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# Sorption of arsenic by iron oxides and oxyhydroxides in soils

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**Abstract**—The concentration of arsenic has been determined in natural iron oxyhydroxides and oxide minerals extracted from soils at the Ashanti mine, Ghana, and was found to vary from 2 to 35,600 mg/kg. The highest concentration of arsenic in these phases occurred in neutral-pH oxidized clay-rich soils, up to 35,600 mg/kg, and in the oxidized surface portion of mine tailings. Where highly acidic soils occurred or reducing conditions were prevalent, lower concentrations of arsenic were measured in the iron oxyhydroxide and oxide fraction (up to 433 mg/kg). Lower concentrations of arsenic in these phases were also recorded from minerals in the organic-rich soils. The proportion of arsenic associated with amorphous iron oxyhydroxides was much greater than that associated with crystalline iron oxyhydroxide and oxide minerals within the studied sample set.

In order to study the effects of pH and soil organic acids on arsenic sorption, the sorbed concentrations of As(V), As(III), monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) on goethite, hematite and lepidocrocite were measured. The sorption decreases in the order as (V) > DMAA = MMAA > As(III) below pH 7 and As(V) > As(III) > MMAA = DMAA above pH 7. Sorption decreased in the order goethite > lepidocrocite > hematite. Increased fulvic acid concentration reduced arsenic sorption on all the iron minerals. Therefore, both a drop in pH and an increase in fulvic acid increases arsenic leaching while greater sorption occurs in solutions in the pH range 4–8.

From the agreement between field observations and laboratory experiments, arsenic sorption by iron oxyhydroxide and oxide minerals would appear to be controlled by Eh and pH and in the presence of other potential sorbents such as organic acids. This has important consequences for the disposal of arsenic in mine tailings where reducing conditions are common and influence the stability of As(III) in place of As(V). This leads to lower sorption and greater leaching of arsenic. Additionally, in organic-rich soils, the competition for binding sites on mineral surfaces between organic acids and arsenic species may also lead to lower levels of arsenic retention.

## INTRODUCTION

ARSENIC is extensively recycled in the surface and near-surface environment (FERGUSON and GAVIS, 1972; ANDREAE 1978; HOLM *et al.*, 1979; AGGETT and O'BRIEN, 1985) particularly in sediments (HOLM *et al.*, 1979; MAHER, 1985; PETERSON and CARPENTER, 1986; BELZIZE and TESSIER, 1990; ABRAHAMS and THORNTON, 1987; O'NEILL, 1990; BOWELL *et al.*, 1994). The solubility and rate of arsenic oxidation are largely controlled by inorganic mechanisms (PETERSON and CARPENTER, 1983; REIMER and THOMPSON, 1988; XU *et al.*, 1991; BOWELL *et al.*, 1994) with arsenic speciation controlled by Eh–pH changes (Fig. 1). In the presence of microorganisms, methylation of arsenic oxyanions can occur, forming monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsenic oxide, trimethylarsine and dimethylarsine. The biomethylation reactions that actually occur depend upon both the microorganism and the arsenic compounds present (JOHNSON, 1972; SANDERS, 1979; PETERSON and CARPENTER, 1983), and the production of these compounds has been observed in natural waters (JOHNSON, 1972; PETERSON and CARPENTER, 1983; BOWELL 1994). These processes are also pH dependent, and consequently, pH variations will affect the distribution of organic, as well as inorganic, arsenic species.

The adsorption of arsenic by iron oxyhydroxides has been the subject of experimental and field studies (SIGG and STUMM, 1980; PETERSON and CARPENTER, 1983; REIMER and THOMPSON, 1988; XU *et al.*, 1991;

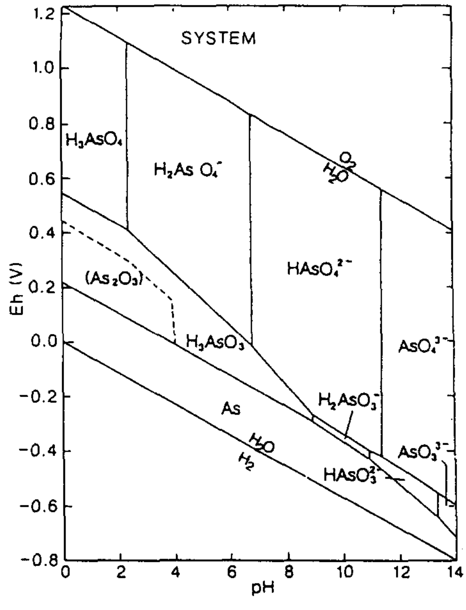

FIG. 1. Eh–pH diagram for arsenic (after data from WAGMAN *et al.*, 1982) [As] = $10^{-6}$M; [S] = $10^{-3}$M; 298 K 1 bar.

WAYCHUNAS *et al.*, 1993; BOWELL *et al.*, 1994). These experimental studies have agreed with the field data that suggest that arsenic can be recycled in the supergene environment and is associated with iron oxyhydroxides. However, the emphasis has been largely on the aquatic environment, and the sorption processes in soils and mine waste are less well understood.

During lateritic weathering of gold–arsenic mineralization at the Ashanti mine, Ghana, arsenic is released into the supergene environment by the oxidation of arsenopyrite (BOWELL, 1992). In groundwaters extracted from soils and spoil heaps, As(V), As (III), MMAA and DMAA have been identified. Total porewater arsenic concentrations up to 1300 mg/l (BOWELL *et al.*, 1994).

