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*Original scientific paper*

# Electrochemical determination of the levels of cadmium, copper and lead in polluted soil and plant samples from mining areas in Zamfara State, Nigeria

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**Abstract**

*The concentrations of lead, copper and cadmium in soil and plant samples collected from Abare and Dareta villages in Anka local government area of Zamfara State, Nigeria have been electrochemically determined. The study was carried out because of the high mortality of women and children under five, reported for these areas in June 2010. The cause was ascribed to the lead poisoning which has been related to the mining and processing of gold-containing ores. Linear sweep anodic stripping voltammetry technique was used with the glassy carbon working, Ag/AgCl reference and platinum auxiliary electrodes. Voltammetric peaks for lead, copper and cadmium that were observed at -495 mV, -19.4 mV and -675 mV, respectively, have formed a basis for construction of the corresponding calibration plots. The concentrations (in mg/kg) of lead, copper and cadmium in the soil samples were found in the ranges of 18.99−26087.70, 2.96−584.60 and 0.00−1354.25, respectively. The concentration values for lead were far above already established USEPA (2002) and WHO (1996) maximum permissible limits for residential areas. The concentrations of lead, copper and cadmium in the food samples ranged between 5.70−79.91, 11.17−41.21 and 0.00−5.74 mg/kg. Several of these values are found well above the FAO/WHO limits of 0.1, 2 and 0.1 mg/kg, respectively. The results indicate that in addition to the lead poisoning, copper and cadmium poisoning may also be responsible for sudden and high mortality in this population.*

**Keywords**

Heavy metals; Mining activities; Soil; Plants; Anodic stripping voltammetry

## Introduction

In June 2010, the Zamfara State Ministry of Health of Nigeria was alerted by Médecins Sans Frontières (MSF) for an increasing number of several deaths and illness among women and children under five years in some villages in Bukkuyum and Anka local government area. They contacted the United States Centers for Disease Control (US CDC) who deployed a response team to assist in investigating the outbreak. At the same time, the Blacksmith Institute, USA, sent a team from Terra Graphics Environmental Engineering Inc. to conduct an environmental assessment of the area. These teams worked with the national and state authorities, MSF, and the country office of the World Health Organization (WHO). The investigations confirmed severe lead poisoning in more than 100 children in the villages of Dareta and Yargalma, having a mean blood lead concentration of 119 μg/dL. Moreover, soil in and some residential areas in Abare exhibited lead concentrations exceeding 100,000 mg/kg. A random sample of 56 children under 5 years from the villages of Abare and Dareta revealed that over 90 % of them had blood lead concentration > 45 μg/dL and over 70 % had concentrations > 0 μg/dL [1]. A high incidence of convulsions and deaths of young children had been recorded in these villages and lead poisoning was implicated. It is generally thought that lead was introduced in the environment by the illegal mining of gold ores.

In the previous study [2], it was reported that our team visited Abare and Dareta villages and observed various processing activities of the ores which could promote metal contamination of the soil, water and vegetables and may constitute health hazards. These include handling the ores with bare hands, eating with unwashed hands, crushing the ores in residential areas, washing the ores in water bodies, exposure of wells to these ores and sometimes drinking polluted water. The concentrations of lead and copper in water from wells, boreholes, ponds and stream from these villages and environs were already reported [2]. Our observations on the research visit to Abare and Dareta villages attributed pollution of soils in the residential areas and farms to the practices of bringing the ores to the residential areas where they are crushed, and irrigating of farmlands by the water already used in processing the ores.

High concentrations of heavy metals in soil would increase potential uptake of these metals by plants and their entering into the food chain [3]. Contamination of food chain becomes increasingly important in a view of its role in human health and nutrition [3-7]. The main threats to human health from heavy metals are associated with exposure to lead, copper, cadmium, mercury and arsenic. These metals may enter the human body through inhalation of dust, consumption of contaminated drinking water and ingestion of food plants grown in contaminated soils [8,9]. The uptake of metals by plants can be affected by several factors which include metal concentrations in soils, soil pH, soil texture, cation exchange capacity, organic matter content of soils as well as the age of the plants [10-12]. Mining activities have been reported to have adverse effects on water resources and farmlands [13] and this could lead to accumulation of heavy metals in plants grown in such contaminated soils.

