Evaluation of Urinary Arsenic as an Indicator of Exposure to Residents of Tarkwa, Ghana

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Abstract

In Ghana, mining plays a significant role in the economic recovery programme. However, the gains are achieved at the cost of environmental and human health. For many years, the extraction of gold involved roasting which released airborne particles and large quantities of arsenic (As). Sampling for this study was conducted in March 2004 to assess the contamination status of trace elements, especially As, in water and mine workers in Tarkwa, which has nearly a century of gold mining history. Water and human urine samples were collected from Tarkwa, in addition to control samples taken from Accra, the capital of Ghana. Arsenic excretion was assessed in the first morning void urine. Concentrations of As and Mn in some water samples from Tarkwa were above the WHO drinking water guidelines. A potential health risk of As and Mn is a concern for the people consuming the contaminated water in this area. Levels of trace elements in water from control site were low compared to levels from Tarkwa. The mean urinary As concentration of 260 $\mu g l^{-1}$ from the study area was comparable to those in As-endemic areas of the world. This indicates relatively high degree of human exposure to As in Tarkwa, Ghana. Relatively low levels of As in water and no significant difference of As concentrations in urine between Tarkwa and Accra may suggest the presence of other sources of As contamination in Ghana, possibly food. This is the first study reporting 23 trace elements in human urine samples from a mining town in Ghana.

Introduction

Arsenic (As) is an ubiquitous element found in several forms in foods and environmental media such as soil, air and water. The predominant form in drinking water is inorganic As, which is both highly toxic and readily bioavailable (Valenzuela *et al*., 2005). Chronic ingestion of inorganic As-contaminated drinking water is, therefore, considered the major pathway behind the risk to human health. It was estimated that 200 million people worldwide are at risk from health effects associated with high concentrations of As in their drinking water (NRC, 2001). Large scale human exposure to As through contaminated groundwater is a serious health threat in many Asian and Latin American countries (Watanabe *et al*., 2001). With the exception of some studies in Taiwan (Tseng, 1977; Hsueh *et al*., 1998), attention has only recently been given to the epidemiological and human toxicological aspects of this contamination.

In Ghana, mining constitutes a great portion of the country's gross national product, and is the bedrock of the country's economic recovery programme. Ghana is a major gold producing country in West Africa and gold accounts for the second largest foreign exchange earner after cocoa. However, the gains are achieved at the cost of environmental and human health. Exploitation of gold puts immense stress on air, water, soil, and vegetation, and also, frequently, poses hazards to human health (Amonoo-Neizer & Amekor, 1993). For many years, the extraction of gold involved roasting which released airborne particles and large quantities of As (14–19 tons) daily in Obuasi (Amonoo-Neizer & Amekor, 1993). The main prospects in Ghana occur at Obuasi, Tarkwa, Prestea, Bibiani, Bogoso and Dunkwa, with the gold occurring in close association with sulphide minerals, especially arsenopyrite and pyrite (Smedley, 1996).

In Obuasi, which is the most important mining area in Ghana, arsenic contamination of food and water has been linked with gold-mining activities. Smedley *et al*. (1996) reported concentrations of up to 350 $\mu g\ l^{-1}$ in stream waters affected directly by mining pollution in Obuasi area, and Amonoo-Neizer & Amekor (1993) reported high As concentrations in food crops (0.12–70.5 mg kg^{-1}) also in Obuasi. At least 10% of Ghana's rural borehole wells have As concentrations exceeding 10 $\mu g\ l^{-1}$ (Mead, 2005). Earlier studies reported that mining operations have resulted in significant, localized surface water, soil, plant, some food items, human hair and atmospheric As pollution in Obuasi (Smedley *et al*., 1996; Smedley & Kinniburgh, 2002; Amonoo-Neizer & Busari, 1980; Amasa, 1975; Amonoo-Neizer, 1980).

The determination of toxic elements in urine is an important clinical screening procedure and has become a matter of wide interest owing to the toxicity of these elements and their influence in controlling the course of biological processes (Horng *et al*., 2002). Urine is easily sampled and, for instance, urinary Pb had been employed in occupational health as a noninvasive surrogate (Alessio & Foa, 1983) especially when subjects were reluctant to allow blood drawing. The arsenic content of urine is generally regarded as the most reliable indicator of recent exposure to inorganic As and is used as the main biomarker of exposure (Mushak & Crocetti, 1995).

Arsenic tends not to accumulate in the body but is readily excreted *via* the kidneys (Vahter & Lind, 1986). Urine is, therefore, a good indicator of environmental As exposure. Urinary As has long been used as a measure of exposure to the element, although, in the early days, the analytical methodology was not sensitive enough to detect the natural background concentration found in all samples (Lai *et al*., 2004). In addition, the urinary profiles of inorganic As metabolites have recently been used in epidemiological studies to assess the capacity of exposed individuals to methylate inorganic As (Valenzuela *et al*., 2005).

Humans are exposed to As in many different ways; by ingestion of contaminated water and food, by inhalation of As-containing dust or volatile As compounds, or by ingestion of As-containing preparations (Luh *et al*., 1973). There is evidence that As (III), once absorbed, may be oxidized to As (V) and or methylated in the human body. When inorganic arsenicals are ingested, urine forms the main route of elimination and the metabolites of inorganic As; dimethy-larsinic acid (DMA) and monomethylarsonic acid (MMA) are the predominant species in urine (Lagerkvist *et al*., 1988). Braman & Foreback (1973) were the first to report on the identification of As species in human urine and Smedley *et al*. (1996) reported a mean urinary total As concentration of 260 $\mu g\ l^{-1}$ from two sample villages, Wumase and Kofikurom, in the Obuasi area of Ghana.

Previous studies (Golow & Adzei, 2002; Adimado & Baah, 2002; Golow *et al*., 1996, Amonoo-Neizer & Amekor, 1993; Amasa, 1975; Smedley, 1996, Smedley *et al*., 1996) have reported mainly on As, Hg and a few trace elements in environmental samples from Ghana. The aim of the study was to assess the extent of trace elements exposure, especially As to mine workers and inhabitants of Tarkwa. This is the first comprehensive study reporting 23 trace element levels in human urine samples from a mining town in Ghana.

Materials and methods

Study area

Tarkwa and its surrounding villages (Fig. 1), which constitute the focus of the study, have nearly a century of gold mining history. The area experiences one of the heaviest and most frequent rains in the country. The choice of this region is important for a number of reasons. Apart from the operations of AngloGold Ashanti Company (formerly Ashanti Goldfields Company Ltd, AGC) at Obuasi in the Ashanti Region, most of the country's gold, diamond, and manganese and bauxite mines are located in this region. Secondly, the area has the largest concentration of mines in a single district on the continent, and, virtually, all the mining companies operating surface mines in the area are international, with mining concessions and operations in several other African countries (Akabzaa, 2000).

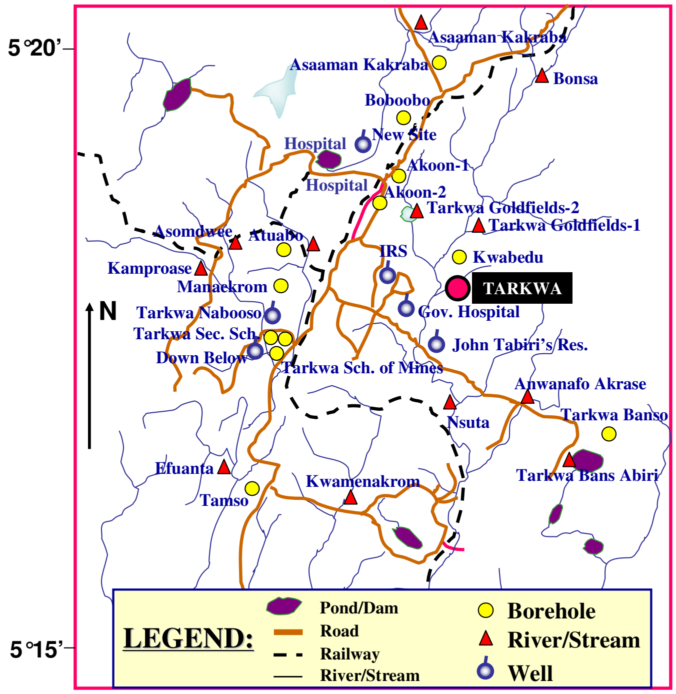


Figure 1. Map showing sampling locations of Tarkwa and surrounding areas.