This paper aims to: (i) report the concentration of arsenic in iron oxyhydroxides and oxides from contaminated and uncontaminated soils, collected from the Ashanti area, Ghana; and (ii) investigate the influence of pH and organic acids in these environments on arsenic sorption by associated laboratory experiments. Iron oxides and oxyhydroxides are common components of natural gossans (BLANCHARD, 1968; BLAIN and ANDREW, 1977), soils (MILNES *et al.*, 1987; BOWELL, in press) and mine waste (BLOWES and JAMBOR, 1990). These minerals are particularly important, environmentally, as it has been proposed that they could be used for the safe disposal of wastes from industrial and mining activities (HARRIS and MONETTE, 1989; HARRIS and KRAUSE, 1993).

## GEOLOGY OF THE ASHANTI AREA, GHANA

At the Ashanti gold mine, arsenic is closely associated with gold in Lower Proterozoic shear zone hosted quartz veins and disseminated sulphide lodes (JUNNER, 1932; GYAPONG, 1980). Arsenic occurs predominantly as arsenopyrite and as a trace element in tetrahedrite, pyrite, aurostibite and bournonite. During lateritic weathering, these minerals are oxidized and this produces a series of secondary arsenate and arsenate–sulphate minerals namely bukovskyite ($Fe_2AsO_4SO_4OH.7H_2O$), kankite ($FeAsO_4.3.5\ H_2O$), pitticite (amorphous hydrated ferric arsenate) and scorodite ($FeAsO_4.2H_2O$) (BOWELL, 1991). In the lower saprolite, arsenopyrite is replaced by secondary arsenates and goethite, and in the upper saprolite, arsenopyrite pseudomorphs are preserved by goethite and hematite. Soils in the Ashanti region are typical ferrasols with a truncated mature saprolite overlain by a thin relatively recent colluvium (BOWELL, 1991).

Arsenic is a good geochemical indicator of bedrock gold mineralization in the thick tropical soil profiles developed in south west Ghana because of the close association between arsenopyrite and gold in the mineralized lodes; the low background arsenic concentrations in the soils (less than 20 mg/kg); and the greater dispersion of arsenic in comparison to other pathfinder elements associated with the mineralization. The elevated arsenic concentration in the ore and high mobility of arsenic also makes it a potential environmental hazard due to wind dispersal and groundwater leaching of arsenic from fine-grained spoil tips and tailings dam material.

## MATERIALS AND METHODS

### *Natural iron oxyhydroxides and oxides from the Ashanti area*

*Sample collection and storage.* Samples were collected from an undisturbed soil profile overlying known bedrock mineralization and from a soil profile overlying unmineralized bedrock on the Sansu prospect, Ashanti, Ghana. Further samples were collected from mine-waste treated soil profiles in the vicinity of the gold processing mill at Obuasi from the Ashanti mine, Ghana. The contaminated samples were of an exposed soil profile (aerobic soil) and from a soil profile covered by a 1.3 m of mine tailings (anaerobic soil). Both of the contaminated soil profiles occurred above unmineralized bedrock. At each sample site, 1 kg samples were collected every 20 cm from the surface to bedrock from the side wall of a newly excavated pit using a piston-hammer core sampler. The cores were stored in air-tight sealed aluminium tubes and the cores opened in the laboratory in an oxygen-free environment so as to preserve reduced species present in the pore waters.

*Soil geochemistry determination.* Arsenic and iron were extracted from a 10 g soil sample (<2 mm size fraction) by digestion with 15 ml of nitric acid (70%) and 15 ml perchloric acid (70%). The reliability of the technique was checked using known standards and found to be ±2% (standards Au-1 and K-1; BURKE, 1985).

Fractionation of arsenic in iron oxides was carried out by successive extractions with $MgCl_2$, citrate–dithionite-bicarbonate (CDB), and ethandioic acid following the procedures of GIBB (1973), KHALID *et al.* (1977) and JACKSON (1958). Magnesium chloride removes the exchangeable arsenic and ethandioic acid and CDB removes arsenic associated with amorphous and crystalline iron oxyhydroxides and oxides. Analysis of the mineral acid digests for arsenic was determined by inductively coupled plasma atomic emission spectrometry (ICPAES, Fisons ARL 3410 minitorch) with a detection limit of 0.5 mg/kg and a precision of ±5%. Iron determination was also carried out by ICPAES. Redox potential and pH were analysed by use of an Oakton field detector kit and total organic matter measured by wet chemistry using hydrogen peroxide (JACKSON, 1958).

### *Laboratory experiments on arsenic sorption*

*Experimental materials.* Typical examples of the common iron oxyhydroxide and oxide minerals were chosen from the collection of the Natural History Museum, London; goethite (BM 26884), hematite (BM 1923,681) and lepidocrocite (581426). The minerals were crushed, air-dried and sieved

Table 1. Surface area and surface area to solution volume ratios of minerals used in laboratory experiments

| Mineral | Surface area/ $cm^2g^{-1}$ | Surface area volume $cm^{-1}$ |
|---|---|---|
| Goethite α-FeOOH | 738 ± 25 | 2.22 ± 0.07 |
| Hematite $Fe_2O_3$ | 689 ± 12 | 2.07 ± 0.03 |
| Lepidocrocite γ-FeOOH | 705 ± 14 | 2.12 ± 0.05 |

with the 350–800 μm fraction retained for use in these experiments. This fraction was selected as being representative of the size fraction of iron oxyhydroxides and oxides found in the soils and spoil heaps in Ashanti. After crushing and sieving, damaged crystal faces and a fine coating of powder on grain surfaces will occur. To minimize any problems of anomalously high dissolution rates, 20 g of sieved material was cleaned ultrasonically in ethanol for 30 s separating any mineral powder into suspension which was then decanted off. The remaining grains were washed in 1 M nitric acid for 1 min to dissolve any remaining powder and remove any sharp or damaged corners. These grains were then rinsed with triply distilled deionized water, then with ethanol to dehydrate the surfaces. Finally, the grains were air-dried. No arsenic could be detected in the mineral grains by electron microprobe (detection limit of 100 mg/l); neither could any other mineral phases be detected prior to the experiments by electron microscopy, X-ray diffraction and Fourier-transform infra-red spectroscopy.