The aim of this study is to ascertain the level of heavy metal contamination of the soils and plants such as guinea corn and maize seeds in Abare, Dareta and environs, using linear sweep anodic stripping voltammetry technique which offers high sensitivity and rapid response time.

## Experimental

### *Collection of soil samples*

Soil samples were collected from 30 sites in Abare, Dareta and environs in July 2010. Sampling was done in a 'W' fashion at sites 10 m apart. Soil samples were taken at 5 cm depth. The sampling sites designated DA 01−10 and AB 05−10 were residential areas in Dareta and Abare, where grinding of the ore was carried out. The mining sites in Dareta were designated DA 11−15. The areas around a pond and at the bank of a stream in Abare where the ores were washed are designated AB 01−05 and AB 11−15, respectively. The coordinates of the sampling stations were recorded using a Garmin 38 global positioning system (GPS) device. About 500 g of each soil sample was collected in polythene bags and labeled. Each sample was then air-dried, sieved (size 2.3 mm) and stored in an air tight glass jar.

*Collection of plant samples*

Samples of various plants and food items were collected from Abare and Dareta in July 2010. The items which included guinea corn and millet leaves were collected randomly from 50 plants in Dareta. The guinea corn leaves and the millet leaves were each mixed thoroughly before analysis. Elephant grass was obtained from the area of cattle grazing in Abare. Guinea corn and millet seeds were purchased from the homes in Abare and Dareta, while the maize and beans were purchased from the homes in Abare.

*Preparation of soil samples*

1.0 g of each soil sample was added to 20 cm$^3$ of a mixture of concentrated $HNO_3$ and $H_2O_2$ (30 %) (Sigma-Aldrich) in the ratio 3:1. The mixture was heated gradually to 120 °C and kept at this temperature for 2 hours till a clear solution was obtained. The solution was allowed to cool and filtered into a 50 cm$^3$ standard flask and supplemented with deionized water before transferring to a pre-cleaned plastic bottle.

*Preparation of plant samples*

The samples were air-dried in a dust-free environment for three weeks and pulverized using a domestic blender. The digestion of samples was carried out by sequential treatment with 65 % $HNO_3$ and $HClO_4$ (Sigma-Aldrich) according to the method earlier reported [14]. 1 g of the fine powder of the sample was digested with 20 cm$^3$ of 65 % $HNO_3$ at 80 °C for one hour. On cooling, 2 cm$^3$ of 70 % $HClO_4$ was added and digested again at 250 °C, until a clear solution was obtained. The mixture was allowed to cool and 20 cm$^3$ of deionized water was added. It was filtered into a 100 cm$^3$ standard flask, supplemented with deionized water and stored in a pre-cleaned plastic container for the heavy metals analysis which was carried out in triplicate within 24 h.

*Voltammetric measurements*

A Basi-Epsilon potentiostat/galvanostat was used in the study. The concentrations of heavy metals were determined by linear sweep anodic stripping voltammetry technique [2,15]. The working electrode (3 mm diameter) was glassy carbon, while platinum electrode (1.6 mm diameter) served as the auxiliary electrode and Ag/AgCl as the reference electrode. The working electrode was polished with alumina powder to obtain a mirror-like image, washed with de-ionized water and placed in a pyranha solution for 2 min, washed with de-ionized water and dried.

