

## Sulphide mining as a source of arsenic in the environment

N. Madhavan and V. Subramanian\*

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110 067, India

**Based on the analysis of various types of environmental samples in the mining and smelter areas associated with the Khetri Cu and Zawar Pb-Zn deposits, it is concluded that zones of exploitation of all sulphide-bearing mineral deposits are potential areas of arsenic (As) contamination. Without identifying the source of As and various natural and anthropogenic concentrating mechanisms for As, such as natural scavenging of As by Fe-Mn hydroxides in sediments and industrial concentration of Cu, Pb and Zn along with the associated As in smelter operations, the pollution and health problems, as known in West Bengal and Bangladesh, cannot be suitably tackled.**

THE presence of arsenic in groundwater poses a threat to human health due to its toxic properties<sup>1</sup>. The World Health Organisation (WHO)<sup>2</sup> and the US Environmental Protection Agency (US-EPA)<sup>3</sup> have set 10 ppb as the limit for arsenic (As) in drinking water. The problems of arsenic contamination of groundwater in West Bengal (India)<sup>4-7</sup> and Bangladesh<sup>8-10</sup> have been widely reported. In its geological occurrence, arsenic is found at high levels in primary sulfide minerals such as arsenopyrite (FeAsS), pyrite (FeS), pyrrhotite (Fe<sub>1-x</sub>S), orpiment (As<sub>2</sub>S<sub>3</sub>) and realgar (AsS)<sup>11</sup>. The estimated large arsenic deposits throughout the world are about  $8.65 \times 10^6$  metric tones (t)<sup>12</sup>. In terms of origin, the hydrothermal volcanic/sedimentary arsenic constitutes  $4.5 \times 10^6$  (t), followed by hydro-mesothermal arsenic  $3.61 \times 10^6$  (t) and hydro-epithermal arsenic deposits  $0.544 \times 10^6$  (t)<sup>12</sup>. The major period of arsenic deposits occurred in the world during carboniferous (about 65% of all As deposits) while at other geological times they are scattered in small quantities<sup>12</sup>. In addition to substitution in sulphide deposits, its ionic radius and valence allow arsenic to substitute in trace amounts for many elements in silicates such as glauconite and other rock-forming silicate minerals<sup>11,13</sup>. The chemical similarities of arsenate (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>) and phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) lead to anion solid solutions between minerals such as pyromorphite Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl and mimetite (Pb<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>Cl (refs 11 and 14). Combining both primary minerals and trace substitution in other minerals, arsenic has an estimated average concentration of 1.5 µg/g in the upper crust<sup>11,15</sup>.

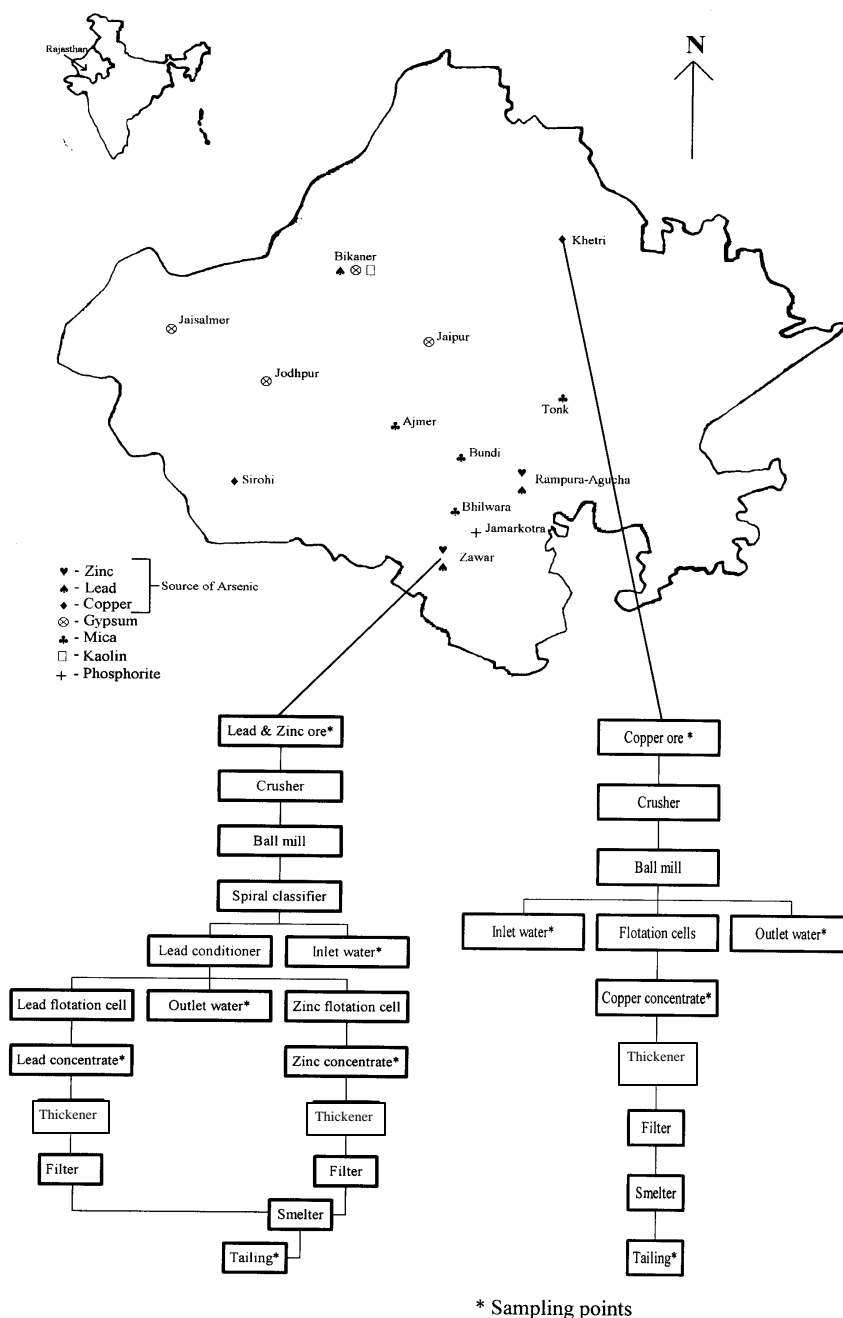
In surficial water systems, arsenic can be dissolved either directly from weathering of minerals<sup>11,16</sup> or through mixing with high-arsenic bearing geothermal