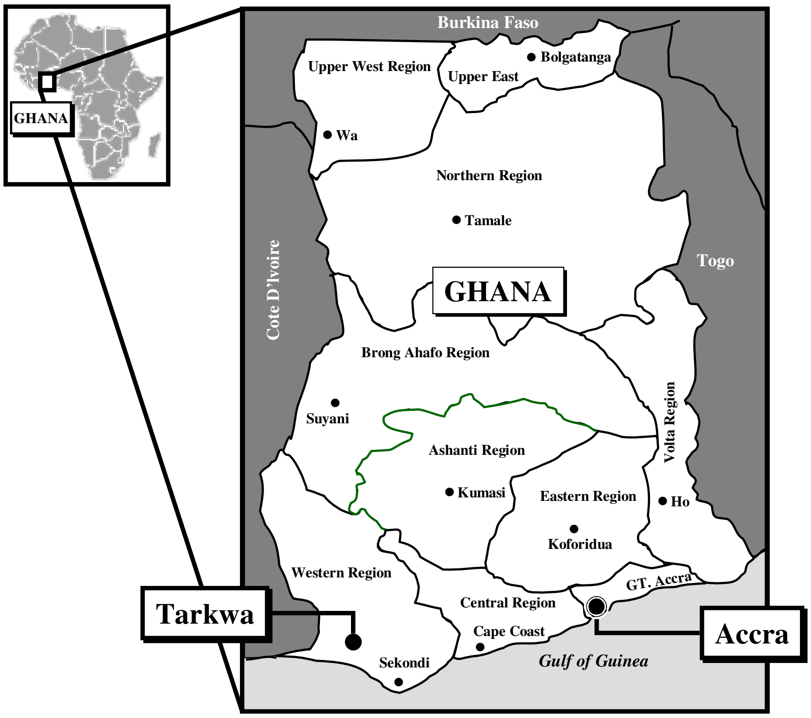


Figure 1a. Map of Ghana showing study area (Tarkwa) and control site (Accra).

The study area is part of the Wassa West District of the Western Region with Tarkwa as its district capital. The district is defined by latitudes 4° N and 5°40’ N, and longitudes 1°45’ W and 2°10’ W. The area falls within the equatorial climatic zone. Rainfall peaks during two periods, April–June and October-November, with an annual mean rainfall of 1933 mm (Akabzaa, 2000). Relative humidity for the area ranges from 83% to 91% with temperature varying between 28 °C and 33 °C (Kuma & Younger, 2001). The Tarkwa District is part of an extensive drainage basin known as the Ankobra basin, comprising the Ankobra river and its tributaries.

Samples

Thirty water and 32 human urine samples were collected from Tarkwa and its environment in March 2004, by a team from the Council for Scientific and Industrial Research-Water Research Institute (CSIR-WRI), Accra, Ghana. The water samples were from boreholes (n = 12), wells (n = 6) and rivers/streams (n = 12). The borehole samples were taken from the standpipes after 30 min of flushing. The wells were selected based on water demand of the surrounding communities as well as the scarcity of water from the public supplies. All well water samples were taken with a water sampler. The streams/rivers were sampled under base flow conditions about 20-30 cm depth from the surface. The *p*H values of the water samples were measured *in-situ*. One control water sample was also taken from a stand pipe located on the premises of the CSIR-WRI in Accra, the capital city of Ghana, and a distance of about 317 km from Tarkwa (Fig. 1a).

Spot urine samples (n = 32) were obtained from patients at the Tarkwa Government Hospital and Aba Hospital (a private hospital), with the assistance of nurses. They included mine workers (14 males and 1 female) and non-mine workers (7 males and 10 females). The ages of the mine workers ranged from 26 to 59 years while that of the non-mine workers varied between 19 and 51 years. As control, urine samples were obtained from four male workers (25–27 years) of the CSIR-WRI in Accra, where no mining occurs. The informed consent was obtained from all the donors in an ethical manner. All the water and urine samples were collected in polyethylene bottles which were pre-screened in Japan. The samples were not subjected to any chemical treatment. They were stored in cold boxes in the field and, on return to the laboratory in Accra, kept in a deep freezer. The frozen samples were air-freighted to the Center for Marine Environmental Studies (CMES) of the Ehime University in Japan, and were kept in an Environmental Specimen Bank (*es-BANK*) at -20 °C until chemical analyses.

Chemical analyses

The water samples were acidified with concentrated sulphuric acid for As and nitric acid for the other trace elements. Milli-Q water acidified with sulphuric or nitric acid was used as a blank. Concentrations of trace elements (V, Cr, Mn, Co, Cu, Zn, Ga, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Tl, Pb and Bi) were measured by an inductively-coupled plasma mass spectrometer (ICP-MS, HP-4500, Hewlett-Packard, Avondale, PA, USA) (Agusa *et al*., 2006). Matrix effects and instrumental drift in the ICP-MS measurements were corrected by the internal standard method with indium as the internal standard. Concentrations of Hg and Se were determined by cold vapour-atomic absorption spectrometry (CV-AAS; Model HG-3000, Sanso, Tsukubu, Japan) and hydride generation atomic absorption spectrometry (HG-AAS; Model HFS-3, Hitachi, Tokyo, Japan), respectively. Arsenic determination was by hydride generation-atomic absorption spectrophotometer (HG-AAS) using a Shimadzu HVG-1 hydride generation system coupled to a Shimadzu AA680 AAS (Shimadzu, Kyoto, Japan).

Urine samples were digested by heating with a mixture of sulphuric acid, nitric acid and perchloric acid for As determination carried out by HG-AAS. For other trace elements, a closed vessel microwave system (Ethos D, Milestone S.r.l., Sorisole, BG, Italy) was used for acid digestion of human urine samples. The digestion programme applied was 2 min at 250 W, 3 min at 0 W, 5 min at 250 W, 5 min at 400 W, 5 min at 500 W, 10 min at 400 W and 5 min for ventilation, respectively.

Statistical analysis

Statistical analysis was performed using SPSS (version 12.0, SPSS Inc., Chicago, Il, USA) for windows. Mann-Whitney *U*-test was used for the detection of differences in trace element concentrations in urine between males and females, mine workers and non-mine workers, as well as people in mine region (Tarkwa) and in control site (Accra). The Spearman rank correlation was used to examine the correlation between age and trace element concentrations in human urine samples. For samples having concentrations below the detection limits of the trace elements, one half of the value of the respective detection limit was substituted and used in statistical analysis. A probability value of $P < 0.05$ was considered as statistically significant in this study.

Results and discussion

Water samples

Groundwaters (wells and boreholes) in this study area recorded *p*H values varying between 4.02 and 6.90 (Table 1). Most groundwaters in southern Ghana, in particular, fall within that range and the reasons are likely related to local geology. Kuma & Younger (2001) reported that the *p*H of the soils in the Tarkwa area varies from very acidic to moderately acidic, a condition attributed to the tropical climate and lush vegetation. Arsenic concentrations in the groundwaters ranged from < 0.1 μg l^{-1} to 4 μg l^{-1} (Table 1). On the other hand, As concentrations in rivers/streams which had relatively high *p*H values between 5.82 and 7.85 were from < 1 μg l^{-1} to 73 μg l^{-1} (mean value of 19 μg l^{-1}). About 33% of the river water samples in this study exceeded the World Health Organization (WHO) guideline value of 10 μg l^{-1} for As in drinking water (WHO, 2004) (Fig. 2). The highest As concentration of 73 μg l^{-1} was from a lake-like water body and downstream of the study area from which the inhabitants draw their domestic water.

