Arsenic in mine waters: an international study

M. Williams

Abstract Hydrochemical data are presented for arsenic (As) in the mine waters of 34 gold and base-metal mining localities in seven countries of south-east Asia, Africa and Latin America, encompassing contrasting climatic settings and at least eight discrete styles of primary mineralization. Peak dissolved As concentrations at these sites range from 0.005–72 mg/l, with the United States Environmental Protection Agency (US-EPA) potable water threshold of 50 μg/l exceeded in 25 cases. Arsenate (As^{5+}) constitutes the dominant species at over 80% of sites. Very high dissolved As concentrations (>1 mg/l) show no systematic between-site relationship with mine water pH/Eh regime. Important determinants of mine water As fluxes include iron hydrochemistry, the presence of cyanic ore processing effluents, site geology, the paragenetic sequence that follows sulphide oxidation, climate and mine management. Human toxicological impacts of As contamination have been recognized at only one case-study site, with a further four considered to warrant more detailed risk assessment.

Keywords Arsenic · Mine waters · Mobility · Speciation · Toxicity

Introduction

Arsenic is a metalloid element with an average crustal abundance of 1.8 mg/kg (Greenwood and Earnshaw 1984). It is strongly chalcophile and can attain percentage-range concentrations in sulphide ore assemblages, most commonly in the form of arsenopyrite (FeAsS) or mono-metallic sulphides such as realgar (As_4S_4). The exploitation of gold and base-metal deposits and the attendant oxidation of As-bearing ore and gangue minerals has been highlighted as a cause of As contamination of surface drainage and groundwater in several countries (Thornton 1994; Williams and Smith 1994; Williams and others 1996). Fergusson (1990) has cited a natural concentration range of 1–10 μg/l for uncontaminated waters, rising to 0.1–5.0 mg/l in many mining areas.

The aqueous chemistry of As differs significantly from most true metals. Inorganic As is predominantly oxyanionic in solution, with pentavalent (arsenate) species (e.g. $H_2AsO_4^-$) stablized at moderate and high redox potentials and trivalent (arsenite, H_3AsO_3) species occurring under reducing conditions at low or circum-neutral pH levels. The kinetics of As^{3+}–As^{5+} transformations are, however, slow, and disequilibrium is common (Fergusson 1990). In addition to its aqueous charge properties, As can be contrasted from most heavy metals by its solubility across a wide pH range (1–12). Contamination of mine waters by As is thus not a hazard exclusively associated with the generation of acid mine drainage (AMD).

The toxicological properties of As have been known for centuries (Abernathy 1993). Symptoms of chronic As poisoning have been recorded in populations reliant on water supplies containing >50 μg/l As in several countries including Chile (Borgoni and others 1980), Mexico (Cebrian and others 1983), Taiwan (Chen and others 1988, 1994), India (Chakraborty and Saha 1987) and Thailand (Williams and others 1996). This value currently constitutes the permissible limit of the European Union (EU), the United States Environmental Protection Agency (US-EPA) and most national governments with respect to As in potable water. Epidemiological evidence of adverse effects at lower exposure levels has, however, prompted the World Health Organization to promote an interim guideline of 10 μg/l (Van Leeuwen 1993).

During the period 1992–1995 the British Geological Survey (BGS) initiated hydrochemical surveys of areas of gold and complex sulphide mining in Malaysia, Thailand, the Philippines and Zimbabwe as a first step towards the quantification of mining-related As hazards worldwide. In 1996, this work, funded jointly by the UK Department for International Development (DFID) and the governments of the host nations, was extended to Argentina, Brazil and Ecuador. This paper summarizes the results of these studies, undertaken using standardized techniques across three continents, and outlines the controls of As mobility, speciation and toxicity in mine waters in the contrasting climatic and geological settings encountered.

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Case-study areas

Data are presented for 34 mining localities (Table 1) with latitude and altitude ranges of 16°N–35°S and 50–2200 m, respectively. Climatically, 25 sites (in Malaysia, Thailand, the Philippines, Brazil and Ecuador) are humid tropical, those in Zimbabwe experience seasonally dry savannah conditions, and those in Argentina lie within a semi-desert regime. The geological settings range from Archean to Tertiary in age (excluding placer deposits of Quaternary to recent origin), with at least eight discrete styles of primary mineralization represented (porphyry, skarn, epithermal vein, shear-zone-hosted mesothermal lode, volcanogenic massive sulphide, banded iron-formation, disseminated volcano-sediment-hosted, pegmatitic veins). Inevitably, certain deposits fail to fit any single descrip-

Table 1
Summary information for BGS case-study sites indicating the commodity produced, method of extraction and beneficiation, status of operation and style of mineralization. Recovery methods: *G* Gravimetric; *Hg* mercury amalgamation; *FF* froth flotation; *CIP* carbon-in-pulp cyanidation; *HL* heap-leach cyanidation; *CAV* Caveat process; *RP* roasting plant; *n.a.* no on-site processing. Status: *O* operative; *P* prospect; *C* closed. Mineralization: *SZH* shear-zone hosted; *VMS* volcanogenic massive sulphide; *BIF* banded iron-formation

Country	Mine/District	Commodity	Operation	Recovery	Status	Mineralization
Peninsular Malaysia	Penjom	Au	Soil pit and adit	G, Hg	C	SZH-mesothermal lodes (Au–Sb)
	Mengapur	Cu, Fe, Ag	–	n.a.	P	Porphyry/skarn (Fe–Cu–Mo–Pb–Ag)
	Sungai Luit	Au	Alluvial	G, Hg	O	Quaternary placer
Sabah (Malaysia)	Mamut	Cu, Au	Open pit	FF	O	Porphyry (Cu–Au)
	Bidu Bidu	Cu, Au	–	n.a.	P	VMS (Fe–Cu–Au)
Sarawak (Malaysia)	Jugan	Au	Open pit	G, Hg	C	Shale hosted epithermal (Au–As)
	Tai Parit	Au	Open pit	CIP	O	Epithermal replacement or skarn (Au–As)
	Kusa	Au	Adit	CIP	C	Carbonate-hosted epithermal (Au–Sb-As)
	Lucky Hill	Au	Adit	RP, CIP	C	Skarn (Au–Sb–As)
	Tai Ton	Au	Adit	CIP	O	Carbonate-hosted epithermal (Au–Sb)
Thailand	Ron Phibun	Sn	Adit/alluvial	FF	SO	Pegmatite veins and placers (Sn–As–W)
	To Mo	Au	Adit	CIP	O	Epithermal (Au–Ag–As–Sb–Ni)
	Pin Yo	Pb, Zn	Adit	CAV	O	Skarn (Sn)
Luzon (Philippines)	Santo Tomas II	Cu, Au	Open pit/adit	FF	O	Porphyry (Cu–Au)
	Antomok	Au	Open pit	CIP	O	Epithermal (Au–As–Cu–Cd)
	Dizon	Cu, Au	Open pit	FF	O	Porphyry (Cu–Au)
Palawan (Philippines)	Santa Lourdes	Hg	Open pit	RP	C	Stratiform marine exhalative (Hg)
Mindanao (Philippines)	Gango	Au	Adit	CIP	O	Epithermal (Au)
	Mainit	Au	Alluvial	G, Hg	O	Epithermal (Au)
	Diwalwal	Au	Adit	CIP	O	Epithermal (Au–As–Cu)
Zimbabwe	Bunyip	Au	–	n.a	P	SZH mesothermal lodes (Au–As)
	Cricket/One step	Au	Open pits and adits	CIP	O	SZH mesothermal lodes (Au–As)
	Indarama	Au, Sb	Shaft and drive	RP, HL	O	SZH mesothermal lodes (Au–Sb–As)
	Globe and Phoenix	Au	Shaft and drive	HL	O	SZH mesothermal lodes (Au–As–Sb–Pb–Zn)
	Wanderer	Au	Adit	RP, HL	SO	BIF (Fe–Au)
	Shamva	Au	Shaft and drive	CIP	O	SZH mesothermal lodes/disseminations (Au)
	Iron Duke	Fe, Au	Adit	n.a.	O	BIF (Fe–Au)
Argentina	Colo-Colo, San Juan	Pb, Zn	Adit	RP	C	Mesothermal lodes
	Mendoza (various)	Pb, Zn	Adit	RP	C	Mesothermal lodes
Ecuador	Ponce Enriquez	Au	Adit	CIP	O	Mesothermal lodes (Au–As–Sb–Pb–Cu–Te)
	Nambija	Au	Adit	CIP	O	Skarn and post-skarn epithermal (Au)
	Portovelo	Au	Adit	CIP	O	Meso- (Au–As–Pb–Cu) and epithermal (Au)
Brazil	Passagem	Au	Adits	n.a.	C	SZH mesothermal lodes (Au–As–Cu)
	Morro Velho	Au	Open pit	RP, CIP	O	SZH-lode and BIF-related (Au)