\*For correspondence. (e-mail: subra@jnuniv.ernet.in) waters<sup>11,17</sup>. In groundwater systems, arsenic can also be derived from the dissolution of arsenic-bearing iron oxides in unconsolidated aquifers<sup>11,18</sup>. Aqueous arsenic concentrations are controlled by anion exchange and coprecipitation with iron and manganese oxyhydroxides, and are therefore a function of Eh and pH<sup>11</sup>. Arsenate anion exchange dynamics are analogous to phosphate, with competition for exchange sites favouring phosphate over arsenate<sup>11</sup>. Competitive exchange reactions show that arsenic can be stored in soils, and then inadvertently released with the addition of a high phosphate source, such as phosphate fertilizer<sup>11,19</sup>.

Thus, As is a highly mobile element in our environment and sulphide mineral deposits even if they contain only traces of As are potential contributors of this toxic element to the environment. It was reported<sup>20</sup> that the sulphosalts of Rampura-Agucha contain enhanced As levels but no such reports are available for the major sulphide mineral belt. Accordingly, an attempt was made to understand the source of As, its movements in the mine waters and its enrichment in the sulphide mining zones of Khetri and Zawar mines and concentrates in smelter operations.

Surface water samples were obtained from Zawar (Pb and Zn sulphides) and Khetri (Cu sulphide) mines and also groundwater from the surrounding residential areas were collected. Figure 1 shows the sampling sites and other mineral mining areas. It should be noted that some of the other mining areas have similar minerals and are therefore potential sites of arsenic contamination. Fresh grains of the sulphide ores, Pb, Zn and Cu concentrates and their tailings were also collected from the ore beneficiation plants at Zawar and Khetri. After collection, water samples were filtered through 0.45 µm membranes, acidified to pH 2 with HCl, and stored at about 4°C until further analysis. Ore, concentrates and tailings were digested in a Teflon bomb. Various geo standards (GXR2, GXR4, GXR5, GXR6, JB-1b, JB2, JCFA-1, JDO1, JG2, JLK1, JR2, JSD2, JSD3 and JS11) were used for instrument calibration. Finally total arsenic in water and other samples were measured by an atomic absorption spectrophotometer (GBC 902) coupled with hydride generator (HG900) using hot vapour technique<sup>21</sup>. For water samples, chemical standards of As were used for calibration.

Table 1 shows the arsenic concentration in various water bodies in the mining areas. In groundwater (Zawar area) the total dissolved arsenic was between 1.4 and 13.8 ppb with an average of  $5.8 \pm 5.5$  ppb. In the Khetri area the concentration was generally below <1 ppb (detection limit). The average total dissolved arsenic in Zawar and Khetri mine inlet water was  $3.0 \pm 2.8$  ppb and <1 ppb, respectively while the mine outlet water had  $130 \pm 14$  ppb and  $3 \pm 1$  ppb arsenic, respectively. Oxidation of metallic sulphides under the action of inlet water produces sulphuric acid<sup>22</sup> and the metals released



**Figure 1.** Map of Rajasthan showing sampling sites and flow sheet of ore beneficiation.

are soluble in this acidic water thus releasing arsenic to the outlet water. Arsenic concentration in lakes, rivers and groundwater in other parts of the world is shown in Table 2 for comparison. Our analysis shows higher concentration of arsenic in Zawar and Khetri ore with an average of  $7683 \pm 4414$  mg As/kg and  $145 \pm 72$  mg As/kg of the sulphide ores, respectively. Table 3 shows the average concentration of Zawar and Khetri ore and tailings with reference to Rampura-Agucha sulphosalts and compares them to other world sulphide ores and tailings. In the second part of Table 3, arsenic enrichment in various aquatic environments such as rivers and lakes are indicated. The average concen-

tration of arsenic in Zawar zinc and Khetri copper tailings was  $1519 \pm 1493$  mg As/kg and  $1179 \pm 1382$  mg As/kg of tailings, respectively. In the metal sulphide smelter, in the zinc concentrate  $10727 \pm 6322$  mg As/kg of the concentrate, in the Pb concentrate  $61 \pm 16$  mg As/kg of the concentrate and in the copper concentrates  $12 \pm 6$  mg As/kg of the concentrate were observed. Processing of Pb-Zn sulphide ores involves first the separation of Zn from the Pb concentrates through addition of chemicals

