Mobility of arsenic in groundwater in the Obuasi gold-mining area of Ghana: some implications for human health

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Abstract: Arsenic in drinking water from streams, shallow wells and boreholes in the Obuasi gold-mining area of Ghana range between < 2 and $175\,\mu g\,l^{-1}$. The main sources are mine pollution and natural oxidation of sulphide minerals, predominantly arsenopyrite (FeAsS). Streamwaters have been most affected by mining activity and contain some of the highest As concentrations observed. They are also of poor bacteriological quality. Some of the streams have a high As(III) content ($As(III)/As_{total} > 0.5$), probably as a result of methylation and reduction reactions mediated by bacteria and algae. Concentrations of As in groundwaters reach up to $64\,\mu g\,l^{-1}$, being highest in deeper (40–70 m) and more reducing (220–250 mV) waters. The As is thought to build up as a result of the longer residence times undergone by groundwaters in the deeper parts of the aquifer. The proportion of As present as As(III) is also higher in the deeper groundwaters. Deep mine exploration boreholes (70–100 m) have relatively low As contents of $5–17\,\mu g\,l^{-1}$, possibly due to As sorption onto precipitating ferric oxyhydroxides or to localized low As concentrations of sulphide minerals.

Median concentrations of inorganic urinary As from sample populations in two villages, one a rural streamwater-drinking community and the other a suburb of Obuasi using groundwater for potable supply, were $42\,\mu g\,l^{-1}$ and $18\,\mu g\,l^{-1}$ respectively. The value for the community drinking groundwater is typical of background concentrations of urinary As. The slightly higher value for the streamwater-drinking community probably reflects different provenance of foodstuffs and higher As concentrations of water sources local to the village. The low value obtained for the inhabitants of the Obuasi suburb, living close to and abstracting groundwater from the area of major mining activity, suggests that groundwater can form a useful potable supply of good inorganic quality provided that deep, long residence time sources are avoided.

Arsenic has long been recognized as a toxin and carcinogen. A relatively high incidence of skin and other cancers has been noted in populations ingesting water with high As concentrations (WHO 1981) and other disorders, especially some dermatological (e.g. Bowen's disease, hyperkeratosis, hyperpigmentation), cardiovascular (Blackfoot disease, Raynaud's syndrome), neurological and respiratory diseases, are linked to arsenic ingestion and exposure (e.g. Gorby 1994). Recent epidemiological evidence has led the WHO to decrease its recommended maximum value for As in drinking water from $50\,\mu g\,l^{-1}$ to $10\,\mu g\,l^{-1}$ (WHO 1993) in recognition of the element's potential health risks, although many regulatory bodies such as the EC and USEPA have not yet followed suit. Arsenic is a relatively common trace element in the environment and this guideline maximum is frequently exceeded in drinking water supplies. Many cases of chronic and acute endemic As poisoning from drinking water have been documented, notably cases in Taiwan (Tseng *et al.* 1968; Chen *et al.* 1994), Argentina (Astolfi 1971), Chile (Zaldivar 1974), China (Wang & Huang 1994) and Mexico (Cebrián *et al.* 1994). Wang & Huang (1994) claimed that no morbidity cases were found where drinking water concentrations were less than $100\,\mu g\,l^{-1}$, but that morbidity increased exponentially as aqueous As increased. Mild As poisoning was observed between 100 and $200\,\mu g\,l^{-1}$.

The average concentration of As in the earth's crust is $1.5–2\,mg\,kg^{-1}$ (National Academy of Sciences 1977). It occurs in many geological materials including clay minerals, phosphorites and iron and manganese ores, but is found in highest concentrations in sulphide minerals, especially arsenopyrite, as well as realgar (AsS), orpiment (As_2S_3) and in solid solution in pyrite (FeS_2). Terrains rich in sulphide-bearing minerals can therefore have high concentrations of dissolved As in rivers and groundwaters derived by sulphide oxidation. In southwest Taiwan for example, water from artesian wells in sulphide-rich black shales has concentrations of As as high as $1.8\,mg\,l^{-1}$. Here, a clear dose–response relationship has been

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found between As ingestion and occurrences of endemic skin cancer, hyperpigmentation, keratosis and Blackfoot disease (Tseng *et al.* 1968).

Mining of sulphide ore bodies can pose a particular problem of As pollution and many ore smeltering operations are well known to release large quantities of As into the environment (e.g. Díaz-Barriga *et al.* 1993; Lagerkvist & Zetterlund 1994). Concentrations of As up to $240\,\mu g\,l^{-1}$ have been found in polluted river water draining a tin-mining area in southwest England (Hunt & Howard 1994). Wilson & Hawkins (1978) found concentrations of As ranging from $5\,\mu g\,l^{-1}$ up to $1.2\,mg\,l^{-1}$ in streamwaters draining the Fairbanks gold-mining district of Alaska. Acidic waters draining a gold-mining area in Zimbabwe were reported to contain up to $72\,mg\,l^{-1}$ of As (Williams & Smith 1994) and high As contents have also been reported in lake sediments affected by former gold mining in the Waverley area of Nova Scotia (Mudroch & Clair 1986).

The town of Obuasi in the Ashanti Region of Ghana has been the centre of large-scale gold-mining activity since the late 19th century. The main gold-bearing ore is arsenopyrite. Mining activity is known to have given rise to substantial airborne As pollution from the ore-roasting chimney in the town as well as riverborne As pollution derived from nearby tailings dams. Some studies of As exposure of mine workers in Obuasi have been carried out (Amasa 1975) but little information is available about the concentrations of As and other potentially toxic metals in the drinking water of rural communities around the town, both as a result of pollution from the mining activity and from natural processes of water–rock interaction and sulphide oxidation. This paper investigates the concentrations of As in drinking water from streams, shallow dug wells and boreholes in a 40 × 40 km area around the town as well as the composition of deep groundwaters (70–100 m depth) from mine exploration boreholes and mining effluent. Arsenic has also been determined in urine samples from volunteers in two selected villages. The main processes of As mobilization in the natural groundwater environment of the Obuasi region and the impact of As on the health of local rural communities are assessed.

Hydrogeochemistry and biogeochemistry of arsenic

Arsenic can occur in the environment in several oxidation states (−3 to +5) but in natural waters is mostly found as an oxyanion in trivalent (arsenite) or pentavalent (arsenate) form. Equilibrium speciation of As has been described in detail by Ferguson & Gavis (1972) and Brookins (1988). In oxidizing environments, arsenate is the dominant form: under acidic conditions (pH less than *c.* 6.5), $H_2AsO_4^-$ may be stabilized, whilst at higher pH, $HAsO_4^{2-}$ will be more stable (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than *c.* 9, the arsenite species $H_3AsO_3^0$ should predominate (Brookins 1988). Arsenic can therefore be stable in dissolved form over a wide range of Eh and pH conditions.

However, under reducing conditions in the presence of sulphur, As concentrations are limited by the low solubility of As sulphide minerals, such as realgar and orpiment. Little information is available about the rates of As reactions in natural waters and specific rate constants are largely unknown. At near-neutral pH, the rate of oxidation of As(III) to As(V) is known to be very slow, but may proceed faster (order of days) under more extreme pH conditions (Ferguson & Gavis 1972).

Water pH has an important impact on As release rates from minerals. Leaching experiments on river sediments contaminated by mine waste have shown that As release to solution is lowest at near-neutral pH; release is enhanced under both acidic and alkaline aqueous conditions (Mok & Wai 1989, 1990).

Most of the As in waters is present in inorganic form (e.g. Cebrián *et al.* 1994). However, organic arsenicals are also known to be stabilized by methylation reactions involving bacteria and algae (Mok & Wai 1994). Monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) have for example been observed, albeit in small quantities, in some river waters and porewaters by biotransformation of inorganic As compounds (e.g. Faust *et al.* 1987). Demethylation reactions are also known to occur in water.

Mobility of As in water is limited by sorption onto ferric oxyhydroxides, humic substances and clays (e.g. Mok & Wai 1994). Wauchope (1975) showed that sorption of As species onto sediments was in the order: arsenate > MMAA > arsenite > DMAA and Bowell (1994) found that sorption onto Fe oxyhydroxides and oxide minerals was in the order As(V) > DMAA = MMAA > As(III) at pH values less than 7, the degree of sorption being greater on amorphous oxyhydroxides (goethite) than on crystalline Fe oxides (haematite). Arsenic should therefore be less mobile in oxidizing environments, because of firstly the greater tendency for sorption of As(V) than As(III) and secondly, the lower solubility of ferric oxyhydroxides under such conditions (Peterson & Carpenter 1986). Dissolved arsenic is therefore more commonly found in reducing waters, often correlating well with dissolved Fe concentrations.

Arsenic toxicity is dependent on both its oxidation state and partitioning between organic and inorganic phases. Reduced forms tend to be more toxic than oxidized forms and inorganic species more toxic than organic, though toxicity of reduced organic forms such as trimethylarsine is relatively high. Toxicity decreases from arsine (–3) through arsenite (inorganic trivalent), arsenoxides (organic trivalent), arsenate (inorganic pentavalent), arsonium compounds to native arsenic (Morton & Dunette 1994). Arsenic(III) is known to be up to 60 times more toxic than As(V) due to its reactivity with, and inhibition of, sulphydryl-bearing enzymes in human metabolism (Squibb & Fowler 1983). However, some *in vivo* reduction of As(V) to As(III) may take place (Vahter & Envall 1983).

