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Biomonitoring of Occupational Exposure to Total Arsenic and Total Mercury in Urine of Goldmine Workers in Southwestern Ghana

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Biomonitoring of total arsenic and total mercury in the urine of goldmine workers in south-western Ghana due to occupational exposure was conducted to determine whether occupational exposure substantially contributes to their overall exposure to arsenic and mercury. The urine was collected after 2-day abstinence from sea foods by the workers and from those with no dental amalgam fillings. Total arsenic and total mercury were simultaneously determined by instrumental neutron activation analysis (INAA). After 1-hour irradiation of the urine in Ghana's miniature neutron source reactor (GHARR-1) to induce ^{76}As and ^{197}Hg radionuclides through nuclear reactions ^{75}As(n, γ)^{76}As, and ^{196}Hg(n, γ)^{197}Hg, the γ-radiation intensity of the induced ^{76}As and ^{197}Hg radionuclides were measured by γ-spectrometry. The validity of the INAA technique for As and Hg determination was checked by analyses of NIST SRM 3103a (As standard solution) and NIST SRM 3133 (Hg standard solution), respectively. The mean mass fractions of arsenic in the urine are 6.76 μg/L ± 1.43, 7.78 μg/L ± 1.33, 8.03 μg/L ± 1.75, 10.44 μg/L ± 1.88, and 14.75 μg/L ± 1.62 for workers in offices 10 km from the mine, 2 km from the mine, 0.5 km from the mine, casual mine workers, and gold ore processing workers, respectively. The levels of arsenic in the urine are all within the 5 to 40 μg As L^{-1} day^{-1} normal range for excretion of arsenic. The observed mass fraction of As was higher in high exposure workers. The mean mass fraction of Hg in the urine are 0.36 μg/L ± 0.11, 0.47 μg/L ± 0.12, 0.51 μg/L ± 0.16, 0.57 μg/L ± 0.14, and 0.56 μg/L ± 0.21 for workers in offices 10 km from the mine, 2 km from the mine, 0.5 km from the mine, casual mine workers, and gold ore processing workers, respectively. The high Hg exposed workers engage in small scale gold mining using mercury. The exposure of the different categories of workers to both total arsenic and total mercury are safe.

Key words: *instrumental neutron activation analyses, mercury, heavy metals, urine, arsenic.*

1. Introduction

The gold mining industry in Ghana is one of the major driving forces of the Ghanaian economy. Extensive gold mining plays an important economic role and provides a livelihood for a large number of people. The economic gains are, however, achieved at a great cost to the health and safety of the mine workers (Camm et al. 2005). The mine workers are exposed to harmful chemicals like arsenic and mercury which are released during the processing of the gold ore. The most common route of occupational exposure to chemicals is through inhalation. Continued exposure of the workers to these harmful chemicals calls for effective and continued monitoring of the workers, in order to determine whether occupational exposure substantially contributes to their overall exposure to arsenic and mercury. Using a biological indicator of exposure, it may be possible to obtain a more precise estimate of the total dose. Urine is the most widely used and accepted matrix to assess internal mercury exposure. The concentration of mercury in urine is considered the most accurate biomarker for understanding the absorbed dose from chronic exposure to mercury vapour. The concentration of arsenic in urine may be used to estimate exposure, since the main route of excretion is via kidneys (WHO 1981). The actual dose may vary to a great extent between individuals due to variations in the burden of work, which will influence the rate of respiration, and due to exposure via other routes, such as ingestion or skin absorption. The total arsenic content in urine is greatly influenced by dietary intake of organic arsenic compounds, mainly arsenobetaine, which may be present in very high concentrations in certain fish species and crustaceans (Buchet et al. 1981a, Cannon et al. 1981, Luten et al. 1982, Momplaisir et al. 1991), and which is rapidly excreted in the urine (Freeman et al. 1979, Tam et al. 1982, Vahter et al. 1983). Consequently, urine samples were collected from the mine workers after 2-day abstinence from sea foods.

Although dental amalgams are a primary source of elemental mercury exposure in the general population, dietary mercury exposure from high fish consumption may contribute to urinary mercury levels (Abe et al. 1995, Suzuki et al. 1993). The urine samples analyzed were collected after 2-day abstinence from sea foods of the workers and of those with no dental amalgam fillings. Analytical methods reported used for arsenic determination in urine include: hydride generation atomic absorption spectrometry (HG-AAS), hydride generation atomic flourescence spectrometry (HG-AFS), inductively coupled plasma/mass spectrometry (ICPMS) and γ-spectrometry of the ^{76}As-induced radionuclide in instrumental neutron activation analysis (INAA). The analytical techniques proposed for the measurement of mercury in urine includes cold vapour atomic absorption spectrometry (CVAAS), hydride generation atomic absorption spectrometry (HG-AAS) and γ-spectrometry of the ^{197}Hg -induced radionuclide in instrumental neutron activation analysis (INAA). The present study investigated the TAs and THg levels in the urine of different categories of goldmine workers in Southwestern Ghana.The aim of the study is to determine whether occupational exposure substantially contributes to the overall exposure of the mine workers to arsenic and mercury based on the individual's work area within the mine.. In addition, the study will provide data on the levels of TAs and THg with the eventual goal of establishing reference levels specifically for Ghanaian gold mine workers.

