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SHORT COMMUNICATION

LEVELS OF ARSENIC IN HUMAN HAIR AS BIOMARKERS OF ARSENIC EXPOSURE IN A MINING COMMUNITY IN GHANA

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ABSTRACT. Arsenic levels were determined in human hair samples collected from a mining and non-mining community in Ghana. Hair samples were digested and analyzed using inductively coupled plasma atomic emission spectrometer (ICP–AES). Elevated levels of arsenic were found in the samples obtained from the mining community, the mean levels in the hair ranged from 0.0142–0.0515 μg/g, whereas arsenic was not detected in the hair samples from the non-mining community. The values obtained from the mining community were all below background levels set by the Agency for Toxic Substance and Disease Registry (ATSDR). The results therefore indicate that arsenic pollution may indeed be associated with mining, inducing human environmental exposure.

KEY WORDS: Arsenic levels, Biomarkers, Human hair, Mining community and human exposure

INTRODUCTION

Arsenic pollution has been on ascendancy owing to the increase in mining and industrial activities [1]. Though arsenic levels in the Tarkwa area landscape are appreciably high, the mining activities and acid mine drainage (AMD) assist in making them available to both plant and animals [2]. There is growing awareness of the environmental legacy of mining activities that have been undertaken with little concern for the environment. The price we have paid for our everyday use of the mineral has sometimes been very high. However, in spite of the positive contributions related to mining, there are adverse effects associated with the extraction and processing which include chemical pollution by heavy metals such as mercury, cadmium, nickel, and arsenic among others, clearance of vegetation and land degradation which leads to increased sediments loads in rivers [3].

Both locally and internationally, there is increasing concern about the health hazards of heavy metals posed by mining. The process of mining involves use of some chemicals including mercury and cyanide. The mine tailings or 'spoils' are the waste material resulting from the processing. Inappropriate disposal and management of mining waste could pollute river bodies and result in uptake of the pollutants in the waste material by crops. Exposed mine tailings have polluted most rivers in mining communities [4-6].

Research has shown that mining activities in the Ankobra Basin has contaminated the river Ankobra with arsenic and mercury and are responsible for high turbidity level of the river at Prestea in the Western Region of Ghana [7, 8].

The primary arsenic-containing mineral is arsenous oxide obtained by separation from roaster or smelter glue glasses. Metallic arsenic is obtained as sublimate by heating the oxide with carbon [9, 10].

Environmental sources of arsenic stem from the continuing use of its compounds such as pesticides, unintended release during the mining of gold and lead (whose ores it commonly occurs), and from the combustion of coal, of which it is a contaminant. The leachate from abandoned gold mines of previous decades and centuries can still be a significant source of arsenic pollution in water systems due to acid mine drainage. Similarity in properties makes arsenic compounds to co-exist with those of phosphorous in nature and so often contaminate

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phosphate deposits and commercial phosphates. Water sources, especially ground water, are a major source of arsenic for most people. There are low background levels of arsenic in many foods and indeed trace amounts are apparently essential to good health [9, 11].

Arsenic compounds can be absorbed by many route although the primary entry is by ingestion and inhalation. There is a common belief that arsenic is a cumulative poison which is largely based on its tendency to accumulate in high concentrations in the tissues such as hair and nails [12].

Absorption of arsenic in inhaled air borne particles is highly dependent on the solubility and the size of particles. Both pentavalent and trivalent soluble arsenic compounds are rapidly and extensively absorbed from the gastrointestinal tract. In many species arsenic metabolism is characterized by a reduction reaction of pentavalent to trivalent arsenic, and oxidative methylation reactions in which trivalent forms of arsenic are sequentially methylated to form mono, - di - and trimethylated products.

Methylation of inorganic arsenic facilitates the excretion of inorganic arsenic from the body as the end products are readily excreted in urine. There are major qualitative and quantitative interspecies differences in methylation, to the extent that some species exhibit either minimal or no arsenic methylation (example marmoset, monkey, guinea pig, chimpanzee). However in humans and most common laboratory animals, inorganic arsenic is extensively methylated and the metabolites are excreted primarily in the urine. Factors such as dose, gender, age and smoking contribute only minimally to the large inter individual variation in arsenic methylation observed in humans [13].

Levels of arsenic or its metabolites in blood, hair, nails and urine are used as biomarkers of arsenic exposure. Blood arsenic is a useful biomarker only in the case of acute poisoning or stable chronic high-level exposure. Arsenic is rapidly cleared from blood and speciation of its chemical forms in blood is difficult. Arsenic in hair and nails is indicators of long-term arsenic exposure, provided care is taken to prevent exogenous contamination of the samples through washing procedures. Arsenic in hair may also be used to estimate relative length of time of an acute exposure [13].