TABLE 1

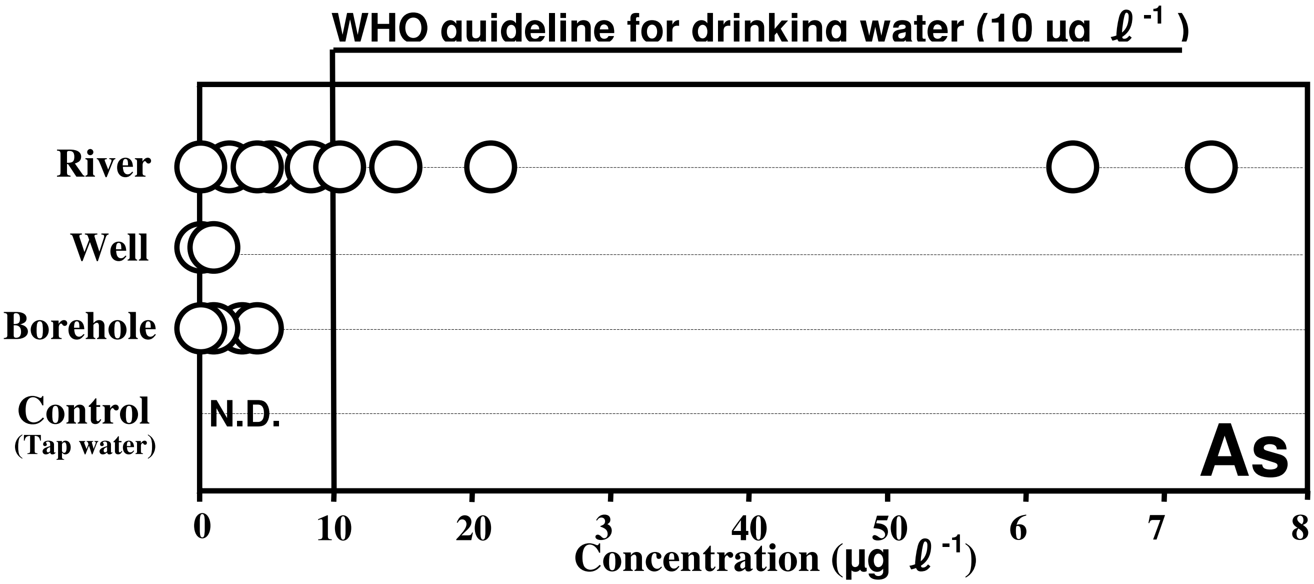
Trace element concentrations (μg/L) in water samples from the study area (Tarkwa) and control site (Accra).

Source	*Type*	*pH*	*V*	*Cr*	*Mn*	*Co*	*Cu*	*Zn*	*Ga*	*As*	*Se*	*Rb*	*Sr*
Tarkwa School of Mines	Borehole	5.70	3.2	2.1	2.2	0.02	11.1	6.88	0.08	2.0	<0.1	0.79	83.3
Tarkwa Secondary School (1)	Borehole	6.90	3.4	0.37	4970	3.3	1.79	3.96	20.9	0.5	<0.1	1.81	1320
Tarkwa Secondary School (2)	Borehole	6.75	1.1	0.12	1450	0.94	1.87	3.64	0.95	1.0	<0.1	0.85	657
Akoon (1)	Borehole	4.04	0.01	0.03	1000	8.9	7.11	21.2	1.54	0.5	<0.1	2.18	38.3
Akoon (2)	Borehole	5.85	1.5	1.5	634	0.13	4.08	5.79	1.18	3.0	<0.1	1.59	522
Atuabo	Borehole	5.49	0.18	0.46	229	0.87	1.19	24.5	0.96	1.0	<0.1	1.51	19.0
Kwabedu (KW 1)	Borehole	5.93	1.1	0.78	145	0.06	4.45	8.14	0.60	1.0	<0.1	0.43	405
Asaman Kakraba (1)	Borehole	6.20	0.47	0.12	268	0.25	1.17	1.82	1.96	4.0	<0.1	0.41	302
Tarkwa Banso (1)	Borehole	5.71	1.2	0.94	3.7	0.07	9.55	10.8	0.24	1.0	<0.1	0.42	35.9
Boboobo (1)	Borehole	5.15	0.13	0.49	386	7.6	4.56	16.2	2.66	0.5	<0.1	1.35	51.3
Tamso	Borehole	4.02	0.21	0.64	324	6.9	3.72	11.4	2.43	1.0	<0.1	0.50	25.0
Manaekrom	Borehole	5.45	0.10	1.8	156	1.2	0.93	9.72	1.29	0.5	<0.1	2.63	33.4
Mean		**5.60**	**1.0**	**0.78**	**797**	**2.5**	**4.29**	**10.3**	**2.90**	**1.3**		**1.21**	**291.04**
Median		**5.71**	**0.77**	**0.57**	**296**	**0.90**	**3.90**	**8.93**	**1.23**	**1.0**		**1.10**	**67.32**
Kamproase Down Below	Well	4.55	0.08	0.31	80.7	1.3	0.87	18.5	0.44	<0.1	<0.1	0.34	5.5
Behind IRS	Well	5.66	0.66	0.66	275	0.43	4.09	42.3	2.28	1.0	<0.1	4.19	38.7
Tarkwa Nabooso	Well	5.56	0.11	0.19	232	3.8	5.10	19.0	2.26	<0.1	<0.1	14.0	64.7
John Tabiri's Residence	Well	4.76	0.07	0.29	43.8	0.31	1.30	31.3	0.70	<0.1	<0.1	0.71	7.6
Government Hospital	Well	5.33	0.10	0.26	108	0.50	1.63	35.2	1.95	<0.1	<0.1	1.65	27.0
New Site	Well	4.49	0.06	0.13	264	1.2	5.19	10.6	4.72	<0.1	<0.1	3.26	33.5
Mean		**5.06**	**0.18**	**0.30**	**167**	**1.2**	**3.03**	**26.2**	**2.06**			**4.02**	**29.5**
Median		**5.04**	**0.09**	**0.27**	**170**	**0.85**	**2.86**	**25.1**	**2.11**			**2.45**	**30.2**
Efuanta (ES1)	Stream	6.40	0.30	0.33	658	0.50	2.36	11.7	1.24	2.0	<0.1	6.41	90.1
Nsuta	Stream	6.32	0.24	0.39	1590	0.90	1.45	7.22	1.12	5.0	<0.1	5.83	60.5
Atuabo	Stream	5.82	0.24	0.45	895	6.9	2.91	10.4	2.02	63	<0.1	2.94	36.6
Asomdwee (AS1)	Stream	5.82	0.22	0.42	318	0.86	1.51	10.5	0.62	8.0	<0.1	3.30	22.6
Kamproase (KS)	Stream	6.47	0.22	0.28	475	0.55	1.48	1495	1.22	2.0	<0.1	4.58	76.1
Asaman Kakraba (AK)	Stream	6.47	0.14	0.23	35.4	0.05	0.97	4.05	1.41	0.5	<0.1	2.09	50.4
Kwamenakrom	Stream	6.27	0.32	0.77	2530	0.78	2.95	80.5	1.00	14	<0.1	15.5	76.8
Tarkwa Goldfields (1)	Stream	7.80	0.02	0.10	11.1	0.08	1.87	3.43	1.51	8.0	<0.1	1.93	578
Tarkwa Goldfields (2)	Stream	7.85	0.05	0.28	18.6	0.15	3.51	4.39	3.17	10	<0.1	3.81	1240
River Anwanafo Akrase	River	6.24	0.61	0.93	440	2.9	9.17	10.7	2.14	21	<0.1	3.25	32.3
River Bonsa	River	6.40	2.0	1.2	929	1.2	1.97	7.15	0.57	4.0	<0.1	3.15	46.7
Tarkwa Bans Abiri	River	7.74	1.1	0.81	283	0.47	1.67	14.5	0.46	73	<0.1	2.97	262
Mean		**6.63**	**0.46**	**0.52**	**682**	**1.3**	**2.65**	**138**	**1.37**	**18**		**4.65**	**214**
Median		**6.40**	**0.24**	**0.41**	**457**	**0.67**	**1.92**	**10.5**	**1.23**	**8.0**		**3.27**	**68.3**
Control Sample	Tap	7.5	0.08	0.08	3.3	0.01	1.76	3.22	1.84	<0.1	<0.1	1.59	39.3

TABLE 1 cont'd

Source	**Type**	**Mo**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Cs**	**Ba**	**Hg**	**Tl**	**Pb**	**Bi**