**Table 1.** Total arsenic in groundwater (ppb), mine water (ppb) and in the sulphide ore, smelter concentrates and tailings (mg/kg) in the Khetri and Zawar region

Zawar	GW	MW <sup>1</sup>	MW <sup>2</sup>	As in ore	As in Zn conc. <sup>x</sup>	As in Pb conc. <sup>x</sup>	As in tailings
1	4.7	6.9	120	3262	6256	49	463
2	13.8	0.9	140	8410	15197	72	2575
3	1.4	0.9	–	5558	–	–	–
4	3.3	3.3	–	13501	–	–	–
Mean	5.8	3.0	130	7683	10727	61	1519
SD	5.5	2.8	14	4414	6322	16	1493
Khetri	GW	MW <sup>1</sup>	MW <sup>2</sup>	As in ore	As in Cu conc. <sup>x</sup>		As in tailings
1	tr	tr	3	70	7		202
2	tr	tr	2	202	16		2156
3	tr	tr	–	105	–		–
4	tr	tr	–	180	–		–
5	tr	tr	–	74	–		–
6	tr	tr	–	241	–		–
Mean	tr	tr	3	145	12		1179
SD	tr	tr	1	72	6		1382

GW, groundwater; MW<sup>1</sup>, mine water inlet; MW<sup>2</sup>, mine water outlet; x, concentrates in the smelter; tr, trace (<1 ppb).

**Table 2.** Dissolved/particulate arsenic levels in diverse environments

Place	Nature of water	As (ppb)
Baitrani, India <sup>35</sup>	River	0.1–2.1
Bangladesh <sup>8</sup>	GW	3–960
Bowen Island, British Columbia <sup>36</sup>	Well	0.5–580
Brahmani, India <sup>35</sup>	River	0.9–13.2
Bunker hill mine, Idaho <sup>37</sup>	GW in level (5 and 9)	0.1–1336
Caron River, England <sup>38</sup>	Water	1–80
Caron River, England <sup>38</sup>	Particulate	1–3800
Coeur d'Alene, Idaho <sup>37</sup>	River aquifer	0.17–2.87
East coast of India <sup>39</sup>	Pulicat lake	35
Fairbanks, Alaska <sup>40</sup>	Stream water	<5–1260
Furtei, South Sardinia <sup>41</sup>	Borehole water	382
Hamilton, New Zealand <sup>25</sup>	Waikato river	32.1
Humber Estuary, NE England <sup>42</sup>	River	0.54–4.07
Madison river vally, Montana <sup>43</sup>	Alluvial GW	26–150
Mahanadi, India <sup>35</sup>	River	0.1–3
Missouri, USA <sup>23</sup>	Well	30–400 As(III)
New Hampshire <sup>12</sup>	Drinking water	<0.0003–180
Northwest Arizona <sup>44</sup>	GW	10–1000
Ohakuri, New Zealand <sup>26</sup>	Lake	38.3–441
Quebec and Ontario, Canada <sup>24</sup>	Lake	97–7297
South Australia <sup>45</sup>	Coastal water	1.1–1.61
South Australia <sup>45</sup>	Particulate	<0.00006–0.013
South McQuesten, Canada <sup>46</sup>	River	<40–220
West Bengal, India <sup>4</sup>	GW	10–3700
Khetri and Zawar, India <sup>P</sup>	GW	<1–13.8
Khetri and Zawar, India <sup>P</sup>	MW <sup>1</sup>	<1–6.9
Khetri and Zawar, India <sup>P</sup>	MW <sup>2</sup>	2–140

GW, groundwater; P, present study; MW<sup>1</sup>, mine water inlet; MW<sup>2</sup>, mine water outlet.

such as potassium ethyl xanthate leading to enhancement of As in the Zn concentrates relative to the Pb concentrates. On the other hand, in the beneficiation of Cu ore, while the concentration of As in the Cu ore is less relative to that in Pb-Zn ores, even the small excess As is eliminated in liquid form in the tailings. Thus, the Cu beneficiation is more harmful to the environment due to direct mixing of As enriched tailing with the immediate aquatic systems

compared to the Zn beneficiation where As is enriched in the Zn concentrates and hence is in solid form.