The most common sources of ingested As are drinking water and food (in the absence of direct pollution sources). Some foodstuffs are known to contain high concentrations of As, especially seafood (up to $40\,\mu g\,g^{-1}$, National Academy of Sciences 1977), although this contains As almost entirely in organic form as arsenobetaine ($(CH_3)_3As+CH_2CO_2^-$) and to a lesser extent as arsenocholine ($(CH_3)_3As^+CH_2CH_2OH$), both of which are of very low toxicity. Most other foodstuffs contain As (in either organic or inorganic form) in the range 0.1–$1.0\,\mu g\,g^{-1}$. Since the most common species in water are inorganic, this represents potentially the most detrimental source of As in the human diet, especially if present in reduced form.

Arsenic tends not to accumulate in the body but is readily excreted via the kidneys (e.g. Vahter & Lind 1986). Urine is therefore a good indicator of environmental As exposure and many studies of populations exposed to airborne As from smelters have been reported. Since seafood is known to be a major source of As (in organic form), most studies report both inorganic and organic (seafood-derived) As content.

Background concentrations of inorganic As in urine are largely reported to lie in the range 10–$23\,\mu g\,l^{-1}$ (Braman & Foreback 1973; Bencko & Symon 1977; Vahter & Lind 1986; Pan *et al.* 1993). Lin *et al.* (1985) quoted a somewhat higher background value of $63.4\,\mu g\,l^{-1}$ although the proportion of As present in inorganic form is not known.

Concentrations of As in urine from smelter workers exposed to airborne As are higher: Kodama *et al.* (1976) reported a value of $56\,\mu g\,l^{-1}$ and Lagerkvist & Zetterlund (1994) gave a mean value of $61\,\mu g\,l^{-1}$ in urine from smelter workers. Concentrations of As in urine of people having recently eaten seafood can reach up to $1000\,\mu g\,l^{-1}$ (Pinto *et al.* 1976), mostly as arsenobetaine.

Obuasi: local environment and geology

Ashanti region is in the tropical rainforest belt of southern Ghana. It receives a high annual rainfall (*c.* 1580 mm) with a pronounced wet season from March to November and a diurnal temperature range of 20–30°C. Evaporation is also high, about $1260\,mm\,a^{-1}$ although rainfall exceeds evaporation for about 8 months of the year (March to October). Much of the Ashanti region comprises natural forest, although many places have been cleared for cocoa and food-crop production. River flows in the region are mainly from northeast to southwest and are dominated by two rivers, the Oda and the Gymi rivers, separated by the Sansu-Moinsi hill range (maximum height *c.* 600 m).

The geology of the area is summarized in Fig. 1. Underlying bedrocks are of Birimian (Proterozoic) metasedimentary and metavolcanic rocks, the Lower Birimian comprising mainly schist, phyllite and metagreywacke as well as granite and the Upper Birimian comprising mainly metavolcanic rocks (Kesse 1985; Fig. 1). These were subjected to intensive folding and faulting and metamorphosed to greenschist grade during the Eburnian orogeny (1830–2030 Ma).

Gold-mining has been the major industry in the Ashanti region since the late 19th century. Ore deposits occur in a major shear zone with a proven lateral extent of 8 km and depth of 1600 m (Amanor and Gyapong 1988). Numerous shafts and surface operations occur along the shear zone in the vicinity of Obuasi (Fig. 1). The gold is present as both disseminated grains in quartz reefs and in association with sulphide minerals, particularly arsenopyrite (Bowell 1992).

Processing of the gold ore is carried out at the Pompora Treatment Plant (PTP) in Obuasi where the ore is crushed, roasted and extracted by a cyanide complexation process. Spent ore is collected in nearby tailings dams and although the liquid effluent from the dams is now recycled in the gold extraction process, at the time of field investigation it was discharged directly into a local stream, the Kwabrafo. This stream flows southerly on the east side of the town, joining the Pompo River 5 km southeast of Obuasi and thereafter flowing into the Gymi River. The

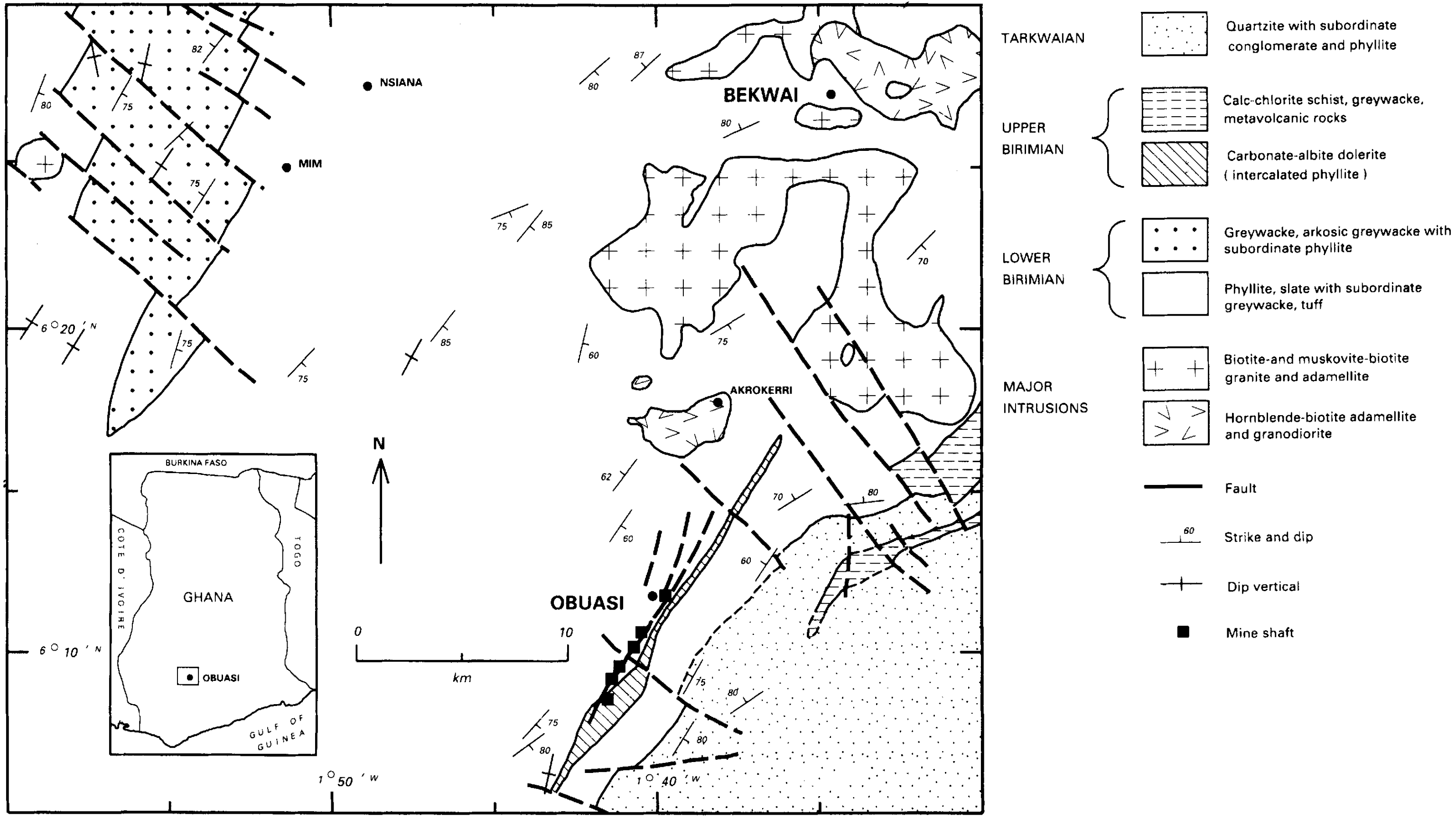

Fig. 1. Geological map of the Obuasi area of Ghana showing the mine shafts of the Ashanti mine complex (after Ghana Geological Survey maps, Obuasi sheets, 1:62 500; Bowell 1992). Location of the study area is indicated in the inset map.

effluent is known to contain large quantities of dissolved As, SO_4 and CN from the extraction and concentration process and as a result has caused serious pollution of the stream waters downstream of the input point. Additional discharges from the mine workings occur from tailings dam overflows, pumping of mine-water drainage into local streams and run-off from slime dams during periods of heavy rainfall.

Arsenic (as arsenic trioxide, As_2O_3) and sulphur (SO_2) were also emitted into the atmosphere via the PTP chimney until the recent installation of an As scrubber which reduced the levels of As emissions considerably (Ashanti Goldfields Corporation Environmental Laboratory, pers. comm. 1993). The prevailing wind direction is northerly and as a result of long-term emissions from the chimney, vegetation on the northerly slopes adjacent to the chimney has been killed or badly damaged. Defoliation as a result of both arsenic and sulphur poisoning has been observed up to 8 km north of Obuasi (Amasa 1975). This has resulted in severe erosion of bare slopes by high rainfall.