*Calibration curve*

Standard solution of each metal was prepared by dissolving the weighed amount of the salt (0.1598 g of $Pb(NO_3)_2$), (0.3929 g of $CuSO_4 \times 5H_2O$) and 0.2745 g of $Cd(NO_3)_2 \times 4H_20$), (all from Sigma-Aldrich) in 100 cm$^3$ of deionized water to give 1000 ppm of lead, copper and cadmium, respectively. From these solutions, serial dilutions were made with 0.1 M acetate buffer, pH 4.50 containing 80 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$ to give the working concentrations of 250, 500, 1000, 2000 and 2500 ppb of each metal. These diluted solutions were used to obtain the calibration curves. For this purpose, 10 cm$^3$ of each of the standard solution of the metal was transferred into the electrochemical cell and purged with nitrogen for 10 min. The pre-concentration of the metal was carried out at -900 mV for 120 s with stirring and after a quiet time of 30 s, the stripping process was carried out by scanning the potential from -900 mV to 200 mV at the scan rate of 20 mV/s. Peak currents for lead, copper and cadmium were observed at -495 mV, -19.4 mV and -675 mV, respectively. These peak current values were used to construct the calibration plots for determination of the concentrations of Pb, Cu and Cd.

*Analysis of samples*

5 cm$^3$ of each digested soil or plant sample was transferred into the electrochemical cell and 5 cm$^3$ of 0.2 M acetate buffer, pH 4.50, containing 160 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$ was added and mixed thoroughly. The solution was purged with nitrogen for 10 min and the potential scanned as described for the standard solutions. The values of the peak current obtained at -495 mV, -19.4 mV and -675 mV were used to determine the concentrations of Pb, Cu and Cd in the samples.

## Results

Similarly to already described determinations of calibration plots for Pb and Cu [2], Figure 1 shows the overlay of voltammograms of standard solutions of Cd, while Figure 2 shows the calibration plot for Cd in the concentration range of 250−2000 ppb.

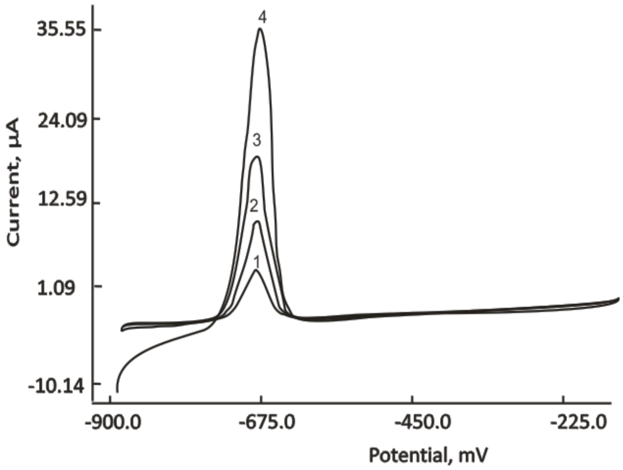


***Fig. 1.*** *Overlay of the voltammograms obtained for standard solutions of $Cd(NO_3)_2\times4H_20$ in 0.1M acetate buffer, pH 4.5 containing 80 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$. Cd concentration: 250 ppb (1), 500 ppb (2), 1000 ppb (3), 2000 ppb (4).*

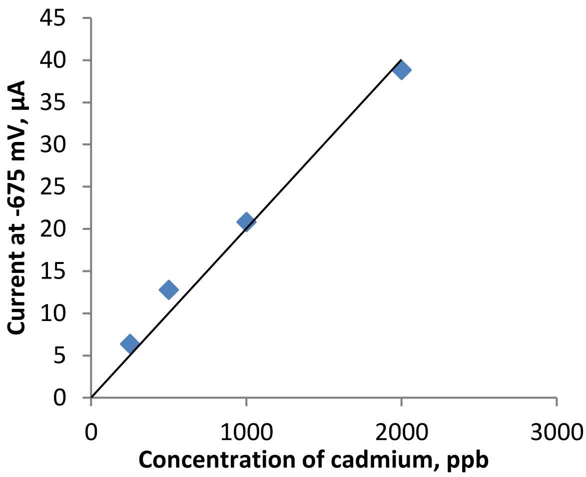


***Fig. 2****. Calibration plot of peak currents at -675 mV against Cd concentration in 0.1 M acetate buffer pH 4.50, containing 80 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$.*

The voltammograms obtained for the determination of metals in soil samples AB 04 and AB 13 are shown in Figures 3 and 4, respectively.