Specific surface areas of the prepared grains were measured on a Quantachrome Corporation Quantasorb, using He–Ar mixtures and the multipoint BET method (Lowell, 1979). The specific surface areas of the three iron minerals are given in Table 1.

A stock solution of As(III) was prepared by dissolving $NaAsO_2$ in triply distilled deionized water. The As(V) solution was prepared from $As_2O_5$. The organic forms MMAA (monomethylarsonic acid) and DMAA (dimethylarsinic acid) were synthesized by methylation of arsenic using the technique developed by Stary *et al.* (1982).

The fulvic acid used in this study was extracted from a tropical ferralsol soil using a modified version of the Ertel and Hedges technique (1983, 1984). Fulvic acid was extracted from the soil into a 0.1 M NaOH–0.1 M $Na_4P_2O_7$ solution at pH 12 for 24 h under nitrogen; the resulting solution was then centrifuged for 30 min at 17,000 rpm to remove insoluble material (largely clay minerals). The clear supernatant was then acidified to pH 2 by the addition of 1 M HCl to precipitate humic acid. The humic acid fraction and any further clay material was collected by centrifugation. The supernatant was subsequently filtered through a 0.45 μm Durapore (polyvinylidene difluoride) filter with the fulvic acid fraction collected in solution in the filtrate. The partly purified fulvic acid was shaken at room temperature for 12 h with distilled water to remove excess salts. This procedure was repeated four times and then the fulvic acid was dialysed for 72 h against pure water. The solutions were then freeze dried. The fulvic acids were characterized by $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy which revealed a range of aromatic phenolic and carboxylic acid groups which are considered to be the core of the fulvic acid structure (Schnitzer, 1978). Attached to this structure are alkane and alkene chains and branches, heterocyclic rings containing nitrogen (pyrrole) and sulphur (primary, secondary and tertiary mercaptans) and subordinate quinone groups. The most abundant aliphatic products are nonvolatile fatty acids of which $C_{16}$ and $C_{18}$ are the most common. The physicochemical characteristics of the fulvic acid used are given in Table 2. All chemicals used in these experiments were of analytical grade and were solutions prepared with triple distilled deionized water.

Table 2. Relative peak area comparison (%) of major $^{13}C$ NMR bands (based on Hatcher *et al.*, 1983), titrable acid groups and composition of fulvic acid used in the laboratory experiments (total element concentrations are the mean of three results by elemental analysis)

| Band (ppm) | Assignment | |
|---|---|---|
| 0–50 | Paraffinic | 26.0 |
| 50–95 | Alcohol, methoxy acetals | 15.0 |
| | Ethers | 23.0 |
| 110–145 | Olefinic, aromatic | 7.0 |
| 165–185 | Carboxyl, ethers | 21.0 |
| 190–200 | Aldehyde, ketone | 4.0 |
| Total area assigned | | 96.0 |
| Titrable carboxylic (meq/g) | | 2.9 |
| Titrable phenolic (meq/g) | | 1.5 |
| Total C (%) | | 42.4 |
| Total H (%) | | 6.8 |
| Total O (%) | | 48.8 |
| Total N (%) | | 1.6 |
| Total S (%) | | 1.4 |

### *Experimental procedure*

Experimental solutions were prepared by adding 0.5 g of mineral matter to a 19 ml arsenic solution. After pH-adjustment, the samples were pre-equilibrated for 3 d. Variable amounts of the four arsenic species were added together to give a known preselected total arsenic concentration in solution of $10^{-6}$ M. Fulvic acid was also added to some solutions. The pH was readjusted to the required pH (using dilute NaOH and $HNO_3$) and the final solution volume adjusted to 20 ml. The samples were shaken for 1 h at room temperature (22 ± 1°C).

Initial experiments showed that equilibrium was achieved after 12 h for As(III), 48 h for As(V) and 72 h for MMAA and DMAA. Following equilibration, the aqueous phase was isolated by centrifugation (7500 rpm for 15 min). An aliquot of this solution was retained for arsenic species analysis by HPLC-graphite-furnace AAS (see below) and the final pH of the solution measured. Redox potential and pH were determined on a 1:1 (v:v) sample to distilled water in the laboratory using a Cambridge instrument meter (SP5) calibrated against standard solutions. At the end of each experiment, the solid residue was dried and examined by Fourier transform infra-red spectroscopy and X-ray diffraction to confirm that no arsenate precipitates had formed.

Arsenic speciation in the samples followed schemes described by Ricci *et al.* (1981), Pacey and Ford (1981), and Haswell *et al.* (1985). A Dionex IonPac AS4A 4 mm column was used to separate the arsenic species in solution. A peristaltic pump set at a flow rate of 1.6 ml/min and two borosilicate glass auto-analyser Y-pieces were used to pump the eluent, hydrochloric acid (6 M) and borohydride (4% solution in 0.1 M sodium hydroxide) solution into the column eluate. Reduction occurred in the short coil and the liberated arsine was flushed with nitrogen into a graphite furnace. Samples (1 ml) were loaded onto the columns through the HPLC injector, with sulphuric acid ($10^{-4}$M) as the eluent at a flow rate of 4 ml/min. After sample loading, 0.1 M ammonium carbonate was used in place of sulphuric acid as the eluent. All reagents used were of analytical reagent grade and standards were made with double distilled and deionized waters. Analysis was carried out using a Perkin Elmer 1100B atomic absorption spectrometer fitted with a graphite L'vov platform with the detection wave-

