, deterioration of groundwater quality associated with a mine tends to be localised, with little or no effect at regional scale (Kuma, 2004; Love and Hallbauer, 1998)

Acidic drainage conditions, coupled with metal pollution, can persist for decades and can result in extensive environmental degradation if not properly managed (Ashton et al., 2001; Kambole, 2003; Love and Hallbauer, 1998; Lupankwa et al., 2004a, 2004b; Ravengai et al., 2004b). AMD has been recognised as a multi-factor pollutant, affecting water chemistry and aquatic ecosystems by a number of direct and indirect pathways (Gray, 1997). The acidification of the water has immediate deleterious effects on aquatic ecosystems. A direct effect is the conversion below pH 4.2 of all carbonate and bicarbonate into carbonic acid, which dissociates into carbon dioxide and water. This destroys the bicarbonate buffer system in the water, which acts as a control on acidity (Ashton et al., 2001). Since many photosynthetic organisms use bicarbonate as their inorganic carbon source, their ability to photosynthesise is limited or destroyed altogether as bicarbonate decomposes and becomes less available. The iron hydroxide flocs block light penetration, thus further limiting photosynthesis (Kelly, 1988).

Decomposition (and hence nutrient cycling) becomes reduced and eventually cease, in water bodies severely affected by acid inflow (Dallas and Day, 1993). Acidic waters also kill some organisms, by destroying ionic balances, or damaging cell components or carbonate exoskeletons (Kelly, 1988). This impacts not only on the affected species, but also on their predators (Bortnikova et al., 2001). The overall impact on the ecosystem is the elimination of species and simplification of the food chain (Gray, 1997).

Mining in Zimbabwe most often takes place in the agriculturally productive source areas of transboundary river systems. This gives rise to conflicts between the mines, which need to dispose of large volumes of waste and wastewater on the one hand, and the water quality needs of the environment, agriculture and other water users (e.g. Ashton et al., 2001; Lupankwa et al., 2004a; b; Musiwa et al., 2004; Ravengai et al., 2004a; b).

Study area

Iron Duke Mine (IDM) is located in north-east Zimbabwe, approximately 40 km north of Harare and 15 km east of Mazowe (Fig. 1). The mine lies at the southern end of a gorge cut through the north-east – south-west trending Iron Mask Mountain Range by the Yellow Jacket River. These mountains stretch from the Iron Cap mine area in the south to the Shamva area in the north-east, forming an arcuate structure. They rise up to 400 m above the surrounding country and are generally steep with sharp ridges of the resistant gossanous ironstones. Drainage is generally dentritic and follows a north-east trend, except where it cuts the Iron Mask range, e.g. Yellow Jacket River which flows north into the larger Mazowe River, which flows along the western edge of the range. IDM is surrounded by a number of commercial farms. Large-scale and small-scale farms draw water from the Mazowe valley, as do the urban areas of Bindura, Goromonzi, Marondera and Mount Darwin. As such, managing the impact of mining operations on the quality of both groundwater and surface water is crucial for sustainable mining operations (Ashton et al., 2001). Furthermore, the Mazowe River is a transboundary water system, flowing into the Zambezi in Mozambique. Zimbabwe, as a signatory to the SADC Protocol on Shared Watercourses, is committed to reducing and controlling the environmental degradation of the Zambezi River (SADC, 2000). As such, managing diffuse pollution in headwaters of the Zambezi's tributaries must be a strategic environmental concern for the nation.

The Yellow Jacket River flows northwards through the mining area (Fig. 2). The mine complex itself is in the south, with the waste dump (tailings dam) and evaporation ponds to the north: Pond 1 is for sewage from the mine complex, Ponds 2 and 3 (now decommissioned) were used for wastewater from underground at the mine and the northern Ponds 4 and 5 are new ponds, replacing Ponds 2 and 3.

The area is part of the highveld of Zimbabwe and receives an average rainfall of 800 to 1 000 mm/a, which normally falls between the months of November and April. Average daily temperatures range from 15°C in winter to 30°C in summer. The vegetation in the area is *Miyombo* woodland that grows extensively on the hills, while large fields of commercially grown crops such as citrus, tobacco, cotton, vegetables, wheat and maize characterise the fertile lowland areas. Along the Yellow Jacket River there are some *Miyombo* woodland and eucalyptus trees that have been planted on its banks. The dominant grasses are mainly creeping grass and *Hyparrhenia philipidum*.

IDM opened in 1914 as a gold mining operation. Mining of iron pyrites started around 1940, a time the mine was being operated by the Rhodesian Broken Hill Development Company Limited. The mine was purchased by Anglo-American Corporation and is now mined solely for pyrite. Currently, the mine produces iron pyrites at the rate of about 60 000t/a, supplying copper mines in Zambia and a fertiliser producing company in Harare. During the mining process, large volumes of waste are also generated and these have historically been dumped as rock piles and a waste dump (tailings dam). In the past the acid derived from both underground workings and surface rock piles would be directed into the Yellow Jacket River since the mine had an exemption permit from the Zimbabwean Ministry of Water Development to discharge 170 m^3/d of wastewater with a pH of 1 from underground workings. This permit expired in 1990 and the mine then constructed evaporation ponds into which wastewater is pumped and left to evaporate.

Previous work

The study area lies in the economically-productive Harare-Bindura-Shamva greenstone belt (Vinyu et al., 1996), with extensive gold-mining and agricultural activities. Previous environmental studies in the area include studies of seasonal variations in the Yellow Jacket and Mazowe Rivers (Magadza and Masendu, 1986; Gratwicke, 1999) and acute acid mine drainage at the IDM waste dump (Williams and Smith, 2000). More recently, a detailed study of the evaporation ponds at IDM by Ravengai et al. (2004c), showed that the ponds were generating large quantities of acid, as well as iron and sulphate, and that this was seeping into groundwater.