Figures 5 and 6 show voltammograms for the determination of Pb, Cu and Cd in millet leaves and guinea corn from Dareta.

The results showing the concentrations of Cu, Cd and Pb in soils from the various sampling sites are presented in Table 1, while the corresponding results for the plants are listed in Table 2.

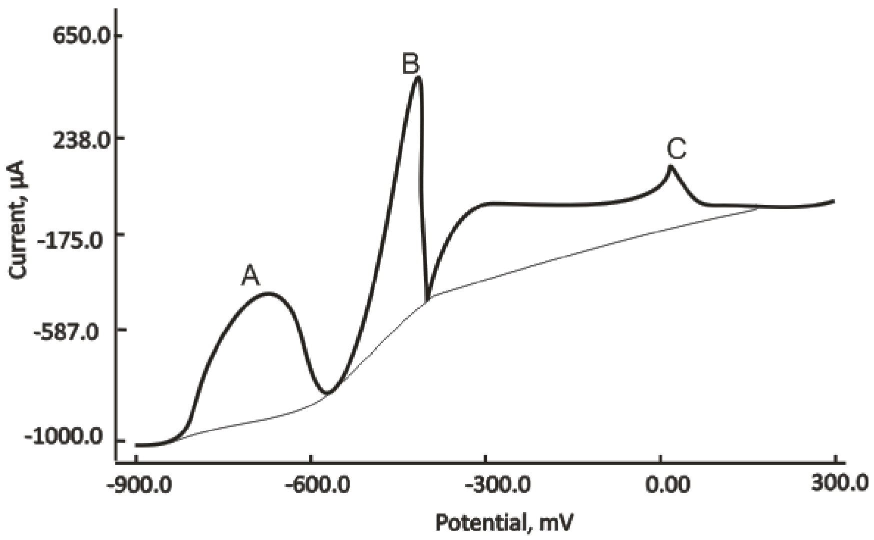


***Fig. 3***. *Voltammograms of the soil sample from Abare AB 04 in 0.1 M acetate buffer, pH 4.5 containing 80 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$. Peaks A, B and C correspond to Cd, Pb and Cu respectively.*

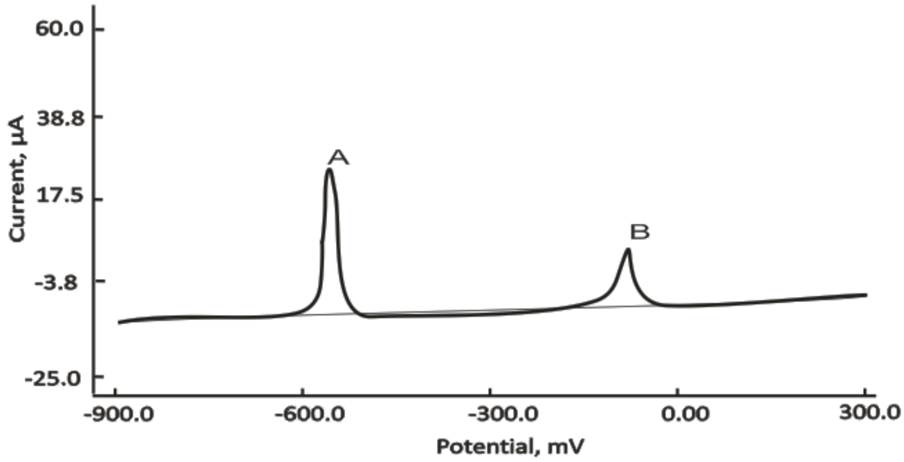


***Fig. 4***. *Voltammogram of the soil sample from Abare, AB 13 in 0.1 M acetate buffer, pH 4.5 containing 80 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$. Peaks A and B correspond to Pb and Cu, respectively.*