tion, or are of uncertain origin. Such problems are highlighted at Mengapur (Malaysia), which exhibits both porphyry and skarn characteristics, Portovelo (Ecuador) which hosts mesothermal polymetallic mineralization with clear epithermal overprints (Pratt and others 1997), and Tai Parit (Sarawak) where siliceous hydrothermal carbonate replacements with skarn characteristics grade to lower temperature jasperoid mineralization with possible Carlin-type affinities.

At the time of sampling, 24 case-study areas hosted operational mines, seven were no longer worked and three remained at the prospect evaluation stage. Gold constitutes either the principal or secondary commodity at all but one of the operative/former extractive sites. Heap-leach (HL) or carbon-in-pulp (CIP) cyanidation technology is, or has been, deployed for Au recovery in over 50% of cases. Froth flotation is deployed at the Cu-Au porphyry mines of Mamut (Malaysia), Santo Tomas II and Dizon (Philippines). Amalgamation of Au with mercury is widely practised at alluvial mining centres such as Sungai Luit (Malaysia) and Mainit (Philippines).

Methodology

Standardized sampling and analytical procedures were applied in all case-study areas, thus maximizing between-site data comparability. Surface waters were drawn directly into a sterile 30-ml polyethylene syringe, then passed through a Millipore 0.45-µm cellulose acetate membrane into a high density polyethylene (HDPE) storage bottle (Nalgene). In localities in which groundwaters were collected, tube wells were pumped continuously for at least 10 min prior to sampling.

Three 30-ml samples were collected at all sampling stations, one of which was acidified with 1% v/v HCl (ARISTAR), another with 1% v/v HNO_3 (ARISTAR), and the third was retained unmodified. Surface water and groundwater pH and Eh values were determined in the field using temperature-compensated glass calomel and Pt electrodes linked to a Radiometer Instruments datalogger. Calibration of the electrodes was undertaken prior to each measurement using buffer solutions of pH 4, 7 and 9, and a 230-mV potassium ferricyanide redox standard.

Total As was initially determined by inductively-coupled plasma emission spectrometry (ICP-ES) analysis of HCl-acidified waters to a practical detection limit of ca. 50 µg/l. Samples holding As at concentrations of <50 µg/l were subsequently re-analysed by hydride-generation atomic absorption spectrophotometry (HG-AAS) to a detection limit of 0.2 µg/l. The proportion of As present as As^{3+} was determined through HG-AAS analysis of subsamples of HCl-acidified water following saturation with ZrCl (an As^{5+} and organoarsenic suppressant). The contribution of As^{5+} was then calculated by subtraction of the As^{3+} value from the total As concentration.

A suite of 15 major and trace cations (Ca, Na, Mg, K, Fe, Mn, Al, Cd, Zn, Cu, Pb, Co, Ni, V, Cr) was determined by ICP-ES analysis of HNO_3-acidified samples. The major anions, Cl, SO_4 and NO_3, were analysed by ion chromatography using unacidified waters.

Results and discussion

Inter-site As concentration range

The maximum aqueous As concentration recorded in each case-study area is given in Table 2. Between-site variations of As concentration span more than four orders of magnitude. The US-EPA potable water limit is exceeded in 25 instances, whereas the 400-µg/l threshold indicated by Fergusson (1990) as critical for the protection of aquatic life is exceeded at 13 sites. The maximum As value of 72 mg/l, recorded at Iron Duke mine, Zimbabwe, constitutes the highest dissolved As concentration published to date for mine waters worldwide (Williams and Smith 2000).

Arsenic speciation

Arsenate (As^{5+}) species were found to be the dominant form of dissolved inorganic As (>50% of the total load) at 29 of the 34 case-study sites. Of these, 19 yielded arsenite (As^{3+}) concentrations equivalent to <5% of total As. Predictably, highest As^{3+} contributions (50–95% of total As) were recorded in waters with redox potentials of <200 mV, exemplified by Lucky Hill (Sarawak), Antomok (Philippines), Diwalwal (Philippines), Colo-Colo (Argentina) and Morro Velho (Brazil).

Hydrochemical controls of As concentration and mobility pH/Eh regime

The 34 BGS case-study sites provide an insight into the hydrochemistry of As under widely differing pH and Eh regimes, with values ranging from 0.52–10.0 and –180–692 mV respectively. The occurrence of anomalous dissolved As concentrations across these ranges confirms that neither pH nor Eh are universal determinants of As mobility. Data presented in Table 2 show three of the ten study locations yielding As values of >1 mg/l to be characterized by pH values of less than 4, with four in the range of 4–8, and two in the pH range of 8–10. With respect to Eh, values in excess of 1 mg/l As are reported for mine waters ranging from mildly reducing (135 mV) to strongly oxidizing (634 mV). These trends are consistent with thermodynamic calculations for the As-S-O-H system (Fig. 1), which indicate the stabilization of soluble oxyanionic As species at pH levels of <1 subject to a redox potential of >400 mV, and at pH 10, given Eh within the range –150–700 mV (Brookins 1988).