2. Materials and methods

Instrumentation. Sample irradiations for neutron activation analysis were carried out in the 30 kW Miniature neutron source reactor (MNSR) at a neutron flux of 5 x 10^{11} neutrons cm^{-2} s^{-1}. The reactor is situated at the Ghana Atomic Energy Commission, Kwabenya, Accra, Ghana.

Study design. Urine samples were collected from 60 mine workers for the study. The urine was collected from workers after 2-day abstinence from sea foods, and from workers with no dental amalgam fillings. Both 'high' and exposure groups were defined based on individual's work area. The urine samples of workers were collected over a period of 24 h into 2.5 L polypropylene sampling vessels with screw caps. After collection, the samples were stored in a cold icebox and transported to our laboratory. Finally the samples were kept in a refrigerator at -20 ºC before use.

Sample preparation. Prior to arsenic and mercury analyses, urine samples were thawed, 1.0 mL was transferred to a vial.The polyethylene vials were turned upside down a few times to thoroughly mix the urine and to ensure that a uniform and representative sample was obtained. This was immediately followed by pipetting 500 mg of the urine into polyethylene irradiation vial (diameter 1.2 cm and height 2.35cm). The vial was heat-sealed. Single standard elements solutions of arsenic (10 µg g^{-1}) and mercury (20 µg g^{-1}) were then prepared in the same manner as the urine samples. The irradiation vials containing the samples and standards were then placed into a bigger irradiation vial (diameter 1.6cm and height 5.5cm) and heat-sealed (double encapsulation). Two standard reference materials with certified values for As and Hg were used to validate the INAA method. The reference materials were: NIST SRM 3133 (Hg standard solution, 10 mg g^{-1} Hg); NIST SRM 3103a (As standard solution, 8 mg g^{-1} As). The standard reference materials were obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA; the values are represented in Table 1

Table 1. Results for validation of INAA method for As and Hg determination

Standard reference material	Concentration of As (mg g^{-1}As)		Concentration of Hg (mg g^{-1} Hg)	
	Certified	Measurement	Certified	Measurement
NIST SRM 3133 (Hg standard solution)	10	10.84 ± 2.69	-	-
NIST SRM 3103a (As standard solution)	-	-	8	9.23 ± 1.19

Sample irradiation and counting. Samples and standards were transferred into the reactor via the pneumatic transfer system at a pressure of 0.6 mPa. The urine samples were irradiated for 1 hour. At the end of the irradiation, the samples and standards were removed from the reactor and allowed to decay for 24-36 hours. The small irradiation vial containing the radioactive urine sample was placed on the coaxial high purity germanium (HPGe) semi-conductor γ-ray detector (Canberra) and the γ-activity of the induced radioisotopes, ^{76}As ($t_{1/2}$ =26 hours; E_γ = 559.1 keV) and ^{196}Hg ($t_{1/2}$ = 64.1 hours; E_γ= 77.3 keV) measured. Measurement time depended on the activities of the induced radioisotopes. That was followed by the measurement of the γ-activity of the induced radioisotopes, ^{76}As and ^{197}Hg, in the standard solution on the same coaxial HPGe γ -ray detector and at the same source-detector distance. A plexiglass source support was mounted on the detector during the measurement in order to ensure easy and reproducible source positioning (De Corte 1987). The ORTEC MAESTRO-32 γ-spectroscopy software was used for γ -spectrum acquisition.

3. Results and discussion

Hg emits three radionuclides at different peak energy levels and with different half lives: ^{196}Hg $(n,\gamma)^{197}$Hg (E_γ = 77.3 keV; $t_{1/2}$ = 64.1 hr); ^{196}Hg$(n,\gamma)^{197m}$Hg E_γ = 134 keV; $t_{1/2}$ = 23.8 hrs); and, ^{202}Hg $(n,\gamma)^{203}$Hg (E_γ = 279.2 keV; $t_{1/2}$ = 46.61 days). Due to inferences from Se at 297.2 keV photopeak and again interference from W and Hf at 134 keV photopeak, the major photopeak counting for Hg occurs at 77.3 keV (Donkor et al. 2006).

The mean concentration of total arsenic and total mercury measured in the urine samples are presented in Tables 2 and 3.