High As concentrations in hair samples of workers from the PTP attest to the former high incidence of airborne As pollution from the mining activity. Amasa (1975) found that hair samples from workers at the PTP ranged between $196 \pm 7\,\mu g\,g^{-1}$ and $1940 \pm 62\,\mu g\,g^{-1}$. Arsenic contents of soils and vegetation were also found to be high (up to $148\,\mu g\,g^{-1}$ and $4700\,\mu g\,g^{-1}$ respectively). Amasa (1975) noted that residents of villages 8–10 km north of the town claimed to have suffered eye inflammations as a result of mine emissions.

Soils in the Obuasi region are leached kaolinite–muscovite laterites with average thicknesses of 1–3 m, although the thickness depends on underlying saprolite lithology, topography and drainage (Bowell 1993). Bowell (1993) studied soil profiles 40 km east of Obuasi and noted that As was concentrated in the upper A horizon of the soils, in association with the higher content of organic matter in this layer. Concentrations of As were noted to be very low at 0.2–$0.3\,\mu g\,g^{-1}$ in the A horizon of profiles not contaminated by mining activity, decreasing to $0.01\,\mu g\,g^{-1}$ in the argillaceous (B) horizon below. Soil As in the Ashanti concession has much higher values of between 1 and $1530\,\mu g\,g^{-1}$ (mean $41.2\,\mu g\,g^{-1}$; N. Bailie, pers. comm. 1993). Saprolite thickness is variable but is mostly in the range 10–20 m (Gibb & Partners 1992). In much of the saprolite, arsenopyrite appears to have been replaced by secondary As- and Fe-bearing minerals, including scorodite ($FeAsO_4.2H_2O$), haematite, arsenolite, amorphous iron oxides and arsenates (Bowell 1992).

Groundwater flow in the Birimian aquifer is predominantly via fracture zones, mostly along quartz veins. Rest-water levels in the Obuasi area are mainly in the range 2.5–7.5 m below ground level with a seasonal variation of several metres (Gibb & Partners 1992), although the piezometric surface for the whole area studied is believed to reflect the surface topography closely. Groundwater flow direction is principally from northeast to southwest.

Health aspects

Many rural communities in the Obuasi area have either never had access to groundwater, or boreholes drilled over the last few years have fallen into disrepair through lack of maintenance. Use of surface waters for potable and domestic supply is therefore common. Education on the relationship between water quality and health is generally poor. As a result, water-borne diseases such as bilharzia and dysentery are common among streamwater drinkers. Guinea worm is rare though present in parts and occasional cholera outbreaks occur, especially during the wet season (J. Ansah, AGC Hospital, Obuasi, pers. comm. 1993). Such water-borne diseases usually have much lower prevalence among communities using groundwater.

Despite the occasional incidence of skin depigmentation and rashes, no diseases which could be unequivocally attributed to As ingestion were observed among the rural communities in the study area.

Sampling and analysis

Water samples from a 40 × 40 km area around Obuasi (Fig. 1) were collected in January 1993, towards the end of the dry season. It was intended to collect samples from boreholes as well as a few hand-dug wells in the area. However, it was found that many rural water-supply boreholes had been abandoned due to lack of ability or willingness to pay maintenance costs and many communities have therefore resorted to surface water sources which are generally highly coloured (humic substances) with high suspended solids and poor bacteriological quality. Since such water sources were the drinking water of many communities, these too were sampled. In all, 65 boreholes, 13 shallow wells and 26 streams used for drinking water were sampled in our study.

On-site analysis comprised temperature, specific electrical conductance (SEC, corrected to

25°C), HCO_3 (measured as total alkalinity), pH, Eh (temperature corrected) and dissolved oxygen, the last three of which were measured in an anaerobic flow-through cell attached in-line to borehole water outlets. Boreholes were pumped until stable readings for these parameters were obtained (usually 15–20 minutes). Streams and shallow wells were not pumped and so pH and dissolved oxygen were measured either at source or from a collected sample (on-site); no Eh readings were taken at these sites. Filtered (0.45 μm) samples were also collected in acid-washed polyethylene bottles for subsequent laboratory analysis. Samples for major-cation, SO_4 and trace element analysis were acidified to 1% HNO_3 (v/v, Aristar), unacidified samples were collected for anion analysis and separate HCl-acidified aliquots were collected for As(III) and total As analysis. Samples were stabilized at *c.* pH 4 for As(III) analysis and subsequently acidified to 2% HCl (v/v Aristar) for As_{total} analysis.

Major cations, SO_4, Si, Al, P, V, Fe_{total}, Mn, Sr and Ba were analysed by ICP-AES using an ARL 34000C optical emission spectrometer; Cl, N species, I and F by automated colorimetry, other trace elements by ICP-MS (Fison's PQ1 instrument) and As by hydride-generation ICP-AES (using an ARL 341 hydride generator). Total As was analysed by pre-reduction of all As(V) to As(III) in samples 24 hours before analysis using 5% KI (2.5 ml 20% KI in 7.5 ml sample solution), followed by on-line hydride generation using 1% w/v $NaBH_4$ in 0.1% w/v NaOH (Trafford 1986). Arsenic(III) was analysed using a modified version of the method given by Driehaus & Jekel (1992). Arsenic(III) was reduced to arsine by $NaBH_4$ at pH > 3.5 using 0.5 M acetic acid as buffer solution (to prevent As(V) also being reduced at lower pH; Driehaus & Jeckel 1992). The acetic-acid method has the limitation that it fails to separate As(III) from DMAA (Anderson *et al.* 1984) and therefore analyses quoted in this paper for As(III) are strictly for the two species. However, since methylated As species usually have very low concentrations in natural waters, the values listed are probably dominated by As(III). The As(III) method used is known to suffer from suppression of the As(III) signal by high concentrations (order of 1 $mg\,l^{-1}$ and above) of Fe, Cu and Ni (e.g. Driehaus & Jeckel 1992). All samples except one of mine-tailings effluent had very low concentrations of Cu and Ni and suppression from these elements is thought to be insignificant. Suppression of the As(III) signal by Fe at the concentrations found in most samples should also be negligible except in some of the minewaters which have up to 20 $mg\,l^{-1}$ Fe. The As(III) data for these, together with the single tailings effluent sample, may have suffered serious suppression of the As(III) signal and must therefore be taken as minimum values (Table 1).

Eighty per cent of samples analysed had ionic charge imbalances of less than 5%. Charge imbalances were poorer for some samples due to low TDS concentrations. The accuracy of ICP-AES and ICP-MS analyses was periodically checked using international reference standards. Mean analyses and 1σ standard deviations for the National Research Council of Canada standard SLRS1 analysed by ICP-AES just prior to the Obuasi samples included (certified values in parentheses; $mg\,l^{-1}$): Na: 9.7 ± 0.2 (10.4 ± 0.6), K: 1.30 ± 0.07 (1.30 ± 0.20), Ca: 29.0 ± 0.7 (25.1 ± 0.9), Mg: 5.8 ± 0.1 (5.99 ± 0.28), Ba: 0.020 ± 0.002 (0.022 ± 0.001), Fe: 0.036 ± 0.006 (0.031 ± 0.002) and Sr: 0.137 ± 0.003 (0.136 ± 0.003; n = 14). Precision of ICP-AES data is typically of the order of 2% RSD (Fe: 5%). Mean concentrations for the National Institute of Standards and Technology standard 1643C obtained by ICP-MS during the course of sample analysis were: Al: 119 ± 67 (certified value: 114 ± 5.1), Cr: 20.4 ± 1.3 (19.0 ± 0.6), Co: 25.8 ± 1.5 (23.5 ± 0.8), Ni: 63.0 ± 3.7 (60.6 ± 7.3), Cu: 22.6 ± 1.3 (22.3 ± 2.8), Zn: 70 ± 11 (73.9 ± 0.9), Sr: 269 ± 8 (263.6 ± 2.6), Mo: 111 ± 3 (104.3 ± 1.9), Cd: 11.7 ± 0.2 (12.2 ± 1.0), Ba: 50.9 ± 0.9 (49.6 ± 3.1), Pb: $35.5 \pm 1.3\,\mu g\,l^{-1}$ (35.3 ± 0.9; n = 3) and Rb: $12.1 \pm 0.2\,\mu g\,l^{-1}$ (11.4 ± 0.2; n = 4). The mean concentration for total As in 1643C by ICP-AES hydride during the course of sample analysis was $75.5 \pm 6\,\mu g\,l^{-1}$ (n = 4, certified value $82.1 \pm 1.2\,\mu g\,l^{-1}$) and SPEX standard EP8 gave a value of $10.5 \pm 0.4\,\mu g\,l^{-1}$ (n = 4, certified value $10.0\,\mu g\,l^{-1}$). Detection limits are quoted as 3σ about the variation of the blank concentration although precision is poorer at these low levels. Detection limits are given as 6σ for As_{total} and As(III) analyses.