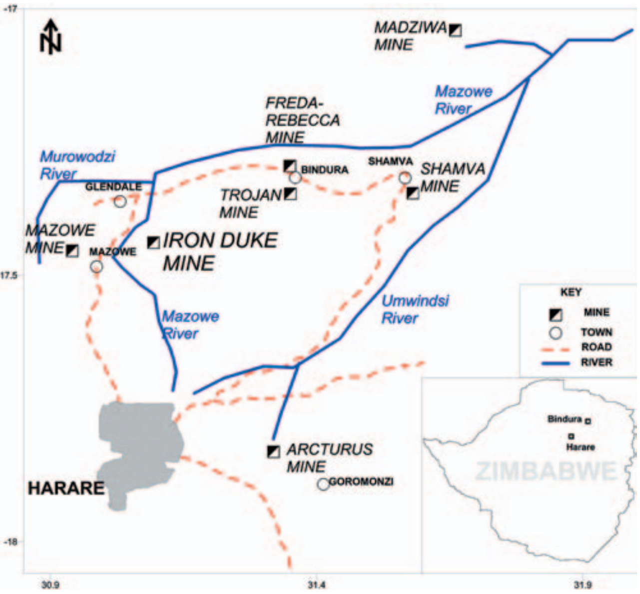

Figure 1
Location of Iron Duke Mine. Inset shows position of study area in north-eastern Zimbabwe.

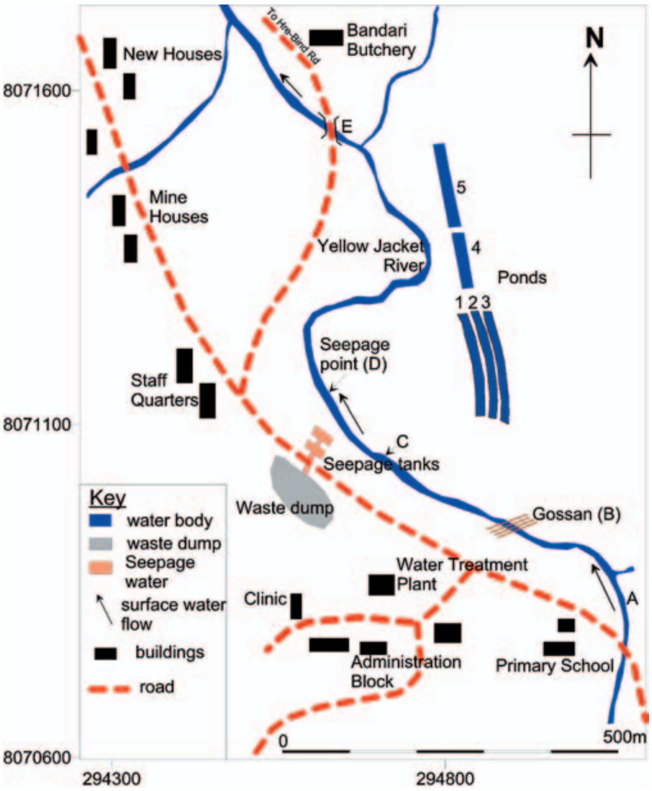

Figure 2
Surface plan of Iron Duke Mine infrastructure in relation to the Yellow Jacket River

It is the objective of this study to describe and explain the surface water chemistry (along the Yellow Jacket River), the groundwater chemistry and flow directions around the Iron Duke Mine area, and their associated effects on aquatic life biodiversity. Previously unpublished results of sampling of surface and groundwater carried out between 2000 and 2001 are also reported. The results are interpreted to provide a detailed and integrated picture of the mining operation's impact on the Yellow Jacket River, local groundwater and aquatic life.

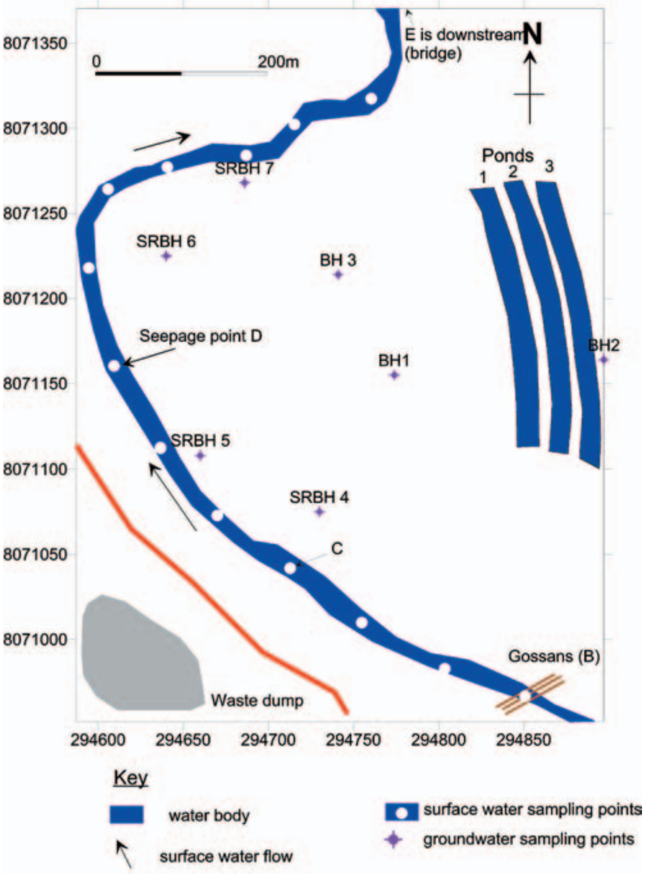

Figure 3
Sampling points in the vicinity of the evaporation ponds and the waste dump, Iron Duke Mine.
Additional sampling points are shown in Fig. 2

Materials and methods

Water sampling

Between August and November 2001, water samples were collected from 25 stations along the Yellow Jacket River during the summer season (Figs. 2 and 3). Samples were taken from upstream of the mining area and of the gossan, from the river as it flows through the mining area and downstream thereof. The sample bottles were rinsed three times with river water, and the river water was filtered through a 0.45 μm membrane filter. Filtering was done to remove suspended organic and inorganic solids that could react with dissolved ions and change the water chemistry. The sample bottles were then filled to the brim to exclude oxygen and acidified with 65% nitric acid (HNO_3) to a pH below 2. The samples were then stored in a cool place for 24h before analysis.