Table 2. Concentration of As for various categories of workers

Sample Identity	Arsenic concentration (µg L^{-1})				
	10 km	2km	0.5km	Casual	Permanent
1	5.71± 1.64	6.12 ±1.05	8.01±1.41	10.53 ± 0.90	11.41 ± 1.46
2	7.41 ± 0.81	5.34 ± 2.13	7.18 ± 1.53	9.35 ± 1.30	14.69 ± 1.03
3	6.61± 1.57	9.77 ± 0.79	8.15 ± 3.02	11.59 ± 2.03	13.82 ± 1.34
4	8.91± 2.29	7.31 ± 1.45	9.19 ± 1.13	12.56 ± 1.42	15.51 ± 1.18
5	5.86 ± 1.64	8.85 ± 1.39	7.26 ± 2.34	10.95 ± 3.18	15.76 ± 2.14
6	6.70 ± 1.42	5.74 ± 1.14	6.81 ± 1.43	9.84 ± 0.83	16.29 ± 2.04
7	5.72 ± 0.79	8.49 ± 1.62	7.87 ± 2.63	11.35 ± 2.71	14.94 ± 1.94
8	6.55 ± 1.25	7.67 ± 0.89	8.25 ± 1.03	8.93 ± 1.55	17.62 ± 2.07
9	8.36 ± 1.29	8.48 ± 1.23	7.21 ± 1.92	9. 78 ± 1.67	13.86 ± 1.79
10	5.89 ± 2.31	8.89 ± 1.74	11.72 ± 1.02	9.68 ± 2.89	14.75 ± 2.23
11	6.78 ± 1.45	7.92 ± 0.51	8.27 ± 2.71	9.81 ± 1.76	16.88 ± 1.37
12	6.57 ± 0.72	8.76 ± 2.01	6.49 ± 0.81	10.87 ± 2.34	11.52 ± 1.45
	***6.76 ± 1.43**	**7.78 ± 1.33**	**8.03 ± 1.75**	**10.44 ± 1.88**	**14.75 ± 1.62**
	****(5.71-8.91)**	**(5.34- 9.77)**	**(6.49-11.72)**	**(8.93-11.59)**	**(11.41-17.62)**

Note: Data are presented as mean ± standard deviation of three replicate measurements;
**average mean concentration;*
*** range of results*

Table 3. Concentrations of Hg for various categories of mine workers

Sample Identity	Mercury Concentration (µg L^{-1})				
	10km	2km	0.5km	Casual	Permanent
1	0.29±0.12	0.43 ± 0.11	0.51±0.24	0.74 ± 0.33	0.51 ± 0.14
2	0.38 ± 0.05	0.56 ± 0.18	0.56±0.17	0.52 ± 0.12	0.64 ± 0.07
3	0.36±0.21	0.45 ± 0.07	0.53±0.26	0.57 ± 0.04	0.57 ± 0.22
4	0.32±0.14	0.49 ± 0.11	0.38±0.06	0.40 ± 0.18	0.53 ± 0.16
5	0.46 ± 0.17	0.51 ± 0.23	0.51±0.21	0.61 ± 0.22	0.76 ± 0.44
6	0.38 ± 0.12	0.52 ± 0.13	0.58±0.08	0.46 ± 0.12	0.49 ± 0.11
7	0.37 ± 0.03	0.47 ± 0.11	0.43±0.14	0.59 ± 0.05	0.52 ± 0.25
8	0.29 ± 0.11	0.38 ± 0.14	0.47±0.19	0.62 ± 0.11	0.47 ± 0.18
9	0.37 ± 0.03	0.48 ± 0.07	0.59±0.23	0.61 ± 0.15	0.38 ± 0.04
10	0.32 ± 0.16	0.53 ± 0.14	0.45 ± 0.17	0.55 ± 0.21	0.56 ± 0.34
11	0.41 ± 0.10	0.36 ± 0.12	0.57 ± 0.11	0.64 ± 0.08	0.60 ± 0.23
12	0.35 ± 0.08	0.43 ± 0.02	0.54 ± 0.06	0.53 ±0.03	0.65 ± 0.32
	***0.36 ± 0.11**	**0.47 ± 0.12**	**0.51 ± 0.16**	**0.57 ± 0.14**	**0.56 ± 0.21**
	****(0.29-0.46)**	**(0.36- 0.56)**	**(0.38-0.59)**	**(0.40-0.74)**	**(0.38-0.76)**

Note: Data are presented as mean ± standard deviation of three replicate measurements;
**average mean concentration;*
*** range of results*

The mean concentration of arsenic concentration for permanent workers at the mine site was found to be the highest (14.75 ± 1.62) whilst that of the catering staff working at about 10km from the mine site was the lowest (6.76 ± 1.43). Also, the mean arsenic concentration of the catering staff was about twice that of the permanent mine workers. The difference between the mean arsenic concentrations of the permanent mine workers and the casual mine workers were relatively small as compared to the other categories of workers.

