Mobilisation and attenuation of arsenic around gold mines, east Otago, New Zealand

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Abstract   Arsenic is released into the environment by decomposition of natural arsenopyrite in gold-bearing veins in east Otago. Natural release is slow, but is accelerated by mining activity. Waters from old mine adits have pH of 6–7, compared to normal groundwater pH of 7–8, and adit waters have arsenic concentrations up to 4 ppm compared to background levels of c. 0.01 ppm. Tailings disposed about 80–90 years ago into what is now a wetland at Barewood have arsenic concentrations of up to 33 000 ppm, principally in the form of the secondary arsenic mineral scorodite. The maximum dissolved arsenic concentration in the Barewood tailings is 0.75 ppm at pH of c. 5.5. Dissolved arsenic release at that pH may be restricted to levels near 1 ppm by the formation of scorodite with solubility and/or kinetic controls on scorodite redissolution. Modern mining activity in the Macraes area has resulted in localised dissolved arsenic concentrations in excess of 200 ppm at pH near 10. Evaporation of this water produces scorodite precipitates. Dissolved arsenic released from arsenopyrite decomposition is attenuated by fine-grained minerals, predominantly phyllosilicates, in soils around weathered veins, and in wetlands downstream from mine workings. Lithic soils can hold at least 50–100 ppm As on the fine fraction (c. 1 μm), and wetland soils can hold hundreds to thousands of parts per million on their fine fractions. Both soil adsorption and scorodite mediation slow the release of arsenic into the environment, allowing more effective dilution by downstream waters to safe arsenic levels.

Keywords   arsenic; scorodite; gold; mining; attenuation; pollution

INTRODUCTION

Arsenic is a common accessory to many metallic mineral deposits, particularly gold deposits. In mesothermal gold deposits, arsenic is the principal anomalous metal, typically at 3–4 orders of magnitude higher concentrations than gold, as arsenic sulphides. Natural erosion of gold deposits releases the arsenic into the environment where it is diluted and the anomaly is destroyed. In areas of high erosion rates, arsenic minerals are physically eroded and transported downstream to be dispersed into sediments. Under low erosion rates, *in situ* chemical oxidation of arsenic sulphides results in dissolution of arsenic and dispersal via stream water.

Gold mining involves extraction and crushing of arsenic-bearing ore, followed by disposal of arsenic-bearing rock as mine tailings; historically these tailings were disposed into the nearest stream. Mining and tailings disposal promotes oxidative arsenic mobilisation by increasing permeability and increasing contact between arsenic sulphides and oxygenated water. Hence, anthropogenic interference accelerates the natural processes of arsenic mobilisation and dispersal into streams.

Historic workings

This study examines the nature and controls of arsenic mobilisation in the vicinity of three different historic gold mining areas in east Otago: Macraes, Nenthorn, and Barewood (Fig. 1). These mining areas are all in unforested grassy uplands which receive 400–800 mm/yr precipitation with a similar amount of evaporation. Broad low-relief interfluves separate steep-sided streams incised 20–100 m below the interfluves. The gold mines were developed in mesothermal fault-hosted quartz vein systems, which have a regional northwest strike and northeastward dip (McKeag & Craw 1989; MacKenzie & Craw 1993). Arsenic in these deposits occurs as arsenopyrite (FeAsS) in primary (unoxidised) ore, and as iron arsenates such as scorodite and pharmacosiderite in naturally oxidised zones (Craw & MacKenzie 1992).

Historic gold mining in these areas occurred between 1875 and 1920 (Williamson 1939), and was mainly underground. Tunnels (adits) and shafts penetrated the upper naturally oxidised zone (c. 20 m thick) into unoxidised primary sulphide-bearing ore. The sulphide-bearing ore was difficult to extract gold from, and most mines quickly became uneconomic in this primary ore and were abandoned. The legacy of this mining activity is a few scattered tunnels which have since become water conduits, and some remnants of mine tailings in streams. Our study examines this legacy for evidence of present arsenic mobilisation, in order to obtain information on the rates of decomposition of arsenic minerals during mining-accelerated oxidation in the 100 yr time frame.

Modern mining

The Macraes area is also the site of a large modern gold mine, and some arsenic concentration data from this site are presented for comparison. The modern Macraes mine is a large open-cut operation producing c. 100 000 ounces of
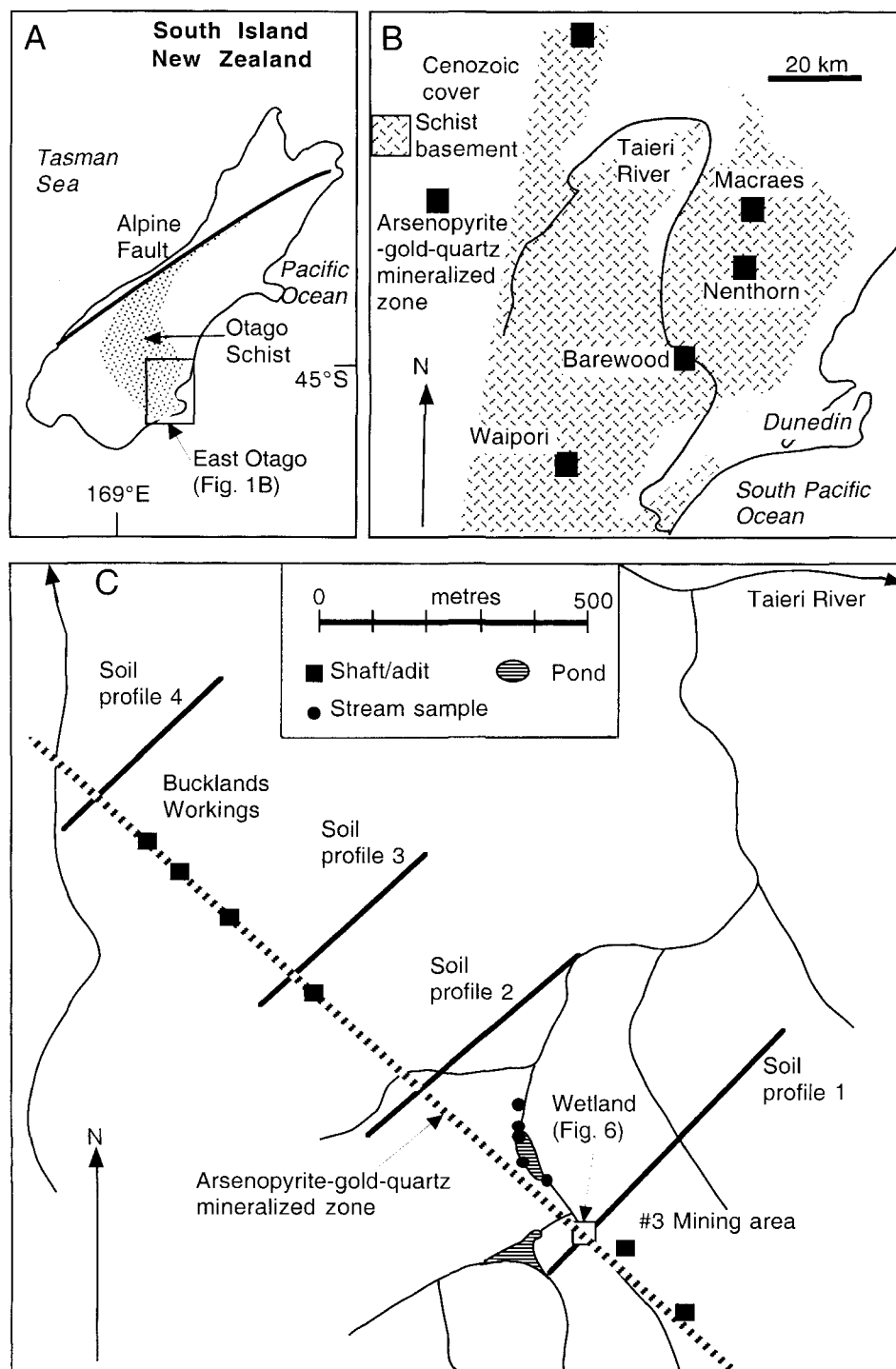
Fig. 1 A, Locality map showing the east Otago portion of the Otago Schist in the South Island of New Zealand. B, The location of principal gold-mining areas in the Otago Schist of east Otago. C, The Barewood gold-mining area with sampling sites, studied wetland, and downstream pond, shown in relation to the gold-arsenopyrite-bearing quartz vein zone.