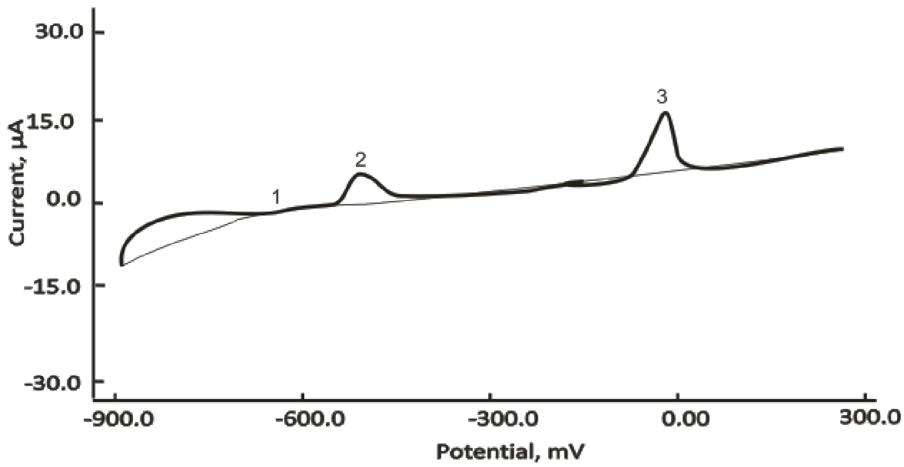


***Fig 5***. *Voltammogram of millet leaves from Dareta in 0.1M acetate buffer, pH 4.5, containing 80 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$. Peaks 1, 2, and 3 correspond to Cd Pb and Cu*

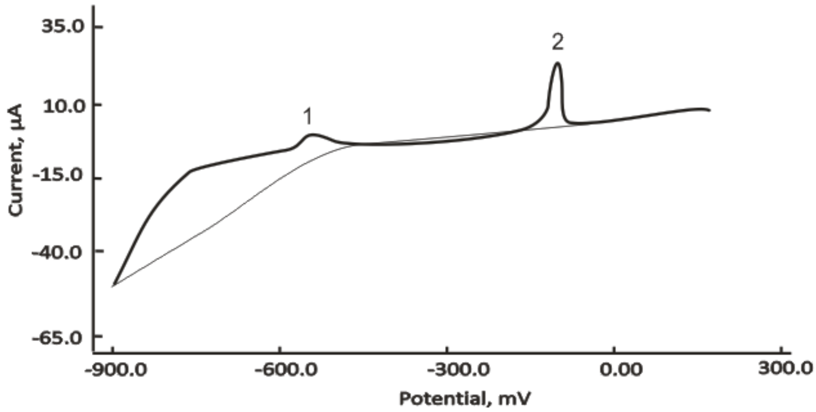


***Fig. 6***. *Voltammogram of guinea corn seed from Dareta in 0.1 M acetate buffer pH 4.5, containing 80 ppm $Hg(NO_3)_2$ and 0.2 M $KNO_3$. Peaks 1 and 2 correspond to Pb (-495 mV) and Cu (-19.4 mV)*