The mean arsenic concentration of the workers who work at about 0.5km (8.03 ± 1.75) from the mine itself was slightly greater than the mean value obtained for workers who work at about 2km from the mine (7.78 ± 1.33). However, some of the mean arsenic concentration recorded did not follow the expected trend. For example, a member of staff working 2km off site recorded an arsenic concentration greater than that of most staff members working 0.5km from the mine site. This could be attributed to the fact that some workers, by the nature of their work, spend more time in the areas of higher arsenic concentration. Even though he is assigned permanently to work 2km from the site he might be spending most of his time in the areas on site that have relatively high arsenic concentration

The highest mercury concentration was recorded by a permanent mine worker (0.76 µg/L ± 0.44) whilst the lowest was recorded by a worker who works 10km (0.29 µg/L ±0.12) off site. However, the casual mine workers recorded the highest mean mercury concentration (0.57 µg/L ± 0.22). It is also worth noting that the mean mercury concentration for the permanent workers was also around the same value (0.56 µg/L ± 0.23). The mine runs a shift system for its workers where some workers come in the morning, the others in the afternoon and the rest at night. However, at peak periods when the mine needs more mine workers, casual workers are brought in to meet its high demand. Mostly, these casual workers engage in artisanal gold mining using mercury when they are off duty at the mine. Therefore, they are exposed to mercury through their artisanal gold mining activities (Donkor et al. 2006). This may have accounted for the higher mean mercury concentration in casual workers.

The As concentration was generally below the WHO recommended range of 5µg/L- 20µg/L, therefore the workers of the mines may be considered not to be at risk (WHO 2001). The As concentration also compared quite well with the urinary total arsenic geometric mean of urine concentrations (in µg/L) for the U.S. population from the 2003-2004 National Health and Nutrition Examination Survey of Non-Hispanic blacks is 11.6 µg/L (9.50-14.1)(Calafat et al. 2007). It could be said that high As concentration can be obtained from the other sources than the mine. The Hg concentrations for the workers were also less than the normal Hg concentration in the urine for the Russian Federation (5µg/L) (WHO 1991). The Hg concentration for the workers also compared well to the urinary mercury geometric mean of urine concentrations (in µg/L) for the U.S. population was found to be 0.476 µg/L (0.413-0.549) (Calafat et al. 2007). The mercury values for experimental subjects were high relative to those recorded from the environmental sample (water soil and sediments) in earlier studies (Donkor et al. 2006, Gati et al. 2000, Serfo-Armah et al. 2004). The body has a mechanism of reducing the excess mercury burden before downloading to excretory organs (e.g. hair tissue) as reproductive waste (Offergelt et al. 1992, Farris et al.). The low levels of mercury in the urine sample may be attributed to the availability of good ventilation facilities in the working surrounding of the mining workers following earlier studies and recommendations. Since mercury is volatile, the chemical could be lost giving good ventilation facilities.

However, there should be routine monitoring of the workers both by the companies and by governmental organisations. There should be routine checks on the mining companies as well to make sure that the high operational standard that might have contributed to the low levels of Hg and As in the workers is maintained. The results of the monitoring process should be made available to the departments responsible for the safety of the workers to serve as a guideline in their dealings. The monitoring programme should take the form of a participatory research involving the workers. The workers should be educated and well informed about the importance of such research studies as some of them were reluctant to provide urine samples.

4. Conclusions

Generally, As concentrations in the urine were higher than the corresponding Hg concentration. This may be due to the stable nature of As; it changes from one form to another. The study also shows that the As can be acquired through other means apart from mining activities. The levels do not suggest any dangerous exposures to the workers. However, there should be carried on further work on the specification of As and Hg in the samples since toxicity depends primarily on the chemical forms of the element.

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Pietvakarių Ganos aukso kasyklų darbuotojų šlapime esančio arseno ir gyvsidabrio koncentracijų stebėjimas

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Straipsnyje siekiama įvertinti, ar arseno ir gyvsidabrio kiekis šlapime priklauso nuo aukso kasyklose išskiriamo arseno ir gyvsidabrio koncentracijų. Šlapimo bandiniai buvo renkami iš žmonių, kurie 2 dienas nevalgė jūros produktų, taip pat kurių dantys neplombuoti. Bendras arseno ir gyvsidabrio kiekis vertintas taikant instrumentinę neutronų aktyvacijos analizę (INAA). Tyrimas parodė, kad abiejų tirtų medžiagų koncentracijos šlapimo bandiniuose yra saugios.