gold per year. The mine mainly exploits primary (unoxidised) ore in which gold is associated with sulphides. The sulphides are separated by flotation before fine grinding (c. 15 μm) and cyanidation. Between 1989 and 1993, the sulphide-rich cyanidation tailings were discharged to a dedicated concentrate tailings impoundment. From late 1993, the concentrate tailings were remixed with the dominant silicate tailings and discharged to a larger flotation tailings impoundment. The concentrate tailings impoundment has since remained unused except for short-term concentrate discharges for temporary operational reasons.

METHODS

Surface-water samples from wetlands in old gold-mining areas have a high content of suspended solids when sampled. These were centrifuged to remove coarse particulate matter (which was analysed separately), transferred immediately to clean glass vials, then filtered (0.45 μm) before analysis by atomic absorption spectrometry (AAS) (Chemsearch Laboratory, University of Otago Chemistry Department) using the hydride method. Precision of analyses is c. 2% at the arsenic levels in this study. Some additional water data were provided by Macraes Mining Co Ltd from their

environmental programme around the active mine, and these were analysed by flame AAS (for As > 0.5 ppm) and graphite furnace AAS (for lower arsenic contents) at Chemsearch. Detection limit for flame AAS is 0.1 ppm and for graphite furnace AAS is 0.005 ppm, and uncertainties in analyses in this study were c. 1% relative for all analyses except those approaching detection limits where uncertainties rose to c. 20%. Pore water in saturated soils and tailings was removed by centrifuge as supernatant, and analysed by AAS as for surface water. Redox potential (Eh) and pH were determined in the field using a portable Oakton WD-35615 meter calibrated with standard pH solutions and ZoBell's solution (Nordstrom 1977).

Soil samples were collected from the surface down to c. 0.2 m, in clean plastic bags. Soils were dried for further processing after pore water had been extracted. Selected soil samples were disaggregated in water by stirring, then dry sieved into different size fractions. The <63 μm fraction was stirred in distilled water then left to settle for 30 s before pouring off remnant suspended fines and drying the settled sediment. The fine suspension was then left to settle for 2 min, and the remnant suspension poured off as the finest fraction and the two suspended fractions dried. These fractions have grain sizes <10 and <1 μm, respectively. The finest fraction was not always present in sufficient quantities for further analysis. Semiquantitative X-ray diffraction analysis showed that finer fractions are dominated by clay minerals and schist micas (muscovite and chlorite), whereas coarser fractions are dominated by quartz and feldspar. Soil samples were prepared as pressed powder discs and analysed by X-ray fluorescence (XRF), which was calibrated using a set of international standards (Govindaraju 1994) for arsenic levels below 500 ppm. A subset of these international standards was used as "unknowns" during routine analysis to check consistency. These analyses have precision of ±5 ppm above a detection limit of 5 ppm, with precision decreasing to ±10 ppm near 500 ppm As content. High-arsenic soil samples were analysed by XRF calibrated with a set of samples from the Macraes mine (Fig. 1) originally analysed by AAS. Precision for analyses above 500 ppm is c. 1% relative. Soil arsenic analyses obtained by Macraes Mining Co Ltd as part of a regional gold exploration programme in the Barewood area were conducted by AAS with detection limit near 1 ppm. Analyses are presented graphically (Fig. 2–8), and are discussed in the following sections. All arsenic analyses are presented in parts per million to facilitate comparison between solid and liquid arsenic contents.

Element maps of mine tailings particles at Barewood (Fig. 1) were constructed by electron microprobe analysis of points on a regular 1 × 1 μm grid. The resulting images, which are 0.3 mm (horizontal in Fig. 9) by 0.4 mm (vertical in Fig. 9) were each constructed from 120 000 individual analyses. Each analysis lasted less than a second, and therefore is only semiquantitative. Maximum values were determined for high spots by conventional microprobe analysis, and are approximately: Fe = 50 wt%; As = 4%; S = 1%; Ca = 5%. The backgrounds in these diagrams for arsenic, sulphur, and calcium are higher than for iron because of the lower peak/background ratio for the elements present at lower weight percentages. Count rates were also lowered by the spongy nature of most of the grains, which therefore include mounting epoxy resin.
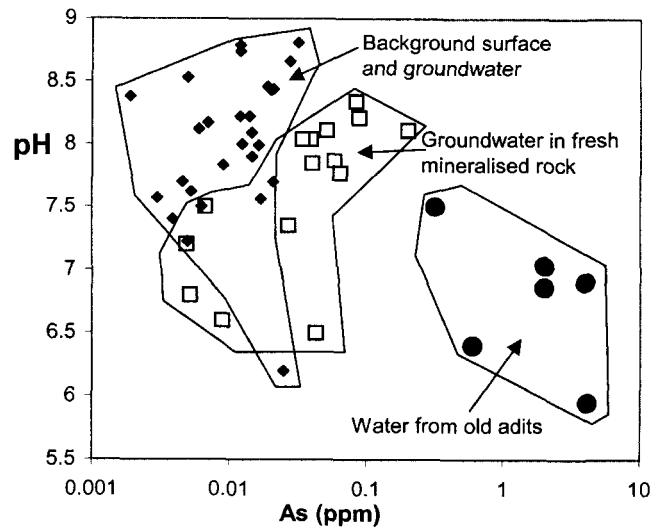

Fig. 2 Comparison of pH and dissolved arsenic concentrations for surface water, groundwater in mineralised rock, and water discharging from old mining adits at Macraes, Nenthorn, and Barewood in east Otago. Logarithmic scales.

