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## **Comparative studies of some heavy metals in the urine of people engaged in mining and non miners**

**J.P.K. Adotey\*, J.K. Bentum, E. J. Koranteng-Addo, F.K. Baah**

*Department of Chemistry, School of Physical Sciences, University of Cape Coast, Ghana*

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### **ABSTRACT**

*This study is an attempt to do comparative analysis on urinary lead, arsenic, nickel and cadmium levels on mine and non miners within the Golden Star Bogoso / Prestea Mines Samples were taken from the Assay Laboratory and Environmental Laboratory Workers of the Golden Star Bogoso/Prestea Mines Company and also Non-miners (students) from the University of Cape Coast as a control. The samples were digested with HNO<sub>3</sub>, HCl and H<sub>2</sub>O<sub>2</sub> and the metals analyzed using the Atomic Absorption Spectra (AAS), Varian 220 model. Lead (Pb) and Nickel (Ni) levels were higher than the permissible level, but that of the arsenic was found to be lower than the permissible level. Cadmium was not detected in any of the urine samples of the mine workers. The students (non-miners) however recorded low levels of all the metals except cadmium which was found to be higher than the permissible levels. The levels of the metals Pb, As and Ni, (except Cd) were found to be higher in the mine workers than those in the non-mine workers.*

**Keywords:** Heavy metals, urine, mineworkers.

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### **INTRODUCTION**

Heavy metals are stable elements that cannot be metabolized by the body and therefore bioaccumulate as it passes up the food chain to human. Most of these do not have any basic function in the body but can be highly toxic. Once the metals are released into the environment through the air, drinking water, food, or countless man-made products and chemicals, they get into the body through inhalation, ingestion and skin absorption.[1] If the heavy metals accumulates in the body tissues faster than the body's detoxification pathways can dispose off the, a gradual build up of this toxins will occur. This can lock into the enzymes sulfuric attachments and block out other molecules from correctly attaching and then suffocate the

enzymes making it useless resulting in weakness of some physiological process in the body [2,3,4].

Heavy metal over load can lead to neurological disease, depression, aggravate conditions such as Osteoporosis and hyperthyroidism, memory loss and poor coordination, muscle pain, anorexia, constipation, vomiting anemia, kidney and liver damage and others [5,6] Heavy metals occur naturally in rock forming and are minerals but human activities have given rise to anomalous high concentration of the metals relative to the normal background levels [7]. The primary route of excretion of heavy metals is the faeces, little trace metals are excreted in urine, hair, breast milk and sweat [8].

Even though urine test for heavy metals exposure is not very good, it still gives an indication of the extent to which one is being exposed and the level of body stored since most of the metals are cleared fairly rapidly[6] In Ghana it is suspected that mining workers and people living in mining areas are frequently exposed to chemicals that contain higher levels of heavy metals. For this reason this paper seeks to compare the levels of Pb, Cd, Ni and As in the urine of some mining workers and people who have never lived in a mining community.

## EXPERIMENTAL SECTION

The samples were collected from two sections of the mining workers at Bogoso Gold Limited that is, Assay Laboratory Workers and Environmental Laboratory Workers. Sixteen samples (52%) were obtained from the Assay Lab workers and 6 other samples (60%) were collected from the Environmental Lab Workers. The samples were collected using 30ml sealed plastic containers. The containers were washed thoroughly with detergent and distilled water to avoid any contamination. 14 samples were also collected in the same container from some students of the University of Cape Coast who are not exposed to any mining activity, and were used as a control. To ensure uniformity, all the samples were fresh morning urine and were digested immediately.

### Sample treatment

Fresh urine tends decompose to become alkaline standing due to the breakdown of urea to ammonium carbonate; but can be stored in a refrigerator. Because of lack of storage facilities, the samples were collected and digested the same day and were kept in a refrigerator for few days before analysis was done using AAS machine (spectra AA220).