While no systematic intersite correlation exists between pH or Eh and the dissolved As loading of mine waters, both variables have been observed to exert an important control on As mobility and attenuation within individual BGS case-study areas. The influence of pH is typically indirect, affecting As by regulating the saturation indices of

Table 2
Maximum concentration and speciation of As and other selected physico-chemical parameters in mine drainage at 34 BGS case-study sites. Data are for surface waters unless otherwise indicated. As^3 values reflect the maximum percentage of total As present as arsenite. Note: Quoted values for pH and Eh are those recorded in the sample yielding the maximum total As concentration. Values for other parameters (including As^3) represent maxima for each case-study area and are thus not necessarily coincident with the quoted As concentration. Blanks signify parameter not determined

Country	Mine	Survey date	Stations	As (μg/l)	As^3 (% total)	pH	Eh (mV)	Fe (mg/l)	Cu (μg/l)	SO$_4$ (mg/l)	Others (mg/l)
Malaysia	Penjom	09.92	31	2970	<5	2.5		27	<10		
(Peninsular)	Mengapur	09.92	9	82	<5	6.6	420				
	Sungai Luit	10.92	8	12	<5	6.2	410				
Sabah (Malaysia)	Mamut	08.93[b]	50	30	38	2.6	611	443	299,000	14,799	Al 1196, Co 6, Ni 15, Zn 90
	Bidu Bidu	06.94	12	365	<5	3.7		1.1	27,050		
Sarawak	Jugan	09.93	17	2910	<5	2.1	435	655	1020	3484	Zn 4.7
(Malaysia)	Tai Parit	09.93	12	460	<5	5.5	370	<1	<10		
	Kusa	10.93	8	1112	<5	6.6		<1	<10		
	Lucky Hill	10.93	12	713	93	7.1	135	<1	<10	2	
	Tai Ton	10.93	4	320	<5	6.3	410	<1	<10		
Thailand	Ron Phibun[a]	08.94[b]	49	5114	39	6.6	366	0.02	91	39	
	To Mo	09.94	10	410	11	5.7		<1			
	Pin Yo	09.94	9	306	<5	7.1		<1			
Luzon (Philippines)	Santo Tomas II	06.94	13	5	<5	2.7	630	373	25,419	4698	Al 425, Co 3.1, Zn 4.2, Ni 0.6
	Antomok	07.94[b]	7	25	60	10.0	100	0.04	9656	1219	Na 236, Mo 125,
	Dizon	07.94	9	63	<5	2.1	692	434	98,964	5326	Zn 7.2, Ni 1.1, Co 1.1
Palawan (Philippines)	Santa Lourdes[a]	12.95	10	40		4.5	510	0.06		245	
Mindanao	Gango	07.95	9	36	<5	6.7	535	0.06	8.2	<1	
(Philippines)	Mainit	07.95[b]	10	20	<5	7.7	554	0.12		33	
	Diwalwal	08.95[b]	21	120	95	8.4	−180	3.09	101	33	Hg 2.9
Zimbabwe	Bunyip	03.93	6	220	<5	5.1		<1	<3		
	Cricket/One step	03.93	9	1005	<5	5.5		<1	<3		
	Indarama	04.93	6	710	<5	5.0		<1	<10		
	Globe and Phoenix	03.93[b]	14	7400	40	8.2	272	0.51	34,467	9194	Na 632, Ni 16, Zn 29, Sb 15
	Wanderer	04.93[b]	5	480		3.9		9.1	21		
	Shamva	03.94	17	325	<5	3.5	530	25.5	145		
	Iron Duke	04.94[b]	13	72,000	3	0.52	634	132,909	20,087	355,425	Al 12,003, Cd 3.7, Zn 55, Ni 24, Cr 18, V 23
Argentina	Colo-Colo, S. Juan	05.97	7	140	50	8.47	196	0.01	<3	211	
	Mendoza (various)	05.97	10	24		8.1	336	0.08	<3	370	
Ecuador	Ponce Enriquez	06.96[b]	35	430		8.1	342	0.16	7277	109	
	Nambija	11.96	12	90		7.1	270	0.98	3	172	
	Portovelo	06.96	5	1200		6.9		<1	27		
Brazil	Passagem[a]	06.97	5	1700	56	7.8	209	0.08	<3	5	
	Morro Velho[c]	06.97	10	7300	50	9.0	35	0.05	1820	1038	

[a] Sites include both surface and groundwater data
[b] Sites were subject to multiple surveys
[c] Sites include tailings pound waters. Survey dates indicate the month and year of the initiation of monitoring

other solutes such as Fe (see below), with which As is prone to coprecipitate. Redox variations in mine waters produce an analogous effect, particularly across the critical ferric-ferrous Fe threshold. A direct Eh control is, however, probable caused by the differential adsorption-desorption of As^{3+} and As^{5+} species (Bowell 1994). Redox-augmented As enrichment in mine waters of moderately high pH (>6.0) has been inferred from the hydrochemical data for several BGS case-study sites in south-east Asia, notably the epithermal and skarn Au-As-Sb deposits of Lucky Hill, Tai Ton and Kusa in the Bau District of Sarawak (Williams and Breward 1995). All are carbonate hosted and mine waters are thus comprehensively buffered at, or very near their source. The surface waters in these localities are, however, relatively eutrophic with high algal productivity and low levels of dissolved oxygen. At Lucky Hill (Fig. 2), a 100-fold increase of dissolved As in a downstream channel section was

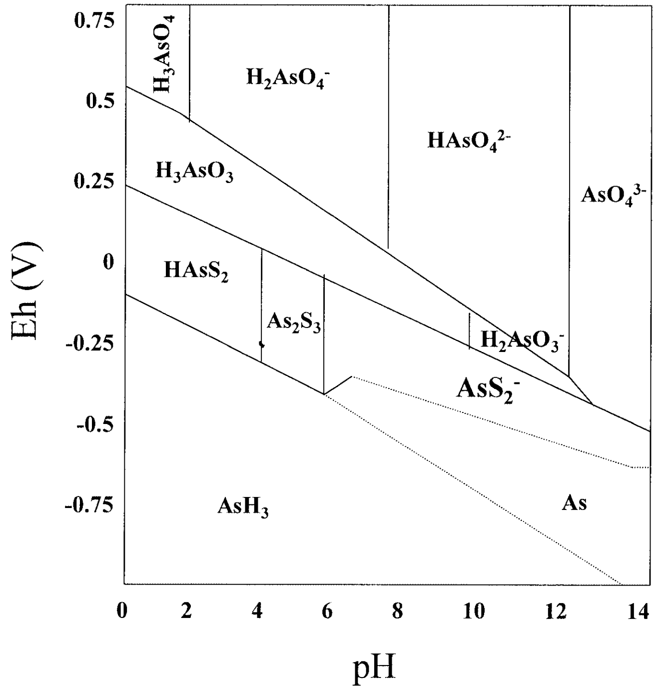

Fig. 1
pH-Eh diagram for the As-S-O-H system (after Brookins 1988)

found to be coincident with a 10-fold reduction of the percentage contribution of As^{5+} to the total As load (i.e. an increase in the significance of arsenite species). No significant fluctuation of pH was recorded; however, Eh values were found to fall from ~400 mV immediately upstream of the mine, to between 100 and 200 mV downstream (Williams and Breward 1995).