Table 3. Composition of soil and spoil heap samples, Ashanti mine Ghana (all concentrations in $\mu g g^{-1}$)

| Soil horizon Depth (cm) | Exchangeable* | Amorph. Fe oxides† | Cryst. Fe oxides‡ | Total As | Total Fe | pH | Eh(V) | %OM§ |
|---|---|---|---|---|---|---|---|---|
| 0–15 | 315 | 361 | 433 | 2990 | 258,000 | 4.6 | 0.612 | 15.2 |
| 15–30 | 229 | 1495 | 295 | 3060 | 296,000 | 5.1 | 0.392 | 8.9 |
| 30–45 | 122 | 2500 | 1280 | 4250 | 329,000 | 5.9 | 0.141 | 2.1 |
| 45–60 | 136 | 2100 | 1400 | 4500 | 435,000 | 6.5 | 0.128 | 1.9 |
| Oxic spoil heap | | | | | | | | |
| 0–15 | 3950 | 20,200 | 2550 | 28,700 | 597,000 | 4.1 | 0.122 | 3.9 |
| 15–30 | 1920 | 18,900 | 1720 | 30,800 | 613,000 | 3.6 | 0.115 | 1.2 |
| 30–45 | 2600 | 35,600 | 2490 | 51,200 | 625,000 | 4.5 | 0.102 | 0.5 |
| Anoxic spoil heap | | | | | | | | |
| 45–60 | 2750 | 17,100 | 1550 | 39,500 | 619,000 | 4.3 | −0.119 | 0 |
| 60–75 | 3950 | 16,200 | 1290 | 39,700 | 621,000 | 4.6 | −0.158 | 0 |
| 75–90 | 9120 | 13,600 | 1020 | 42,000 | 598,000 | 4.2 | −0.218 | 0 |
| 90–105 | 8500 | 11,500 | 995 | 37,900 | 639,000 | 4.7 | −0.225 | 0 |

*Extractable in $MgCl_2$; †extractable in ethandioic acid; ‡extractable in citrate dithionite bicarbonate; §% organic matter (Jackson, 1958).

length adjusted to 193.7 nm. Three replicates were analysed for each sample.

## RESULTS

### *Arsenic concentration in natural iron oxyhydroxides and oxides*

The concentrations of arsenic in the soil profiles are listed in Table 3. The highest concentration of arsenic occurred in the mine waste spoil heaps and was an order of magnitude greater than in soils overlying mineralization, and several orders of magnitude greater than soils overlying unmineralized bedrock. In the uncontaminated soils above bedrock mineralization, arsenic concentration increased with depth. In the profile above unmineralized bedrock, a broad decrease is observed with a slight enrichment at surface, possibly due to sorption by organic matter. In the contaminated soils, concentration was more variable due to the input of arsenic from aerosol dispersion. The proportion of arsenic associated with amorphous iron oxyhydroxides was much greater than that associated with crystalline iron minerals. Up to 2500 mg/kg arsenic was present in the ethandioic fraction, dominated by poorly crystalline goethite, while up to 1400 mg/kg arsenic was extracted by CDB from crystalline iron minerals (dominantly hematite). The highest proportion of arsenic in the iron minerals occurred in pH 6–7, oxidized clay-rich soils and in the oxidized near-surface portion of mine tailings (over 70% of total arsenic, Table 3). Where highly acidic soils or reducing conditions occurred in the mine tailings, the concentration of arsenic in the iron minerals was an order of magnitude lower and the exchangeable concentrations much higher (Table 3). Lower concentrations of arsenic in the CDB and ethandioic acid fractions also occurred in organic-rich soils.

### *Laboratory experiments on arsenic sorption*

*Influence of pH.* Distribution coefficients of arsenic sorbed were calculated from the decrease in arsenic species concentration in solution and the surface area of the mineral grains used, and agree with previous studies (Sigg and Stumm, 1980; Xu *et al.*, 1991). The sorption of As(V) onto goethite, hematite and lepidocrocite are plotted against the pH of the final solution (Fig. 2). Sorbed As(V) showed a maximum concentration with goethite and lepidocrocite around pH 6 and for hematite between pH 7 and 8. The sorption of As(III) is less dependent on pH than As(V), but displays a sorption maximum at pH 6 with goethite, pH 7 with hematite and with lepidocrocite at pH 8 (Fig. 2). The sorption of MMAA and DMAA is diffuse but show an enhanced adsorption at low pH (Fig. 2).

Arsenic sorption is greater on goethite and lepidocrocite than on hematite for all arsenic species studied (Fig. 2). The chemical sorption of As(V) by the minerals studied is greater than for the other arsenic species over the pH range 3–9, but only slightly greater at both extremely acidic ($pH < 3$) and alkaline ($pH > 9$) conditions.

*Influence of arsenic concentration.* Sorption isotherms of the arsenic species on goethite are shown in Fig. 3 at pH 7. For all species, greater sorption occurs with increased arsenic concentration (at total arsenic concentration, $10^{-6}$ M), i.e. a higher sorption capacity occurred for As(V) on goethite than for the other arsenic species, which show a similar magnitude of sorption capacity (Fig. 3).