***Table 1.*** *Concentrations of Pb, Cu and Cd in soil samples from Dareta and Abare villages in Zamfara State*

| Soil sample | Coordinate | Content of Pb, mg/kg | Content of Cu mg/kg | Content of Cd, mg/kg |
|---|---|---|---|---|
| DA 01 (Grinding site) | N 12$^0$ 01’50.2’’ E 005$^0$ 57’30.5’’ | 1175.00 ± 8.40 | 36.604 ± 6.00 | ND |
| DA 02(Grinding site) | N 12$^0$ 01’42.6’’ E 005$^0$ 57’18.7’’ | 40.04 ± 1.10 | 2.96 ± 0.28 | ND |
| DA 03(Grinding site) | N 12$^0$ 01’41.6’’ E 005$^0$ 57’18.7’’ | 36.16 ± 0.18 | 10.86 ± 1.80 | ND |
| DA 04(Grinding site) | N 12$^0$ 01’29.6’’ E 005$^0$ 57’44.0’’ | 18.99 ± 0.70 | 32.84 ± 0.50 | ND |
| DA 05(Grinding site) | N 12$^0$ 01’39.5’’ E 005$^0$ 57’32.1’’ | 21.06 ± 0.24 | 6.56 ± 0.11 | ND |
| DA 06(Grinding site) | N 12$^0$ 01’51.8’’ E 005$^0$ 57’21.3’’ | 26087.70 ±16.20 | 78.51 ± 1.66 | ND |
| DA 07(Grinding site) | N 12$^0$ 01’51.7’’ E 005$^0$ 57’21.2’’ | 438.56 ± 2.20 | 9.73 ±1.27 | ND |
| DA 08(Grinding site) | N 12$^0$ 01’52.0’’ E 005$^0$ 57’20.9’’ | 438.56 ± 1.30 | 9.73 ± 0.54 | ND |
| DA 09(Grinding site) | N 12$^0$ 01’51.7’’ E 005$^0$ 57’21.2’’ | 701.30 ±0.91 | 33.26 ± 1.20 | ND |
| DA 10(Grinding site) | N 12$^0$ 01’51.8’’ E 005$^0$ 57’21.0’’ | 339.46 ± 1.10 | 38.69 ± 1.10 | ND |
| DA 11(Mining site) | N 12$^0$ 01’15.8’’ E 005$^0$ 57’34.0’’ | 1128.51 ± 26 | 123.08 ± 2.91 | 804.50 ± 5.60 |
| DA 12(Mining site) | N 12$^0$ 01’15.3’’ E 005$^0$ 57’34.3’ | 630.70 ± 1.22 | 54.30 ± 1.80 | ND |
| DA 13(Mining site) | N 12$^0$ 01’15.0’’ E 005$^0$ 57’34.0’’ | 167.54 ± 1.00 | 54.30 ± 1.40 | ND |
| DA 14(Mining site) | N 12$^0$ 01’14.7’’ E 005$^0$ 57’34.0’’ | 3760.96 ± 4.1 | 213.80 ± 2.80 | 1354.25 ± 7.50 |
| DA 15(Mining site) | N 12$^0$ 01’14.9’’ E 005$^0$ 57’34.2’’ | 481.14 ± 6.50 | 48.64 ± 1.80 | ND |
| AB 01(Washing site) | N 12$^0$ 04’41.2’’ E 005$^0$ 57’29.1’’ | 900.40 ± 1.30 | 92.53 ± 3.50 | ND |
| AB 02(Washing site) | N 12$^0$ 04’42.1’’ E 005$^0$ 57’30.6’’ | 4051.76 ± 28 | 458.37 ± 1.50 | ND |
| AB 03(Washing site) | N 12$^0$ 04’41.5’’ E 005$^0$ 57’29.0’’ | 606.14 ± 2.80 | 33.71 ± 2.50 | ND |
| AB 04(Washing site) | N 12$^0$ 04’41.2’’ E 005$^0$ 57’29.7’’ | 3720.62 ± 3.00 | 584.60 ± 2.85 | 1216.25 ± 9.50 |
| AB 05(Washing site) | N 12$^0$ 04’40.6’’ E 005$^0$ 57’29.2’’ | 390.79 ± 5.10 | 50.91 ± 3.50 | ND |
| AB 06(Grinding site) | N 12$^0$ 04’41.3’’ E 005$^0$ 57’26.2’’ | 38.16 ± 0.87 | 15.16 ± 1.25 | ND |
| AB 07(Grinding site) | N 12$^0$ 04’40.7’’ E 005$^0$ 57’26.2’’ | 489.48 ± 1.80 | 17.19 ± 0.68 | ND |