10ml each of urine samples were measured with a measuring cylinder into a 150ml beaker and 10ml of 1:1 nitric acid was added. The mixtures were covered with a watch glass and was heated using an adjustable hot plate and were allowed to reflux for 10-15minutes without boiling. It was then allowed to cool and 15ml of concentrated nitric acid was added and allowed to reflux for 30 minutes. The last step was repeated and the mixtures were allowed to evaporate to about 5ml without boiling. It was allowed to cool and 2ml of water and 3ml of 30% Hydrogen peroxide was added. The beaker was covered with a water glass and placed on a hot plate and was allowed to heat until the effervescence was minimal. It was then allowed to cool and 5ml of concentrated HCl and 10ml of water was added and heated and refluxed for 15 minutes without boiling.

The samples were finally diluted to 100ml volume with distilled water after cooling and were then filtered using suction filtration to remove any particulate matter. [9] The digested samples were then analyzed for As, Pb, Ni and Cd using Atomic Absorption Spectrum (Varian 220). The control and the blank were digested in the same way.

## RESULTS AND DISCUSSION

The proficiency testing indicated the recovery of the metals were within the acceptable limits of  $\pm 15\%$

The results of analysis of lead, arsenic, nickel and cadmium in the urine of some mining and non-mining workers are shown in Tables 1-4.

**Table 1: Metals in urine of mine workers**

Sample	Concentration of metal (mg/L)		
	As	Ni	Pb
BA-01	0.015	0.034	0.314
BA-02	0.011	0.036	0.277
BA-03	0.011	0.024	0.307
BA-04	0.01	0.025	0.255
BA-05	0.013	0.038	0.492
BA-06	ND	0.054	0.276
BA-07	0.010	0.029	0.312
BA-08	0.008	0.015	0.299
BA-09	ND	0.038	0.327
BA-10	0.011	0.038	0.334
BA-11	0.009	0.034	0.313
BA-12	0.008	0.030	0.319
BA-13	0.002	0.054	0.274
BA-14	ND	0.043	0.311
BA-21	0.009	0.027	0.290
BA-22	0.005	0.011	0.164
BE-16	0.010	0.056	0.342
BE-17	0.003	0.062	0.355
BE-18	0.009	0.052	0.304
BE-19	0.009	0.044	0.337
BE-20	0.002	ND	0.127
BE-25	ND	ND	0.078

LOD= 0.005 ppm

**Table3: Metals in urine of environmental laboratory mine workers**

Samples	Concentration of metals (mg/L)		
	As	Ni	Pb
BE-16	0.010	0.056	0.342
BE-17	0.003	0.062	0.355
BE-18	0.009	0.052	0.304
BE-19	0.009	0.044	0.337
BE-20	0.002	ND	0.127
BE-25	ND	ND	0.078

**Table 2: Metals in urine of Assay laboratory mine workers**

Samples	Concentration of metals (mg/L)		
	As	Ni	Pb
BA-01	0.0150	0.0340	0.3140
BA-02	0.0110	0.0360	0.2770
BA-03	0.0110	0.0240	0.3070
BA-04	0.0100	0.0250	0.2550
BA-05	0.0130	0.0380	0.4920
BA-06	ND	0.0540	0.2760
BA-07	0.0100	0.0290	0.3120
BA-08	0.0080	0.0150	0.2990
BA-09	ND	0.0380	0.3270
BA-10	0.0110	0.0380	0.3340
BA-11	0.0090	0.0340	0.3130
BA-12	0.0080	0.0300	0.3190
BA-13	0.0020	0.0540	0.2740
BA-14	ND	0.0430	0.3110
BA-21	0.0090	0.0270	0.2900
BA-22	0.0050	0.0110	0.1640