Tarkwa School of Mines	Borehole	0.18	0.15	0.15	0.01	0.02	<0.1	<0.1	1.6	<0.5	0.01	0.21	0.02
Tarkwa Secondary School (1)	Borehole	2.19	0.15	0.16	0.13	0.31	0.2	0.2	520	<0.5	0.14	0.32	0.14
Tarkwa Secondary School (2)	Borehole	1.79	0.09	0.03	0.02	0.04	<0.1	0.1	23	<0.5	0.02	0.24	0.02
Akoon (1)	Borehole	0.13	0.10	0.09	<0.01	<0.01	<0.1	0.4	35	<0.5	<0.01	0.01	0.00
Akoon (2)	Borehole	0.36	0.45	0.03	0.01	0.05	<0.1	0.2	28	2.3	0.01	0.25	0.01
Atuabo	Borehole	0.13	0.17	0.06	0.04	0.12	0.1	0.1	20	<0.5	0.05	0.25	0.04
Kwabedu (KW 1)	Borehole	0.08	0.28	0.07	0.02	0.06	<0.1	0.1	13	<0.5	0.02	0.20	0.02
Asaman Kakraba (1)	Borehole	0.14	0.13	0.02	0.01	0.02	<0.1	0.3	43	<0.5	0.02	0.09	0.01
Tarkwa Banso (1)	Borehole	0.08	0.03	0.01	<0.01	0.01	<0.1	<0.1	5.1	<0.5	<0.01	0.18	0.01
Boboobo (1)	Borehole	0.23	0.11	0.05	<0.01	<0.01	<0.1	0.1	57	<0.5	<0.01	0.02	<0.01
Tamso	Borehole	0.06	0.09	0.06	<0.01	0.01	<0.1	<0.1	52	<0.5	<0.01	0.08	0.01
Manaekrom	Borehole	0.05	0.03	0.03	0.02	0.02	<0.1	0.1	28	<0.5	0.03	0.06	0.02
Mean		**0.45**	**0.15**	**0.06**	**0.03**	**0.07**		**0.2**	**69**		**0.04**	**0.16**	**0.03**
Median		**0.14**	**0.12**	**0.06**	**0.02**	**0.03**		**0.1**	**28**		**0.02**	**0.19**	**0.02**
Kamproase Down Below	Well	0.04	0.14	0.05	0.01	0.02	<0.1	<0.1	9.3	<0.5	0.01	0.43	0.01
Behind IRS	Well	0.09	0.18	0.08	<0.01	0.12	0.2	0.1	49	<0.5	0.03	43	0.01
Tarkwa Nabooso	Well	0.05	0.16	0.07	<0.01	0.02	<0.1	0.1	55	<0.5	0.03	0.30	<0.01
John Tabiri's Residence	Well	0.05	0.17	0.04	<0.01	0.06	0.1	<0.1	15	<0.5	0.01	0.67	<0.01
Government Hospital	Well	0.09	0.29	0.06	<0.01	0.17	<0.1	<0.1	43	1	0.02	1.04	<0.01
New Site	Well	0.04	0.14	0.06	<0.01	0.01	<0.1	<0.1	110	<0.5	0.04	1.27	<0.01
Mean		**0.06**	**0.18**	**0.06**		**0.07**			**47**		**0.02**	**7.76**	
Median		**0.05**	**0.17**	**0.06**		**0.04**			**46**		**0.02**	**0.86**	
Efuanta (ES1)	Stream	0.56	0.28	0.13	<0.01	0.03	0.1	<0.1	27	<0.5	<0.01	1.09	0.01
Nsuta	Stream	6.50	0.09	0.01	<0.01	0.01	0.2	<0.1	25	<0.5	<0.01	0.32	<0.01
Atuabo	Stream	0.29	0.15	0.03	<0.01	0.03	0.2	<0.1	44	<0.5	0.01	0.72	0.01
Asomdwee (AS1)	Stream	0.13	0.15	0.00	<0.01	0.02	<0.1	<0.1	13	<0.5	<0.01	0.28	<0.01
Kamproase (KS)	Stream	0.45	0.13	0.05	0.01	0.02	<0.1	<0.1	26	<0.5	0.01	2.01	0.01
Asaman Kakraba (AK)	Stream	0.08	0.02	0.00	<0.01	0.01	<0.1	<0.1	31	<0.5	<0.01	0.16	<0.01
Kwamenakrom	Stream	1.57	0.12	0.08	<0.01	0.05	0.1	0.1	21	<0.5	<0.01	1.01	<0.01
Tarkwa Goldfields (1)	Stream	0.72	0.04	0.00	<0.01	<0.01	<0.1	0.3	36	<0.5	<0.01	0.04	<0.01
Tarkwa Goldfields (2)	Stream	1.54	0.04	0.00	<0.01	<0.01	0.1	0.8	75	<0.5	<0.01	0.02	<0.01
River Anwanafo Akrase	River	0.73	1.35	0.03	0.01	0.08	0.5	<0.1	44	<0.5	0.01	3.71	0.04
River Bonsa	River	1.19	0.09	0.02	<0.01	0.01	0.1	<0.1	12	<0.5	<0.01	0.45	<0.01
Tarkwa Bans Abiri	River	223	0.09	0.12	<0.01	0.02	15	0.1	9.6	<0.5	<0.01	0.42	<0.01
Mean		**19.7**	**0.21**	**0.04**		**0.03**	**2.0**		**30**			**0.85**	
Median		**0.73**	**0.10**	**0.03**		**0.02**	**0.1**		**27**			**0.43**	
Control Sample	Tap	0.25	0.01	<0.01	<0.01	0.01	<0.1	<0.1	38	<0.5	<0.01	0.05	<0.01



The relatively high levels of arsenic in river waters suggest that people living in this area might be at risk. The highest As concentration exceeded the highest levels in some studies from literature for either ground or river water;14.4 µg l^{-1} (Tamasi & Cini, 2004), 22 µg l^{-1} (Rios-Arana *et al*., 2003), 13.8 µg l^{-1} (Naicker *et al*., 2003), 21 µg l^{-1} (Miller *et al*., 2004), 49.3 µg l^{-1} (Meza *et al*., 2004) and 64 µg l^{-1} (Smedley, 1996) but were much less than concentrations observed in regions, where chronic health problems related to As, have been detected; < 0.01 – 2.5 mg l^{-1} (Anawar *et al*., 2002), < 1 – 535 µg l^{-1} (Watanabe *et al*., 2001), 3.05 µg l^{-1} (Berg *et al*., 2001) and 1,654 µg l^{-1} (Chakraborti *et al*., 2003). In the present study, relatively high As concentrations in the river waters may reflect the oxidation/weathering of arsenopyrite and, probably, other sulphide-bearing mine tailings.

Mercury was detected in only two of the water samples, and one of them from a borehole (2.3 µg l^{-1}) exceeded the WHO guideline level of 1 µg l^{-1} for Hg in drinking water (WHO, 2004). In a related study carried out in a small-scale gold mining town of Dumasi in Ghana, Hg concentrations in boreholes varied from 0.12 to 0.27 µg l^{-1} (n = 8) and concentrations in river water samples were more variable, ranging between 0.18 and 0.76 µg l^{-1} (n = 5) (Babut *et al*., 2003). Although Hg contamination by gold mining is also of concern in Tarkwa, the results suggest that, currently, it is not so serious. However, the study might have failed to detect some Hg contamination because the detection limit (< 0.5 µg l^{-1}) for Hg in this study was higher than those in other studies (Babut *et al.,* 2003; Golow & Mingle, 2003). The highest lead concentra-tion of 43 µg l^{-1} was measured from a well. This well is located in a commercial area, and lead-contaminated street dust or residential soil and lead-based paint from the buildings in the vicinity could have contributed to the elevated value (Banerjee, 2003; Montgomery & Mathee, 2005). The rest of the samples were all below the WHO guideline value of 10 µg l^{-1} for drinking water (WHO, 2004).

Manganese is also an essential element but a known mutagen (Beckman *et al*., 1985). The accumulation of Mn may cause hepatic encephalopathy. Moreover, the chronic ingestion of Mn in drinking water is associated with neurological damage (Kondakis *et al*., 1989). Interestingly, about 33% of the boreholes and 58% of the river waters exceeded the WHO guideline value of 400 µg l^{-1} for Mn in drinking water (WHO, 2004) (Fig. 3). Thus, a health risk to the people of Tarkwa consuming Mn-contami-nated water is of great concern. The geology of the Tarkwa area consists of Tarkwaian and Birimian systems (Kuma & Younger, 2001) and manganese-bearing horizons are quite ubiquitous in rocks of the Birimian suite.