Fe hydrochemistry

The dynamics of Fe constitute an important control on aqueous As mobility, particularly in acid ($pH < 4.0$) ferruginous mine waters, exemplified in the BGS database by Iron Duke and Wanderer (Zimbabwe), Penjom (Malaysia), and the porphyries of Mamut (Malaysia) and Dizon (Philippines). During BGS surveys, these sites yielded peak dissolved Fe concentrations (mainly present as uncomplexed Fe^{2+} and $FeSO_4^{aq.}$; Williams and others 1994; Williams and Smith 2000) in the range 9–132,909 mg/l, with corresponding pH values of 0.52–3.5. At Iron Duke, Wanderer and Mamut, the precipitation of this substantial Fe load at downstream distances of 50 m to 5 km from AMD sources has been shown to prompt a one- to two-order of magnitude reduction in the concentration of dissolved As.

The controls on, and solid products of, Fe precipitation in mine waters at the above sites vary substantially. At Iron Duke (Zimbabwe) and Mamut (Malaysia), leachate from highly pyritic waste-piles was confirmed by geochemical modelling to be acutely Fe super-saturated, and kinetically constrained precipitation was observed at distances of 20–500 m along the flowpath (Fig. 3). In cases such as Wanderer (Zimbabwe) and Penjom (Malaysia), initially undersaturated waters with an Fe load of ca. 9–27 mg/l, precipitate Fe within a few hundred metres of the mine water source because of buffering and/or dilution through mixing with uncontaminated drainage, rising pH and a consequent reduction of the saturation-indices for thermodynamically favoured Fe minerals. Hydrous oxides such as goethite, limonite and a complex range of poorly/non-crystalline phases have been found to be the dominant Fe precipitates at virtually all BGS case-study sites. However, at Iron Duke (Zimbabwe),

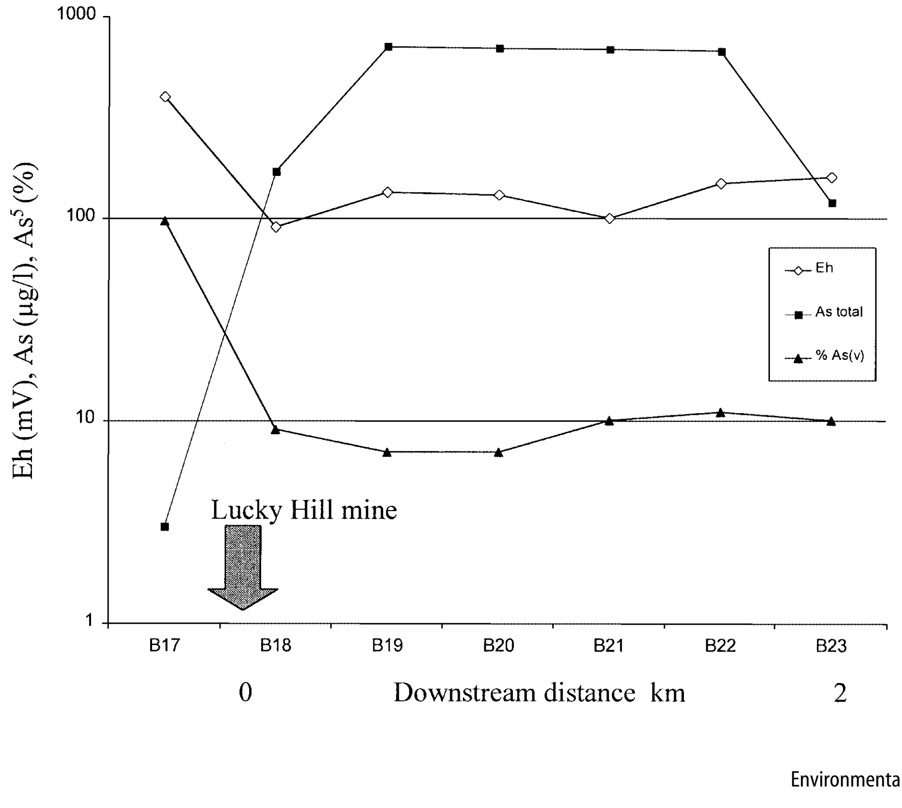

Fig. 2
Total As, As^3 and Eh profiles downstream of Lucky Hill mine, Sarawak, Malaysia

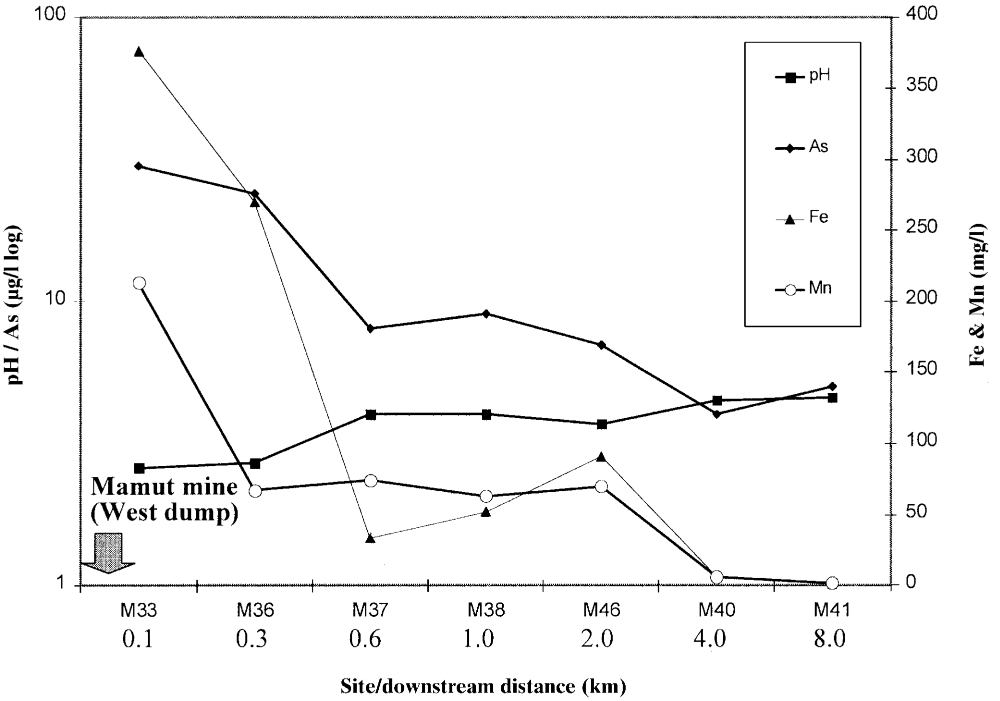

Fig. 3
Total Fe, Mn, As and pH gradients downstream of one of three major waste rock piles at Mamut mine, Sabah, Malaysia. The initial losses of Fe from solution, and the attendant coprecipitation of As, occurs at a kinetically constrained rate. Downstream of station M36, hydrochemical adjustments are predominantly thermodynamically controlled

equilibrium hydrous oxide precipitation is preceded along the mine water flowpath by the precipitation of an Fe sulphate, melanterite ($FeSO_4.7H_2O$), and accounts for the removal of >99% of the initial (super-saturated) Fe load (Williams and Smith 2000).