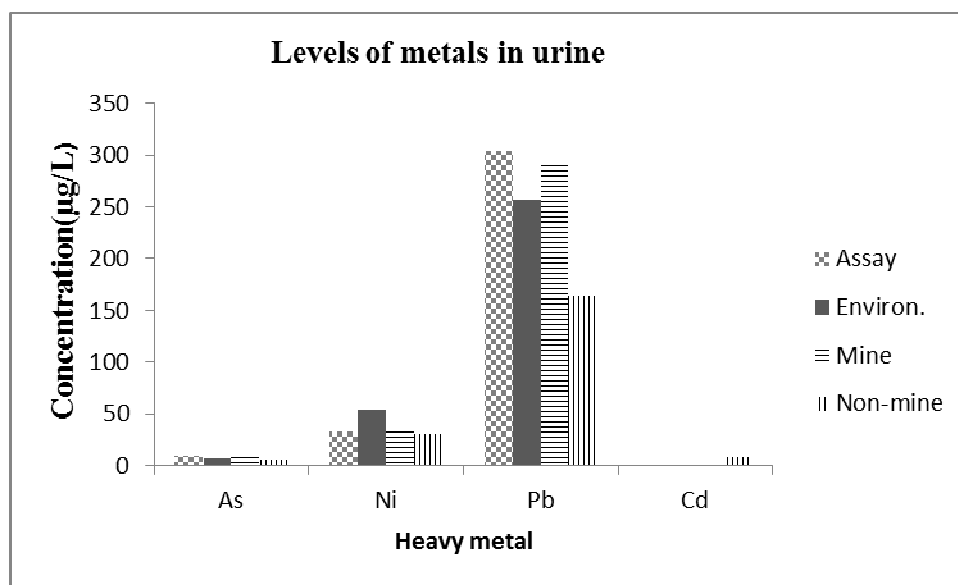
**Table 4: Metals in Urine of Non- mining workers**

Samples	Concentration of metals (mg/L)			
	As	Ni	Pb	Cd
US-01	0.0020	0.0390	0.1460	ND
US-02	ND	ND	0.1400	0.0080
US-03	ND	ND	0.1300	ND
US-04	ND	ND	0.1670	0.0070
US-05	ND	ND	0.1480	0.0060
US-06	ND	ND	0.1300	0.0070
US-07	0.0190	ND	0.2010	ND
US-08	ND	ND	0.1460	0.0100
US-09	0.0020	ND	0.2380	0.0090
US-10	ND	ND	0.2010	0.0090
US-11	ND	ND	0.1850	0.0100
US-12	ND	ND	0.1700	0.0080
US-13	ND	0.0120	0.1770	0.0080
US-14	0.0020	0.0430	0.1260	0.0090

The concentration ( mean  $\pm$  rsd ) and median of these metals As, Ni and Pb in the urine of the assay laboratory mine workers were  $9.4 \pm 3.31 \mu\text{g/L}$ , (  $10.0 \mu\text{g/L}$  );  $33.10 \pm 11.78 \mu\text{g/L}$ , ( $34.0 \mu\text{g/L}$ ) and  $304.0 \pm 64.26 \mu\text{g/L}$ , ( $30.9 \mu\text{g/L}$ ). Their ranges in  $\mu\text{g/L}$  were As,  $<0.001 - 20$ ; Ni,  $10 - 50$ ; and Pb,  $160 - 490$ . The mean and (median) levels of the metals in the urine of the environmental mine workers were: As,  $6.6 \pm 3.78 \mu\text{g/L}$  (  $9.0 \mu\text{g/L}$ ); Ni,  $53.5 \pm 7.6$  ( $54.0 \mu\text{g/L}$ , and Pb  $257.2 \pm 121.97 \mu\text{g/L}$ . The respective ranges were  $< 0.001 - 10.0$ ;  $40 - 60$  and  $0.80 - 360 \mu\text{g/L}$ . Cd was not detected in any of the urine samples from the mine workers. Generally the assay laboratory workers had higher levels of As, Ni and Pb. Also there were variations in the levels of

heavy metals in the samples. The levels of all the metals in the urine of the environmental laboratory were more varied than those of the Assay laboratory workers as indicated by the percentage relative standard deviation. For both workers the order of variation were As < Ni < Pb. Pb was detected to have the highest level and As the least, The mean levels of the metals in all the mining workers were As,  $8.6 \pm 3.57$ ; Ni,  $37.2 \pm 13.73$  and Pb  $291.2 \pm 83.35$   $\mu\text{g/L}$ .