From Table 3 it can be seen that As is introduced into the aquatic environment through sulphide mining activities. Lithologic logs in North America<sup>23</sup> show As asso-

**Table 3.** Dispersal of arsenic from source to aquatic environment

Place	Nature of sample	Primary minerals	Valuable elements	As (mg/kg)	Cu %	Fe %
Khetri, Jhunjhunu <sup>P</sup>	Ore	ccp	Cu, Co	145	4.3	59.6
Khetri, Jhunjhunu <sup>P</sup>	Unoxidized tailings	–	–	1179	0.09	–
Zawar, Udiapur <sup>P</sup>	Ore	sp	Ag, Pb and Zn	7683	0.03	6.7
Zawar, Udiapur <sup>P</sup>	Unoxidized tailings	–	–	1519	0.01	–
Rampura-Agucha, Bhilwara <sup>20</sup>	Sulphosalt Freibergite	sp	Pb and Zn	9300	15.06	5.46
Rampura-Agucha, Bhilwara <sup>20</sup>	Sulphosalt Argentian pearcite	–	–	5000	5.13	0.03
Bowen Island, British Columbia <sup>36</sup>	Vein deposits	asp	–	16.4–17.2	–	7.0–7
California, USA <sup>11</sup>	Playa brine	–	B, Li	100	–	–
Cleveland Deposits, New Mexico <sup>47</sup>	Ore	ccp, sp, gn	Au and Ag, Zn	98	1.3	21.1
Cleveland Deposits, New Mexico <sup>47</sup>	Tailings	–	–	4–190	0.07–3.1	2.1–3
Cyprus-Pinos Altos, New Mexico <sup>47</sup>	Ore concentrate	ccp, sp, gn	Cu, Fe with Au & Ag	290	10	24
Cyprus-Pinos Altos, New Mexico <sup>47</sup>	Tailings	–	–	42–110	0.07–0.9	10–1
Ingaldhal, Chitradurga, Karnataka <sup>48</sup>	Cobaltite mineral	col	Co	44.8–47.4	–	2.0–4
Killingdal, Norway <sup>49</sup>	Ore	ccp, sp, py	–	1200	1.03	34.1
Laver, Norrbotten, Sweden <sup>50</sup>	Unoxidized tailings	ccp, po	Cu	68	0.1	2.4
Laver, Norrbotten, Sweden <sup>50</sup>	Oxidized tailings	–	–	109	0.03	2.7
Li Hir Island, Papua New Guinea <sup>51</sup>	Volcanic marine sediments	–	–	1200–4900	0.01	17.7–1
Lokken, Norway <sup>49</sup>	Ore	ccp, sp, py	Cu, Zn	40	2.2	37.1
Maria De La Paz, Mexico <sup>52</sup>	Slag tailings	–	Ag, Au, Cu, Pb and Zn	3800	0.4	–
New Brunswick, Canada <sup>53</sup>	Tuff	–	Ag, Cu, Pb, Zn	45	0.003	1.8
New Brunswick, Canada <sup>53</sup>	Rhyolite	–	Ag, Cu, Pb, Zn	62	0.001	1.3
New Mexico, USA <sup>54</sup>	Empire zinc mine tailings	ccp, sp	Ag, Au, Cu, Fe, Pb and Zn	3.8–185	0.05	–
Rio Tinto, Spain <sup>11</sup>	Ore field	–	Cu, As, Se	6000	–	–
Skorovas, Norway <sup>49</sup>	Ore	ccp, sp, py	–	500	1.3	–
Slave Province, N. America <sup>55</sup>	Cupin mine, Contwoyto lake	–	Au, Ag, Cu	4.20	0.03	–
South America <sup>56</sup>	Volcanic hosted	stn	Ag, Au, Sb	638–7032	–	–
South America <sup>56</sup>	Sediment or volcanic hosted	stn	Ag, Au, Sb	12–3109	–	–
South America <sup>56</sup>	Sediment hosted	stn	Ag, Au, Sb	1–326	–	–
Southern Tuscany, Italy <sup>57</sup>	Gabellino (floatation tailings)	ccp, gn, po, py, sp	Cu	50–388	0.03	–
Southern Tuscany, Italy <sup>57</sup>	Fontalcinaldo (waste rock dump)	–	–	55–1075	0.003	–
Stekenjokk, Sweden <sup>50</sup>	Unoxidized tailings	py, po, sp, ccp	Cu and Zn	1178	0.2	9.7
Sudbury, Ontario <sup>27</sup>	Ore	–	Ni, Cu	2.2–26	–	–
Twin Creeks, Nevada <sup>58</sup>	Arsenian pyrite	–	Au (595–1465 ppm)	1.05–2.43	–	–
Western Australia <sup>55</sup>	Nevoria mine	–	Au, Ag, Cu	500	0.023	–
Western Australia <sup>55</sup>	Marvel Loch mine	–	Au, Ag, Zn	2875	0.008	–