Four water samples were also collected from Ponds 2 and 3 during the same fieldwork period. No water sample was collected from Pond 1 since it is a sewage pond and did not form part of the study. The sampling procedure was the same as that for the surface water except that the samples were not preserved with nitric acid since the water in these ponds was already around pH 2.

Seven groundwater samples were taken from the boreholes during the time of the fieldwork – see Fig. 2. This included the water from four boreholes that were drilled by the researcher, and three pre-existing boreholes. The sampling procedures for groundwater were the same as those for surface water except that the boreholes were flushed six times before water was collected, so that the water sampled would be representative of the aquifer around that borehole.

Chemical analyses

Field measurements for pH, electrical conductivity (EC) and temperature were measured using electronic HANNA EC and pH meters. For the 2001 sampling campaign, iron was analysed by inductively-coupled plasma spectrophotometry and sulphate by gravimetry at the Agricura Laboratories in Harare. For the 2000 sampling campaign, metals were analysed at the laboratories of the Geology Department, University of Zimbabwe (UZ) by atomic absorption spectrophotometer.

Biotic sampling

No direct bio-monitoring program was performed at the time of this study, however, the standard South African Scoring System (SASS) Version 4 (Chutter, 1998) was used to sample the benthic macroinvertebrate fauna in the river. The basic principals of biological monitoring are well-known and have been tested in many parts of the world (Armitage et al., 1983; Thirion et al., 1995; Gratwicke, 1998). Stations were selected 1000m above the mine, at the mine, 1000m downstream of the mine and 2000m downstream from the mine and sampled monthly from January-September 1998 (Gratwicke, 1999), June 1999 and June 2000, (Gratwicke, 2001)

Results and discussion

Evaporation pond water chemistry

Levels of Fe, SO_4^{2-} and acidity in the ponds are presented in Table 1, clearly showing that the pond water chemistry is dominated by acid mine drainage. The solubility of Fe and SO_4^{2-} in water is 486 g/ℓ (Weast, 1988). The results indicate that the evaporation pond water is under-saturated with respect to Fe and SO_4^{2-}. This means that the pond water can dissolve still more Fe and SO_4^{2-} from the solid material below it and this will increase the chemical load to groundwater.

Surface water chemistry

In Figs. 4 and 5 (2000 and 2001 sampling campaigns respectively), the changes in concentration of various parameters are shown, going downstream along the river. The location of the gossan (immediately upstream of the mining area) and the discharge point from the waste dump (tailings dam) is shown on the profiles.

pH measurements from both years (Figs. 4 and 5) indicate that the river water quality degrades downstream (the changes in pH are much clearer in Fig. 4 than in Fig. 5, since far more sampling points were used in the 2001 sampling campaign, on which Fig. 4 is based). Upstream, the pH of the water is approximately neutral (pH~7). As the water cuts through the gossan, the pH drops (Point B, pH ~6.0). This is to be expected since gossans often contain unreacted sulphides, which react under bacterial catalysis to release acid – see Eqs.(1) - (5).

However, this input of acidity quickly gets diluted as the water flows downstream and the river pH rises (pH~7.0, between Points B and C). This pH rise causes a decrease in the concen-

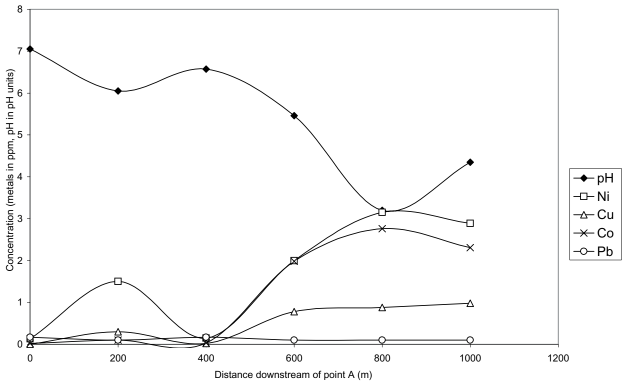

Figure 4
Surface water chemistry, Yellow Jacket River, 2000 sampling campaign

trations of Fe and SO_4^{2-}, as both species become increasingly insoluble with rising pH. As the water approaches Point C, the river water pH drops again (initially to pH~6.5, then dropping further to 6.0). At this point, the water attains a lightly greenish colour with some brownish suspended material. This point corresponds to the position of the waste dump (tailings dam) and the drop in pH can be attributed to seepage of acidic effluent from the waste dump and/or discharge from the waste dump's seepage tanks (Fig. 2). Williams and Smith (2000) showed that the light-green colour of the water is due to the presence of dissolved iron (II) sulphate ($FeSO_4$). This material is generated by acid mine drainage, as shown in Eq. (1) above.

Downstream from Point C, the pH slightly rises (pH of 6.5), but then falls towards Point D (pH of 4). This is likely due to recharge of surface water with acidic groundwater. There are two possible sources of acidic groundwater: Williams and Smith (2000) suggest that there could be east-trending fracture-controlled groundwater flow, from a plume developed beneath the waste dump (tailings dam). Ravengai and others (2004c) demonstrated that seepage from the evaporation ponds would be highly acidic, as well as containing large amounts of dissolved Fe and SO_4^{2-}. However, neither flow path has been directly demonstrated. The contaminated recharge (from either source) is likely to be the cause of the further decrease in pH beyond Point D, as the water gets to the bridge (Point E, pH~3.0).

The changes in Fe and SO_4^{2-} levels below Point C can also be explained by recharge of the river with contaminated groundwater from either the evaporation ponds, or the waste dump (tailings dam) or both. At a pH of above 4 (the pH between Points C and D), a form of ferric hydroxide precipitates out of solution. The medium-low pH and the large amounts of SO_4^{2-} present hinder the precipitation of ferric hydroxide in the pure form. Instead, a complex SO_4^{2-} mineral called schwetmannite – $Fe_8O_8(OH)_6SO_4$ – precipitates. This forms as a yellowish-brownish precipitate known as "yellow boy", "yellow jacket" or ochre deposit. These deposits were observed on the bed of the Yellow Jacket River from Point D, onwards for several hundred metres downstream during the course of the fieldwork. This feature explains the name of the river itself. With the pH decreasing below 4 immediately after Point D, schwetmannite redissolves, liberating Fe and SO_4^{2-} into solution. This causes the sudden peaks in Fe and SO_4^{2-} concentrations which fall away quickly, as this sudden (and once-off) loading of dissolved Fe and SO_4^{2-} is diluted and dispersed.