Antimony is a well-known toxic element at high doses (Navas-Acien *et al*., 2005). It shares similar chemical and toxicological properties with arsenic (Gebel, 1997), and they are frequent co-exposures (Gebel *et al*., 1998). Antimony in drinking water has been reported to modulate the toxicity of arsenic (Gebel, 1999), and the severity of As poisoning might be magnified by exposure to Sb (Frisbie *et al*., 2002). Incidentally, the same sample that recorded the highest As concentration of 73 µg l^{-1} had the highest Sb concentration of 15 µg l^{-1}, exceeding the WHO drinking water guideline value of 5 µg l^{-1} for Sb. The rest of the samples were below the detection limit of 0.1 µg l^{-1}. The concentrations of the other trace elements in the water samples were generally low with most concentrations below the limits of detection (Table 1). Arsenic was not detected in the control sample and the concentrations of the other trace elements in the control sample were predominantly low and within the WHO safe limits for drinking water (Table 1).

Urine samples

Urinary As concentrations from the study area varied between 34 and 700 µg l^{-1} with a mean of 260 µg l^{-1} (Table 2). The highest values of 700 µg l^{-1} and 650 µg l^{-1} were from a female (unknown occupation) and a male mine worker, respectively. The urinary As levels of the control samples ranged from 120 to 280 µg l^{-1} (mean value of 200 µg l^{-1}). In terms of sex, the mean values for males and females were 250 and 260 µg l^{-1}, respectively. Statistically, there was no difference between males and females ($P = 0.876$). There was also no correlation between urinary As concentration and age of males and females ($r = 0.056$) (Fig. 4). In this study, the youngest female (21 years) and oldest female (51 years) had urinary As levels of 290 µg l^{-1} and 43 µg l^{-1}, respectively. The onset of menopause may add to the explanation of the change of urinary As levels in women (Kristiansen *et al*., 1997). The distribution of urinary As concentrations among the miners and non-miners (from the study area) and control samples is shown in Fig. 5 and, statistically, there was no difference among the three groups.

TABLE 2

Trace element concentrations (µg/l) in urine samples from the study area (Tarkwa) and control site (Accra)

Subject	*Occupation*	*Age (yrs)*	*Sex*	*V*	*Cr*	*Mn*	*Co*	*Cu*	*Zn*	*Ga*	*As*	*Se*	*Rb*	*Sr*
T1	Mine worker	30	Male	1.3	11	4.5	1.0	263	146	0.10	85	23	207	69.7
T2	Mine worker	29	Male	2.0	12	13.3	1.5	503	620	0.61	380	99	3250	383
T3	Mine worker	59	Male	1.0	11	4.5	0.8	244	64.1	<0.01	34	8	1170	21.0
T4	Mine worker	40	Male	3.1	20	9.4	1.3	453	757	0.21	220	81	5920	442
T5	Mine worker	45	Male	2.8	21	3.8	1.0	367	699	0.21	330	48	1720	229
T6	Mine worker	29	Male	4.1	27	5.0	1.7	648	1230	0.21	650	58	2270	292
T7	Mine worker	41	Male	4.4	24	7.4	1.7	615	681	0.42	230	68	1280	545
T8	Mine worker	41	Male	4.6	24	6.1	2.4	535	719	0.21	270	52	3630	243
T9	Mine worker	48	Male	4.3	22	7.8	1.9	676	562	0.10	480	69	3310	260
T10	Mine worker	42	Male	4.9	27	4.6	2.3	516	220	0.21	170	38	2190	210
T11	Mine worker	26	Male	2.3	15	2.6	1.2	174	393	0.20	160	21	520	397
T12	Mine worker	36	Male	2.8	15	7.8	1.7	417	317	0.10	140	80	2250	162
T13	Mine worker	29	Male	6.0	25	8.1	1.8	349	928	0.10	260	74	6790	87.6
T14	Mine worker	43	Male	6.2	34	12.3	1.7	421	279	0.21	400	270	8120	224
T15	Mine worker	45	Female	4.8	29	25.1	1.4	388	801	0.20	260	70	6380	93.1
T16	Food vendor	30	Female	3.5	22	7.9	0.8	332	660	0.10	250	54	1170	163
T17	Caterer	24	Male	4.7	25	6.9	1.1	533	537	0.21	210	66	3580	558
T18	Trader	31	Female	4.0	20	12.0	2.1	363	1170	0.62	130	39	3970	306
T19	Nurse	44	Male	5.5	32	7.3	1.0	465	646	0.11	240	82	4500	132
T20	Nurse	51	Female	1.5	9.4	3.7	0.2	72.7	166	0.10	43	4.7	210	71.7
T21	Cleaner	34	Male	2.8	17	6.4	1.3	163	2020	0.10	430	111	7310	192
T22	Military	25	Male	2.1	18	5.6	0.8	132	495	0.10	130	61	2020	44.1
T23	Unknown	26	Male	3.1	19	5.2	1.3	221	1100	0.10	270	71	7830	112
T24	Unknown	34	Female	6.4	29	6.4	2.1	580	159	0.21	230	62	3350	273
T25	Unknown	20	Female	3.0	23	6.2	2.4	272	958	0.10	60.0	18	6100	155
T26	Unknown	25	Female	2.6	19	103	2.9	358	628	0.52	700	123	9660	15.6
T27	Unknown	19	Male	4.8	22	8.0	3.6	528	695	0.20	150	76	6320	192
T28	Unknown	43	Female	3.8	22	9.3	2.3	516	770	0.31	285	56	2400	342
T29	Unknown	26	Male	2.7	17	8.3	1.1	489	294	0.10	70	43	3580	103
T30	Unknown	32	Female	4.1	21	42.7	3.3	377	850	0.41	300	52	1680	382
T31	Unknown	27	Female	19	28	262	3.2	476	719	5.65	310	122	6350	135
T32	Unknown	21	Female	2.6	22	5.3	4.1	490	1600	0.31	290	85	2270	534
Mean		**34**		**4.1**	**21**	**19.6**	**1.8**	**404**	**684**	**0.40**	**260**	**68**	**3850**	**230**
Median		**32**		**3.6**	**22**	**7.4**	**1.7**	**419**	**670**	**0.21**	**250**	**64**	**3330**	**201**
Control														
C1	Lab. Technician	26	Male	4.7	24	4.8	1.9	536	531	0.10	170	77	2890	76.6
C2	Lab. Technician	26	Male	5.1	24	3.6	1.6	593	333	0.10	120	70	1710	224
C3	Lab. Technician	25	Male	4.4	22	4.9	1.7	708	666	0.10	220	47	2150	303
C4	Lab. Technician	27	Male	5.3	31	3.1	2.2	636	697	0.10	280	76	2420	448
Mean		**26**		**4.9**	**25**	**4.1**	**1.8**	**618**	**557**	**0.10**	**200**	**68**	**2290**	**263**
Median		**26**		**4.9**	**24**	**4.2**	**1.8**	**614**	**598**	**0.10**	**200**	**73**	**2290**	**263**

TABLE 2 cont'd

Subject	*Occupation*	*Age (yrs)*	*Sex*	*Mo*	*Ag*	*Cd*	*In*	*Sn*	*Sb*	*Cs*	*Ba*	*Hg*	*Tl*	*Pb*	*Bi*
T1	Mine worker	30	Male	18.2	<0.01	0.10	0.03	2.4	0.1	5	0.8	1.3	0.30	2.0	<0.01
T2	Mine worker	29	Male	258	0.82	0.72	0.04	3.1	0.3	8	9.3	7.1	0.41	6.1	0.05
T3	Mine worker	59	Male	10.0	0.20	0.10	0.01	6.1	0.1	1	0.5	0.5	0.10	1.0	<0.01
T4	Mine worker	40	Male	146	0.51	0.92	0.03	2.3	0.2	14	3.5	4.5	0.41	8.2	0.01
T5	Mine worker	45	Male	134	<0.01	0.72	0.03	2.2	0.2	5	0.9	2.4	0.41	5.1	<0.01
T6	Mine worker	29	Male	78.1	<0.01	0.82	<0.01	0.9	0.1	8	2.2	1.4	0.21	2.1	<0.01
T7	Mine worker	41	Male	60.2	1.4	0.63	0.11	1.1	0.2	6	5.4	9.4	0.42	5.3	0.08
T8	Mine worker	41	Male	147	0.21	0.62	0.03	2.3	0.1	8	1.5	3.5	0.21	6.2	0.01