The heterogeneous surface charge properties of hydrous oxides make them efficient scavengers of both cations and anions in mine waters. The precise mechanisms have been described elsewhere (e.g. Calvert and Price 1977) and may involve coprecipitation, adsorption, surface complex formation, ion exchange and lattice penetration (Ottesen and Theobald 1994). While Mn oxides often precipitate earlier than Fe oxides in mine waters, their isoelectric points are characteristically below 3.0 and they are hence electronegative (i.e. cation scavengers) in all but the most acid systems. For common Fe oxides, including goethite and ferrihydrite, Schwertmann and Fechter (1982) give isoelectric points of >pH 5.0, indicating a propensity for the adsorption of oxyanionic solutes such as H_2AsO_4 at pH levels below this threshold (see Fig. 3).

Aqueous complexing agents

Dissolved As concentrations of >7 mg/l in mine effluents at Globe and Phoenix (Zimbabwe) and Morro Velho (Brazil) have been interpreted as the product of complexation with CN^- derived from HL and CIP cyanidation process waters. These waters, plus those yielding site maxima for As at Ponce Enriquez (Ecuador) and Antomok (Philippines) are conspicuously alkaline and variably rich in Na (derived from the $NaCN^-$ feed), SO_4 and Cu. At Globe and Phoenix (Fig. 4), Williams and Smith (1994) have modelled, using WATEQ4F, the hydrochemistry of alkaline waters (pH 7.5–9.5) impacted by seepage from a HL pad, and confirmed theoretical super-saturation with respect to As, Sb, Cu, Ni and Zn. At this site and elsewhere, this phenomenon has been found to be extremely localized and thus of strictly limited environmental concern. With downstream dilution, falling pH levels (to <7.5) induce the volatilization or oxidation of CN^- and precipitation of the metalloids and heavy metals formerly complexed.

Site geological control of aqueous As concentrations

The strong influence of site geological characteristics, particularly ore and gangue mineralogy and host-rock lithology, on mine water composition is well recognized. Plumlee and others (1993) have summarized first-order controls as (1) the abundance of pyrite and other proton-liberating sulphides, sulphide susceptibility to weathering (a function of structure, stoichiometry, purity and granulometry), (2) orebody and waste permeability (with respect to both H_2O and air), (3) microbial activity and species types, and (4) buffering capacity of gangue minerals and host lithologies (afforded by carbonates, aluminosilicates and hydrous oxides). Such variables interact to produce infinite site-specific scenarios, yet particular metallogenic settings and deposit types have, nonetheless, been shown to yield recurrent mine water drainage signatures with respect to pH and dissolved heavy metal loading (Plumlee and others 1993).

In similar fashion, the range of As concentrations recorded for mine waters incorporated in the BGS study can, to a great extent, be interpreted as a predictable function of site geology. Figure 5 shows the maximum As concentration plotted against pH for each site, and highlights discrete fields for several of the deposit types encountered. A highly arsenical, acid (<pH 4) signature is,

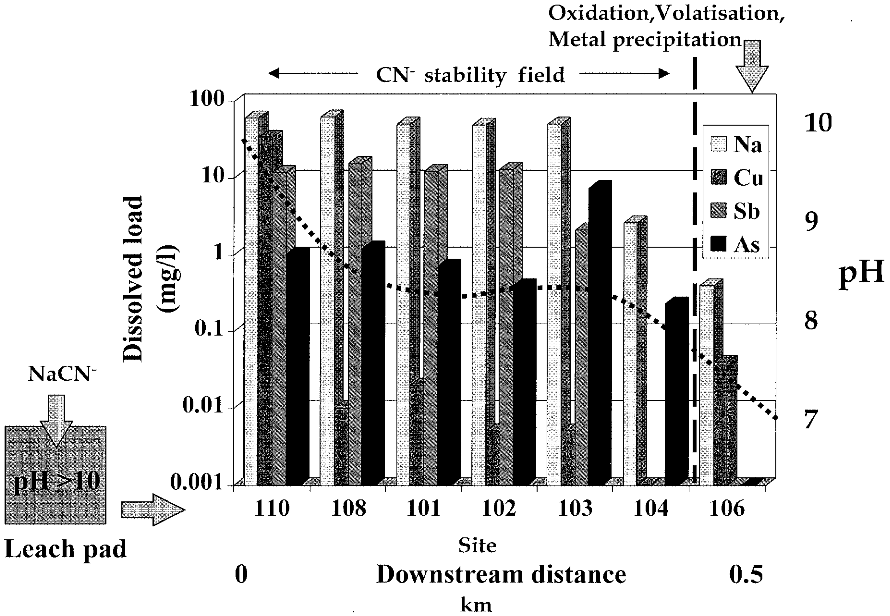

Fig. 4
Total As, Sb, Cu, Na and pH (*dotted line*) in discharge close to a heap-leach cyanidation operation at Globe and Phoenix mine, Zimbabwe. High dissolved As and Sb concentrations in the upper reaches of the drainage may reflect complexation with cyanide. The complexes degrade at pH<7.5, accounting for the loss of As from solution downstream of station 104

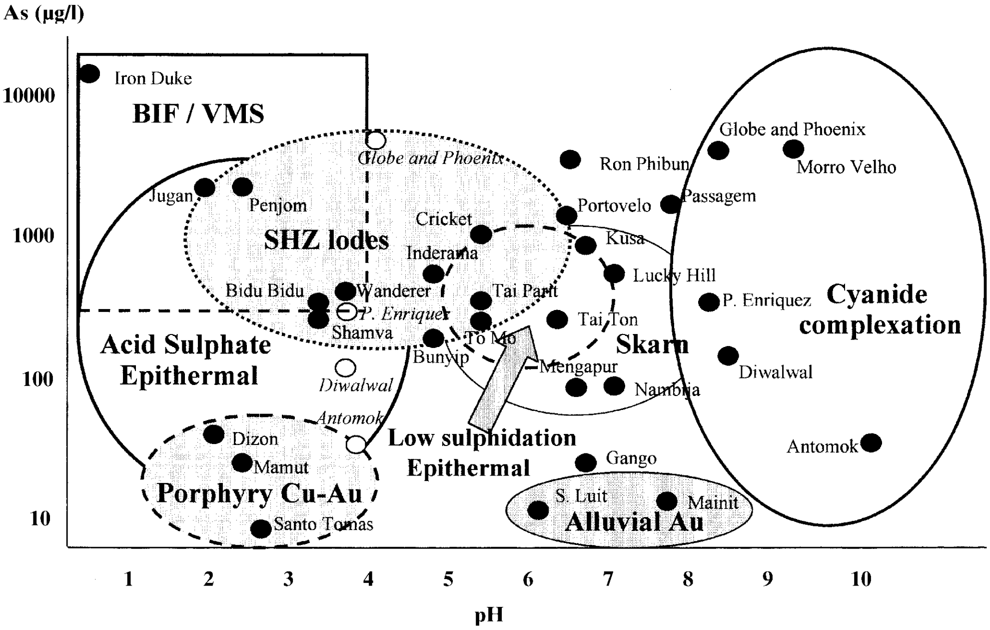

Fig. 5
Peak dissolved As versus pH in mine waters from BGS case-study sites, showing postulated fields for specific deposit types