# RESEARCH COMMUNICATIONS

**Table 3.** (Contd.)

Bangladesh <sup>59,60</sup>	Ganges (Padma) river sediments	–	–	1.18–2.61	0.002–0.003	2.5–1
Bangladesh <sup>59,60</sup>	Brahmaputra (Jamuna) river sediment	–	–	1.41–5.93	0.002–0.005	3.1–(
Bangladesh <sup>59,60</sup>	Meghna river sediment	–	–	1.3–5.55	0.001–0.007	3.8–(
Blackbird creek, Idaho <sup>61</sup>	Stream sediments	col, ccp, py	Co	42–2550	0.1–0.3	–
Bullit County, Kentucky <sup>62</sup>	New Albany raw shale	oil shale	–	14	0.03	2
Central Newfoundland, Canada <sup>63</sup>	Lower till (pyrite 5%)	asp, gn, sp, py	–	10–20	–	2.3
Central Newfoundland, Canada <sup>63</sup>	Meltout till (pyrite 10–20%)	–	–	30–90	–	4.7–(
Elba-Argetario, S. Tuscany, Italy <sup>64</sup>	Sediments	–	–	4–120	0.01	–
Fairbanks, Alaska <sup>40</sup>	Suspended sediments	au, stn, gn, sel	Au	0.005–18	–	–
Fairbanks, Alaska <sup>40</sup>	Sediment	–	–	5–4114	–	–
Fal Estuary, Cornwall, UK <sup>65</sup>	Tresillian river sediment	asp, ba, ccp, py, sp	–	508	0.1	–
Indian subcontinent <sup>66</sup>	Ganges river sediment	–	–	2.0–9.0	0.002	2.5
Indian subcontinent <sup>66</sup>	Brahmaputra river sediment	–	–	2.0–6.0	0.005	2.9
Indian subcontinent <sup>66</sup>	Yamuna river sediment	–	–	3.0–11.0	0.006	2.4
Indian subcontinent <sup>66</sup>	Narmada and Tapti river sediment	–	–	3.0–5.0	0.001–0.005	1.09–(
Indian subcontinent <sup>66</sup>	Godavari river sediment	–	–	4.0–14.0	0.005	5.8
Indian subcontinent <sup>66</sup>	Krishna river sediment	–	–	2.0–5.0	0.003	2.9
Indian subcontinent <sup>66</sup>	Cauveri river sediment	–	–	2.0–4.0	0.003	1.5
Japan <sup>67</sup>	Lake Biwa sediment	–	–	198	–	–
Lake Ohakuri, New Zealand <sup>26</sup>	Sediment pore water	–	–	0.98–6.43	–	–
Missouri, USA <sup>23</sup>	Bulk soil	–	–	7	(nearer to smelter)	–
Missouri, USA <sup>23</sup>	Limonite separates	len	–	4.4–84	–	1.8–(
Monchegorsh, Russia <sup>68</sup>	Top soil (0–5 cm) (near smelter)	–	Ni	11–60	0.2	1.6
New Brunswick, Canada <sup>53</sup>	Sediment	–	Ag, Cu, Pb, Zn	42	0.02	3.9
Northern Tyrrhenian Sea <sup>69</sup>	Silty clays	ba, sp,	Co, Cu, Ni, Pb, Zn	24–38	0.004	–
Northern Tyrrhenian Sea <sup>69</sup>	Clayey silts	–	–	23–25	0.004	–
Orissa, India <sup>70</sup>	Mahanadi river sediment	–	Cu, Fe, Pb	~4	–	–
Orissa, India <sup>70</sup>	Brahmani river sediment	–	Cu, Fe, Pb	~8	–	–
Orissa, India <sup>70</sup>	Baitarani river sediment	–	Cu, Fe, Pb	~7	–	–
Qubec & Ontario, Canada <sup>24</sup>	Lake sediments	–	–	0.67–40	–	0.2–1
Smith County, Tennessee <sup>62</sup>	Chattanooga raw shale	oil shale	–	11	0.01	0.7
South Carolina, USA <sup>71</sup>	Coal fly ash tank water	–	–	1300–48900	2.6–3.0	22.0–(
South Carolina, USA <sup>71</sup>	Suspended solids	–	–	23–870	0.01–0.02	21.1–(
Sudbury, Ontario <sup>27</sup>	Lake (suspended particles)	–	–	6.5–38	(nearer to smelter)	–
Sudbury, Ontario <sup>27</sup>	Kelly Lake sediment (max)	–	–	650	–	–

asp, arsenopyrite; au, placer gold; ba, barite; ccp, chalcopyrite; col, cobaltite; gn, galena; len, lemnite; po, pyrroprhotite; py, pyrite; sel, sheelite; stn, stibnite; sp, spalerite; P, present study.

ciation with limonite in the alluvial sediments. Variations in redox conditions modify the concentration of dissolved species and may effect the amount of adsorbed arsenic<sup>24</sup>. As redox conditions become increasingly reducing at depths, the ferric iron is reduced to ferrous iron, resulting in mobilization of some of the adsorbed arsenic. Under prolonged reducing conditions, essentially all of the adsorbed arsenic may be reduced to As<sup>3+</sup> (ref. 23). In this connection it is noteworthy that *Anabaena oscillaroides*, a bacteria isolated from the Waikato river is capable of reducing As<sup>5+</sup> to As<sup>3+</sup> which is more toxic and about 25 times more soluble than the former<sup>25</sup>. Thus post-depositional changes in redox potentials and pH can potentially modify the movement of As to and from dissolved and solid phases with speciation of As playing an important role in its upward or downward mobility with depth either due to simple inorganic reactions or biochemical reactions. Since some of the sulphide mines are at greater depths, the transport of As in the aquatic environment in the mining areas is very important.