Beyond this point, as the river progresses towards Point E, the ongoing recharge of the river (from contaminated groundwater) is liable to carry with it more dissolved Fe and SO_4^{2}. Since

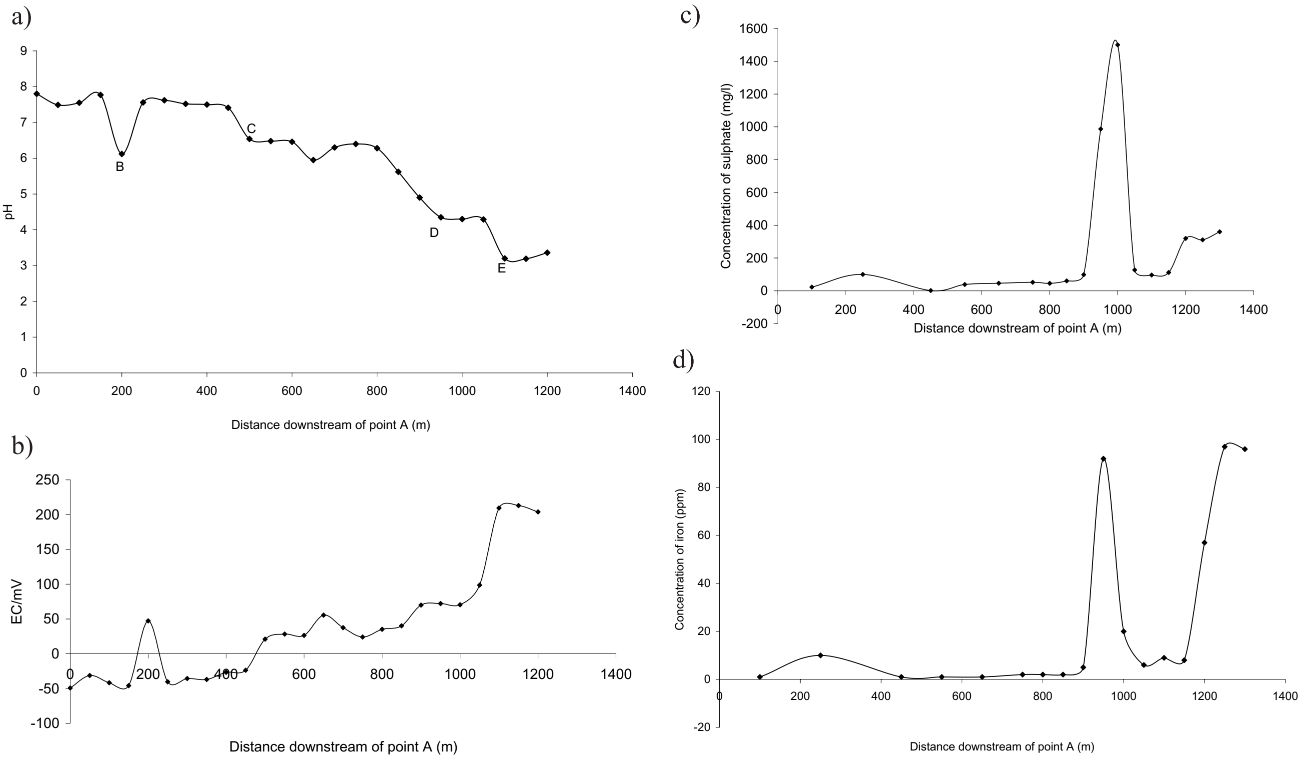

Figure 5
Surface water chemistry, Yellow Jacket River, 2001 sampling campaign.
a) pH; b) Electrical conductivity in mV; c) Dissolved iron; d) Dissolved sulphate