NATURAL ARSENIC CONCENTRATIONS

Surface water in the vicinity of Macraes mine (Fig. 1, 2) has background arsenic concentrations near the recommended drinking water limit (0.01 ppm; USEPA 1994). Groundwater in unmineralised rock has similar arsenic content to the surface water, reflecting the close relationship between surface water and groundwater in this area. In contrast, some groundwater from unoxidised mineralised rock (arsenopyrite bearing) has distinctly higher arsenic contents, up to 0.2 ppm (Fig. 2).

Background arsenic content of host schist basement is 2–6 ppm, and arsenic contents in gold-bearing quartz veins is typically 2000–10 000 ppm (Fig. 3) (McKeag & Craw 1989; Craw & MacKenzie 1992). Soil arsenic content in unmineralised areas reflects that of the underlying schist and is typically c. 5 ppm. Soil in areas with mineralised veins commonly has 5–10 ppm As over large areas except at the veins themselves where peaks of 50–1000 ppm As occur (Fig. 3) (Lee et al. 1992). The higher arsenic contents above veins are distributed unevenly through the soil grain-size spectrum, with relatively high concentrations at the millimetre scale and in the finest fractions at Nenthorn (Fig. 4).

ADIT DRAINAGE

Each of the studied mining areas is penetrated by several adits, which are gently inclined upwards to facilitate drainage during mining. Post-mining collapse at all entrance portals has created low dams (c. 1 m high) which impound discharging groundwater for c. 20 m back up the adits. Water oozes through the dams and flows slowly down low-gradient channels originally constructed for drainage outside the portals. The low-gradient channels below the dams have largely silted up and now form wetlands.

Water issuing from the adits is chemically different from surrounding background surface water and groundwater. In
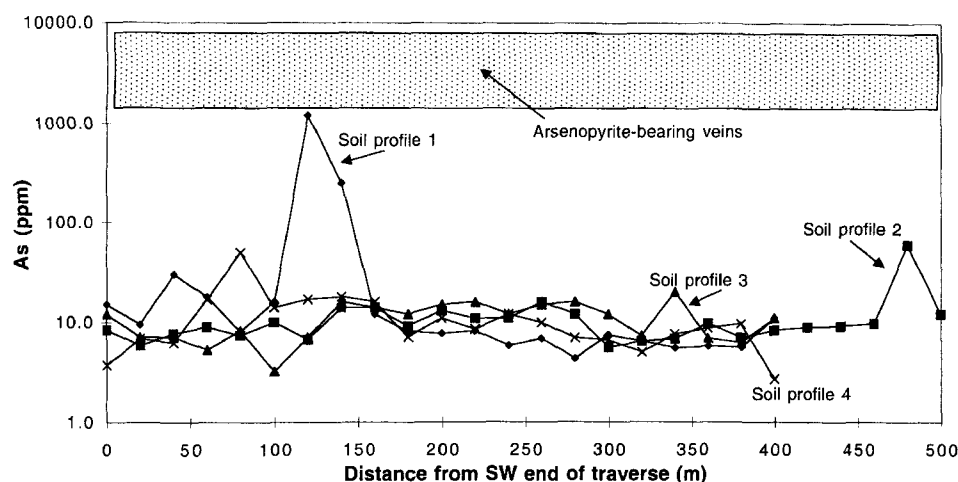
Fig. 3 Arsenic concentrations in soil samples taken every 20 m along traverses across the Barewood mineralised fault zone (Fig. 1C). Typical arsenic content of mineralised quartz veins at Barewood (stippled; after Craw & MacKenzie 1992) is shown for comparison. Logarithmic scale.
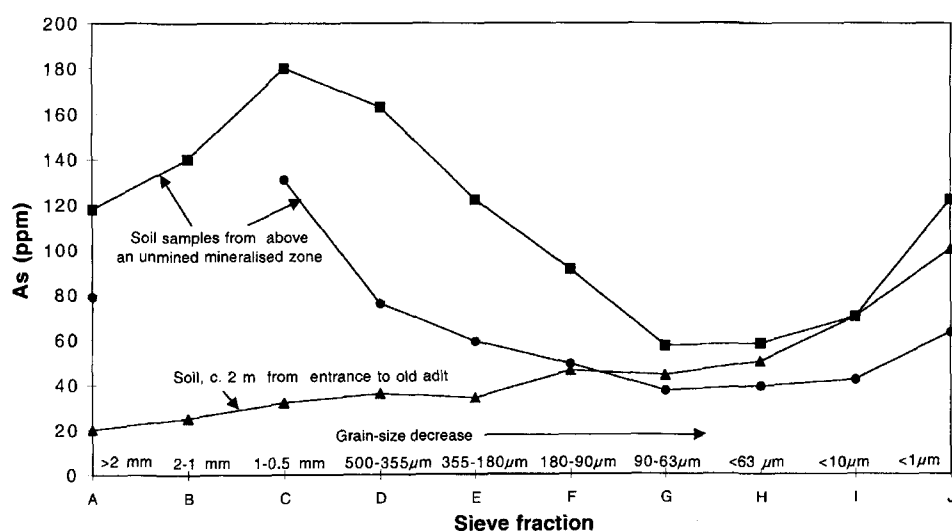

Fig. 4 Arsenic concentrations in various grain-size fractions of Nenthorn (Consolidated Lode) soil samples (see text for methods) taken from above an unmined portion of a mineralised quartz vein (top two curves) and from the entrance to an old adit on the same vein.

particular, the adit water arsenic content is distinctly higher, and the pH is generally lower, than most east Otago waters (Fig. 2). Sulphate content of adit water (c. 150 ppm) is generally higher than regional groundwater (<20 ppm) as well, and locally the smell of hydrogen sulphide emanates. However, Eh of the discharging water is +200 to +300 mV, implying that sulphate greatly dominates over sulphide (Garrels & Christ 1965). Arsenic content of adit water can be up to 4 ppm and is commonly between 0.1 and 1 ppm (Fig. 2, 5). The arsenic content of adit water decreases generally downstream in the wetlands, although there is considerable variation (Fig. 5).