In order to predict the distribution of arsenic between dissolved and particulate phases in a wide range of ecosystems shown in second part of the Table 3, the key role played by Fe oxyhydroxides in the chemistry of dissolved arsenic concentration in oxic aquatic environments must be considered. Many studies have reported the distribution of arsenic among the Fe oxyhydroxides of oxic sediments and the associated interstitial and overlying waters in a variety of lakes<sup>24,26,27</sup>. Distributions of dissolved As and Fe concentrations suggest a close association of both elements in a dissolution–diffusion–precipitation cycle for Fe and adsorbed As<sup>24</sup>. Aquatic plants play a key role in remobilizing As at depths which can be illustrated by the following observations.

To gain a better understanding of the impact of rhizosphere/burrow oxidation by wetland plants and burrowing invertebrates on the biogeochemistry of metals and metalloids in the ecosystem, it was hypothesized<sup>28,29</sup> that salt marsh plants and burrowing invertebrates could accumulate Fe, Zn and As through oxidation of the rhizosphere/burrow wall. The mechanism behind the accumulation would be as follows: Oxidation of ferrous iron to its ferric form would lead to precipitation of iron oxyhydroxides in the rhizosphere (iron plaque), which in turn would lead to a decreasing concentration gradient of dissolved iron oxyhydroxides in the rhizosphere, that in turn would lead to a decreasing concentration gradient of dissolved iron towards the plant roots. The iron oxyhydroxides in turn would bind arsenic and zinc, again creating a decreasing concentration gradient of both elements towards the roots. These gradients would lead to the diffusion of iron, arsenic and zinc in the direction of the roots. Assuming that uptake of the elements by the root is slower than the supply through diffusion, an increase in concentration of all three elements would be expected to occur in the solid phase of the rhizosphere<sup>28</sup>. Therefore arsenic contained in sediments or in sulphide ores/concentrates can be released, either as soluble (As<sup>3+</sup>) or insoluble (As<sup>5+</sup>) species. In either case, it will be a poison released from the medium and pose a threat to the environment. While the As levels in the groundwater in West Bengal, Bangladesh, outer Mongolia and Japan<sup>30</sup> have been widely reported for a long time, it is surprising that As has not been analysed in the sulphide ores of Singhbhum base-metal

belt that is in the hinterland of the As-contaminated area in India. Along with Cu, Pb and Zn, As may also be amenable to efficient bioleaching processes from sulphide ore deposits<sup>31</sup>. With regard to the As problem in Bangladesh and West Bengal, Fe-oxyhydroxides are reported<sup>32</sup> to be the carriers of As in the Gangetic alluvium, and upon redox changes associated with water-table fluctuation in response to withdrawal of water through millions of tube-wells in the area, they release As to the water in soluble form. Also, there are weathered base metal deposits underlying the Gangetic basin<sup>33</sup> which could be the source of As as observed for the sulphide deposit in the present study. Arsenic-bearing phosphatic fertilizers also could be an additional source of As<sup>33</sup>. The chemical speciation of arsenic as well as the Eh values of affected groundwater in Bangladesh indicate the tendency towards reducing environment<sup>34</sup>. Furthermore, comparison between total arsenic and iron content in groundwater, aquifer soil, suspended river sediment, bank sediment and surface soil does not indicate strong correlation<sup>34</sup>, thereby contradicting earlier work<sup>32</sup> in Fe–As relationship. Thus mobilization of As needs to be carefully studied in future from the source to the aquifer region. However, in the Khetri–Zawar region, the As problem may not be associated with movement in aquifers like in the Bengal delta area and thus different mechanisms of transport of As in the aquatic system may operate in various regions and no single mechanism can account for all observations.

Thus our observation indicates that from the sulphide ores the mine water leaches out As under redox and acidic conditions and further As concentration takes place in the metal sulphide beneficiation activities. Thus no specific As-enriched mineral such as arsenopyrite is required in the neighbouring lithology but all sulphide mining and smelter sites are potential locations of future As-contaminated areas and should not await an episodic event to unleash an environmental disaster. Arsenic studies should therefore precede mining/smelter operations as a precaution in all sulphide-related mineral resources exploitation.