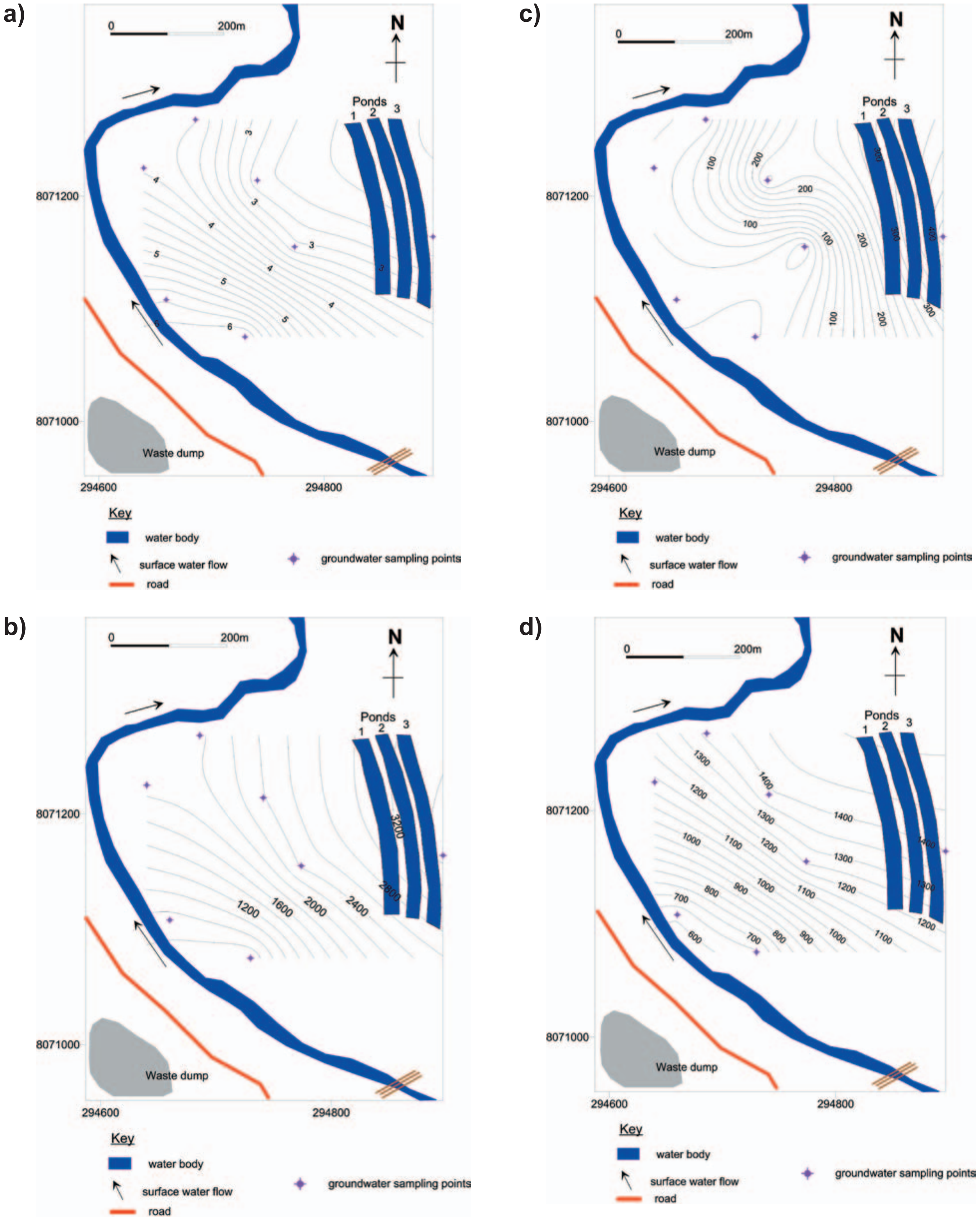

Figure 6

Groundwater chemistry around the Iron Duke Mine ponds shown as contour plots, 2001 sampling campaign. a) pH; b) electrical conductivity, c) dissolved iron in mg/ℓ; d) dissolved sulphate in mg/ℓ

the pH is below 4, the Fe and SO_4^{2-} being added to the river is in dissolved form only. This accounts for the steady rise in Fe and SO_4^{2-} levels, after the earlier peak.

The electrical conductivity profile (Fig. 5b) has an inverse relationship with that of pH (Fig. 5a). This is mainly due to the relatively high H^+ concentration - its conductance would dominate at low pH as the metal ions are in relatively low concentration, concentration (although indeed at higher concentrations than at higher pH). Conversely, under high pH most species are in their undissolved states and therefore unable to conduct elec-

TABLE 1
Results of chemical analyses of evaporation pond water, Iron Duke Mine

Sampling point (pond)	Fe (mg/ℓ)	SO_4 (mg/ℓ)	pH	Date
Pond 2	2232	2159	2.0	03/09/2001
Pond 3	7845	7167	2.0	03/09/2001

TABLE 2
Metal levels in three boreholes around the Iron Duke Mine ponds, 2000 campaign

Sampling point (borehole)	Metal concentrations (mg/ℓ)					
	Fe	Ni	Cu	Co	Pb	Zn
BH 1	441.0	1.065	0.306	0.920	0.15	1.409
BH 2	341.7	0.958	0.509	0.848	0.49	1.821
BH 3	245.5	4.763	0.584	5.506	0.25	3.928

tricity. Therefore the trends observed for EC can be explained in the same way as those of pH.

Considering metals (Fig. 4), the river is not contaminated upstream of the mine, but becomes contaminated as the river passes through gossans, which are associated with releasing low pH as a result of pyrite oxidation. However, the most important thing to note in the graphs is that the concentration of the elements increases with decreasing pH. Of greatest importance is the fact that when the pH has the lowest values, all the elements show marked increase in water. The very low pH is associated with the elements becoming soluble and mobile. The lowest pH corresponds to the proposed seepage points where contaminated groundwater from the waste dump and the evaporation ponds enters the river (see Fig. 2).

Groundwater chemistry

Groundwater results from the 2001 sampling campaign are presented in Fig. 6 and metal results from 2001 in Table 2.

The contour plot for pH shows that groundwater pH is very low closer to the evaporation ponds. With increasing distance from the ponds, pH slowly increases in the north-west direction towards the river but much faster towards the west and south-west. This suggests that the plume of contaminated water is moving preferentially towards the north-west, and to a lesser extent towards the west and south-west. The groundwater pH (3 to 4) in the area is generally higher than the pH of the water in the ponds (pH 2) due to mixing of the seepage water with water recharging the aquifer from rainfall and seepage from the sewage water in Pond 3. The electrical conductivity results (Fig. 6) show an inverse relation to pH, as expected. The poor quality of this groundwater makes it unsuitable for domestic or agricultural use and its suitability for industrial use is also doubtful (DWAF, 1996; WHO, 1996).

The distribution patterns of Fe (Fig. 6c) and of SO_4^{2-} (Fig. 6d) are similar to those of acidity (low pH) and electrical conductivity (Figs. 6a and 6b, respectively). This follows from their increased solubilities at low pH. The values for Fe and SO_4^{2-} are also high in all the boreholes. The high values have been attributed to the oxidation of pyrite in the generation of acid mine drainage in the ponds – see Eq. (1). These values are well above the World Health Organisation drinking water guidelines (WHO, 1996), Zimbabwe wastewater quality limits (MRRWD, 2000) and the South African domestic water use standards (DWAF, 1996).

Metals other than Fe were only analysed in three boreholes during the 2000 sampling campaign. With so few boreholes, the data cannot reasonably be contoured, and are presented in Table 2.

In addition to the high Fe values already considered above, concentrations of Pb, Ni, and Zn in all the boreholes are above the World Health Organisation drinking water guidelines (WHO, 1996), Zimbabwe wastewater quality limits (MRRWD, 2000) and the South African domestic use standards (DWAF, 1996).

Effect of water quality on aquatic life

No direct bio-sampling programme was connected with this study, but the impact of acid mine drainage on the Yellow Jacket River has been an issue of concern to local residents and mine authorities for many years due to the bright yellow colour of its sediments. The first published work noting the biological impacts on the Yellow Jacket River reported on studies conducted during 1983 (Magadza and Masendu, 1986) and since then mine authorities have made several attempts at long-term remedial action (Smythe, 1995), e.g. rehabilitation of the waste dump and installation of the evaporation ponds (thus ending direct discharge of effluent into the river).