T9	Mine worker	48	Male	149	0.31	0.92	0.3	3.1	0.4	9	1.6	4.3	0.61	10.2	0.20
T10	Mine worker	42	Male	82.2	0.10	0.52	0.01	1.5	0.1	6	1.4	2.4	0.21	2.1	<0.01
T11	Mine worker	26	Male	34.2	0.20	0.10	<0.01	1.0	0.1	3	4.0	2.8	0.10	4.0	<0.01
T12	Mine worker	36	Male	31.9	0.62	0.62	0.04	2.0	0.2	6	1.4	2.0	0.31	2.1	0.03
T13	Mine worker	29	Male	60.8	0.41	0.41	0.03	1.1	0.1	10	0.8	3.5	0.52	5.2	0.01
T14	Mine worker	43	Male	29.9	0.83	1.03	0.04	1.5	0.3	12	1.2	3.0	0.62	7.2	0.01
T15	Mine worker	45	Female	36.8	0.82	0.41	0.1	4.8	0.2	6	3.5	5.9	0.51	3.1	0.02
T16	Food vendor	30	Female	43.9	0.92	0.92	0.01	1.0	0.1	5	1.4	2.3	0.20	2.0	0.02
T17	Caterer	24	Male	140	0.83	0.73	0.02	0.9	0.2	12	3.2	4.9	0.83	4.1	0.03
T18	Trader	31	Female	49.2	1.5	0.31	0.04	2.1	0.1	6	13	3.6	0.31	3.1	0.01
T19	Nurse	44	Male	38.8	0.75	0.43	0.03	0.6	0.1	7	1.6	3.2	0.32	3.2	0.02
T20	Nurse	51	Female	25.3	0.51	0.20	0.03	0.9	0.1	1	1.1	1.1	0.10	1.0	0.02
T21	Cleaner	34	Male	42.5	0.41	0.52	0.02	0.8	0.2	13	0.9	12	0.52	7.3	0.03
T22	Military	25	Male	153	0.92	1.03	0.02	0.6	0.1	5	0.6	2.7	0.21	2.1	0.02
T23	Unknown	26	Male	90.9	0.51	0.61	0.02	1.4	0.2	11	0.7	4.5	0.31	3.1	0.03
T24	Unknown	34	Female	57.8	0.62	0.83	0.03	1.8	0.1	6	4.1	7.6	0.21	2.1	0.03
T25	Unknown	20	Female	39.1	0.62	0.10	0.02	1.4	0.2	7	0.6	1.1	0.41	4.1	0.08
T26	Unknown	25	Female	141	0.42	0.83	0.04	1.6	0.2	22	8.9	8.2	0.63	6.3	0.03
T27	Unknown	19	Male	40.9	0.51	0.31	0.04	1.1	0.1	7	3.5	4.0	0.41	3.1	0.01
T28	Unknown	43	Female	74.0	1.0	0.82	0.02	0.8	0.1	7	2.8	2.8	0.21	2.1	0.02
T29	Unknown	26	Male	89.6	0.10	0.31	<0.01	1.6	0.1	7	1.9	3.4	0.21	4.1	0.01
T30	Unknown	32	Female	102	0.20	0.72	0.01	3.7	0.2	6	6.7	2.5	0.20	7.2	<0.01
T31	Unknown	27	Female	69.0	0.42	1.9	0.27	2.8	1	10	86	5.2	0.63	<0.01	0.26
T32	Unknown	21	Female	14.2	0.10	0.61	0.01	1.5	0.2	9	3.7	4.6	0.31	7.1	0.01
Mean	**34**		**77.7**	**0.58**	**0.62**	**0.05**	**1.9**	**0.2**	**8**	**5.6**	**4.0**	**0.35**	**4.2**	**0.04**	
Median	**32**		**60.5**	**0.51**	**0.62**	**0.03**	**1.5**	**0.2**	**7**	**1.7**	**3.4**	**0.31**	**4.0**	**0.02**	
CONTROL															
C1	Lab. Technician	26	Male	71.4	<0.01	0.31	<0.01	1.8	0.1	6	0.8	5.5	0.21	1.0	<0.01
C2	Lab. Technician	26	Male	59.0	<0.01	0.41	<0.01	2.0	0.2	4	2.8	2.0	0.10	1.0	<0.01
C3	Lab. Technician	25	Male	107	<0.01	0.31	<0.01	1.1	0.1	5	1.9	3.5	0.21	2.1	<0.01
C4	Lab. Technician	27	Male	328	<0.01	0.42	<0.01	1.2	0.1	7	1.5	1.4	0.31	3.1	<0.01
Mean		**26**		**141**		**0.36**		**1.5**	**0.1**	**6**	**1.7**	**3.1**	**0.21**	**1.8**	
Median		**26**		**89.1**		**0.36**		**1.5**	**0.1**	**6**	**1.7**	**2.8**	**0.21**	**1.6**	

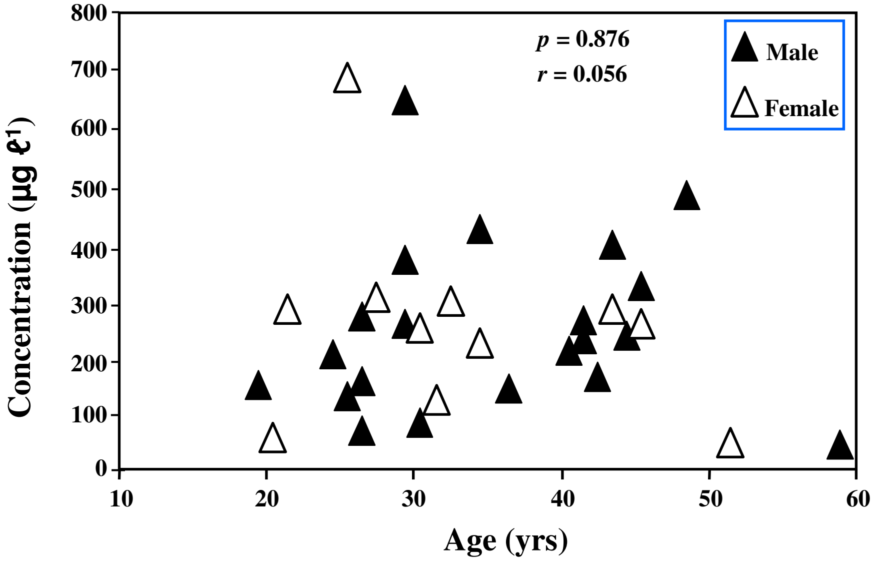


Figure 4. Correlation between urinary arsenic concentration and age of males and females.

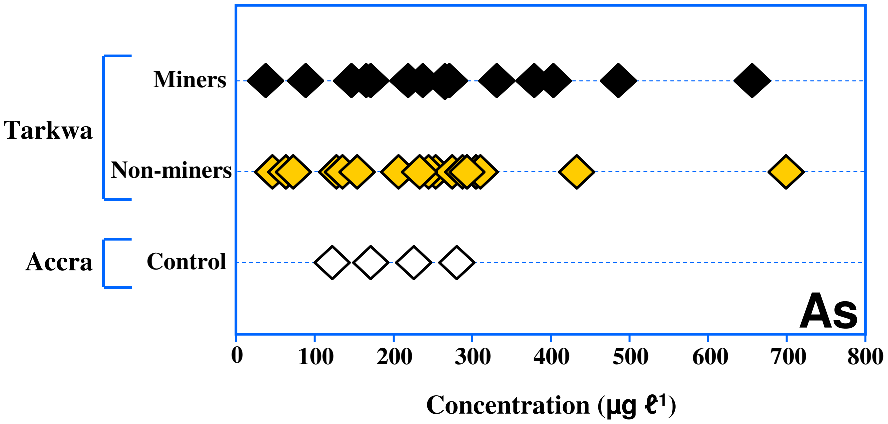


Figure 5. Urinary arsenic concentrations in miners, non-miners and control subjects.