1. Azcue, J. M. and Nriagu, J. O., *Arsenic in the Environment*, John Wiley, New York, 1994, pp. 1–17.
2. WHO Guidelines for Drinking Water Quality, Recommendations, 2nd edn, World Health Organisation, Geneva, 1993, vol. 1, p. 41.
3. US Environmental Protection Agency (US-EPA), *Quality Criteria for Water*, US-EPA, Washington DC, 1976.
4. Mandal, B. K., Roy Chowdhury, T., Samanta, G., Basu, G. K., Chowdhury, P. P., Chanda, C. R., Lodh, D., Karan, N. K., Dhar, R. K., Tamili, D. K., Das, D., Saha, K. C. and Chakraborti, D., *Curr. Sci.*, 1996, **70**, 976–986.
5. Mandal, B. K., Roy Chowdhury, T., Samanta, G., Basu, G. K., Chowdhury, P. P., Chanda, C. R., Lodh, D., Karan, N. K., Dhar, R. K., Tamili, D. K., Das, D., Saha, K. C. and Chakraborti, D., *Curr. Sci.*, 1997, **72**, 114–117.
6. Bagla, P. and Kaiser, J., *Science*, 1996, **274**, 174–175.
7. Saha, D. P. and Subramanian, K. S., *Science*, 1996, **274**, 1285–1289.
8. Dhar, R. K., Biswas, B. K., Samanta, G., Mandal, B. K., Chakraborti, D., Roy, S., Jafar, A., Islam, A., Ara, G., Kabir, S., Khan, A. W., Ahmed, S. A. and Hadi, S. A., *Curr. Sci.*, 1997, **73**, 48–59.