Soil samples from the wetlands downstream of adits also have variable and locally high arsenic contents, with the highest concentrations near the upstream end of the wetlands (Fig. 5). However, there is a strong grain-size effect on arsenic contents of some samples, with highest concentrations in the finest material (Fig. 4, 5).
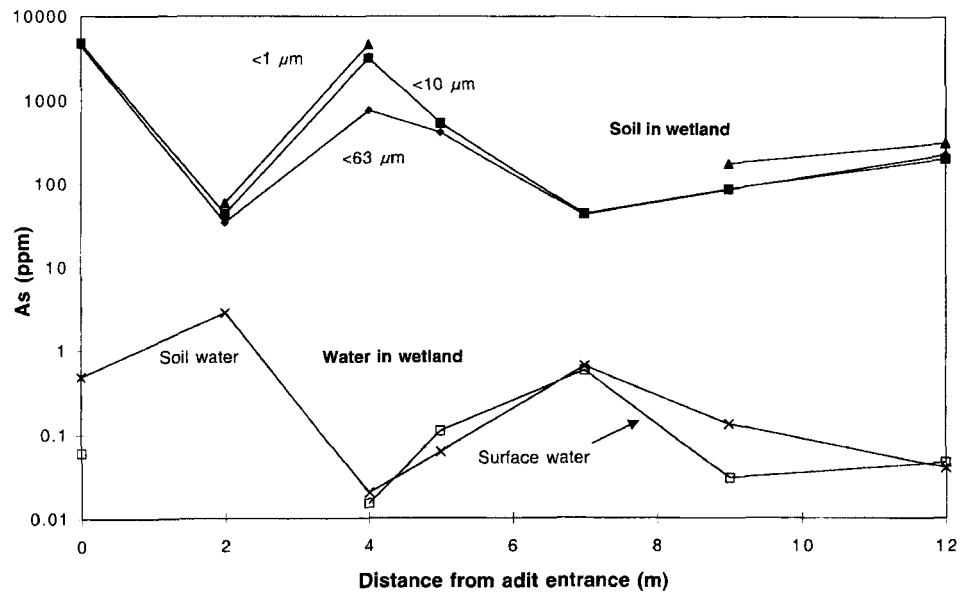
BAREWOOD WETLAND

A wetland has developed in a natural stream in the wake of mining activity (1890–1911; Ingram 1980) at the Barewood #3 mining area (Fig. 1C), which locally disturbed the streambed. This wetland is immediately downstream of

natural outcrops of an arsenopyrite-bearing quartz vein 1–2 m thick. These outcrops have been partially mined for gold at the surface, and deep (c. 40 m; Ingram 1980) shafts provided access to deeper levels where most mining occurred. Small (2 m scale) piles of mined but uncrushed arsenopyrite-bearing quartz lie near one shaft on the upstream end of the wetland. A cyanidation plant was located immediately downstream of the wetland, where an associated dam and pond still survive (Fig. 1C). Tailings from the plant were disposed into the stream, and remnants of tailings are still present in the wetland.

The wetland has an irregular shape due to mining activities, but is broadly elongate along the stream valley axis (Fig. 1C, 6A). Samples of soil and soil water were taken at 2 m intervals on a long (25 m) transect approximately parallel to the stream valley, and on three transects at a high angle to this long profile (Fig. 6A). Measurements of pH and Eh of soil water were made at each sample site. Data from these sample sites are contoured in Fig. 6B, C, and D to depict gross differences in data over the wetland. High soil-arsenic contents (Fig. 6B) were found where old mine tailings are preserved and in the axis of the stream draining the mineralised outcrops and mine dumps. Soil-water arsenic content (Fig. 6C) generally mirrors the associated soil arsenic content (Fig. 6B), but variations are less dramatic. Similarly,

Fig. 5 Arsenic concentrations in soil and water in samples taken on a traverse through a wetland formed at the entrance to an adit (as in Fig. 4) at Nenthorn. The three finest fractions of soil were analysed separately, and soil water was extracted by centrifuge. Surface water was slow moving across the top of the wetland. Logarithmic scale.

the lowest pH values (Fig. 6D) were found near where soil arsenic contents are highest, and Eh values are highest where pH was lowest (c. +260 to +300 mV).

In detail, data from the sampled points show considerable variation from point to point. Arsenic content of wetland soil varies widely along the long profile (Fig. 7A). Bulk samples of soil from the streambed and pond floor downstream of the wetland (Fig. 1C, 7B) are almost entirely mud, and have much lower arsenic contents than in the wetland upstream. The finest grain-size fraction of each wetland sample has the highest arsenic concentration (Fig. 7A). The irregular downstream variation in soil arsenic content is reflected consistently in all grain-size fractions (Fig. 7A). Arsenic content of soil water is variable (Fig. 7C, D).

OLD TAILINGS AT BAREWOOD

High arsenic contents of soil in the downstream part of the wetland are due to the presence of remnants of mine tailings, presumably residue from the cyanidation plant located in the area (Ingram 1980). Transect 3 (Fig. 6A) extends westward into the main tailings area, where analysed soil arsenic concentrations are up to 33 000 ppm (Fig. 8). The soil pore-water arsenic content is also high in these old tailings, but it forms a compositional plateau near 0.75 ppm rather than rising steadily like the associated soil arsenic content (Fig. 8). The soil water in this area is distinctively orange-brown due to suspension of fine-grained iron oxyhydroxide, which is readily stirred up from the associated saturated soil. The old tailings are generally finer grained than the background wetland soils and have uniform grain size (<63 μm).

Tailings mineralogy

The tailings material which makes up the soil in this area consists mainly of irregular particles 1–40 μm across. These particles are principally iron oxyhydroxide with a variety of subordinate silicate minerals of similar grain size,

particularly quartz, muscovite, and epidote. Iron oxyhydroxide grains are spongy in appearance, with irregular margins. Some grains are zoned, with central portions displaying weak greenish grey internal reflection colours (possibly scorodite, see below) against the brownish grey of iron oxyhydroxide.