Urine samples were collected from sample populations in two villages (30 volunteers in each) in the Obuasi area. Samples were collected in 30 ml sterile containers and frozen before analysis. Each represented a single, rather than 24-hour bulked sample. Records were made of villagers' age, occupation, sex, general health and dietary intake over the previous 24 hours. Sample digestion for reducible As was achieved by adding 4 ml concentrated HCl to 2 ml of urine and refluxing in an air condenser for 2–3 hours. Condensers were then washed down and the wash added to the sample; 1 ml 20% KI was added and the sample made up to 20 ml using deionized water. The reducible fraction is strictly inorganic As(III), As(V) and the methylated metabolite MMAA but the method does not quantitatively reduce DMAA. Since MMAA is usually a minor constituent of urine (Naqvi *et al.* 1994), the reducible fraction can be taken mainly to represent the concentration of inorganic As species. Digestion for total As involved mixing 2 ml of urine with 1 ml of a concentrated HNO_3-$HClO_4$-H_2SO_4 solution in the ratio 20:10:1. Samples were heated from 150°C to 300°C in steps of 30°C every 15–20 minutes and the resultant salt residue then dissolved in 5 ml deionized water and 4 ml HCl. Finally, 1 ml of KI was added to each sample and made up to 20 ml using deionized water. All solutions were heated to 90°C for 20 minutes prior to analysis to ensure total reduction of all As to As(III). Both total As and reducible As were analysed by the National Poisons Unit, Guy's Hospital, London by hydride-generation atomic absorption spectrometry.

Results and discussion

Mine effluent discharge

Chemical data given by Gibb & Partners (1992) for tailings effluent from the Obuasi mine reveal it to be a highly toxic cocktail of chemicals including especially As and CN derived from the roasting and extraction process. These have historically been discharged directly to nearby streams with no prior treatment or control. One sample taken during this study of the effluent being pumped directly into the Kwabrafo stream on the east side of Obuasi (Table 1) showed this to be an alkaline solution (pH 8.3) incorporating a range of toxic substances including dissolved As of 1.8 mg l^{-1}, SO_4 of 1750 mg l^{-1} and CN of 30 mg l^{-1} (CN analysed for this study by Ashanti Goldfields Corporation laboratory). Concentrations of NH_4, P, B, Co, Ni, Cu, Zn, I, Mo, Sb, Ag, Au and W are also very high in this effluent (Table 1). The As(III) content of the sample is only 50 μg l^{-1} and suggests that most of the As in the effluent is present as oxidized As(V). However, for reasons stated above, the low As(III) value may be an artefact of the analytical method and the ratio of As(III) to As total may be higher than that quoted. The high concentrations of dissolved solutes in the effluent are most likely due to the formation of CN complexes.

The concentration of As in the Kwabrafo stream just a few metres downstream of the effluent discharge point (sample collected January 1993) was 7.9 mg l^{-1} and SO_4 1130 mg l^{-1}. Concentrations of P, B, I, Ni, Co, Mo, Ag and Sb were 1.4 mg l^{-1}, 740 μg l^{-1}, 533 μg l^{-1}, 62 μg l^{-1}, 68 μg l^{-1}, 7.2 μg l^{-1}, 0.24 μg l^{-1} and 10 μg l^{-1} respectively. A sample of Kwabrafo streamwater taken at the same time from several hundred metres upstream of the effluent discharge point also revealed a high total As concentration (though much lower than the effluent; 0.35 mg l^{-1}), probably as a result of wash-in of pollutants to the stream from various points upstream in the mine area.

The quality of the Pompo and Gymi river systems downstream of the mine complex has not been investigated in this study although it is thought to have been seriously impaired over a distance of many kilometres. Concentrations of CN are expected to diminish downstream due to degradation in the aerobic environment. This may lead to decreased trace metal mobilization as CN complexes break down but will result in increased concentrations in stream sediments. Conversely, mobilization of many trace elements, notably As, is expected to be enhanced in the streams by binding to organic matter and colloids.

Regional water quality

Representative chemical data for streams, wells and boreholes are given in Table 1 and median values are summarized in Table 2. Waters are usually acidic (median values for streams, wells and boreholes are 6.4, 5.4 and 5.8 respectively) with low total dissolved solids contents (TDS; 70, 52 and 101 mg l^{-1} respectively; Table 2). The low overall TDS concentrations suggest that the waters have had short contact times with host rock materials and that water interaction has been relatively small. Bicarbonate (HCO_3) concentrations are also usually low but reach higher values in the groundwaters (median value 67 mg l^{-1}; Table 2). This suggests that the deeper groundwaters have undergone a greater degree of water–rock interaction than the streams and shallow-well waters. All waters sampled are undersaturated with respect to calcite and reflect the general paucity of carbonate in the aquifer, although carbonate is present as a gangue mineral in the auriferous shear zones (Leube *et al.* 1990). The waters are saturated with respect to quartz, reflecting the dominance of silicate–water interaction processes.

The surface waters are almost universally brown, being rich in organic matter and colloidal Fe. Bacterial counts are usually high, with mean concentrations of aerobic hetero-

Table 1. *Chemical analyses of representative water samples from streams, shallow dug wells and boreholes from the Obuasi area, Ghana.*

Sample type	Units	Odumase stream Akokoaso	Ankasa stream,	Dwete stream	Wumase	Abedwum	Mile Fourteen	Meduma	Manso Atwere	Kofikurom	Tweapease	Obuasi mine, bore 1	Obuasi mine, bore 2	Obusai, tailings outflow
Sample type		stream	stream	stream	well	well	borehole	borehole	borehole	borehole	borehole	exploration borehole	exploration borehole	tailings effluent
Longitude	(1°W)	39.23	38.20	35.67	41.91	39.63	49.61	35.64	51.22	40.92	44.33	39.57	39.56	39.71
Latitude	(6°N)	9.76	19.81	13.41	5.28	18.26	13.47	16.11	27.27	11.89	8.92	12.21	12.24	13.39
Water level	m				2.91	3.54	2.9	14.96		6.52	2.23	41.35	36.75	
Temperature	°C	24.2	22.7	25.6	25.0	25.0	25.5	26.3	25.5	26.4	26.1	26.6		32.3
Well depth	mbgl				3.76	5.85	64	53		38	43	70	70	
pH		6.53	6.65	5.99	5.57	5.58	6.20	5.87	6.18	5.44	5.70	5.94	6.17	8.45
Eh	mV						332	419	296	399	307	279	258	
DO	mg l^{-1}	4.6	4.4	1.4	1.1	5.4	<0.1	3.7	<0.1	1.6	<0.1			
SEC	μS cm^{-1}	169	55.9	50.3	82	67.4	213	110	275	113	152	956	631	2960
Ca	mg l^{-1}	6.9	2.51	1.05	7.29	6.6	22.14	5.92	43.6	6.81	10.12	87.3	58.7	435
Mg	mg l^{-1}	4.18	1.71	1.03	0.81	0.45	6.03	3.34	4.17	3.83	4.01	77.1	42.5	9.76
Na	mg l^{-1}	8.4	6.8	3.5	6.5	3.1	16.9	10.8	16.3	9.5	16.8	26.3	23.9	349
K	mg l^{-1}	0.54	0.4	<0.1	0.81	0.67	0.71	3.33	0.4	0.92	0.51	0.76	0.74	33.8
HCO_3	mg l^{-1}	54.3	25.5	8.1	28.6	25.2	130	62.5	187	38.2	82.4	110	135	154
SO_4	mg l^{-1}	1.9	0.7	2.2	3.0	0.2	0.3	0.2	<0.1	0.3	0.8	507	253	1746
Cl	mg l^{-1}	6.2	4.2	3.9	8.2	4	6.7	2.8	7	8.5	8	11.2	10.2	184
NO_3–N	mg l^{-1}	<0.2	<0.2	<0.2	<0.2	0.3	<0.2	<0.2	<0.2	3	<0.2	<0.2	<0.2	7.3
NO_2–N	μg l^{-1}	<5	<5	<5	8	<5	<5	<5	<5	<5	<5	14	6	408
NH_4–N	mg l^{-1}	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.02	17.7
Si	mg l^{-1}	8.6	7.3	4.3	7.4	5.6	31.3	28.7	30.2	12.1	28.5	7.9	12.3	4.5
Al	mg l^{-1}	0.04	0.09	0.04	0.17	<0.02	<0.02	<0.02	<0.02	0.05	<0.02	0.07	<0.02	0.03
P_{total}	mg l^{-1}	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.1	0.3	<0.1	0.2	<0.1	<0.1	1.4
V	μg l^{-1}	<3	<3	<3	18	<3	<3	<3	<3	6	<3	4	4	<3
Fe_{total}	mg l^{-1}	1.08	0.68	0.14	0.21	0.067	0.032	<0.020	0.75	0.053	0.702	20.4	4.16	0.702
Mn	mg l^{-1}	0.048	0.027	0.004	0.053	0.032	0.201	0.001	0.56	0.029	0.066	8.79	5.01	0.079
As	μg l^{-1}	7	43	10	<2	<2	54	3	57	<2	10	8	5	1810
As(III)	μg l^{-1}	4	5	<3	<3	<3	12	<3	11	<3	4	*3	*<3	*50
II	μg l^{-1}	12.3	6.5	6.0	6.0	20.0	9.6	4.0	5.2	8.0	12.6	16.0	21.2	775
FF	μg l^{-1}	80	30	30	30	40	310	90	130	30	200	350	170	490
Sr	μg l^{-1}	44.7	26.8	7.7	35.5	50.1	334	109	364	66.2	172	395	305	1496
Ba	μg l^{-1}	8.3	14.6	5.5	41.7	28.6	8.5	129	4.0	39.3	6.6	54.7	29	22.7
Li	μg l^{-1}	1.65	6.43	1.08	13.4	2.46	32.7	18.3	31.9	9.18	36.4	14.3	11.8	6.42
Be	μg l^{-1}	<0.3	<0.3	<0.3	0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
B	μg l^{-1}	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	343
Cr	μg l^{-1}	0.38	0.33	0.40	0.51	<0.30	<0.30	1.91	<0.30	<0.30	<0.30	<0.30	<0.30	0.62
Co	μg l^{-1}	0.13	0.48	0.15	2.18	1.60	4.60	0.05	3.48	1.93	2.52	65.9	22.41	261
Ni	μg l^{-1}	0.47	1.18	0.43	4.67	2.19	0.61	3.79	1.20	4.16	4.29	161	61.8	1471
Cu	μg l^{-1}	3.6	2.3	1.2	3.0	2.7	1.8	7.9	0.5	6.8	1.2	8.3	31	9219
Zn	μg l^{-1}	3.2	3.3	3.9	27.2	33.2	6.0	5.3	20.8	14.8	11.2	909	2502	631
Y	μg l^{-1}	0.024	0.36	0.11	0.28	0.47	<0.020	0.036	0.063	0.11	<0.020	35.3	1.42	0.062
Mo	μg l^{-1}	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	0.7	173
Ag	μg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.1	<0.02	<0.1	<0.1	<0.1	19.6
Cd	μg l^{-1}	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	1.2	0.6	0.2
Pb	μg l^{-1}	0.12	0.15	0.19	0.11	0.27	<0.07	0.37	<0.07	0.10	<0.07	0.23	<0.07	<0.07
Rb	μg l^{-1}	0.76	0.68	0.12	1.25	1.58	2.04	1.98	0.63	1.33	1.24	2.23	1.68	34
Cs	μg l^{-1}	<0.2	<0.2	<0.2	<0.2	<0.2	0.63	<0.2	0.41	0.32	<0.2	2.9	1.7	0.63
Sb	μg l^{-1}	0.27	<0.04	0.06	0.14	0.07	0.11	<0.04	<0.04	<0.04	<0.04	1.63	1.65	93
Tl	μg l^{-1}	<0.020	<0.020	<0.020	<0.020	<0.020	0.024	<0.020	<0.020	<0.020	<0.020	2.30	0.030	<0.020
U	μg l^{-1}	0.014	0.011	<0.005	0.076	0.028	0.098	0.060	0.13	0.008	<0.005	0.17	0.11	0.13
Au	μg l^{-1}													120
W	μg l^{-1}													911