The mean urinary As concentration of 260 µg l^{-1} was higher than values from a study of 22 people from arsenic-affected villages in West Bengal, India (Samanta *et al.*, 2000). In the West Bengal study, mean urinary As concentrations of 170.4 µgl^{-1} (adult males), 169 µgl^{-1} (adult females) and 151.9 µgl^{-1} (children) were reported (Samanta *et al.*, 2000). Similarly, the mean urinary As concentration from this study was higher than other studies that involved communities depending on tube wells and other water sources with diverse arsenic concentrations for drinking and cooking purposes. Concentrations measured were 18.9–93.8 µgl^{-1} (Meza *et al.*, 2004), 1.6–40 µgl^{-1} (Kristiansen *et al.*, 1997) and 0.7–19.4 µgl^{-1} (White *et al.*, 1998). However, the range of concentration in this study 34–700 µgl^{-1}, was much lower than that of Semria Ojha Patti village 24–3,696 µgl^{-1} in West Bengal, India, and Samta village 110–3,085 µgl^{-1} in Bangladesh (Chakraborti *et al.*, 2003). Nevertheless, the results indicate relatively high degree of human exposure to arsenic in Tarkwa, Ghana, when compared to some well-known heavily arsenic-affected countries of the world (Fig. 6).

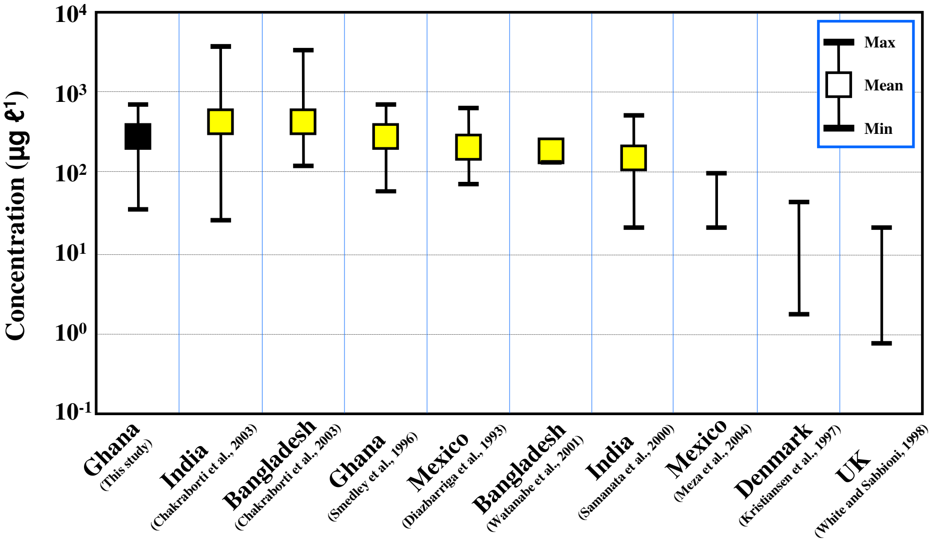


Figure 6. Comparison of urinary arsenic concentrations from this study with other countries.

Factors, such as how often fish is consumed, time of alcohol consumption, number of amalgam fillings, as well as working hours are probably important to the evaluation of Hg contamination of people occupationally exposed to Hg vapours (Santa Rosa *et al*., 2001). In this study, Hg concentrations ranged from < 0.5–12 µg l^{-1} with a mean of 4 µg l^{-1}. The range in this present study fell below the range of 0.02–183 µg l^{-1} reported in a study involving four towns around the Ankobra and Tano river basins in south-western Ghana of which the 217 subjects (12–18 years) were of school going age and might be involved in illegal mining 'galamsey' activities (Adimado & Baah, 2002). Van Straaten (2000) also reported Hg concentration of 172 mg l^{-1} in a 29-year old male involved in small-scale gold mining in Tanzania. The reason for the low Hg levels in the present study could be that the subjects were not into small-scale gold mining which involves amalgamation of the gold concentrate and later heating the amalgam to vapourise Hg.

In this study, concentrations of Cd varied between 0.10 and 1.9 µg l^{-1} (mean of 0.62 µg l^{-1}), and fell below the urinary Cd concentration of 20 µg l^{-1}, generally considered as normal (Horng, 1996). The concentrations of urinary Cr in this study ranged from 9.4 µg l^{-1} to 34 µg l^{-1} with a mean value of 21 µg l^{-1}. The range was significantly higher than some reference studies: 0.04–1.5 µg l^{-1} (Minoia *et al*., 1990), 0.1–0.52 µg l^{-1} (Brune *et al*., 1993) and < 0.7 µg l^{-1} (Paschal *et al*., 1998). It must, however, be emphasized that the subjects in this present study were quite different from the reference studies in that samples were taken mainly from patients who were likely to be exposed.

Copper concentrations in this study ranged from 72.7 to 676 µg l^{-1} and levels of Zn varied from 64.1 to 2020 µg l^{-1}. Some reported urinary Cu concentrations are 12–80 µg l^{-1} (Iyengar & Woittiez, 1988) and 4.2–50 µg l^{-1} (Minoia *et al*., 1990) while that for urinary Zn are 180–850 µg l^{-1} (Schramel *et al*., 1985), 266–864 µg l^{-1} (Minoia *et al*., 1990) and 361–599 µg l^{-1} (Iyengar & Woittiez, 1988). Higher concentrations of Cu were observed in the control site compared with the study area, suggesting the existence of some exposure sources in the control site. Since the samples, especially from control site (n = 4), were limited, further study is required to confirm the regional difference of trace element levels. For urinary trace elements, the pattern of elemental abundance was Rb > Zn > Cu > As > Sr > Mo > Se > Cr > Mn > Cs > Ba. On the other hand, concentrations of Sb, In and Bi were low or below detection limits. Fig. 7 shows the comparison of urinary trace element concentrations between miners and control subjects.

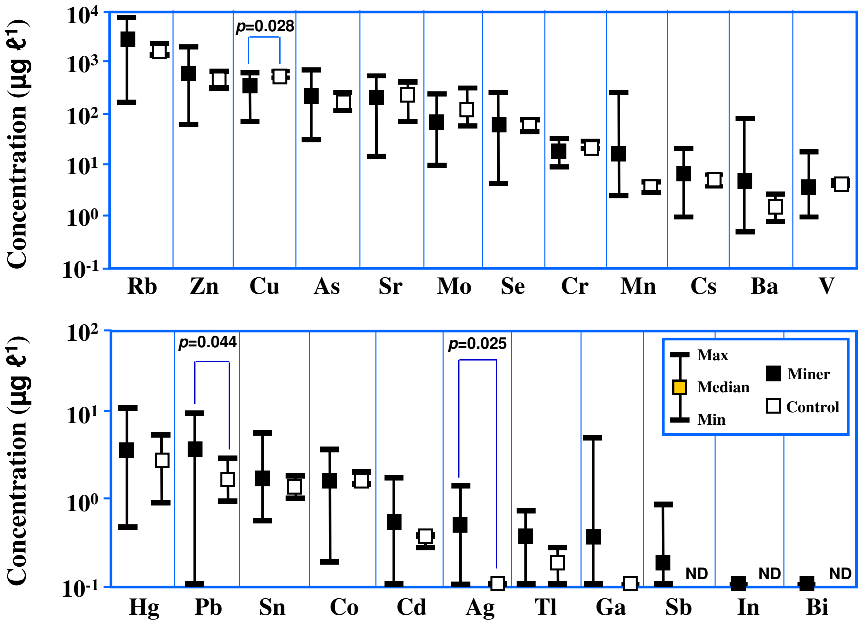


Figure 7. Comparison of urinary trace element concentrations between miners and control subjects.

Relationships between concentrations of As in water and human urine samples

In an attempt to assess the arsenic contamination in Ghana and identify the possible exposure route, a graph of arsenic concentration in urine against arsenic level in water from some well-known arsenic-affected countries of the world was plotted (Fig. 8). Consumption of groundwater is an important exposure route of As to residents in As-contaminated regions such as Bangladesh and India (West Bengal). For Bangladesh, India (West Bengal), Chile and Mexico, as the concentrations of arsenic in water increased the corresponding levels in urine also increased significantly (r = 0.651, P = 0.022), implying that the source of As in urine could be from drinking water. Both studies in China were conducted in the Guizhou Province, an area of endemic arsenicosis, where a unique type of exposure resulting from the burning of As-rich coal is found. Guizhou inhabitants commonly use this coal for cooking, heating, and drying their dietary staples of corn and hot peppers.