*Influence of fulvic acid concentration.* The effects of fulvic acid concentration (at 10 mg/l, 25 mg/l and 50 mg/l) on sorption by goethite are shown in Fig. 4. Increasing fulvic acid concentration decreased the sorption of arsenic over the pH range 4–9. With the

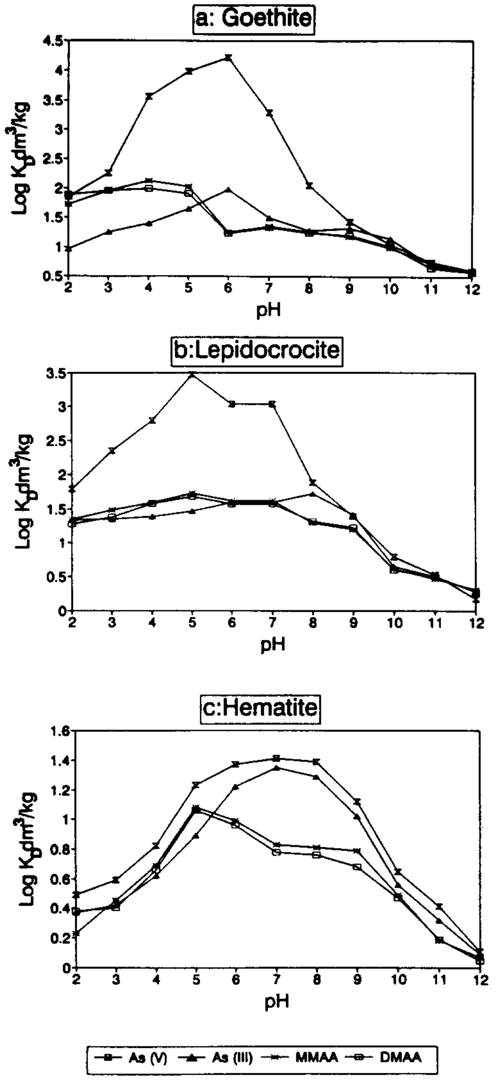

FIG. 2. Adsorption of arsenic species as a function of pH. Plot of log distribution coefficient ($K_D$, dm$^3$kg$^{-1}$). [As] = $10^{-6}$M. (a) Goethite; (b) lepidocrocite; (c) hematite.

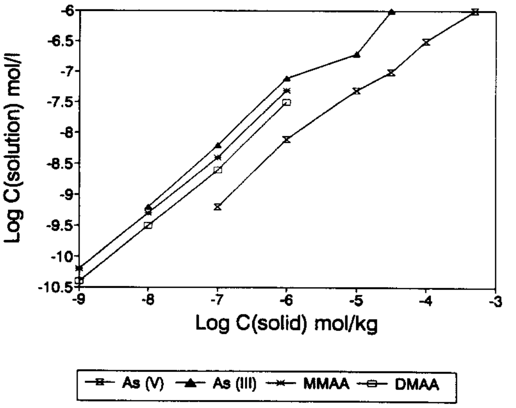

FIG. 3. Sorption isotherms for arsenic species on goethite (pH 7, adsorbent solution = 25 g/l).

organo-arsenic species, the reduction in sorption in the presence of fulvic acid is greater than with the inorganic arsenic species, possibly pointing to a similar sorption mechanism for the organo-arsenic species and fulvic acid. In strongly acidic and alkaline solutions, the effect of fulvic acid on arsenic sorption was negligible.

## DISCUSSION

Sorption of the arsenic species by goethite, hematite and lepidocrocite, can be related to arsenic speciation and to the variable surface properties of the iron oxyhydroxides and oxide, both of which are pH dependent. The difference between total arsenic and the sum of arsenic leached from the iron oxyhydroxides and oxides, from Ashanti, can be explained by the presence of residual iron arsenates (observed in XRD traces and FTIR spectra) and partly due to arsenic sorption by soil organic matter. The distribution of arsenic species in solution can be calculated from known stability constants (Table 4) with variable pH (Fig. 5). Many oxide surfaces, including goethite and hematite, change from being positively charged at low pH to negatively charged at high pH (PARFAIT, 1980). With increasing $OH^-$ concentration, such surfaces become increasingly negatively charged and thus can adsorb more cations. The pH at which the change occurs (i.e. the point at which there is a net zero charge (pzc) on the mineral surface) can be used as an indicator of whether a surface is likely to be negative or positively charged at a given pH. The pzc for goethite is 7.6–8.1 hematite, 6.5–8.6; and for lepidocrocite, 7.8–8 (PARKS and DEBRUYN, 1962).

The main As(V) species are $H_2AsO_4^-$ and $HAsO_4^{2-}$, and these are attracted to the oxides when the mineral surfaces are positively charged, i.e. when $pH < pH_{pzc}$ (PARFAIT, 1980). This would explain why, when $pH > 7$, As(V) sorption decreases rapidly. The low sorption of As(V) at $pH < 4$ could be related to release of $Fe^{3+}$ from the oxide surface, although $FeAsO_4$ was not observed in the final residue of any of the solutions. However, $Fe^{3+}$ may form soluble $Fe^{3+}-H_2AsO_4^-$ complexes which would reduce sorption by the solid material.

By contrast, $H_3AsO_3$ is the dominant form of As(III) below pH 9. The maximum sorption of As(III) decreases in strongly acidic and alkali solutions when the surface of the iron oxides would be strongly positively or negatively charged, respectively.