All sources listed are used for drinking water supply apart from the Obuasi mine exploration boreholes and the Obuasi tailings effluent. DO, dissolved oxygen; SEC, specific electrical conductance (corrected to 25°C); bgl, below ground level; *represents a minimum value. Charge imbalances are all <3% except tailings outflow (–5.6%).

Table 2. *Median values for major elements and parameters of health significance in Obuasi drinking waters (streams, wells and boreholes)*

		Streams	Wells	Boreholes	WHO maximum
n		26	13	65	
Temperature	°C	24.3	25.2	26.3	
Well depth	m		3.5	48	
pH		6.42	5.37	5.84	
Ca	mg l^{-1}	4.8	3.9	7.0	
Mg	mg l^{-1}	3.1	0.82	3.9	
Na	mg l^{-1}	8.5	6.6	13.8	(200)
K	mg l^{-1}	1.4	1.1	0.55	
HCO_3	mg l^{-1}	41	21	67	
SO_4	mg l^{-1}	1.5	1.1	0.44	500
Cl	mg l^{-1}	6.2	6.2	6.0	(250)
NO_3-N	mg l^{-1}	< 0.2	0.3	< 0.2	10
NO_2-N	μg l^{-1}	< 5	< 5	< 5	910
NH_4-N	mg l^{-1}	< 0.01	< 0.01	< 0.01	(1000)
TDS	mg l^{-1}	70	52	101	
Si	mg l^{-1}	8.7	8.0	21.3	
Al	mg l^{-1}	0.03	< 0.02	< 0.02	0.2
Fe_{total}	mg l^{-1}	0.5	0.07	0.2	0.3
Mn	mg l^{-1}	0.03	0.03	0.08	0.5
Sr	μg l^{-1}	44	38	94	
Ba	μg l^{-1}	19	29	16	700
As(III)	μg l^{-1}	< 3	< 3	< 3	
As_{total}	μg l^{-1}	7	< 2	< 2	10
Cd	μg l^{-1}	< 0.2	< 0.2	< 0.2	3
Cu	μg l^{-1}	1.3	1.5	3.7	
Ni	μg l^{-1}	1.0	2.2	3.4	
Co	μg l^{-1}	0.34	1.55	1.33	
Zn	μg l^{-1}	3.9	27	18	
Sb	μg l^{-1}	< 0.04	< 0.04	< 0.04	5
Ag	μg l^{-1}	< 0.02	< 0.02	< 0.02	
Pb	μg l^{-1}	0.09	0.11	0.06	10
F	μg l^{-1}	65	50	70	1500
I	μg l^{-1}	9.1	10.1	6.7	

WHO (1993) maximum guideline values are given for comparison (values in parentheses are for elements for which no recommended guideline maximum is given, but the value represents the limit above which taste problems might occur). TDS, total dissolved solids.

trophic bacteria of 5700 colony-forming units ml^{-1}. Many of the shallow dug wells also have high bacterial populations (mean aerobic heterotrophs 4700 CFU ml^{-1}), but organic water quality is usually much better in the hand-pumped groundwaters (mean 860 CFU ml^{-1}; West *et al.* 1995).

Most of the groundwaters are oxidizing with Eh values between ≥ 300 and 500 mV but some deeper waters have lower redox potentials of around 220–250 mV. These are relatively high values for reducing waters but reflect the low pHs of the sources investigated.

Dissolved SO_4 concentrations are usually very low in the Obuasi waters, median values for streams, wells and boreholes being 1.5, 1.1 and 0.4 mg l^{-1} respectively (Table 2). All drinking water sources are undersaturated with respect to barite. Iron contents are variable, the median values for streams being 0.5 mg l^{-1}, wells 0.07 mg l^{-1} and the boreholes 0.2 mg l^{-1}.

Three groundwater samples collected from exploration boreholes penetrating to 70–100 m depth at the mine complex have different compositions with much higher TDS values of 500–800 mg l^{-1}. They are moderately reducing with Eh values of 260–280 mV. Dissolved oxygen was only measured at one site but gave a low value of 0.1 mg l^{-1}. These groundwaters have high dissolved SO_4 (200–500 mg l^{-1}) and Fe (4–20 mg l^{-1}) concentrations as well as other trace elements such as Mn, Co, Ni, Cu and Zn (e.g. Table 1). Iron was observed to oxidize and precipitate over the course of several minutes from water abstracted during sampling. These waters are saturated with respect to barite. The

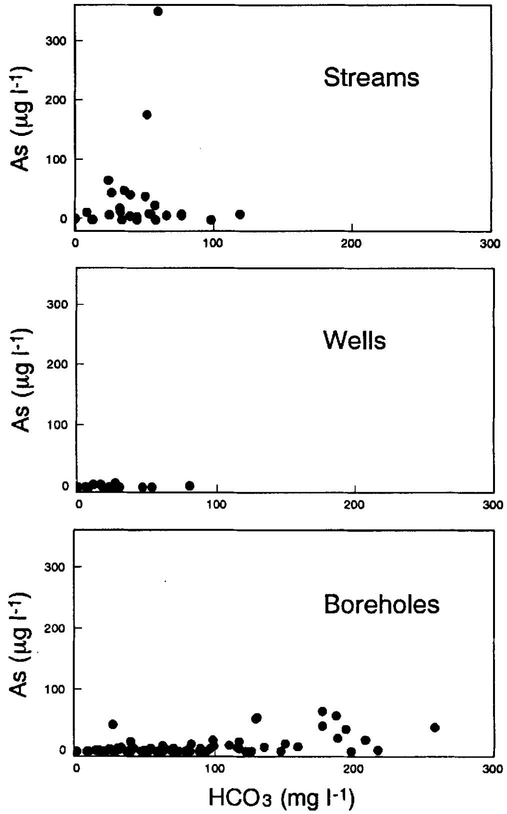

Fig. 2. Variation of As_{total} with bicarbonate (HCO_3) in water from streams, shallow wells and boreholes in the Obuasi area.

high concentrations are most likely the result of oxidation of Fe and related sulphides. One sample of mine drainage being pumped from shafts into a local stream has a particularly high TDS of $1322 mg l^{-1}$, high SO_4 of $926 mg l^{-1}$ and Fe of $7.6 mg l^{-1}$. The sample is saturated with respect to goethite and ferrihydrite. This appears to have undergone extensive sulphide oxidation, probably as a result of introduction of atmospheric oxygen via the open shaft workings.