Two scorodite X-ray diffraction peaks, the highest intensity (122) peak at 3.18 Å and a broad multiple peak at 4.5 Å, are detectable in diffractograms of the tailings. The tailings were also investigated in chemical detail using electron microprobe element mapping. Most of the grains contain some iron, so grain outlines are indicated in Fig. 9A. Many of the more iron rich grains are zoned, with an iron-rich core and rim and a lower Fe annulus between. These latter grains are commonly richest in arsenic in their cores (Fig. 9B) and are presumed to be arsenopyrite decomposed to scorodite. Localised impregnation of iron-rich grains by low levels of sulphur (Fig. 9C) and calcium (Fig. 9D) in subequal proportions may indicate the presence of gypsum. Irregular phosphorus concentrations (energy-dispersive analysis) also occur in iron oxyhydroxide grains and in their rim zones.

There is no optical or chemical evidence for relict sulphide minerals within the tailings particles. However, particle textures described above formed within present particle shapes, after particle formation in the processing plant, and are a result of postdepositional alteration over the past 90 years.

ACTIVE MACRAES MINE SITE

There are four process-related waters associated with this operation that are of interest to this study. Analyses of these waters has been conducted regularly by Macraes Mining Co Ltd, and this database has been supplemented during this study. Results are variable due to periodic incursion of rainwater and mixing with other process waters. Hence, we have used only relatively high arsenic analyses for each dataset (Fig. 10), discounting the more dilute data for clarity.
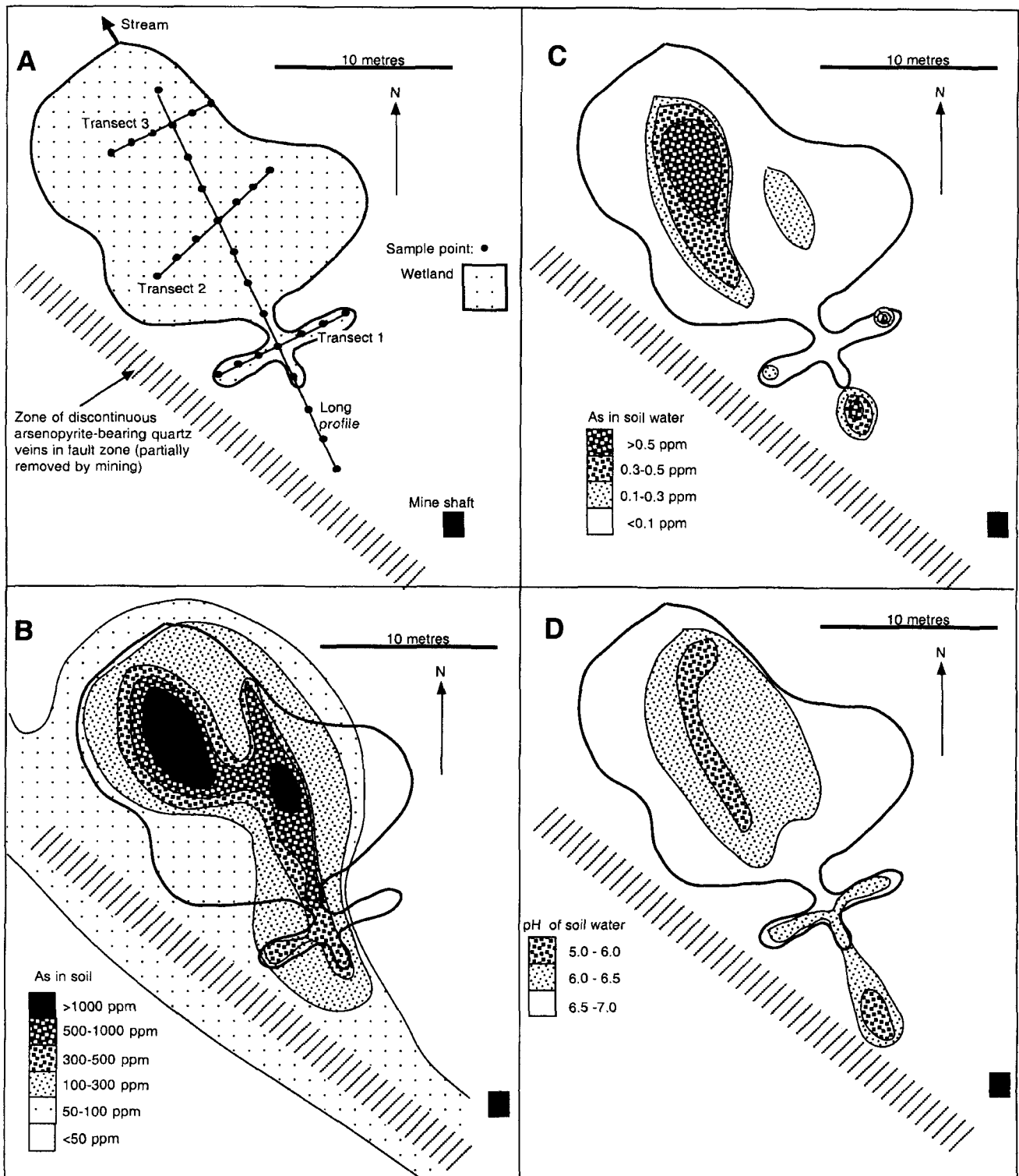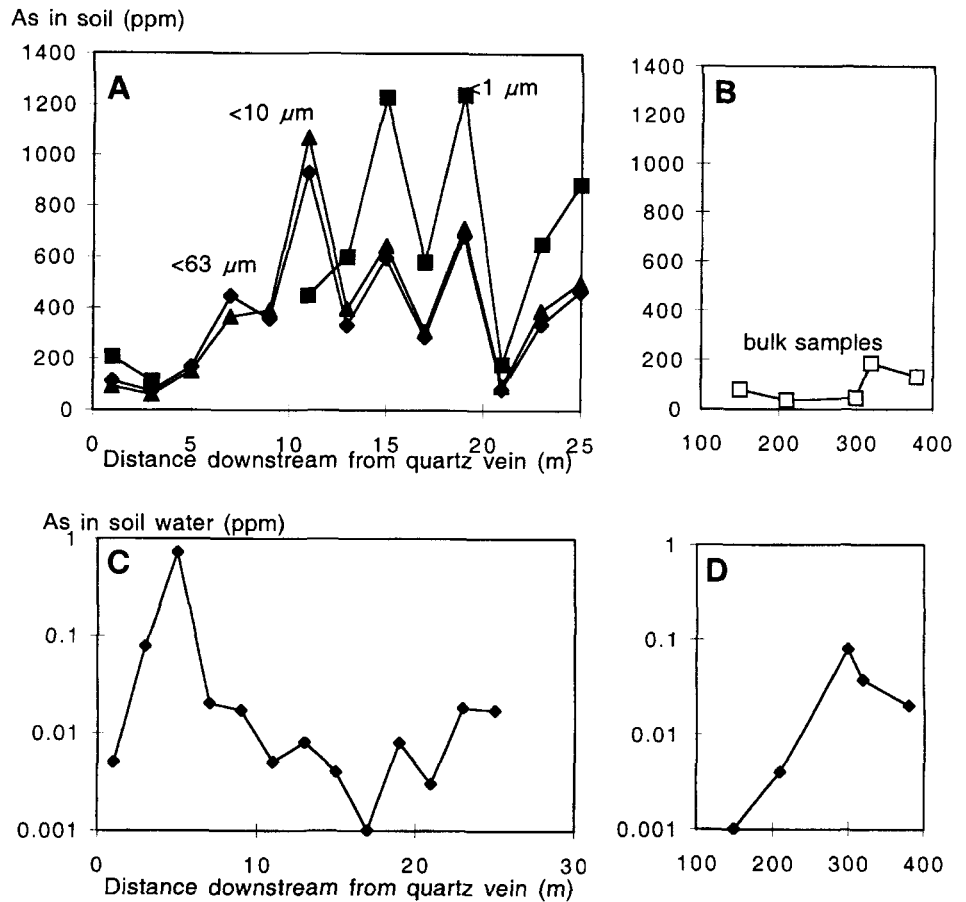
Fig. 6 Sketch maps of the studied wetland in the Barewood #3 mining area (Fig. 1C). **A**, General outline of the wetland in relation to the mineralised vein system, showing the sampling sites. **B**, Contoured (by hand) arsenic content of soils in and around the wetland, based on the sample sites in (A) and the data in Fig. 3. **C**, Contoured (by hand) arsenic contents of wetland soil water extracted by centrifuge. **D**, Contoured (by hand) pH of wetland soils measured *in situ*.