The organo-arsenic complexes, MMAA and DMAA, are also deprotonated at high pH and show a low sorption. The higher sorption at low pH cannot simply be due to electrostatic attraction and may be due to some form of colloidal attraction between goethite surfaces and the organic acids, as proposed for clays and humic acids (SLAVEK and PICKERING, 1981). Fulvic acid acts as an anion and competes for

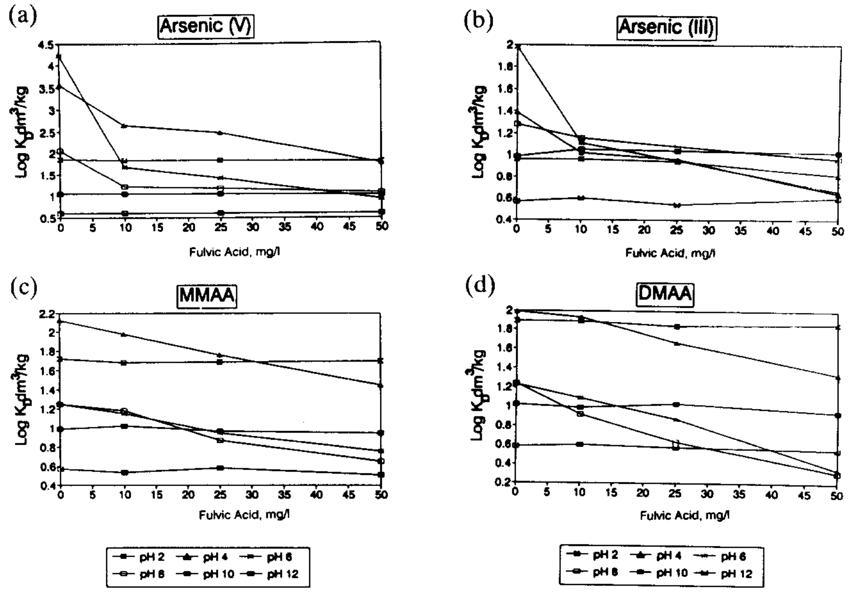

FIG. 4. Sorption of arsenic species on goethite as a function of pH and fulvic acid concentration. [As] = $10^{-6}$M. (a) As(V); (b) As (III); (c) MMAA; (d) DMAA.

Table 4. Dissociation constants of arsenic species (from WAGMAN *et al.*, 1982)

| Arsenic species | $pK_{a1}$ | $pK_{a2}$ | $pK_{a3}$ |
|---|---|---|---|
| $H_3AsO_4$ | 2.20 | 6.97 | 11.53 |
| $H_3AsO_3$ | 9.22 | 12.13 | 13.4 |
| $CH_3AsO(OH)_2$ | 3.60 | 8.22 | |
| $(CH_3)_2AsO(OH)$ | 6.20 | | |

sites with As(V) species and thus reduces As(V) sorption with increasing fulvic acid concentration (TIPPING and COOKE, 1982). A strong reduction in As(III), MMAA and DMAA adsorption also occurs and is more noticeable with increasing pH as well as fulvic acid concentration, possibly implying a similar sorption mechanism for As(III), MMAA and DMAA. For As(III), MMAA and DMAA, some form of site specific adsorption is the dominant mechanism while for As(V), electrostatic attraction is the most likely mechanism (PETERSON and CARPENTER, 1983; XU *et al.*, 1991).

In sediments, under oxidizing conditions, arsenic porewater concentrations are generally low and increase with decreasing Eh (ANDREAE, 1978; PETERSON and CARPENTER, 1986; BELZIZE and TESSIER, 1990). Based on the Eh–pH relations of inorganic arsenic species (Fig. 1), As(V) would be the dominant species in oxidizing conditions and be readily sorbed by iron oxides and hydroxides (PETERSON and CARPENTER, 1983). Consequently, solution arsenic concentration is low. With a drop in Eh, As(III) becomes more important and as shown in this study is less readily sorbed, leading to higher arsenic concentrations in solution. At low pH, iron oxides and hydroxides would also dissolve, thus releasing any arsenic sorbed, increasing arsenic concentrations in solution. At very low Eh, if reduced sulphur is present, arsenic sulphides could be precipitated, decreasing the arsenic concentration in porewaters.

In the soils and spoil heaps at the Ashanti mine, the sorption of arsenic, as As(V) is favoured in the neutral pH soils and oxidizing weakly acidic portions of the spoil heaps where pH < $pH_{pzc}$ of the iron minerals. Where reducing conditions occur (leading to a higher As(III)/As(V) ratio), or where negatively charged mineral surfaces are favoured due to system pH or the presence of organic acids, arsenic sorption is not favoured and arsenic is leached. This is exhibited in the higher proportion of $MgCl_2$-extractable arsenic from the anoxic mine waste and organic-rich soil samples. The production of MMAA and DMAA leads to greater leaching of arsenic as these species are less readily sorbed and compete with other sorbents for sites on the mineral surfaces.

## CONCLUSIONS

Field and laboratory data suggest that the sorption of arsenic by goethite, hematite and lepidocrocite, is related to chemical speciation dependent on pH, Eh and the presence of competing compounds such as fulvic acid. The sorption of As(V) is greater in the pH range 4–8 and involves electrostatic attraction between the arsenate anion and a positively charged mineral surface. The sorption of As(V) is greater than As(III) or organo-arsenic species. The presence of fulvic acid reduces arsenic sorption by competing for binding sites. A reduction in pH combined with low Eh will increase the As(III)/As(V) ratio leading to greater arsenic leaching. A pH decrease in the