Distribution of arsenic. Total arsenic concentrations in the Obuasi waters vary between < 2 (detection limit) and $350 \mu g l^{-1}$, although the highest value observed in drinking-water supplies was $175 \mu g l^{-1}$. Twenty per cent of supplies studied exceed the WHO guideline maximum of $10 \mu g l^{-1}$, although only 6% exceed the former WHO and current EC guideline maximum of $50 \mu g l^{-1}$. Concentrations are plotted for streams, wells and boreholes against HCO_3 content as a measure of degree of water-rock (mainly silicate) interaction in Fig. 2. The streams have the highest values observed. The highest concentration ($350 \mu g l^{-1}$) is from the Kwabrafo upstream of the effluent discharge point and is manifestly affected by mine pollution. Unlike all other samples given in Fig. 2, this is not a drinking water supply source.

Shallow wells have universally low As_{total} contents as well as HCO_3 as indicated in Table 2. The HCO_3 contents of the groundwaters range up to higher values ($258 mg l^{-1}$ maximum) as would be expected for groundwaters having infiltrated to deeper levels in the aquifer and having had longer residence times for chemical reaction. The increase in HCO_3 also corresponds with increasing borehole depth (not shown).

Figure 2 shows that the total As concentration of the groundwaters notably increases with increasing HCO_3 concentration and suggests that As mobilization is achieved through greater aquifer residence time. This is corroborated by the observed correlation between As_{total} and borehole depth in at least some of the groundwaters given in Fig. 3; deeper groundwaters should have had longer periods in contact with aquifer material and hence have undergone

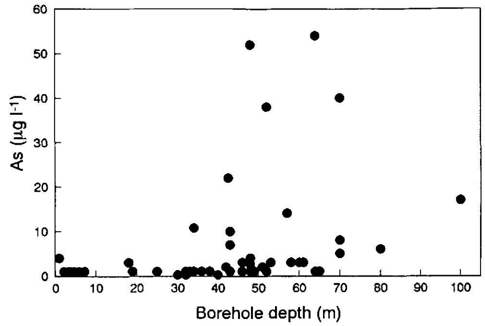

Fig. 3. Variation of As with total borehole depth (depth below ground level) in groundwaters (from wells and boreholes) in the Obuasi area.

greater water–rock reaction with As-bearing mineral phases, particularly sulphides. These deeper groundwaters also have lower redox potentials.

Investigation of the distributions of As_{total} in waters from the Obuasi area (Fig. 4) shows that the highest values in streams are mainly found to the north of Obuasi town. Groundwaters in this tract of land do not show correspondingly high As concentrations and so it is unlikely that the streamwater As is derived from the bedrock. Since the prevailing wind direction is towards the north, it is suggested that the high As streamwater values result from airborne pollution derived from the PTP chimney stack in Obuasi. Although an As scrubber has now been fitted to the plant, it is considered that the observed As represents relict pollution which has not yet been flushed from the natural surface water system because of sorption and precipitation processes involving the soil. Groundwater As_{total} concentrations reach the highest values in the western part (Fig. 4). This corresponds with deeper (and more reducing) groundwaters in this area.

Concentrations of As(III) (strictly As(III) plus DMAA) are presented in Tables 1 and 2 and ratios of As(III) to As_{total} are plotted in an Eh–pH diagram in Fig. 5. The smallest symbols shown in Fig. 5 represent those samples for which Eh and pH values were determined but either As(III) or As_{total} or both were below detection limits. Figure 5 shows that the more reducing groundwaters (Eh values $\leq 300\,mV$) not only have higher As_{total} contents, but also largely have higher As(III)/As_{total} ratios. The higher As_{total} contents of deeper groundwaters may therefore also be due to the lower tendency for sorption of As(III) to Fe species than As(V), together with the lower potential for Fe(III) precipitation under reducing conditions. Since As(III) is much more toxic than As(V), these deeper groundwaters are more a cause for concern with respect to As than the oxidized shallower groundwaters.

Histograms of the distribution of As(III)/

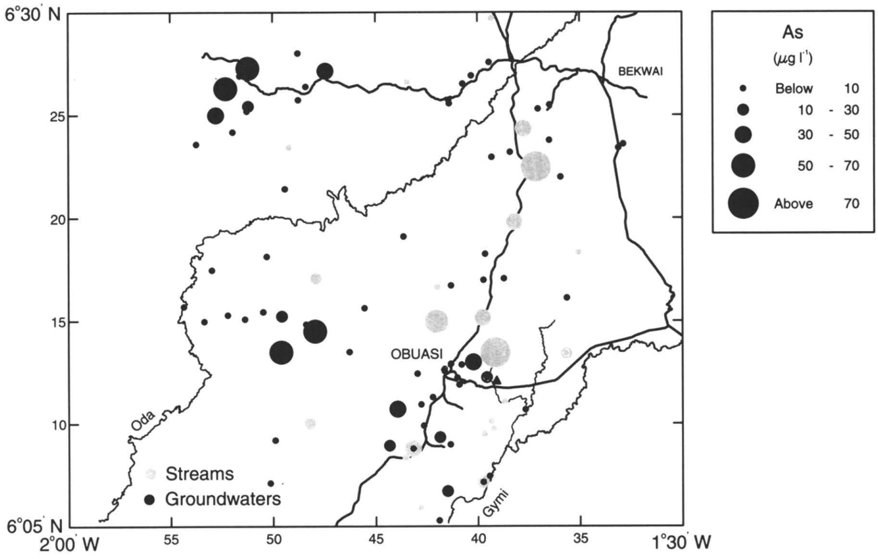

Fig. 4. Regional distribution of As_{total} in waters from the Obuasi area. Groundwaters are denoted by solid symbols and surface waters by stipple. As_{total} concentration is proportional to symbol size. Location of the Gymi and Oda rivers (and tributaries of the Gymi River) are indicated along with major roads. ▲, location of the Pompora Treatment Plant (PTP).

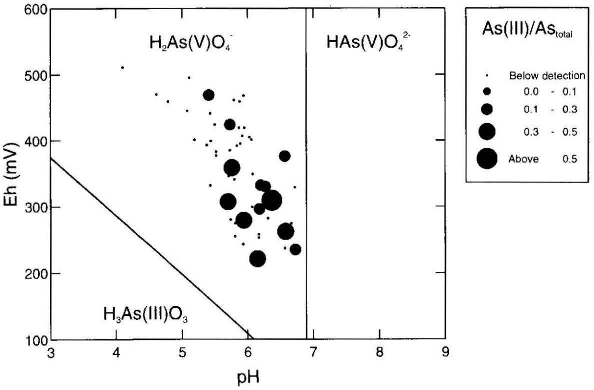

Fig. 5. Part of the Eh–pH diagram for the As system (after Brookins 1988) showing the principal stability fields of arsenate (As(V)) and arsenite (As(III)) species together with measured As(III)/As$_{total}$ ratios in water samples from the Obuasi area. The smallest symbols represent those samples for which Eh and pH determinations were made but As(III) or As$_{total}$ values were less than detection limits.

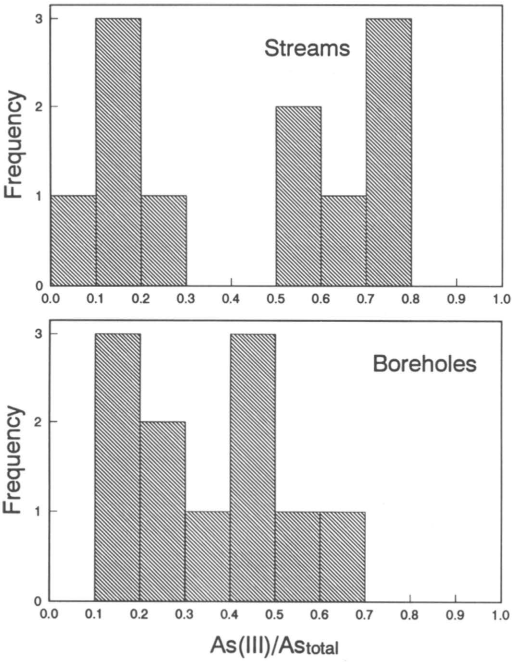

Fig. 6. Histograms of measured As(III)/As$_{total}$ ratio in streams and borehole waters.

As$_{total}$ in streams and borehole waters are given in Fig. 6. Whilst most of the groundwaters have ratios lower than 0.5 (the higher values corresponding to the deeper reducing waters), the streams have an apparent bi-modal distribution. Some have values less than 0.3 as would be expected for surface waters in contact with atmospheric oxygen. However, many have As(III)/As$_{total}$ ratios greater than 0.5. Remembering that the streams in the area have high humic and colloidal Fe contents and high bacterial counts, it is possible that oxidized As(V) has been reduced to As(III) by bacterial activity and that biomethylation reactions have generated DMAA in some of the surface waters.