Concentrate decant pond

This pond formed on the surface of the concentrate tailings impoundment and has persisted through the life of the impoundment. The water was derived from the cyanidation plant process, and accumulates as the concentrate tailings dewater immediately after deposition. The tailings slurry develops appreciable dissolved arsenic contents due to dissolution of arsenopyrite (up to 50 000 ppm As) as it passes through the cyanidation process. This process involves some oxidation which produces predominantly As(V) in solution

Fig. 7 Variations in arsenic content of soil and soil water along the length of: (**A**) the Barewood wetland (long profile, Fig. 6A); (**B**) the stream and the pond downstream of the wetland (Fig. 1C); (**C**) the water in the soil in the wetland; and (**D**) the water in the soil downstream of the wetland. Logarithmic scale for C and D.

(Pacheco 1999). While the concentrate impoundment was active, this water was discharged with a pH near 10. Dissolved arsenic contents reached 250 ppm, and were commonly over 100 ppm (Craw et al. 1999). When the concentrate impoundment was not in use, the arsenic-rich

Fig. 8 Arsenic content of soil, and water centrifuged from that soil, along transect 3 in the Barewood wetland (Fig. 1C). Logarithmic scale.

decant pond water was commonly recycled but discharged into the flotation tailings impoundment. The concentrate decant pond has been maintained to partly cover the tailings, but influx of fresh water has periodically diluted the arsenic content to c. 10 ppm, and pH has dropped to near 8.

The surface of the concentrate tailings dried over 4 years of inactivity where the decant pond has receded due to water recycling. This surface zone has undergone some oxidation, with development of secondary iron oxyhydroxide, gypsum, and scorodite. Scorodite is most abundant in a dry crust (10–20 mm thick), where it forms pale-green smears (few micrometres thick) on tailings depositional bedding surfaces, mixed with, or separate from, iron oxyhydroxide smears. Some of this scorodite coats desiccation cracks formed perpendicular to the tailings surface, also with iron oxyhydroxides.

Concentrate tailings pore water

Some of the concentrate tailings water was trapped as pore water in the settling sediment. Samples of this water, extracted by centrifugation from tailings sediments up to 2 m below surface, have pH between 7 and 10 (Craw et al. 1999) and dissolved arsenic contents between 4 and 140 ppm (Fig. 10).