A nine-month study of the Yellow Jacket River in 1998 showed that water quality in the stream near the mine was poor, with conductivity ranging from 125 to 5 000 µS/cm and pH values ranging between 2.8 and 6.9 (Gratwicke, 1999). This was accompanied by a marked reduction in the number of aquatic macroinvertebrate taxa. About 5 invertebrate families present were recorded each month in the river directly below the mine; this was just 30% of the number being recorded each month at an unimpacted reference site on the Mazowe River with about 15 families. Aquatic diversity improved downstream as the acid became neutralised; each month an average of 7 and 9 taxa were recorded 2 and 4 km downstream of the mine respectively. Only caddis fly larvae (Leptoceridae), dragonfly larvae (Corduliidae) and midge larvae (Chironomidae) that are tolerant of acid mine drainage were found regularly in the river immediately below the mine. The worst effects of the acid mine drainage were limited to the 3 km stretch of the Yellow Jacket River between the mine and its confluence with the Mazowe River, after which the lowest recorded pH was 6.2 (Gratwicke, 1999). However, it is suspected that a fish kill in July 1998 in the Mazowe River that involved over 1 000 fish and five different species (*Labeo cylindricus, Labeobarbus marequensis, Tilapia rendalli, Serranochromis robustus* and *Clarias gariepinus*) was related to mine effluent because this was the only time that the yellow iron hydroxide sediment characteristic of the Yellow Jacket River was observed at this station in the Mazowe River. In addition to the direct toxic effects of low pH on many invertebrates, fish, amphibians and plants, solubilised metals can become dissolved in acidic stream-water posing further threats to plant and animal life (Dallas and Day, 1993).

Since the 1998 survey, the mine has made a concerted effort to rehabilitate its dumps and the Yellow Jacket River water quality and its associated aquatic invertebrate diversity have improved slightly, but remain impacted, with the worst impact in the areas around and immediately downstream of the waste dump (tailings dam) and the evaporation ponds. These are the areas with the lowest pH and highest metal levels in the river. The "yellow boy" sediments that characterise the stream bed of the Yellow Jacket River especially from the bridge, makes it virtually fish-less by coating the river bed with precipitating iron hydroxides. Depletion of the numbers and diversity of benthic (bottom dwelling) species occurs because the precipitate has a smothering effect, decreasing the levels of dissolved oxygen and covering the bed with precipitates. The low pH can be directly toxic, causing damage to fish gills. Dissolved metals mobilised by these acidic conditions are extremely toxic to fish (Dallas and Day, 1993).

Fish, amphibians, invertebrates and other forms of life may temporarily recolonise parts of the Yellow Jacket River during the rainy season when the acidic conditions have been diluted, but the problem is a recurring chronic one and the mine needs to implement a vigorous and innovative adaptive management programme to create a long-term solution to this problem. It is clear that the rehabilitation of the mine dumps has not solved the chronic acid mine drainage problem, and that the evaporation ponds are strongly affecting water quality in the Yellow Jacket stream. In the light of these results, the next step needed is to phase out use of the evaporation ponds and to neutralise the acidic soils. In the future, mine effluent needs to be neutralised completely using a watertight acid-proof tank system. Precipitated solids should be removed using settling tanks and incorporated into the mine dumps, while the remaining effluent should be carefully chemically tested before deciding on an environmentally appropriate means of its disposal.

Conclusions

The specific conclusions from the study of Iron Duke Mine are:

- Mine water pumped to the evaporation ponds as well as seepage from the waste dump (tailings dam) contaminates the local groundwater and the Yellow Jacket River, which shows the characteristics of bacterially-mediated acid mine drainage. Although microbial identification was beyond the scope of this study, the low pH levels recorded are consistent with an active micro-flora.
- The acidic water continues to dissolve the finely ground rock particles in the dump and ponds, resulting in ongoing groundwater pollution by transition metals and sulphate even though the ponds no longer receive mine water
- Consequently the aquifer unit below the ponds is acidic (pH of 3) and is contaminated with transition metals and sulphate, and this will continue, unless remedial action is taken
- pH, EC, heavy metals and sulphate measurements show that the Yellow Jacket River is not polluted upstream and supports aquatic life
- Low pH and formation of "yellow boy" sediments by acid mine drainage has impaired the aquatic life in the Yellow Jacket River downstream of the Iron Duke Mine.

Accordingly the following general conclusions and recommendations are made: The study highlights the inadvisability of using unlined "evaporation ponds" for disposal of acidic mine effluent, since this practice has transferred the problem of acid mine drainage to surface water to the much longer-term problem of seepage resulting in serious groundwater contamination. Because of their capacity for continuing generation of acid and other pollutants, decommissioned sulphide-rich dumps and facilities such as IDM's evaporation ponds require careful, long-term management, for example by the use of a cover. Clay covers can be highly effective at decreasing oxidation (Koffi et al., 2003), but reactive coverings are more effective in the long term. The cover could contain lime or limestone, which would react with infiltrating water to raise its pH. This would mean that water infiltrating into the waste pile in the old pond would have a buffering capacity. Additionally or alternatively, a reactive cover could contain organic carbon. This stimulates the activity of sulphate-reducing bacteria and thus counters AMD (Aykol et al., 2003). One possibility would be the use of lipids with two hydrophobic tails, such as some glycerols and egg fats, which have been shown to suppress pyrite oxidation (Elsetinow et al., 2002). Many such lipids are locally available in industrial wastes (Moyce et al., 2004). Other forms of organic carbon, such as granulated activated carbon or carbon-steel wool, could also be considered (Aykol et al., 2003). Such alternatives are more effective than municipal waste, but much more costly.

A reactive barrier could also be developed through the soil and weathered rock zone downflow of the evaporation ponds - i.e. between the ponds and the Yellow Jacket River. Such a barrier could contain lime, limestone or organic materials, such as municipal compost. The latter has been shown to be effective in removing Fe and SO_4^{2-} from groundwater into the barrier (Herbert et al., 2000).