The levels of the heavy metals As, Ni, Pb and Cd in the urine of non-mining workers or people who have never resided in mining communities were respectively  $6.2 \pm 8.50$ ,  $31.30 \pm 16.86$ ;  $164.6 \pm 39.93$  and  $8.3 \pm 1.27$   $\mu\text{g/L}$ . Except for Cd which was not detected in the urine samples of the mine workers, the levels of all the other heavy metals were higher than levels found in urine of non-mine workers (Fig 1).



**Figure 1: Levels of heavy metals in urine samples of mining and non-mining workers**

The environmental mine workers had the highest level of Ni and higher than the mean for the mine workers. Also the mean level of Pb in the urine assay laboratory workers was higher than the mean for the mining workers. The levels of As and Ni in the urine of the non-mine workers was comparable to the As in the urine of the environmental mine workers Ni in the urine of the assay lab workers. The observations suggest that the environmental workers are exposed to higher levels of Ni than the Assay lab workers, while the assay lab workers are also exposed to higher levels of Pb. The non-mine workers however, had higher levels of Cd.

**Table 5: Correlation coefficient of regression analysis of metals in the urine of non-mining workers**

	As	Ni	Pb	Cd
As	1	*	*	*
Ni		1	1	1
Pb			1	*
Cd				1

There was no significant correlation between any two of the metals detected in the urine samples of the assay, environmental or the mine workers in general, implying that they were exposed to varied sources of metal, from food, emission from vehicles and mining activities. Apart from As,

the levels of metals detected in the urine of the non-mining workers however, showed very strong correlations at the 0.01 confidence level (Table 5). The very high correlation coefficient of  $r = 1$  for correlation between Ni and Pb, and Ni and Cd; and the fact that there was no significant correlation between Pb and Cd may imply that generally the two metals were from different sources.

The presence of these metals in the urine of both mining and non-mining workers is an indication of the prevalence of these metals in the environment and food samples, and that exposure to heavy metal is common, particularly Pb. The relatively higher levels of the heavy metals in the urine of the mining workers suggests that they are exposed to higher levels of heavy metals compared to non-mining workers agree with observations made by [6] The very high levels indicate that it is hard to avoid lead due to its sources and widespread distribution in the environment. The metals are also components of exhaust emissions, and have the potential to affect the individual through inhalation. These metals are absorbed either through the lungs or the gastrointestinal tract. These metals get into the human body through inhalation, ingestion and skin. They are found in the soil, ocean and pesticides and therefore present in foods [5,6]

Accumulation of high levels of these heavy metals, above permissible levels, in the human body may cause health hazards such as fatigue, memory loss, dementia, depression, anxiety, and insomnia. The higher level of the metals in the urine analyzed is an indication of higher levels stored in the human body. This can have significant health impacts in the long term.

Apart from Arsenic which were found to have levels lower than the Bio-standard for heavy metals and metalloids set by [10]. The levels of all the other metals were much higher than the Bio-standards; of As, 15-40  $\mu\text{g/L}$ ; Ni, 0.5-6.1  $\mu\text{g/L}$ , Pb 150  $\mu\text{g/L}$  and Cd 1.5  $\mu\text{g/L}$ .

## CONCLUSION

Arsenic, Nickel, Lead and Cadmium were detected in the urine samples. All the four were found in the urine samples of the non-mining workers, but only Cd was not found in the urine samples of the mining workers. The levels of the metals in samples from the miners were higher than those found in the urine of non-mining workers. The assay lab workers had highest levels of Pb and As whiles the environmental workers had the highest level of Ni. Ni showed very high significant correlation of  $r = 1$  with Pb and Cd, No significant relation was observed for the metals in the urine of the mining workers implying they are exposed to varied sources the metals. Both mining and non-mining workers are likely to be exposed to heavy metals.

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