for example, characteristic of BIF and VMS deposits (e.g. Bidu Bidu, Sabah and Iron Duke, Zimbabwe), whereas the porphyries of Santo Tomas II, Dizon (Philippines) and Mamut (Sabah) plot within a strongly acidic ($pH < 3$), As-poor (< 70 µg/l) field. Most mesothermal shear-zone hosted Au-lode deposits of the Zimbabwe greenstone belts (e.g. Shamva, Cricket, One-Step, Indarama) and Peninsular Malaysia (Penjom) occupy the centre-left of the diagram within a field delimited by pH 2 −5.5 and As 0.3–3.0 mg/l. Other mesothermal lode deposits, such as Globe and Phoenix (Zimbabwe), Ponce Enriquez (Ecuador) and possibly Morro Velho (Brazil), should probably also occupy this field; however, their position along the pH axis is substantially modified by the presence of alkaline Au cyanidation effluents in their drainage waters.

Significance of sulphide oxidation products

The paragenetic sequence that follows the oxidation of As-bearing sulphides exerts a major control on aqueous As mobilization. In most cases arsenopyrite is the primary carrier, the oxidation of which generally results in the in situ formation of scorodite ($FeAsO_4.2H_2O$) or similar ferric arsenate coatings (e.g. Fig. 6a). Scorodite is of limited solubility under most pH/Eh conditions, and its formation has been observed to constrain the generation of As-rich leachates from mine waste at the majority of BGS case-study sites. However, contrasting scenarios have

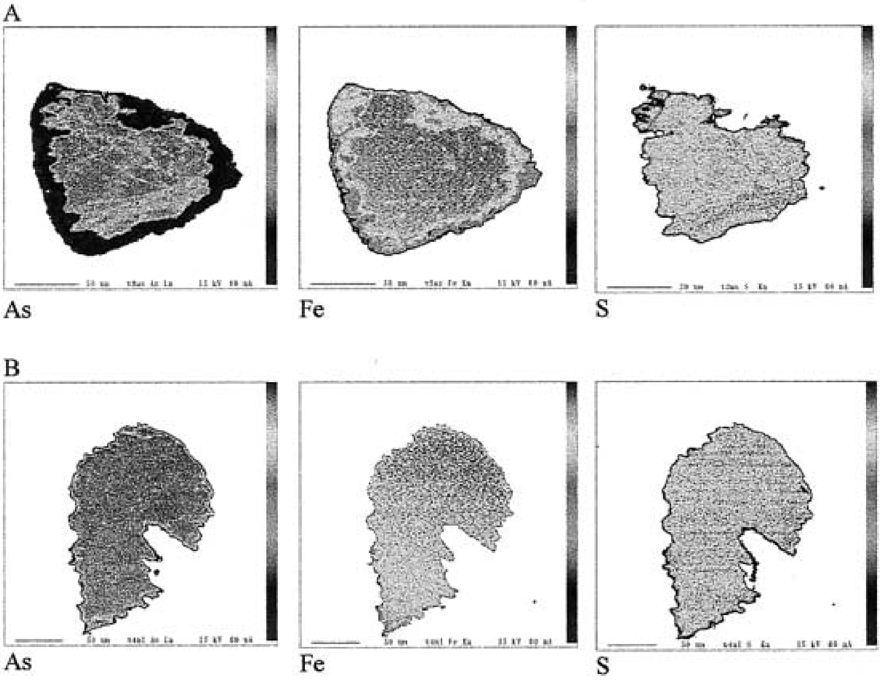

Fig. 6
Microprobe images showing contrasting weathering parageneses of arsenopyrite grains from alluvium near Ron Phibun, Thailand: **A** encapsulation of FeAsS by ferric arsenate,
B degradation through the superficial formation and dissolution of arsenolite

been recorded at Ron Phibun (Thailand), Globe and Phoenix (Zimbabwe) and Kusa (Sarawak), and at least partially account for the severe As contamination of surface waters and shallow groundwaters in these localities (5.1, 7.4 and 1.1 mg/l As respectively, see Table 2). In the former two cases, microprobe studies (Williams 1997) have shown the principal product of disseminated arsenopyrite oxidation in mine tailings and alluvium to be arsenolite (As_2O_3), a high-solubility phase that readily liberates As into the interstitial pore-waters (Fig. 6b). At Kusa, ore deposition from highly alkaline, reducing hydrothermal fluids has produced an unusual primary assemblage dominated by native As and the monometallic sulphides realgar (As_4S_4) and orpiment (As_2S_3), now variably coated by arsenolite and As-jarosite overgrowths. Scorodite precipitates as an arsenopyrite alteration product under most pH/Eh conditions, given a suitable ambient concentration of reactive Fe. For most case-study sites, total Fe concentrations in soils and mine waste samples have been recorded in the range 12–24% (Williams and Breward 1995). Values of $<4\%$, however, characterize alluvium samples from Ron Phibun (Fordyce and others 1994) and floodplain deposits outwashed from mine tailings at Globe and Phoenix (Williams and Smith 1994), thus possibly explaining the predominance of arsenolite at these sites. At Kusa, the formation of arsenical jarosites is considered to result from unusual conditions that facilitate (1) arsenolite precipitation following realgar/orpiment oxidation, (2) dissolution of arsenolite in SO_4-rich standing waters (e.g. flooded open pits), (3) evaporative saturation of water with respect to a range of sulphates, and coprecipitation of As.

Climatic influences

Although of secondary importance to site geology, climate is a universal regulator of the flux of elements to the hydrosphere, and is thus an important factor in the post-mining mobilization of As from arsenic wastes. Sulphide oxidation rates increase with temperature and humidity, hence compositionally analogous mine wastes may yield differing contaminant fluxes under contrasting climatic regimes.