Centimetre-scale iron oxyhydroxide-rich oxidation bands, with variable scattered gypsum grains, cut irregularly across depositional banding in these partially dried tailings (Craw et al. 1999). These bands occur sporadically to depths of up to 1.5 m below the surface, where the tailings are being evaporatively dried via desiccation cracks. Scorodite
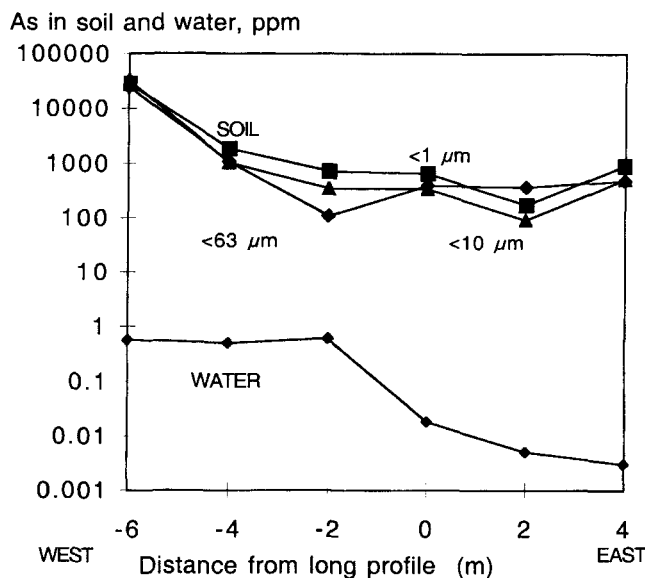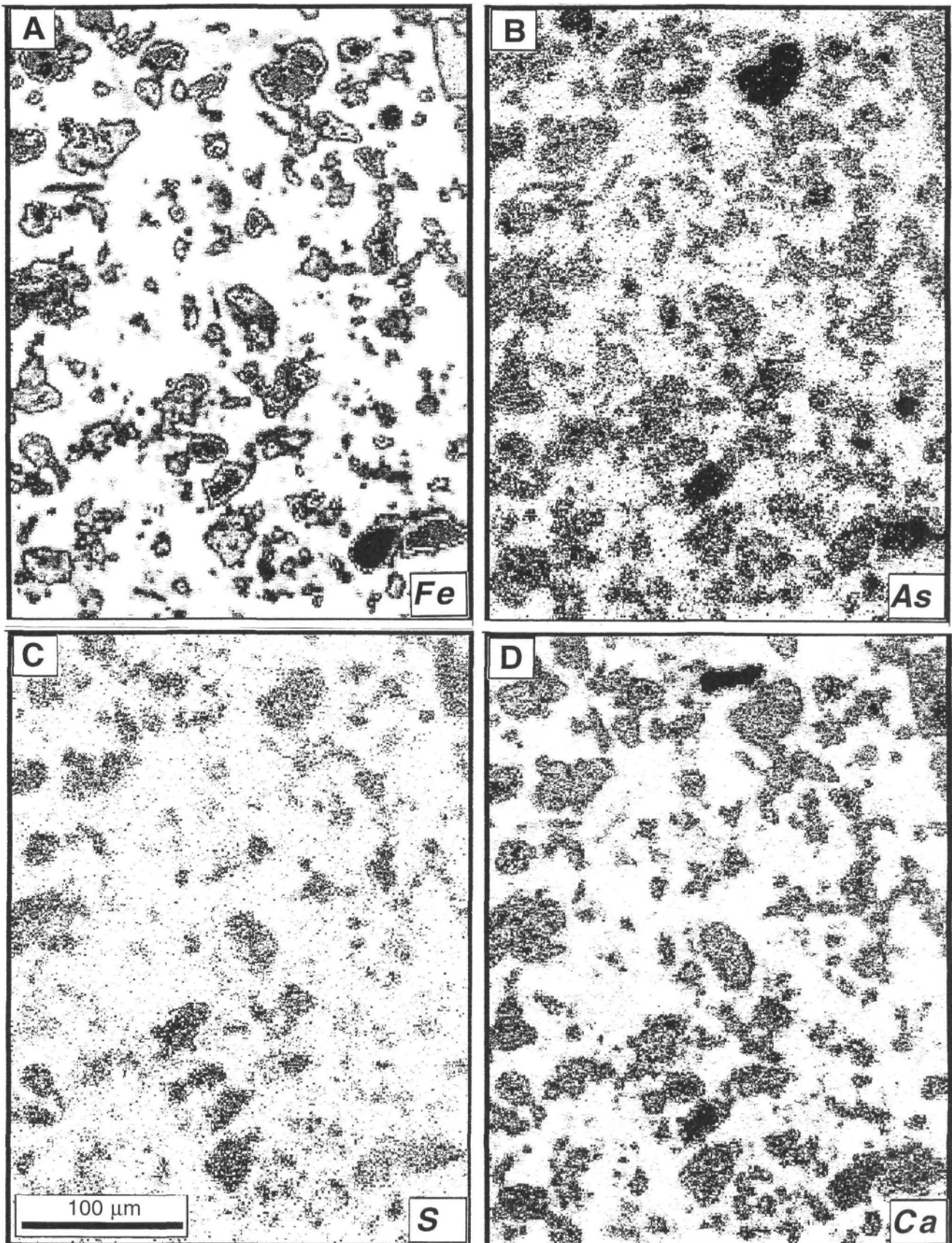
Fig. 9 Microprobe element maps showing distribution of Fe (**A**), As (**B**), S (**C**), and Ca (**D**) in a portion of an epoxy resin mount of dried tailings from the west end of transect 3 in the Barewood wetland (Fig. 1C) (see text). Horizontal width is 0.3 mm and vertical width is 0.4 mm.
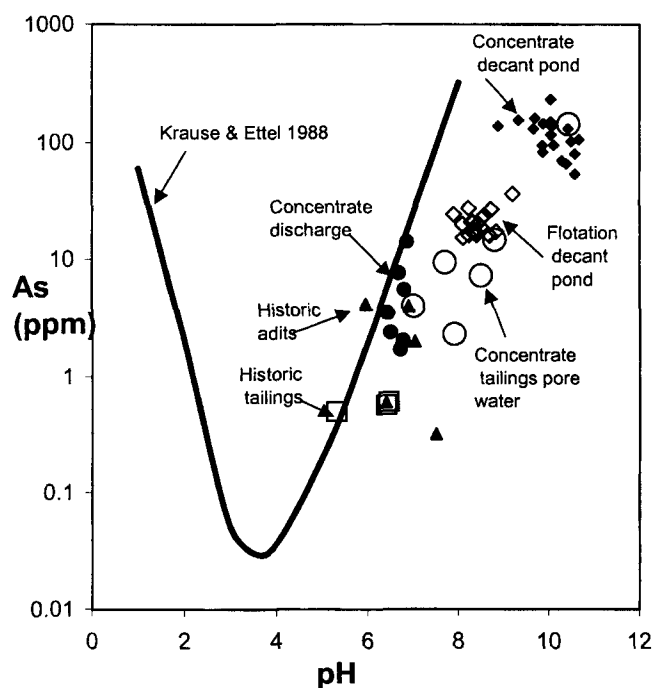
Fig. 10 Summary diagram showing the variations of maximum dissolved arsenic concentrations with mine water pH for historic tailings at Barewood (open squares), historic adits at Barewood, Nenthorn, and Macraes (filled triangles), and modern tailings waters at Macraes (as labelled), as outlined in the text. The laboratory-determined scorodite dissolution curve from Krause & Ettel (1988) is shown for comparison. The part of this curve above pH of c. 2 is for incongruent scorodite solubility to form iron oxyhydroxide and dissolved arsenic.

commonly accompanies the iron oxyhydroxide bands (Craw et al. 1999). The scorodite is very fine (sub-micrometre grains) and intimately intermixed with tailings minerals and iron oxyhydroxides, and is too fine grained for optical resolution of individual grains. No X-ray diffraction confirmation has been possible because the tailings contain a wide variety of crystalline minerals, silicates, and sulphides, which interfere with the scorodite diffraction spectrum. The scorodite was identified by electron microprobe scanning and elemental mapping, which showed that the green material consists of iron and arsenic, but no sulphur.

Concentrate tailings discharge water

Process water lost from the concentrate tailings by leakage through the impounding dam passed through permeable zones in the dam to collection systems at the base of the structure. The discharging water mixed with natural surface water and groundwater, which lowered the pH of the mixture to between 6 and 7. The discharging water mixture had arsenic concentrations up to 12 ppm (Fig. 10).

Flotation decant pond

Most tailings are discharged to the larger flotation tailings impoundment, upon which a large decant pond has formed. This decant pond has had pH between 8 and 9 for most of its life, and low arsenic contents (<5 ppm). This is because flotation tailings typically have relatively low arsenic contents (<500 ppm) compared to the concentrate tailings.