Arsenic mobilization. Given the regional distribution of As-bearing minerals in the Obuasi area, the most likely source of the As in the waters is arsenopyrite (FeAsS) although minor amounts could also be derived by desorption from clays or secondary minerals (scorodite, arsenolite) formed after arsenopyrite oxidation. Oxidation of pyrite and arsenopyrite by oxygen may be described respectively by the equations:

$$4FeS_2 + 14O_2 + 4H_2O = 4Fe^{2+} + 8SO_4^{2-} + 8H^+ \quad (1)$$

and

$$4FeAsS + 13O_2 + 6H_2O = 4Fe^{2+} + 4AsO_4^{3-} + 4SO_4^{2-} + 12H^+ \quad (2)$$

The equations show that the oxidation process releases Fe and SO_4 (and arsenopyrite releases As) into solution. As noted above, with the exception of the minewaters, SO_4 contents of Obuasi groundwaters are generally quite low. However, the amount of arsenopyrite oxidation required to generate the observed dissolved As concentrations is also small. Assuming a congruent and complete reaction, oxidation of 0.85 mmol of arsenopyrite would be required to produce the highest observed As concentration in the drinking water boreholes ($64\,\mu g\,l^{-1}$). This would produce a corresponding SO_4 concentration of only $82\,\mu g\,l^{-1}$ and Fe of $48\,\mu g\,l^{-1}$. Iron is present in some of the waters in reducing acidic or organic-rich conditions, but molar Fe/S ratios are usually much lower than the value of 0.5 expected for stoichiometric oxidation of pyrite (and indeed the value of 1.0 expected for oxidation of arsenopyrite). This is likely due to Fe precipitation as ferric oxyhydroxide in aerobic waters. Even the reducing waters from the mine exploration boreholes have Fe/S ratios significantly less than 0.5 and suggest that some loss of Fe(III) has occurred by precipitation of minerals such as goethite and ferrihydrite, although the possibility of non-stoichiometric release of As from sulphide minerals under reducing conditions cannot be ruled out.

Arsenic concentrations in the mine-waters are relatively low compared to the highest values observed in the study area: the three boreholes sampled had groundwater concentrations of 5, 8 and $17\,\mu g\,l^{-1}$ As. This may be due to increased sorption of As by ferric oxyhydroxide in waters particularly enriched in dissolved iron, or due to oxidation of larger amounts of As-poor sulphide, particularly pyrite.

Despite the clear potential for As problems in the Obuasi groundwaters, only some of the deeper more reducing waters have concentrations above the WHO recommended limit and are considered potentially hazardous to health. Although streamwaters are also largely below the limit, concentrations are higher than in the shallow groundwaters, probably as a direct result of mining pollution. This concentration of As, together with their poor bacteriological quality renders them undesirable as sources of drinking water and their use should be discouraged.

Other elements. Although the high concentrations of solutes in the mine-tailings effluent from the Obuasi mine complex are the result of CN complexing rather than natural processes, the composition gives an indication of the range of other elements in local drinking waters which may be present and potentially problematic as a result of both pollution and natural sulphide oxidation. Equations (1) and (2) demonstrate that in the natural system, the oxidation process generates a large amount of acid (H^+), arsenopyrite even more so than pyrite. Consequent lowering of water pH gives greater potential for mineral dissolution and desorption reactions and under such conditions Fe, Mn and Al are more stable in solution. Also, other trace elements may be present in the sulphide ores which are released as oxidation proceeds, for example, Ni, Co, Cu, Zn, Mo and Ag.

Other elements of potential health concern have been examined in the Obuasi waters. Most are, however, not problematic: the waters largely have low TDS concentrations and so major elements are of low concentration. Chloride is mostly $<20\,mg\,l^{-1}$, SO_4 $<4\,mg\,l^{-1}$, Na $<30\,mg\,l^{-1}$, Ca in the range 0.2–$54\,mg\,l^{-1}$ and Mg in the range 0.1–$10\,mg\,l^{-1}$. Concentrations of constituents commonly attributed to agricultural pollution (NO_3, K and P) are also usually low: only one sample investigated has a concentration of NO_3–N higher than the WHO recommended limit and most are $<5\,mg\,l^{-1}$, K values are mostly $<3\,mg\,l^{-1}$ and P concentrations are $<0.3\,mg\,l^{-1}$.

Aluminium concentrations are quite high in some samples: around 10% of the drinking water supplies sampled had concentrations above the WHO guideline maximum of $200\,\mu g\,l^{-1}$, especially some of the streams and shallow wells, the Al largely occurring in colloidal form. The high concentrations reflect the acidic character of the waters (Table 1).

Iron, although not detrimental to health, is often mentioned together with Mn in a health context because of aesthetic and acceptability problems. Iron is often quite high in Obuasi waters, notably the more reducing sources and surface sources with heavy particulate matter and humic loads. The WHO guideline maximum value for Fe in drinking water is $0.3\,mg\,l^{-1}$ but an upper limit of $1\,mg\,l^{-1}$ should suffice for most purposes (WHO 1993). About 27% of drinking waters sampled had Fe concentrations greater than $1\,mg\,l^{-1}$. Manganese is less problematic, with 3% of sources having concentrations

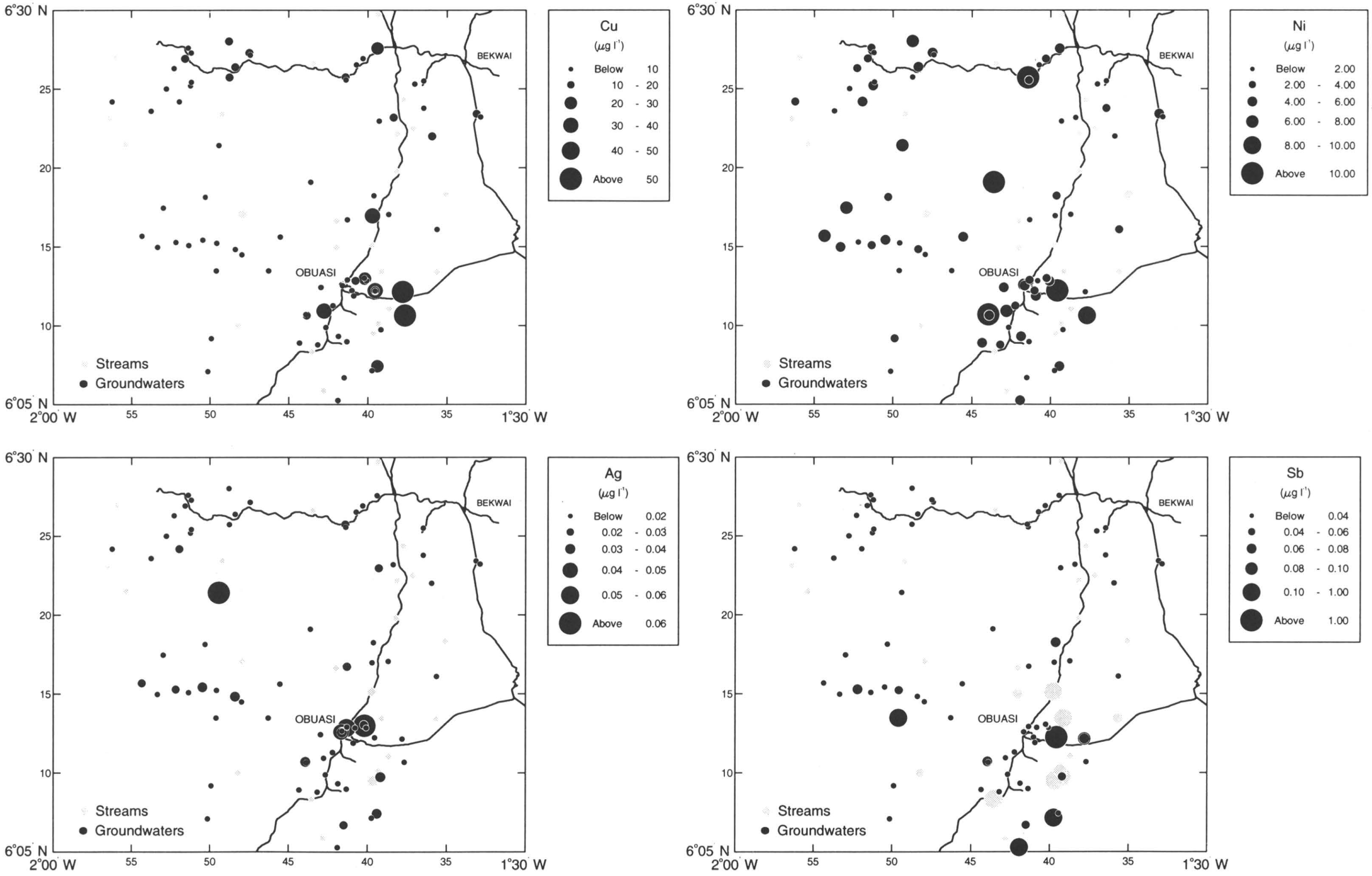

Fig. 7. Regional distributions of Cu, Ni, Ag and Sb in waters (streams, wells and boreholes) in the Obuasi area.

Table 3. *Median concentrations and ranges of As in urine from sample populations of two villages in the Obuasi area*

Village	Water source	No. villagers studied	Age range	Median total As (μg l^{-1})	Range (μgl^{-1})	Median inorganic As* (μg l^{-1})	Range (μgl^{-1})
Wumase	Stream	30	10–62	297	55–532	42	4–112
Kofikurom	Borehole	30	15–60	224	58–679	18	4–68

*Strictly includes the methylated metabolite MMAA.

greater than the provisional WHO guideline maximum of 0.5 mg l^{-1}.

Concentrations of halogens in drinking waters, notably I and F, have frequently been linked with health problems, principally goitre (I deficiency) and dental problems respectively. Median I concentrations in Obuasi waters are 7–10 μg l^{-1} (Table 2) and are not thought to promote a health problem locally; indeed goitre has not been identified as an endemic problem in the Obuasi area. Fluoride concentrations are generally low (median values 50–70 μg l^{-1}, Table 2) and much lower than the WHO recommended maximum value of 1.5 mg l^{-1}. Dental caries (commonly associated with dietary F deficiency) was identified as a common problem in the study area, although high sugar intake and poor dental hygiene are additional likely causes.