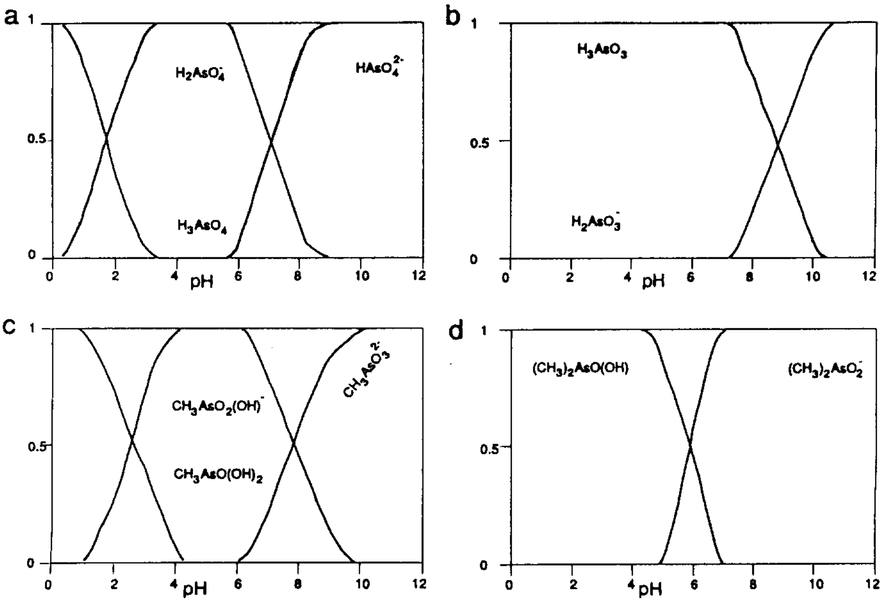

FIG. 5. Distribution of arsenic species with pH (p$K_a$ values shown in Table 4). (a) As(V); (b) As (III); (c) MMAA; (d) DMAA.

range 5–7 under oxidizing conditions could lower arsenic concentration in solution by decreasing the As(III)/As(V) ratio and leading to greater arsenic sorption by the mineral phases. The formation of organo-arsenic species is related to microbiological activity and any decrease in activity (for example at low pH) would consequently reduce the production of organic arsenic complexes.

The mobility of arsenic in the near surface and surface environment is dependent on pH. Under low Eh conditions, the predominance of As(III) over As(V) and the dissolution of iron oxides and oxyhydroxides would enhance the leaching of arsenic leading to increased arsenic concentrations in solution. Under oxidizing conditions, a lowering of pH would enhance sorption due to a decrease in the As(III)/As(V) ratio and possibly lead to the coprecipitation of arsenic with iron. A large drop in pH (<4) enhances arsenic leaching at high Eh. Similarly, leaching is enhanced in the presence of fulvic acid which competes for binding sites on the mineral surfaces.

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*Note added in proof*—Recently it has been brought to the author's attention that a similar experimental study has been reported by XU *et al.* (1991). These workers examined the adsorption of As species onto goethite, quartz, and corundum. As in this study, they found the order of adsorption to be As(V) > As(III) > MMAA = DMAA above pH 7 and As(V) > MMAA = DMAA > As(III) below pH 7. Goethite showed maximum adsorption in their study as well. They also postulated that As(V) adsorption was largely influenced by surface charge while MMAA and DMAA were influenced by covalence factors. This agreement between the two experimental studies strengthens the findings of both studies.

## REFERENCES

ABRAHAMS P. W. and THORNTON I. (1987) The distribution and extent of land contaminated by arsenic and associated metals in the mining regions of southwest England. *Trans. Inst. Min. Metall.* (sec. B Appl. Earth Sci.) **96,** B1–B8.

AGGETT J. and O'BRIEN G. A. (1985) Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. *Envir. Sci. Tech.* **19,** 231–238.

ANDREAE M. O. (1978) Distribution and speciation of arsenic in natural waters and certain algae. *Deep Sea Res.* **25,** 391–402.

BELZIZE N. and TESSIER A. (1990) Interactions between arsenic and iron in lacustrine sediments. *Geochim. cosmochim. Acta* **54,** 103–109.

BLAIN C. F. and ANDREW R. L. (1977) Sulphide weathering and the evaluation of Gossans in mineral exploration. *Miner. Sci. Eng.* **9,** 119–149.

BLANCHARD R. (1968) Interpretation of leached outcrops. *Nev. States Bur. Mines Bull.* **66,** 160 pp.

BLOWES D. W. and JAMBOR J. L. (1990) The pore-water geochemistry and mineralogy of the vadose zone of sulphide tailings, Waite Amulet, Quebec, Canada. *Appl. Geochem.* **5,** 327–346.

BOWELL R. J. (1991) The mobility of gold in tropical rain forest soils. PhD thesis. University of Southampton. 438 pp.

BOWELL R. J. (1992) Supergene gold mineralogy at the

Ashanti mine, Ghana: Implications for the supergene behaviour of gold. *Miner. Mag.* **56,** 545–560.

Bowell R. J. (1993) Mineralogy and geochemistry of a tropical weathering profile, Ashanti region, Ghana. *Chem. Geol.* (in press).

Bowell R. J., Din V. K. and Morley N. E. (1994) Arsenic speciation in porewaters, Ashanti mine, Ghana. *Appl. Geochem.* **9**, 9–16.

Burke K. E. (1985) First cooperative study on four tropical soil samples and one laterite bauxite proposed as geochemical reference samples. *Geostandards Newsl.* **9**, 69–78.

Ertel J. R. and Hedges J. I. (1983) Chemical and spectroscopic properties of marine and terrestrial humic acids, melanoidins, and synthetic compounds. In *Aquatic and Marine Humic Materials* (eds R. Christman and E. Gjessing), pp. 143–163. Ann Arbor Sci, MI.

Ertel J. R. and Hedges J. I. (1984) The lignin component of humic substances: Distribution among soil and sedimentary humic, fulvic, and base insoluble fractions. *Geochim. cosmochim. Acta* **48,** 2065–2074.

Ferguson J. F. and Gavis J. (1972) A review of the arsenic cycle in natural waters. *Water Res.* **6,** 1259–1274.

Gibb R. J. (1973) Mechanisms of metal transport in rivers. *Science* **180,** 171–173.