Finally, the effect of "evaporation ponds" in polluting the groundwater needs monitoring by routine, but possibly infrequent, analysis of samples from a number of boreholes distributed around the ponds.

Acknowledgements

This research was supported by Iron Duke Pyrites (Pty) Ltd, by a University of Zimbabwe post-graduate scholarship to S Ravengai and by a Mineral Resources Centre travel grant to S Ravengai. The community of Iron Duke Mine is thanked for their hospitality during the fieldwork. Review of an earlier draft of this manuscript by two anonymous reviewers improved the quality of this work.

References

ARMITAGE PD, MOSS D, WRIGHT JF and FURSE MY (1983) The performance of a new biological water quality score system based on macroinvertebrates over a wide range of unpolluted running water sites. *Water Res.* **17** 333-347.

ASHTON PJ, LOVE D, MAHACHI H and DIRKS P (2001) An Overview of the Impact of Mining and Mineral Processing Operations on Water Resources and Water Quality in the Zambezi, Limpopo and Olifants Catchments in Southern Africa. CSIR report to the Minerals, Mining and Sustainable Development Project, Southern Africa.

AYKOL A, BUDAKOGLU M, KUMRAL M, GULTEKIN AH, TURHAN M, ESENLI V, YAVUZ F and ORGUN Y (2003) Heavy metal pollution and acid drainage from the abandoned Balya Pb-Zn sulfide Mine, NW Anatolia, Turkey. *Environ. Geol.* **45** 198-208.

BENNER SG, GOULD WD and BLOWES DW (2000) Microbial populations associated with the generation and treatment of acid mine drainage. *Chem. Geol.* **169** 435-448.

BIGHAM JM and NORDSTROM DK (2000) Iron and aluminum hydroxysulfates from acid sulfate waters. In: Alpers CN, Jambor JL and Nordstrom DK (eds.) *Sulfate Minerals: Crystallography, Geochemistry and Environmental Significance. Rev. Econ. Geol.* **40** 351-404.

BOND PL, DRUSCHEL GK and BANFIELD JF (2000) Comparison of acid mine drainage microbial communities in physically and geochemically distinct ecosystems. *Appl. Environ. Micriobiol.* **66** 4962-4971.

BORTNIKOVA SB, SMOLYAKOV BS, SIDENKO NV, KOLONIN GR, BESSONOVA EP and ANDROSOVA NV (2001) Geochemical consequences of acid mine drainage into a natural reservoir: Inorganic precipitation and effects on plankton activity. *J. Geochem. Explor.* **74** 127-139.

CHUTTER FM (1998) Research on the Rapid Biological Assessment of Water Quality Impacts in Streams and Rivers. Water Research Commission Report No. 422/1/98, Pretoria.

DALLAS HF and DAY JA (1993) The Effect of Water Quality Variables on Riverine Ecosystems: A Review. Water Research Commission Report No. TT 61/93, Pretoria.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY) (1996) *South African Water Quality Guidelines.* **Volume 8**: *Field Guide*. Government Printer, Pretoria.

EDWARDS KJ, BOND PL, GIHRING TM and BANFIELD JF (2000a) An Archaeal iron-oxidizing extreme acidophile important in acid mine drainage. *Sci.* **287** 1796-1799

EDWARDS KJ, BOND PL, DRUSCHELGK, McGUIRE M, HAMERS RJ and BANFIELD JF (2000b) Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California. *Chem. Geol.* **169** 383-397.

ELSETINOW AR, BORDA MJ, SCHOONEN AA and STRONGIN DR (2002) Suppression of pyrite oxidation in acidic aqueous environments using lipids having two hydrophobic tails. *Adv. Environ. Res.* **8** 87-95.

GRATWICKE B (1998) An introduction to aquatic biological monitoring. *Zim. Sci. News* **32** 75-78.

GRATWICKE B (1999) The effect of season on a biotic water quality index: A case study of the Yellow Jacket and Mazowe Rivers, Zimbabwe. *S. Afr. J. Aquat. Sci.* **24** 24-35.

GRATWICKE (2001) Personal communication. Department of Biological Sciences, University of Zimbabwe.

GRAY NF (1997) Environmental impact and remediation of acid mine drainage: A management problem. *Environ. Geol.* **30** 62-71.

HERBERT RBJR, BENNER SG and BLOWES DW (2000) Solid phase iron-sulfur geochemistry of a reactive barrier for treatment of mine drainage. *Appl. Geochem*. **15** 1331-1343.

JAMBOR JL, NORDSTROM DK and ALPERS CN (2000) Metal-sulfate salts from sulfide mineral oxidation. In: Alpers CN, Jambor JL and Nordstrom DK (eds.) *Sulfate Minerals: Crystallography, Geochemistry and Environmental Significance*. *Rev. Econ. Geol.* **40** 305-350.

KAMBOLE MS (2003) Managing the water quality of the Kafue River. *Phys. Chem. Earth* **28** 1105-1109.

KEITH DC, RUNNELLS DD, ESPOSITO KJ, CHERMAK JA, LEVY DB, HANNULA SR, WATTS M and HALL L (2001) Geochemical models of the impact of acidic groundwater and evaporative sulfate salts on Boulder Creek at Iron Mountain, California. *Appl. Geochem.* **16** 947-961.

KELLY M (1988) *Mining and the Freshwater Environment*. Elsevier, London.

KIM JY and CHON HT (2001) Pollution of a water course impacted by acid mine drainage in the Imgok creek of the Gangreung coal field, Korea. *Appl. Geochem*. **16** 1387-1396.

KIRBY CS and ELDER BRADY JA (1998) Field determination of Fe^{2+} oxidation rates in acid mine drainage using a continuously-stirred tank reactor. *Appl. Geochem*. **13** 509-520.

KNICKERBOCKER C, NORDSTROM DK and SOUTHAM G (2000) The role of "blebbing" in overcoming the hydrophobic barrier during biooxidation of elemental sulfur by *Thiobacillus thiooxidans*. *Chem. Geol.* **169** 425-433.