The BGS case-study sites facilitate a comparison of As mobilization in semidesert, humid tropical and seasonally dry tropical settings. Data for the arid San Juan and Mendoza provinces of Argentina suggest that highly arsenical Pb-Zn mineralization and associated mining wastes in these areas (much dating to the 19th century) exert little impact on the As loading of perennial drainage. The highest surface water As concentrations (140-μg/l) have, on the basis of their association with NaCl-dominated, B and Li rich waters, been interpreted as derived from evaporites rather than sulphide ores (Rawlins and others 1997). Chemical weathering in this environment is slow relative to the humid tropics; however, leachate production, rather than weathering or mineralogical constraints, is considered the principal rate control on As dispersal. Humid tropical climates, represented by all BGS case-study sites in south-east Asia, induce particularly high rates of oxidation and hydrolysis (the principal mechanism of alumino-silicate gangue mineral degradation), whereas year-round precipitation ensures an abundance of leachate for the transport of As from mine wastes into surface water and groundwater. Mineralogical rather than climatic rate-controls on As mobilization are thus probably most critical at these sites. Fordyce and others (1994) describe a 6000-m^3 flotation waste pile at Ron Phibun,

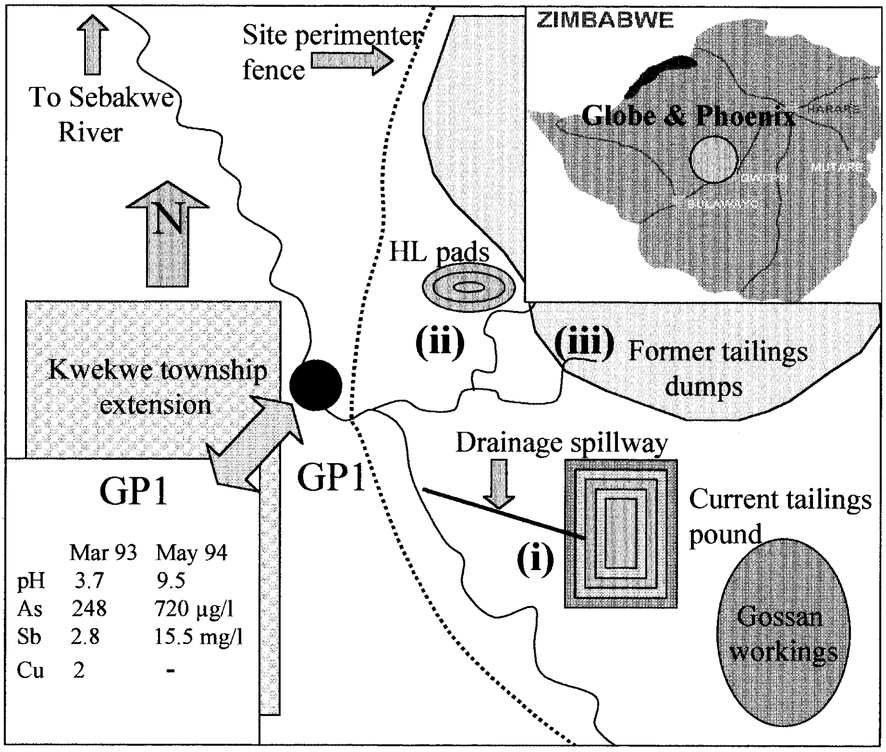

Fig. 7
Globe and Phoenix mine operation, Zimbabwe highlighting mine-derived drainage sources: *i* the contemporary tailings pile, *ii* HL pads, *iii* older tailings wastes. The location of BGS sampling station GP1 is also indicated, with selected wet and dry season hydrochemical data for this site (*inset*)

Thailand, originally containing several percent arsenopyrite in a quartzo-feldspathic matrix, which within ca. 50 years has been deeply degraded to kaolinite and other clays, with little residual sulphide. Despite such rapid weathering and high rainfall, the leachates from this waste are reported to be relatively As poor (<200 µg/l) because of the dominance of scorodite as an arsenopyrite alteration product.

In seasonally arid environments, pronounced seasonal contrasts of mine water chemistry have been demonstrated. Globe and Phoenix, Zimbabwe (Fig. 7), a north-flowing tributary of the Sebakwe River, was found to receive contributions from at least three sectors of the mine (Williams and Smith 1994): (1) the contemporary tailings pile, (2) the HL pads and (3) a ca. 4 km^2 area of older tailings (much dating to the early 20th century) during wet season conditions in March–April 1993, but only the first two of these sources in the dry season of the following year. The older tailings of Globe and Phoenix constitute the site's major AMD source. Consequently strongly acid downstream waters (e.g. pH 3.7 at BGS station GP1) are replaced by alkaline flows (pH 8) in the dry season (Fig. 7). Williams and Smith (1994) have suggested that the aqueous mass transfer of As and other sulphide-derived contaminants from Globe and Phoenix is greatest during the rains because of active leaching of the old tailings. Highest concentrations of As in downstream drainage nonetheless occur in the dry season when discharges are ca. 95% lower and are sufficiently dominated by HL effluents to maintain a pH conducive to cyanometallic As transport.

The production of acute contaminant pulses (with respect to low pH, dissolved metalloids and heavy metals) at the onset of rainfall is an important mine water management consideration in seasonally dry climates. Such events reflect the leaching of oxidation products and evaporative sulphosalts accumulated on mine waste surfaces during prolonged dry periods. They are of particular ecotoxicological significance, as many aquatic fauna suffer mortality or disrupted life cycles in response to short-term (1–24 h) water quality phenomena (US-EPA 1989).

Mine and waste management

Control of sulphide oxidation

Dissolved As is mobile across a wide pH/Eh range; however, its initial liberation from primary sulphides is strongly pH/Eh dependent. In mine waste management, an understanding of the thermodynamic controls of sulphide oxidation is thus fundamental to minimizing the flux of As (and also heavy metals) into the hydrosphere. At Globe and Phoenix mine, the most recent of several tailings piles (see Fig 7) has been constructed using alternating horizons of clay and arenaceous tailings. Although, primarily used to augment physical stability, these clay layers also restrict permeability and thus maintain a reducing environment and inhibit sulphide oxidation within the waste-pile. Mineralogical studies of Globe and Phoenix tailings have confirmed a range of As-bearing sulphides to be present, including gersdorffite (NiAsS), tetrahedrite-tennantite ($(CuFe)_{12}(SbAs)_4S_{13}$) and arsenopyrite, yet leachate from the modern tailings construction has been found to be neither strongly acid nor As contaminated (<100 µg/1; Williams and Smith 1994). A contrasting scenario has been recorded by BGS at Ron Phibun, Thailand, where placer tin deposits with As con-

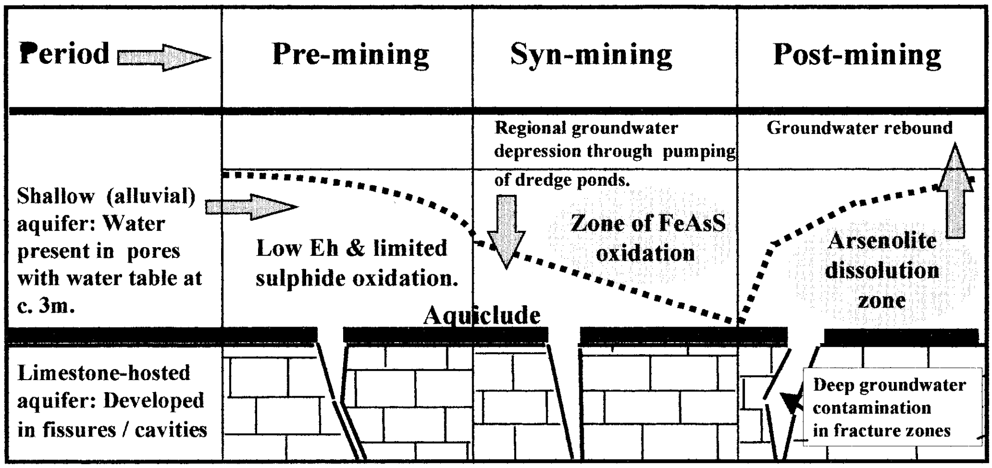

Fig. 8
Model of As mobilization into shallow groundwater at Ron Phibun, Thailand following de-watering by alluvial mining activities and oxidation of disseminated sulphides. *Dotted line* depicts the temporal water table trend during and after mining