9. Biswas, B. K., Dhar, R. K., Samanta, G., Mandal, B. K., Chakraborti, D., Faruk, I., Islam, K. S., Chowdhury, Md. M., Islam, A. and Roy, S., *Curr. Sci.*, 1998, **74**, 134–145.
10. Mushtaque, A., Chowdhury, R. and Jakariya, M., *Science*, 1999, **284**, 1621.
11. Peters, S. C., Blum, J. D., Klaue, B. and Karakas, M. R., *Environ. Sci. Technol.*, 1999, **33**, 1328–1333.
12. Laznicka, L., *Econ. Geol.*, 1999, **94**, 455–474.
13. Onken, B. M. and Hossner, L. R., *Soil Sci. Soc. Am. J.*, 1996, **60**, 1385–1392.
14. Klein, C. and Hurlbut, C. S., *Manual of Mineralogy*, John Wiley, New York, 1985, 20th edn.
15. Taylor, S. R. and McLennan, S. M. *The Continental Crust: Its Composition and Evolution*, Blackwell Scientific Publications, Boston, 1985.
16. Baker, L. A., Aureshi, T. M. and Wyman, M. M., *Water Resour. Res.*, 1998, **34**, 1543–1552.
17. Wilkie, J. A. and Hering, J. G., *Environ. Sci. Technol.*, 1998, **32**, 657–662.
18. Korte, N., *Environ. Geol. Water Sci.*, 1991, **18**, 137–141.
19. Peryea, F. J., *Soil Sci. Soc. Am. J.*, 1991, **55**, 1301–1306.
20. Mukherjee, A. D., Samhita Glahiri and Bhattacharya, H. N., *J. Geol. Soc. India*, 1991, **37**, 132–135.
21. GBC 902 and HG 900, *Operation Manual for the Hydride Generator*, 1986, pp. 1–12.
22. Mok, W. M., Riley, J. A. and Wai, C. M., *Water Res.*, 1988, **22**, 769–774.
23. Korte, N., *Environ. Geol. Water Sci.*, 1991, **18**, 137–141.
24. Belzile, N. and Tessier, A., *Geochim. Cosmochim. Acta*, 1990, **54**, 103–109.
25. McLaren, S. J. and Kim, N. D., *Environ. Pollut.*, 1995, **90**, 67–73.
26. Aggett, J. and Kriegman, M. R., *Water Res.*, 1988, **22**, 407–411.
27. Nariagu, J. O., *Geochim. Cosmochim. Acta*, 1983, **47**, 1523–1526.
28. Otte, M. L., Kearns, C. C. and Doyle, M. O., *Bull. Environ. Contam. Toxicol.*, 1995, **55**, 154–161.
29. Doyle, M.O. and Otte, M. L., *Environ. Pollut.*, 1997, **96**, 1–11.
30. Guo Xiao-Juan, Report, News Letter 2, Asia Arsenic Network (AAN), 1999.
31. Natarajan, K. A., in *Biogeochemistry of Rivers in Tropical South and Southeast Asia* (eds Ittekkot, V., Subramanian, V. and Annadurai, S.), Heft 82, SCOPE Sonderband, Mitt. Geol.-Paläont. Inst., Univ. Hamburg, 1999, pp. 55–72.
32. Nickson, R., McArthur, J., Burgess, W., Ahmed, K. M., Ravenscroft, P. and Rahman, M., *Nature*, 1998, **395**, 338.
33. Acharyya, S. K., Chakraborty, P., Lahiri, S., Raymahashay, B. C., Guha, S. and Bhowmik, A., *Nature*, 1999, **401**, 545–547.
34. Safiullah, S., Khanal, D. P., Tareq, S. M. T. and Khan, M. M. K., in *Biogeochemistry of Rivers in Tropical South and Southeast Asia* (eds Ittekkot, V., Subramanian, V. and Annadurai, S.), Heft 82, SCOPE Sonderband, Mitt. Geol.-Paläont. Inst., Univ. Hamburg, 1999, pp. 125–130.
35. Konhauser, K. O., Powell, M. A., Fyfe, W. S., Longstaffe, F. J. and Tripathy, S., *Environ. Geol.*, 1997, **29**, 132–141.
36. Boyle, D. R., Turner, R. J. W. and Hall, G. E. M., *Environ. Geochem. Health*, 1998, **20**, 199–212.
37. Mok, W. M., Riley, J. A. and Wai, C. M., *Water Res.*, 1988, **22**, 769–774.
38. Johnson, C. A. and Thornton, I., *Water Res.*, 1987, **21**, 359–365.
39. Periakali, P., Research proposal submitted to the Department of Science and Technology, New Delhi, 1998.
40. Wilson, F. H. and Hawkins, D. B., *Environ. Geol.*, 1978, **2**, 195–202.
41. Cidu, R., Caboi, R., Fanfani, L. and Frau, F., *Environ. Geol.*, 1997, **30**, 231–237.
42. Neal, C., Simith, C. J., Jeffery, H. A., Jarvie, H. P. and Robson, A. J., *J. Hydrol.*, 1996, **182**, 37–64.
43. Sonderegger, J. L. and Ohguchi, T., *Environ. Geol. Water Sci.*, 1988, **11**, 153–161.
44. Rosner, U., *Environ. Geol.*, 1998, **33**, 224–230.
45. Maher, W. A., *Water Res.*, 1985, **19**, 933–934.
46. Kwong, Y. T. J., Roots, C. F., Roach, P. and Kettley, W., *Environ. Geol.*, 1997, **30**, 98–107.
47. Boulet, M. P. and Larocque, A. C. L., *Environ. Geol.*, 1998, **33**, 130–142.
48. Devaraju, T. C. and Alapieti, T. T., *J. Geol. Soc. India*, 1997, **49**, 597–598.
49. David Banks, Paul L. Younger, Rolf-Tore Arnesen, Egil R. Iversen and Sheila, B. B., *Environ. Geol.*, 1997, **32**, 157–174.
50. Holmstrom, H., Ljungberg, J. and Ohlander, B., *Environ. Geol.*, 1999, **37**, 267–280.
51. Pichler, T., Giggenbach, W. F., McInnes, B. I. A., Buhl, D. and Duck, B., *Econ. Geol.*, 1999, **94**, 281–288.
52. Manz, M. and Castro, L. J., *Environ. Pollut.*, 1997, **98**, 7–13.
53. Lentz, D. R., *Econ. Geol.*, 1999, **94**, 57–86.
54. Walder, I. F. and Chavez, W. X. Jr., *Environ. Geol.*, 1995, **26**, 1–18.
55. Muller, G. A., *Econ. Geol.*, 1997, **92**, 181–209.
56. Dill, H. G., Perfold, Z. and Riera, K. C., *Econ. Geol.*, 1997, **92**, 623–632.
57. Benvenuti, B., Mascaro, I., Corsini, F., Lattanzi, P., Parrini, P. and Tanelli, G., *Environ. Geol.*, 1997, **30**, 238–243.
58. Simon, G., Kesler, S. E. and Chryssoulis, S., *Econ. Geol.*, 1999, **94**, 405–422.
59. Datta, D. K. and Subramanian, V., *Environ. Geol.*, 1997, **30**, 181–188.
60. Datta, D. K. and Subramanian, V., *Environ. Geol.*, 1998, **36**, 93–101.
61. Mok, W. M. and Wai, C. M., *Water Res.*, 1989, **23**, 7–13.
62. Sullivan, P. J. and Yelton, J. L., *Environ. Geol. Water Sci.*, 1988, **12**, 181–186.
63. Klassen, R. A., *Environ. Geol.*, 1998, **33**, 154–169.
64. Leoni, L. and Sartori, F., *Environ. Geol.*, 1997, **32**, 83–91.
65. Pirrie, D., Camm, G. S., Sear, L. G. and Hughes, S. H., *Environ. Geol.*, 1997, **29**, 58–65.
66. Subramanian, V., Van Grieken, R. and Van T’Dack, L., *J. Geol. Soc. India*, 1987, **30**, 217–226.
67. Takamatsu, T., Kawashima, M. and Koyama, M., *Water Res.*, 1985, **19**, 1029–1032.
68. Reimann, C., Boyd, R., Caritat, P. de., Halleraker, J. H., Kashulina, G., Niskavaara, H. and Bogatyrev, I., *Environ. Pollut.*, 1997, **95**, 45–56.
69. Leoni, L., Sartori, F., Saitta, M., Damiani, V., Ferretti, O. and Viel, M., *Environ. Geol. Water Sci.*, 1971, **17**, 23–46.
70. Konhauser, K. O., Powell, M. A., Fyfe, W. S., Longstaffe, F. J. and Tripathy, S., *J. Hydrol.*, 1997, **193**, 258–269.
71. Newman, M. C., Alberts, J. J. and Greenhut, V. A., *Water Res.*, 1985, **19**, 1157–1165.

Received 17 September 1999; revised accepted 31 December 1999

## Antimicrobial activity of artemisinin and its precursors