KOFFI K, LeBLANC M, JOURDE H, CASIOT C, PISTRE S, GOUZE P and ELBAZ-POULICHET F (2003) Reverse oxidation zoning in mine tailings generating arsenic-rich acidic water (Carnoulès, France). *Mine Water Environ.* **22** 7-14.

KUMA JS (2004) Is groundwater in the Tarkwa gold mining district of Ghana potable? *Environ. Geol*. **45** 391-400.

LOOS MA, CONRADIE JM, WHILLIER PA, MARÉ J and BOSCH C (1990) Research on the Inhibition of Bacterial Oxidation of Pyrite and Concomitant Acid Mine Drainage: Part 1. Investigation of Gold Sand Dumps. Water Research Commission Report No. 132/1/90, Pretoria.

LOVE D and HALLBAUER DK (1998) Characterisation of groundwater contamination in a dolomitic aquifer: A case study from the Far West Rand. In: *Ext. Abs. Geological Society of South Africa Conference Geocongress 98*. Pretoria, South Africa.

LUPANKWA K, LOVE D, MAPANI BS and MSEKA S (2004a) Impact of a base metal slimes dam on water systems. Madziwa Mine, Zimbabwe. *Phys. Chem. Earth* **29** 1145-1151.

LUPANKWA K, LOVE D, MAPANI BS, MSEKA S and SMITH V (2004b) Influence of the Trojan Nickel Mine rock dump on run-off quality, Mazowe Valley, Zimbabwe. In: *Ext. Abs., 5th WaterNet-WARFSA Symposium*. Windhoek, Namibia.

MABVIRA-MECK ML, LOVE D and MAPANI BS (2004). Zimbabwean mine dumps and their impact on river water quality – A reconnaissance study. In: *Ext. Abs., 5th WaterNet-WARFSA Symposium*. Windhoek, Namibia.

MAGADZA CHD and MASENDU H (1986) Some observations on effluent in the Yellow Jacket stream, Zimbabwe. *Zim. Sci. News* **20** 11-15.

MET (MINISTRY OF ENVIRONMENT AND TOURISM) (2003) National Climate Database. Unpublished digital records, Harare.

MOYCE W, NYAMA Z, LOVE D, WUTA M, MUSIWA K and ZINGONI E (2004) Influence of Golden Quarry landfill on groundwater quality, Westlea suburb, Harare, Zimbabwe. In: *Ext. Abs., 5th WaterNet-WARFSA Symposium*. Windhoek, Namibia.

MRRWD (MINISTRY OF RURAL RESOURCES AND WATER DEVELOPMENT) (2000) Water (Waste and Effluent Disposal) Regulations, Statutory Instrument 274 of 2000, Republic of Zimbabwe.

MUSIWA K, LOVE D and OWEN R (2004) Impact of a gold mine on water systems – Athens Mine, Mvuma, Zimbabwe. In: *Proc. 1st SANTREN Conference and Exhibition*. Gaborone, Botswana.

NORDSTROM DK and ALPERS CN (1999) Geochemistry of acid mine waters. In: Plumlee GS and Logsdon MJ (eds.) *The Environmental Geochemistry of Minerals deposits. Part A; Processes Techniques and Health Issues*. *Rev. Econ. Geol*. **6A** 133-160.

RAVENGAI S, LOVE D, LOVE I and KAMBEWA C (2004a) The impact of gold mine dumps on water quality around the Arcturus group of mines, Mazowe Valley, Zimbabwe. In: *Proc. IWA Specialist Group Conference on Water and Wastewater Management for Developing Countries*. Victoria Falls, Zimbabwe.

RAVENGAI S, LOVE D, MABVIRA-MECK ML, MUSIWA K and MOYCE W (2004b) Water quality in an abandoned mining belt, Beatrice, Zimbabwe. In: *Ext. Abs., 5th WaterNet-WARFSA Symposium*. Windhoek, Namibia.

RAVENGAI S, OWEN RJS and LOVE D (2004c) Evaluation of seepage and acid generation potential from evaporation ponds, Iron Duke Pyrite Mine, Mazowe Valley, Zimbabwe. *Phys. Chem. Earth* **29** 1129-1134.

ROSE S and GHAZI AM (1998) Experimental study of the stability of metals associated with iron oxyhydroxides precipitated in acid mine drainage. *Environ. Geol.* **36** 364-370.

RÖSNER T, BOER R, REYNEKE R, AUCAMP P and VERMAAK J (2000) A Preliminary Assessment of Pollution Contained in the Unsaturated and Saturated Zone Beneath Reclaimed Gold-Mine Residue Deposits. Water Research Commission Report No. 797/1/01, Pretoria.

SADC (2000) Revised Protocol on Shared Watercourses in the Southern African Development Community. Southern African Development Community, Gaborone.

SMYTHE GR (1995) Iron Duke acid mine drainage. In: *Proc. Mining and Environment in Zimbabwe*, 21-24, Institute of Mining and Metallurgy in Zimbabwe, Harare.

THIRION C, MOKE A and WOEST R (1995) Biological Monitoring of Streams and Rivers Using SASS4 – A User Manual. Institute for Water Quality Studies, Dept. of Water Affairs and Forestry, South Africa.

VINYU ML, FREI R and JELSMA, HA (1996) Timing between granitoid emplacement and associated gold mineralization: examples from the ca. 2.7 Ga Harare-Shamva greenstone belt, northern Zimbabwe. *Can. J. Earth Sci.* **33** 981-992.

WEAST RC (1988) *Handbook of Chemistry and Physics*. CRC Press, New York.

WILLIAMS TM and SMITH B (2000) Hydrochemical characterisation of acute acid mine drainage at Iron Duke mine, Mazoe, Zimbabwe. *Environ. Geol.* **39** 272-278.

WHO (WORLD HEALTH ORGANISATION) (1996) *Guidelines for Drinking Water Quality* (2nd edn.) **Volume 2**: *Health Criteria and Other Supporting Information*. World Health Organisation Press, Geneva.

ZÄNKER H, MOLL H, RICHTER W, BRENDLER V, HENNIG C, REICH T, KLUGE A and HÜTTIG G (2002) The colloid chemistry of acid rock drainage solution from an abandoned Zn–Pb–Ag mine. *Appl. Geochem.* **17** 633-648.