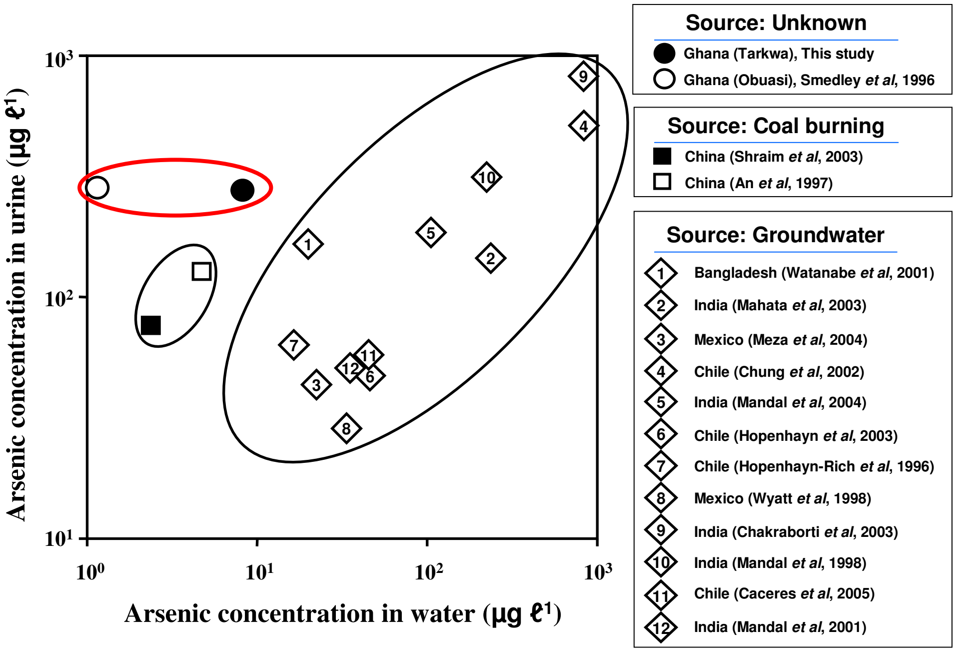


Figure 8. Relationships between concentrations of As in water and human urine in different populations.

The coal is burned in open stoves without chimneys, resulting in contamination of both the indoor air and the foods being prepared. In this present study, although the arsenic levels in water samples were much lower than those in other highly As-endemic regions, the concentrations in human urine were comparable (Fig. 8). A similar trend was also observed in an earlier study in the Obuasi area of Ghana by Smedley *et al*. (1996) who analyzed As concentrations in urine and groundwater, and suggested that the high levels of total As in urine and low levels of total As in drinking water reflected high fish intake. However, since they did not analyze arsenobetaine (AB) and metabo-lized inorganic arsenicals such as monome-thylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Fig. 9) in urine samples, fish may not always be a significant source of As exposure.

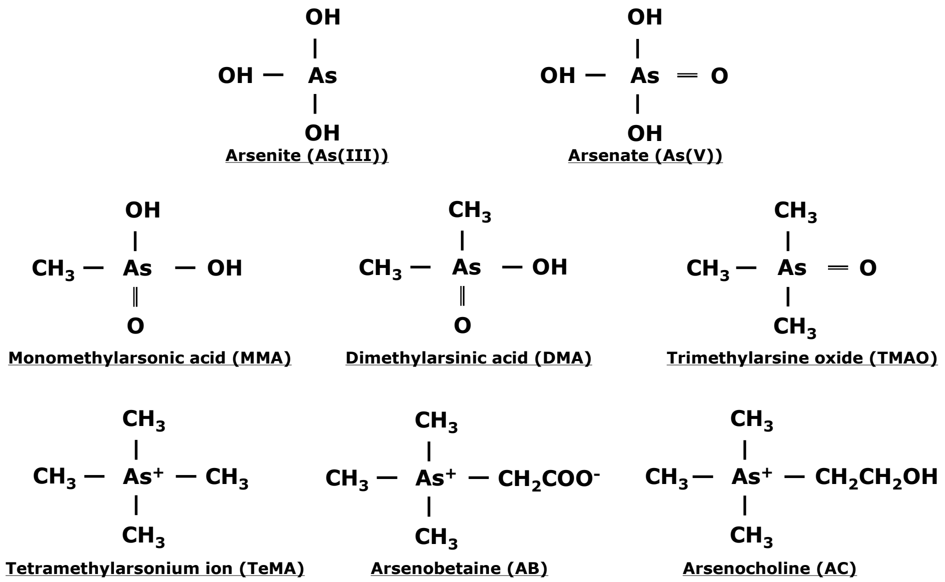


Figure 9. Chemical structures of arsenic species.

Some foodstuffs are known to contain high concentrations of As. Seafood consumption may contribute intakes of As because seafood has high As concentrations and As is generally present as organic species such as arsenobetaine (Cullen & Reimer, 1989), and, to a lesser extent, arsenocholine, both of which are of very low toxicity. Arsenobetaine, which is ingested through the marine products, is rapidly excreted into urine without change (Le *et al.,* 1993). Thus, total As in urine measured in this study may not be an appropriate measure of inorganic As exposure because of the dietary artifacts associated with certain types of seafood containing arsenobetaine, arsenocholine and arseno-sugar (organoarsenic compounds), which are excreted through urine without metabolic transformation. When total urinary As is measured, intake of all forms of arsenic is detected. Organic As is, however, consi-dered relatively low-toxic.

Conclusion

Unlike other areas of the developing world, e.g. Bangladesh, West Bengal in India, southern Taiwan, Chile, Vietnam, Argentina and Mexico, where endemic As poisoning is prevalent, groundwaters from the study area are apparently less vulnerable to the generation of high dissolved As concentra-tions. Primary sulphide minerals could have been leached and As present in the system strongly bound to ferric oxide products rather than being significantly mobilized into solution. Nevertheless, based on the results of this study, As, Mn, Pb and Hg contamination in some water sources is a cause for concern. Other elements that showed high urinary concentrations relative to the control samples are Pb, Ag, Mn, Rb, Zn, Cd, Ba, Tl, Sb and Ga.

Tarkwa is an important case study for assessing the health effects of As and other trace elements because it depicts a typical mining town. Urinary As concentrations were comparable to those in some well-known arsenic-affected countries of the world. Relatively low As levels in water and no significant difference in urinary As concentrations between the study area and control site suggest other sources of As contamination in Ghana, possibly food.

The health of the population within the area surveyed as well as the economic resources are threatened by As contamina-tion and other trace elements arising from mining activities. If the geologic and groundwater conditions that promote high As concentrations are known, they may be helpful to identify high-risks areas. Social conscience about health risks and consequences of environmental pollution has to be developed and the actual situation must be taken into account by authorities (Environmental Protection Agency, Minerals Commission, Ghana Chamber of

Mines, etc.) to achieve a definite solution to the problem. For example, the powers of the district assemblies should be enhanced to monitor activities and enforce regulations on polluting discharges into the environment from mining companies and also check the illegal activities of small-scale miners.

Arsenic is a serious health threat as exposure to this element, particularly in the inorganic form, can lead to cancer. Recent studies have shown that As acts as an endocrine disruptor at very low concentra-tion (Kaltreider *et al*., 2001). Total As was determined in this study. In future, an attempt should be made to determine the different species of As in drinking water, human urine, and fish and food items to evaluate the intake of inorganic As in Ghana. Since the most common As species in water are inorganic, this represents potentially the most detrimental source of As in human diet. Arsenic analysis in human hair and nails may also be interesting as it depicts long term accumulation.

Acknowledgement

The authors are grateful to Messrs Sampson K. Abu and Kwame Danso of CSIR-WRI, and the Tarkwa Government Hospital and Aba Hospital, for their help in sampling. They also acknowledge Mr Masahiro Kunimoto and Miss Noriko Tsunehiro, staff in the Environmental Specimen Bank (*es-BANK*), CMES, Ehime University, Japan, for their support in sample management. This study was supported by 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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