Gyapong W. A. (1980) Factors controlling ore localization at Ashanti mine, Ghana. MSc thesis, Imperial College, London. 180 pp.

Harris G. B. and Krause E. (1993) The disposal of arsenic from Metallurgical processes: its status regarding ferric arsenate. *Extractive Metallurgy of Nickel, Cobalt, and Associated Metals. TMS Annual Meeting, Denver,* February 21–25. Abstracts volume.

Harris G. B. and Monette S. (1989) The disposal of arsenical solid residues. In *Productivity and Technology in the Metallurgical Industries, Proceedings of a Joint TMS-AIME/GDMB Joint Symposium, Cologne, Germany,* September 17–22, 1989. pp. 545–546.

Haswell S. J., O'Neil P. and Bancroft K. C. (1985) Arsenic speciation in soil minewaters from mineralized and unmineralized areas of south-west England. *Talanta* **32,** 69–72.

Hatcher P. G., Berger I. A., Dennis L. W. and Maciel G. E. (1983) Solid state $^{13}$C NMR of sedimentary humic substances: new revelations on their chemical composition. In *Aquatic and Marine Humic Materials* (eds R. Christman and E. Gjessing), pp. 37–82. Ann Arbor, MI.

Holm T. R., Anderson M. A., Iverson D. G. and Stanforth (1979) Heterogenous interactions of arsenic in aquatic systems. In *Chemical Modelling in Aqueous Systems* (ed. E. A. Jenne), 710–736. Amer. Chem. Soc., Washington DC.

Jackson M. L. (1958) *Soil Chemical Analysis.* Prentice-Hall, Englewood Cliffs, NJ. 650 pp.

Johnson D. L. (1972) Bacterial reduction of arsenate in seawater. *Nature* **240,** 44–45.

Junner N. R. (1932) *The Geology of the Obuasi Goldfield.* 2, Memoir Gold Coast Survey, 65 pp.

Khalid R. A., Patrick W. H. and DeLaune R. D. (1977) Phosphorus sorption characteristics of flooded soils. *Soil Sci. Soc. Am.* **41,** 305–310.

Lowell S. (1979) *Introduction to Powder Surface Area.* Wiley Interscience, N.Y. 450 pp.

Maher W. A. (1985) Mode of occurrence and speciation of arsenic in some pelagic and estuarine sediments. *Chem. Geol.* **47,** 333–345.

Milnes A. R., Bourman R. P. and Fitzpatrick R. W. (1987) Petrology and mineralogy of laterites in southern and eastern Australia and southern Africa. *Chem. Geol.* **60,** 237–250.

O'Neill P. (1990) Arsenic. In *Heavy Metals in Soils* (ed. B. J. Alloway), pp. 83–99. Blackie, Glasgow.

Pacey G. E. and Ford J. A. (1981) Arsenic speciation by ion-exchange separation and atomic absorption spectrophotometry. *Talanta* **28,** 935–938.

Parfait R. L. (1980) Chemical properties of variable charge soils. In *Soils with Variable Charge* (ed. B. K. G. Theng), 167–194. New Zealand Society of Soil Science.

Parks G. A. and DeBruyn P. J. (1962) The zero point charge of oxides. *J. Phys. Chem.* **66,** 967–973.

Peterson M. L. and Carpenter R. (1983) Biogeochemical processes effecting arsenic species in an intermittently anoxic fjord. *Mar. Chem* **12,** 295–321.

Peterson M. L. and Carpenter R. (1986) Arsenic distribution in the Puget sound, Lake Washington, B. C. *Geochim. cosmochim. Acta* **50,** 353–369.

Reimer K. J. and Thompson J. A. J. (1988) Arsenic speciation in marine interstitial water. The occurrence of organoarsenicals. *Biogeochem.* **6,** 211–237.

Ricci G. R., Shepard L. S., Colovos G. and Hester N. E. (1981) Ion chromatography with atomic absorption spectrometric detection for determination of organic and inorganic arsenic species. *Analyt. Chem.* **53,** 610–613.

Sanders J. G. (1979) Microbial role in the demethylation and oxidation of methylated arsenicals in seawater. *Chemosphere* **8,** 135–137.

Schnitzer M. (1978) Humic substances: chemistry and reactions. In *Soil Organic Matter* (eds. M. Schnitzer and S. Khan), pp. 1–64. Elsevier, Amsterdam.

Sigg L. and Stumm W. (1980) The interaction of anions and weak acids with the hydrous goethite surface. *Colloid. Surface* **2,** 101–117.

Slavek J. and Pickering W. F. (1981) The effect of pH on the retention of Cu, Pb, Cd, and Zn by clay-fulvic acid mixtures. *Wat. Air Soil Pollut.* **16,** 209–221.

Stary J., Zeman A. and Kratzer K. (1982) Synthesis and separation of arsenic species. *Radiochem. Radioanal. Lett.* **52,** 263–271.

Tipping E. and Cooke D. (1982) The effect of adsorbed humic substances on the surface charge of goethite in freshwaters. *Geochim. cosmochim. Acta* **46,** 75–80.

Wagman D. D., Evans H. H., Parker V. B., Schumm R. H., Harlow I., Bailey S. M., Churney K. L. and Butall R. L. (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and organic substances in SI units. *J. Phys. Chem.* Ref. Data II, supp. 2: 392 pp.

Waychunas G. A., Rea B. A., Fuller C. C. and Davies J. A. (1993) Surface chemistry of ferrihydrite: Part I: EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. cosmochim. Acta* **57,** 2251–2269.

Xu H., Allard B. and Grimvall A. (1991) Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Wat. Air Soil Pollut.* **57–58,** 269–278.