Figure 7 shows the regional distributions of Cu, Ni, Ag and Sb in Obuasi waters. Antimony has been included because of its known association with As in mine wastes and high concentrations in mining areas (e.g. Mok & Wai 1990). Although the elements given in Fig. 7 are all well below levels considered detrimental to health, their concentrations are higher in the vicinity of Obuasi. This may largely reflect natural water–rock interaction processes in the main sulphide vein-bearing zone (Fig. 1). Concentrations of most of these elements are higher in groundwaters than streams but some streamwaters around Obuasi also have high Sb concentrations, probably due to binding with colloidal-Fe and organic materials. It is also possible that the trace element anomalies around Obuasi are caused by recharge of polluted water from the Pompo and Gymi river systems to the Birimian aquifer, rather than natural water–rock interaction processes. This would also give rise to elevated concentrations of the elements shown in Fig. 7 in the groundwaters as a result of mixing. Further investigation of the distributions of elements concentrated in the tailings effluent such as Cl, SO_4, CN, Sr, B and Rb would help to determine whether this localized area of trace element anomaly is pollution-derived or natural, although CN should not have long-term stability in oxidizing conditions in river systems. Further work on the hydrogeology of the Obuasi area would also help to determine whether the groundwater quality is severely affected by mine waste recharge.

Urine samples

Statistical results for urine samples from the two villages studied in the Obuasi area are given in Table 3. One village, Kofikurom, situated about 2 km west of the Obuasi mine, is a suburb of Obuasi where the inhabitants have used groundwater from borehole supplies for many years. The chemical analysis for borehole water from this village is given in Table 1: As concentration was low at $< 2\,\mu$g l^{-1}. The other village, Wumase, is located 14 km south of Obuasi, where the water supply has traditionally been from a stream source (although a few shallow dug wells are available). Total arsenic concentration from one of the wells was $< 2\,\mu$g l^{-1} (Table 1) but higher in the local stream (the main source) at 5 μg l^{-1}. The As_{total} concentration of unfiltered streamwater from this site was found to be 8 μg l^{-1}, the excess over dissolved concentration probably bound to suspended solids or organic acids. People from both villages eat a diet of rice, cassava, plantain, yam, maize, occasional meat and fish (most volunteers having eaten fish, mostly local freshwater types, within the 24-hour period preceding the sampling). Villagers from Wumase obtain vegetables mainly from local farms, whilst those from Kofikurom obtain vegetables from Obuasi market and a farm at Anyenim (Obuasi). Ages of the volunteers were 10–62 and 15–60 in Wumase and Kofikurom respectively (Table 3). Occupations of volunteers in Wumase were mainly farmers, housewives and schoolchildren, whilst those in Kofikurom had a more varied range of occupations and included miners, farmers, traders, security staff and housewives.

Within each community, urinary As concentrations did not vary significantly with age, sex or occupation. Median values of total As concentration were 297 μg l^{-1} for Wumase and

224 $\mu g\,l^{-1}$ for Kofikurom. These values are very high compared to concentrations quoted elsewhere in the literature, but reflect the content of organic As (arsenobetaine, arsenocholine) derived from recent ingestion of fish in both populations. Inorganic (reducible) As contents were much lower at 42 and 18 $\mu g\,l^{-1}$ respectively (Table 3). The median concentration for Kofikurom falls within the range of background urinary As values given by other studies. The value for Wumase is somewhat higher and could be a result of ingestion of drinking water with more As (albeit at a concentration below the WHO recommended maximum) or due to differences in provenance of foodstuffs such as vegetable crops: those purchased at Obuasi market by the Kofikurom inhabitants are likely to be exotic rather than grown locally in potentially As-rich soils. There is also the possibility that Wumase residents use water from the polluted Gymi river since this flows very close to the village. This is, however, unconfirmed.

Since Kofikurom is a suburb of Obuasi, situated close to the mine complex and using groundwater abstracted from the vicinity of the auriferous vein systems, the low concentration of inorganic As in Kofikurom urine samples is particularly encouraging and provides further evidence that local shallow groundwater is of good quality with respect to As.

Conclusions

The distribution of As and other trace elements has been investigated in streams, shallow wells and boreholes providing drinking water to rural communities in the Obuasi area. Concentrations of total As range between $< 2\,\mu g\,l^{-1}$ and $175\,\mu g\,l^{-1}$, 20% of sources exceeding the WHO guideline maximum value for As of $10\,\mu g\,l^{-1}$ (although only 6% exceed the current EC and USEPA maximum of $50\,\mu g\,l^{-1}$). The high As loads of some local streams and groundwaters result from both mine-derived pollution and natural water–rock interaction processes. Pollution results from the discharging of tailings effluent and mine drainage into streams around Obuasi and historic atmospheric emissions of As trioxide and sulphur dioxide from roasting operations at Obuasi mine. High concentrations of As are also derived from natural oxidation of As-rich sulphide ores, notably arsenopyrite, as well as derivation from secondary As-bearing minerals.

Some of the streamwaters contain the highest concentrations of As, particularly those in the path of former mine emissions, to the north of Obuasi. Many of the As-rich streamwaters have high colloidal-Fe concentrations and are highly coloured, suggesting a high organic-acid content. The high As concentrations are likely to be facilitated by strong binding to these compounds. Arsenic(III)/As_{total} ratios have a bimodal distribution, some with values less than 0.5 dominated by As(V) and some dominated by As(III) and possibly DMAA (values greater than 0.5) which are likely to have resulted from biomethylation and reduction reactions involving bacteria and algae.

Arsenic concentrations are universally low in shallow wells (median value $< 2\,\mu g\,l^{-1}$) but reach higher levels (up to $64\,\mu g\,l^{-1}$) in groundwater from some of the deeper, more reducing boreholes (40–70 m depth). Deep mine-waters (70–100 m) rich in Fe and SO_4 indicative of Fe-sulphide oxidation have As concentrations between 5 and 17 $mg\,l^{-1}$. This range is lower than observed local maxima and probably results from As sorption by precipitating ferric oxyhydroxide although oxidation of As-poor sulphide minerals such as pyrite may also be responsible for the relatively low concentrations.

Positive correlations between As, borehole depth and bicarbonate content in groundwaters suggest that high As is controlled by depth of circulation and results from greater degrees of water–rock interaction with sulphide minerals, afforded by longer residence times in the aquifer. The higher concentrations in the deeper boreholes are generally accompanied by higher proportions of As(III) which is the stable species under more reducing conditions.

As(III) is known to be more toxic than As(V). The deeper borehole waters and some streams are therefore a greater health concern, both because of higher As_{total} contents and higher proportions of As(III). However, possible risks from As(V) should not be ignored because of the potential for *in vivo* reduction to As(III).

The quality of Obuasi drinking waters with respect to other inorganic constituents is generally good. Concentrations of the major elements are low with Cl mostly $< 20\,mg\,l^{-1}$, SO_4 $< 4\,mg\,l^{-1}$ and Na $< 30\,mg\,l^{-1}$. There is also little evidence of significant agricultural pollution since concentrations of NO_3, K and P are usually low. Trace metals, particularly those associated with sulphide oxidation and gold-mining activity (e.g. Co, Ni, Cu, Zn, Pb, Ag, Sb) are also all below WHO guideline maxima in drinking waters analysed in this study. However, higher values are observed to the east and south of Obuasi, either as a result of recharge of polluted river water to the aquifer or from natural sulphide oxidation in the area where the greatest concentration of ore veins occurs.

Microbiological quality of some Obuasi drinking waters is less good, particularly streamwaters and some shallow wells which have high bacterial counts and are often associated with water-borne diseases (West *et al.* 1995). This, together with potentially high As concentrations, renders the streamwaters largely unsuitable for potable supply.

Use of borehole water should therefore be encouraged in the area, with the exception of deeper groundwater sources with potentially high As concentrations. The local geological and geochemical environment in Obuasi is typical of the Ashanti gold belt in general and it is therefore likely that the As mobilization processes outlined above are representative of the region as a whole.

Urinary total As concentrations in volunteers from two villages, one a rural community 14 km south of Obuasi and the other a suburb of the town, are very high with median values at 297 and 224 $\mu g\,l^{-1}$ respectively and reflect the high intake of fish in the diet. Inorganic As contents are much lower at 42 and 18 $\mu g\,l^{-1}$ respectively. Differences between the two probably reflect differences in As content of water supplies and provenance of vegetable foods. In particular, the low median value for the village using groundwater, despite its proximity to mining activity and to potential sources of As, attests to the overall good quality of shallow groundwater with respect to As in the Obuasi area.

Concentrations of As in river sediments downstream of the pollutant discharge points were not investigated in this study. This would be an interesting topic for further research since large amounts of aqueous As are known to sorb onto sediments. Since As release from sediments is thought to be achieved more readily under acidic conditions, the river sediments can have a large impact on potential for As dispersion downstream of the pollution injection point and on recharge to the aquifer. This has large implications for groundwater resource protection in the area to the south and east of Obuasi.

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