Research by [14] and associated scientists have reported that arsenic acts specifically in the progression phase of carcinogenicity. Research findings indicate that arsenic may be related to its ability to cause gene amplification but not gene mutations. Data collected regarding humans who are occupationally exposed to arsenic indicates that exposure to arsenic appears to act at a later stage in the carcinogenic process. Thus, scientists postulate that amplification of an altered or activated oncogene may be a late stage in neoplastic progression [14].

Occupational exposure to arsenic, primarily through inhalation, is causally associated with lung cancer. Chronic arsenic exposure in Taiwan has been shown to cause black foot disease, a severe form of peripheral vascular disease which leads to gangrenous changes [13].

In Ghana, gold is mined almost everywhere, from the coast to the north of the country and the fact that arsenic is associated with gold mining makes it very important for this study. Arsenic is found in the earth crust and the activities of underground mining involving the excavation of the earth, exposes arsenic. The metal is leached into water bodies, takes up by plants, thereby ingested and inhaled by people living in that community. Surface mining activities have worsened it all, since their tailings are a direct source of exposure of the environment. As such, adverse consequences are a big potential threat as compared to deep mining. Illegal mining operations popularly called ‘galamsey’ in Ghana has also contributed immensely to this problem. Arsenic accumulation in humans who reside in mining areas is becoming a health concern.

The objective of this paper was to determine the concentration of arsenic in human hair as biomarkers of exposure of arsenic in a mining community.

EXPERIMENTAL

The research was carried out at Tarkwa, a mining community in the Western Region of Ghana, located on latitude 5^{o} 17 N and longitude 1^{o} 59 W [15]. Hair samples were chosen instead of urine and blood for the analysis because human hair bio-accumulates metals through gastrointestinal absorption and inhalation. In addition, some metals bio-accumulates through exogenous contamination or external contamination [16]. Hair sampling is non-invasive method and does not require the services of medical personnel or special equipment or condition for storage. The study may reveal about total amount of metals through exogenous and endogenous accumulation.

Sampling. Three sets of thirty (n = 30) human hair samples were collected from thirty people (n = 30) according to their age. They were categorized into three age groups: (5–10), (11–19) and (> 20) years. This was done to indicate exposure period, since the people sampled had lived in the community most of their time. Twenty one (n = 21) hair samples were from mining community (Tarkwa) and nine (n = 9) were from non-mining community (Koforidua), which was used as a control.

Volunteers' were taken to barbering shops, barbed and their hair samples were collected. It was ensured that the hair samples were put in a labelled envelope separately, labelled, and sealed until analyzed.

Reagents and equipments. Concentrated hydrochloric acid (BDH, UK), high purity ICP 1000 mg/L arsenic stock standards (Spectrascan), Liberty ICP–AES (USA), Glassware's: Simax (Czech Republic) and Schott Duran (Germany), crucibles: Haldenwanger (Germany), furnace: Fischer Scientific, water: double distilled water, oven: Galenkamp (UK), were used.

Pre-treatment of the sample. Each hair sample was soaked in detergent, rinsed with water and double distilled water three times. This was to ensure that it was dust free and free from oils and absorbed arsenic on the hair samples [17].

Digestion method. About 3.00 g of the hair sample was weighed into a clean crucible. This was burnt to partial dryness but not to total dryness because that can cause an explosion. It was then masked at a temperature of 480 ^{o}C for about 25 min [18, 19]. The crucible was then removed from the furnace and allowed to cool. 5 mL of concentrated HCl was added to each sample. Each digested sample was transferred into a 100 mL volumetric flask and made up to the mark. The solution was analyzed with an inductively coupled plasma atomic emission spectrometer.

The sample was carried into the hot plasma at the head of the tubes by argon flowing at 1 mL/min through the central quartz tube. Ionization of the flowing argon is initiated by a spark from a tesla coil. The resulting ions, and their associated electrons, then interact with the fluctuating magnetic field produced by the induction coil. This interaction causes the ions and electrons within the coil to flow in the closed annular paths.

Calibration of instruments was checked after every ten samples by analyzing the calibration standards. A re-analysis would have been necessitated if the calibration standards indicated that, the instrument had drifted out of calibration (> 3 % of original values) [20].

Quality control analysis. Three standard solutions 1 mg/L, 4 mg/L and 6 mg/L were prepared from high purity ICP 1000 mg/L arsenic stock standards using de-ionized water and analysed with the ICP-AES. This was done thrice to check the reproducibility and recovery of the ICP-AES used in the analysis.

RESULTS AND DISCUSSION

The result obtained after the analysis of the standard solutions for quality control is given in Table 1. The average concentration of arsenic (μg/g) in hair samples from Tarkwa a mining community and Koforidua a non-mining community is given in Table 2.

Table 1. Quality control results.