However, when concentrate tailings were mixed with the flotation tailings, dissolved arsenic in the flotation decant pond rose to >20 ppm at times (Fig. 10).

DISCUSSION AND CONCLUSIONS

Arsenic attenuation in soil

Arsenic is known to be readily adsorbed onto surfaces of minerals such as clays (Xu et al. 1991; Sadiq 1997) and iron oxyhydroxides (Hem 1977; Bowell 1994; Webster et al. 1994), particularly at pH of 5–7 (Xu et al. 1991; Bowell 1994). Hence, in all the settings described in this paper, arsenic adsorption should be expected. Because of the high solubility of secondary arsenate minerals (see below), it is not possible to test this experimentally. Also, natural wet-dry cycles in the unsaturated zone may cause arsenic adsorbed onto iron oxyhydroxide to precipitate as crystalline or amorphous arsenate minerals such as scorodite or pharmacosiderite (Craw & MacKenzie 1992). Similar reactions may occur during sample preparation for analysis. Low levels of arsenic in iron-rich grain rims of the Barewood tailings (Fig. 9A, B) may be due to these processes. Attenuation of arsenic in soils in this environment is clearly a combination of adsorption and localised (temporary) formation of secondary arsenic minerals.

Despite the difficulties in defining the precise nature of arsenic attenuation processes, the analytical data (above) allow some quantification of the magnitude of attenuation of arsenic by soil around the old mine workings. It is notable that soil arsenic contents are typically <200 ppm, and are only rarely up to 1000 ppm (Fig. 3, 4), whereas the primary veins have up to 10 000 ppm As (Fig. 3) (Lee et al. 1992). These levels indicate that there has been major loss of arsenic in solution from the soil over geological time. The remaining arsenic represents a combination of attenuated arsenic in temporary sites, and relict vein material.

Arsenopyrite in the mineralised veins is typically coarse grained, especially at Nenthorn and Barewood, where grains up to 3 mm are common. We suggest that remnants of these coarse grains are responsible for the relatively high arsenic contents of some of the coarser fractions of the soils sampled over a mineralised vein at Nenthorn (Fig. 4, A–D fractions). These remnants may be arsenopyrite or scorodite pseudomorphs of arsenopyrite. Some adsorption of arsenic onto iron oxyhydroxides in these fractions is also probable. In contrast, the moderate arsenic levels in the finest fraction (Fig. 4, J fraction) are probably due almost entirely to adsorption or arsenate precipitation onto the iron oxyhydroxides and clays which dominate the fine fraction in these soils (Churchman 1978). Lithic soil from near an adit entrance shows a similar pattern of high adsorbed arsenic in the fine fraction (Fig. 4). If this interpretation is correct, further decomposition of any relict material should progressively decrease the anomalous levels of arsenic in the coarse-grained material, while the arsenic levels in the finest fraction could remain approximately constant or increase as arsenic passes from primary minerals to adsorption onto fine-grained minerals.

Wetland soil at the entrance to the Nenthorn adit (Fig. 5) is in an ideal setting to adsorb arsenic from water passing through the wetland from the adit. The wetland soil is generally finer grained with no coarse fractions, compared to soils from the nearby vein (Fig. 4), as it is clay-mineral-

rich silt and mud deposited in a wetland setting. The arsenic contents of all size fractions (Fig. 5) are higher than equivalent size fractions in the vein soils (Fig. 4), suggesting substantial attenuation of arsenic in this wetland setting of 100s or even 1000s of ppm. The apparent antithetic variation in soil and water arsenic contents in Fig. 5 may have some significance, and a direct chemical relationship between soil and water is possible. Similar but more subtle relationships may exist in the Barewood wetland (Fig. 7A, C).

The degraded tailings at the western end of transect 3 at Barewood (Fig. 8) appear to have preserved most of their primary arsenic content, with formation of arsenate minerals, mainly scorodite. Adsorbed arsenic may have also become attached to the numerous grains of iron oxyhydroxide in these tailings (Fig. 9). Presence of phosphorus in some of these grains may attest to adsorption competition between arsenate and phosphate ions (Peryea & Kammereck 1997). Farther from these tailings, Barewood wetland soils show a similar pattern of higher arsenic in the fine-grained fraction (Fig. 7A, 8) to that in natural arsenic-rich soils (Fig. 4), probably due to adsorption. However, the soil within the tailings is fine grained (Fig. 8) and is readily suspended in water, so widespread physical dispersal through the wetland may have occurred. Hence, the high levels of arsenic in wetland soils (Fig. 7A) may be partly due to physical input of arsenic-rich sediment as well as adsorption/arsenate deposition.

Limits to dissolved arsenic

Despite the widespread decomposition of arsenopyrite in old mine workings described above, dissolved arsenic concentrations never exceed a few parts per million. Arsenic concentration control by scorodite formation in degraded mine tailings has been suggested by Dove & Rimstidt (1985), and similar control is suspected in east Otago. This type of control is implied by data in Fig. 8, which show that, despite an increase in soil arsenic concentration of 2–3 orders of magnitude along transect 3 at the Barewood wetland (Fig. 6A), the arsenic concentration of the pore water reaches a limit of c. 0.75 ppm. This dissolved arsenic limit occurs for a pH of c. 5.3–6 and lies on the solubility curve for scorodite (Krause & Ettel 1988) (Fig. 10). Likewise, water discharged from old adits in east Otago generally has pH near 6–6.5, at which scorodite solubility is slightly higher (1–4 ppm) than in the Barewood wetland tailings (Fig. 2, 10). Measured redox potential at these sites (above) suggests that at times of sampling, As(V), the oxidation state of arsenic in scorodite, was stable (Bowell 1994; Vink 1996). The presence of scorodite in the old workings and old tailings (above) shows that oxidised conditions prevail at other times as well.

At higher pH, scorodite solubility increases dramatically (Fig. 10) (Krause & Ettel 1988), and no observed Otago water compositions approach the experimental curve. However, it is notable that maximum observed dissolved arsenic concentrations increase with increasing pH (Fig. 10). Scorodite has precipitated in Macraes mine concentrate tailings where evaporation has increased local arsenic concentrations (as As(V); Pacheco 1999) to levels even higher than those observed.

Deposition of scorodite may limit arsenic discharge into waterways, particularly at low pH of the old mine sites in this study. This limitation of dissolved arsenic may be due

to scorodite solubility and/or kinetics of scorodite dissolution. Attenuation by iron oxyhydroxides and phyllosilicate minerals is important at the same sites, however. Downstream dilution is also an important part of pollution remediation, and is reliable except in times of drought.

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