centrations of up to 6000 mg/kg (Fordyce and others 1994) were mined for several decades until 1986. During exploitation, excavation of the alluvium was accompanied by hydraulic pumping, lowering the water table locally by up to 10 m. Williams (1997) has proposed that enhanced arsenopyrite oxidation caused by dewatering, arsenolite precipitation in the Fe poor alluvial matrix, and subsequent dissolution of this soluble phase during post-mining groundwater rebound may account for the extremely high As concentrations recorded in alluvial aquifers of the Ron Phibun area (max. 5.1 mg/l, Table 2) during the past decade (Fig. 8).

Control of process waters

The role of CN^- in augmenting As mobility in alkaline mine waters has been described above. Although inherently unstable and non-persistent in most natural waters, the degradation of cyanic complexes prior to the introduction of HL or CIP effluents into rivers or aquifers is critical, given the toxicity of both cyanide and the metals or metalloids often complexed. In large mines, tailings impoundments for the receipt of CIP plant residues facilitate careful management of effluent residence times and discharge rates, as exemplified at Shamva (Zimbabwe) and Morro Velho (Brazil). In the latter case, the effect of waters with maximum pH and As levels of 9.0 and 7.3 mg/l respectively (see Table 2) within the tailings impoundment are virtually undetectable immediately beneath the spillway, for which Rawlins and others (1997) report a pH of 7.5 and dissolved As concentrations of <50 µg/l. Contrasting conditions are, however, common in the vicinity of smaller cyanidation operations, exemplified at Diwalwal, the Philippines. Although not highly arsenical, surface waters in this locality receive effluents from a cooperative artisanal CIP operation and have been recorded as pH 8.4, with Eh –180 and dissolved concentrations of 43 mg/l Na and >1.5 mg/l Hg.

Toxicological significance

Environmental As exposure is a causal factor in human carcinogenesis and numerous non-cancer health disorders (Williams and others 1998). Chronic exposure symptoms include hyperkeratosis, hyperpigmentation, skin malignancies and peripheral arteriosclerosis (blackfoot disease), all of which are known in populations consuming water with 100–1000 µg/l As (Chen and others 1988; Williams and others 1996). The development of liver, bladder and kidney cancer (notably, unique to humans) has been demonstrated at similar exposures through clinical (Sesieni and Cuzick 1993) and epidemiological (Chen and others 1994) studies. Acute As toxification induces gastrointestinal irritation, loss of peripheral nerve response and, ultimately, cardiovascular failure. Abernathy (1993) reports an estimated lethal dose of 70–180 mg.

Water is the dominant human As exposure pathway (Abernathy 1993). The interaction of As-bearing effluents with potable water supplies is thus a critical determinant of the overall As risk at most sites investigated. Soluble inorganic As species are readily absorbed in the gastrointestinal tract and are considered 100% bioavailable for purposes of risk assessment (Chaney and others 1993). Inorganic solid phases are typically of much lower bioavailability (Tsuji 1993). Williams and others (1998) report combined stomach and gastrointestinal As absorption quotients of 18–35% (of total As) for Ron Phibun mine waste and soils exposed to a physiologically-based extraction test (PBET).

The toxicity of As is species-dependent, generally decreasing through the sequence $As^{3+} > As^{5+} >$ methyl As. The toxicity differential between dissolved arsenate and arsenite species is approximately an order of magnitude (Abernathy 1993) and, to a large extent, accounts for the steep As dose–response curves produced for populations dependent on deep anoxic aquifers, exemplified in the 'Blackfoot zone' of Taiwan (Chen and others 1994). Most waters investigated in the present study are arsenate dominated; however, speciation factors require full consideration in risk assessment in areas of mining related As contamination. At Ron Phibun, Thailand, the advantage arising from the replacement of shallow alluvial groundwater that holds up to 5.1 mg/l total As in As^{5+} species, with potable supplies from a deep carbonate aquifer holding no more than 140 µg/l As, has been partially offset by the prevalence in the latter of up to 39%

total As as arsenite. For the purpose of risk assessment, Williams and others (1996) have calculated an 'arsenate equivalent' in this carbonate aquifer of up to 626 μg/l. Although over 60% of BGS case-study sites yielded peak As values in excess of the US-EPA potable water limit (50 μg/l) and over 30% display acute (though often localized) As contamination (>1 mg/l), human toxification has been confirmed only in the case of Ron Phibun, Thailand (Williams and others 1996). Of the remaining sites, 12 present no plausible risk because of their remoteness from human populations. Seven, with resident or downstream populations of 500–30,000 (Mamut, Santo Tomas, Antomok, Dizon, Gango, Mainit and Nambija) are considered at low risk because of the systematically low As concentrations of their leachates (<100 μg/l). Four sites warrant more detailed risk assessment of which two, Ponce Enriquez and Portovelo (Ecuador), have recently been subject to population exposure studies under a major World Bank funded programme (SES 1998). In Zimbabwe, the impact on a high-density township adjacent to the Globe and Phoenix mine, and the elevated As in both shallow groundwater and maize plantations to the north-west of the site (Williams and Smith 1994; Williams and Breward 1995), remains to be evaluated. At Iron Duke, the effect of acid-metalliferous groundwater plumes documented by Williams and Smith (2000) on both potable supplies and irrigation waters is also unknown.

Conclusions

This study has confirmed As to be a significant mine water contaminant in a diverse range of geological and climatic settings. In contrast to heavy metals, the mobilization of As across a wide pH/Eh indicates a requirement for technology other than that conventionally applied to AMD in the treatment of many As-contaminated systems. Empirical data, collected using standardized methodologies, can enhance understanding of the factors controlling the magnitude and spatial extent of As pollution arising from Au and base metal mining. Ultimately this should improve problem prediction ahead of deposit exploitation (i.e. at the impact assessment stage), thus facilitating early implementation of appropriate preventative controls. Inevitably, several inherent determinants of the potential for As contamination (including climate, geological and hydrogeological setting and ore/gangue mineralogy) are beyond management influence. Important controls of the rate of As flux into the hydrosphere, for example, solid-fluid interactions within waste-piles, sulphide oxidation rates, and the fate of ore beneficiation effluents, can, however, be regulated and optimized. Once in solution, As attenuation rates can also be regulated, given an adequate understanding of the hydrochemical processes involved. It requires emphasis that the toxicological significance (and hence the urgency for remedial treatment) of the mine waters investigated is a function of both hydrochemical composition and human utilization. Although more than 60% of case-study sites have been shown to hold As at concentrations in excess of the US-EPA potable water threshold, a human toxicological risk is probable in no more than five cases.

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