Standard (mg/L)	Result after the ICP-AES analysis of standard (mg/L)			Mean	Standard deviation	Recovery (%)
Standard 1 (1.00)	0.982	0.965	0.975	0.9738	0.0085	97.38
Standard 2 (4.00)	3.885	3.925	3.915	3.9083	0.0208	97.71
Standard 3 (6.00)	5.652	5.842	5.757	5.7503	0.0952	95.84

From Table 1, the percentage of arsenic recovered from the standard solutions was between 96–98 % with a standard deviation between 0.0085-0.0952 and a standard error of 0.04. It shows that the method used in analytical analysis was precise and accurate.

Arsenic concentration in human hair samples. The results presented in Table 2, show elevated levels of arsenic exposure in mining community (Tarkwa) which is most likely as a result of the mining operations. This is because the concentrations of the samples from the non–mining community (Koforidua) were all below the detection limit of 0.001 μg/g of the instrument.

Table 2. Average concentration of arsenic (μg/g) in hair samples sampled from Tarkwa a mining community and Koforidua a non–mining community.

Age category (years)	Sample code	Average concentration of arsenic (μg/g) in hair samples		
		First group of people sampled from Tarkwa	Second group of people sampled from Tarkwa	Third group of people sampled from Koforidua (control)
5 – 10	A1	0.0236±0.0035	0.0480±0.0072	BD
	A2	0.0178±0.0027	0.0200±0.0030	BD
	A3	0.0041±0.0006	0.0059±0.0009	BD
	A4	NS	0.0046±0.0007	BD
11 - 19	B1	0.0043±0.0007	0.0158±0.0024	BD
	B2	0.0244±0.0037	0.0148±0.0022	BD
	B3	0.0234±0.0035	0.0491±0.0074	NS
	B4	0.0050±0.0008	NS	NS
> 20	C1	0.0615±0.0092	0.0644±0.0097	BD
	C2	0.0369±0.0055	0.0502±0.0075	BD
	C3	0.0116±0.0017	0.0398±0.0060	BD
	C4	0.0238±0.0003	NS	NS

BD = below limit of detection (0.001 μg/g). NS = No samples were obtained.

People living near mining areas are likely to face a high risk of arsenic pollution due to deep and surface mining as a result of the roasting operation in gold processing mining at Tarkwa. Arsenic concentrations in soil and water in many rural areas of Australia are high because of both natural geohydrologic conditions and the presence of contamination resulting from gold mining operations, industrial wastes, and runoff from agricultural land [21, 22]. Surface soil and groundwater have been found to contain high concentrations of arsenic in areas where gold mining has been undertaken [22]. Town water supplies that are based on groundwater extraction have been found to have elevated arsenic concentrations in some rural areas of Victoria [22].

The results obtained shows high levels of arsenic in a mining community (Tarkwa) even though they were all below arsenic background levels [23, 24] except the samples from

Koforidua which served as control had values which were all below the detection limit of 0.001 μg/g of the ICP-AES used. This shows that the mineral species containing arsenic such as arsenopyrite could be present in mining areas [25].

Arsenic levels varied with age categories for example, 5–10 years old had a mean of 0.0196 μg/g, from 11–19 years old experienced a higher concentration of 0.0266 μg/g, then there was a considerable increase at > 20 years old [26, 27]. These people have been living in the mining community for most of their life time. This suggests that arsenic accumulation could be depending on the duration of exposure. Because arsenic accumulates in hair and nails and has limited mobility once incorporated into keratin, their analysis for arsenic concentration is used as an index of longer term (several months) exposure to inorganic arsenic [28, 29]. Analysis of nails is considered to be a good reflection of long-term exposure because nails - after rapid growth - remain isolated from other metabolic activities in the body [29].

Reported background and elevated levels of arsenic in human urine and hair are highly variable and depend on a many factors including the individual diet. The Agency for Toxic Substance and Disease Registry (ATSDR) has noted that normal levels of arsenic in hair or nails are less than 1 μg/g (1 mg/kg). However, National Medical Services Laboratory, who performed the analysis for arsenic in hair, reported a normal background level 0.08 to 0.69 μg/g (0.08-0.69 mg/kg) [23, 24]. This suggests that people living in such mining communities may be exposed to arsenic levels which invariably may affect their health [26, 27].

The results obtained from the analysis of the samples using inductively coupled plasma atomic emission spectrometer techniques shows that both deep and surface mining of gold at Tarkwa could result in the release of arsenic to the environment, inducing exposure levels that are potentially harmful to human beings.

Studies done within Tarkwa and its environment shows an elevated levels of arsenic in both surface and ground water sources as well as in some food crops [30] and these sources could be a major route of arsenic exposure to the people living in the community. This means that alternative sources of livelihood ought to be made available to the inhabitant of mining communities to avert any serious health related problems.

CONCLUSIONS

The result of the analysis of all the samples recorded varying values indicating arsenic exposure in the mining environment. There is therefore a need for intensive education on the effects of mining to the inhabitants. Human hair samples could be used as biomarkers for monitoring levels of arsenic in the environment.

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