| Soil sample | Coordinate | Content of Pb, mg/kg | Content of Cu mg/kg | Content of Cd, mg/kg |
|---|---|---|---|---|
| AB 08(Grinding site) | N 12$^0$ 04'41.3'' E 005$^0$ 57'26.4'' | 111.899 ± 2.10 | 24.35 ± 1.35 | ND |
| AB 09(Grinding site) | N 12$^0$ 04'40.7'' E 005$^0$57'26.8'' | 1615.79 ± 3.20 | 49.10 ± 3.50 | ND |
| AB 10(Grinding site) | N 12$^0$ 04'41.3'' E 005$^0$ 57'27.0'' | 207.89 ± 1.85 | 10.86 ± 1.67 | ND |
| AB 11(Washing site) | N 12$^0$ 04'22.7'' E 005$^0$ 57'28.3'' | 287.54 ± 0.87 | 92.69 ± 2.50 | 8.03 ± 1.35 |
| AB 12(Washing site) | N 12$^0$ 04'21.7'' E 005$^0$ 57'27.6'' | 1323.68 ± 4.51 | 204.52 ± 3.45 | ND |
| AB 13(Washing site) | N 12$^0$ 04'23.1'' E 005$^0$ 57'28.8'' | 205.56 ± 1.25 | 40.04 ± 2.31 | ND |
| AB 14(Processing site) | N 12$^0$ 04'22.9'' E 005$^0$ 57'29.3'' | 390.79 ± 3.10 | 69.91 ± 1.40 | ND |
| AB 15(Washing site) | N 12$^0$ 04'23.1'' E 005$^0$ 57'29.5'' | 51.586 ± 1.20 | 23.55 ± 1.48 | ND |

ND: Not detected.

***Table 2.*** *Concentrations of metals in samples of plants and food from Abare and Dareta, Zamfara State.*

| Plant/food SAMPLE | LOCATION | Content of Pb, mg/kg | Content of Cu mg/kg | Content of Cd, mg/kg |
|---|---|---|---|---|
| Elephant grass | Abare | 24.63 ±0.05 | 27.37 ± 0.08 | ND |
| Guinea Corn seeds | Abare | 15.60 ± 0.15 | 11.17 ± 0.07 | ND |
| Maize | Abare | 24.56 ± 0.04 | 12.72 ± 0.06 | 5.74 ± 0.13 |
| Beans | Abare | 10.64 ± 0.05 | 30.41 ± 0.10 | ND |
| Millet seeds | Abare | 5.70 ± 0.06 | 14.84 ± 0.06 | ND |
| Guinea corn seeds | Dareta | 79.91 ±0.07 | 41.21 ± 0.05 | ND |
| Guinea corn leaves | Dareta | 36.86 ± 0.10 | 19.05 ± 0.03 | ND |
| Millet seeds | Dareta | 22.29 ± 0.09 | 11.53 ± 0.10 | ND |
| Millet leaves | Dareta | 22.76 ± 0.09 | 40.58 ± 0.20 | 5.34 ± 0.08 |
| FAO/WHO (2011) | -- | 0.1 | 2 | 0.1 |

ND: Not Detected

## Discussion

### *Soil analysis*

The concentration levels of Pb, Cu and Cd in soil samples listed in Table 1 can be considered based on the processes carried out at each specific location. DA 01−10 are residences where grinding of ores is carried out by women and children. DA 11−15 denote the mining sites located 3.5 km from Dareta. Sites AB 01−05 are located around a pond in Abare. Sites AB 06−10 are grinding areas located in residences in Abare, while AB 11−15 are sites located by the stream in Abare where the processors wash the powdered ores to obtain gold.

Data in Table 1 show that in the residential areas in Dareta (DA 01−DA 10), concentrations of Pb were detected in the range 18.99-26087.70 mg/kg, Cu was detected in the range 2.96−78.51 mg/kg, while Cd was not detected at all. At the mining sites in Dareta (DA 11−DA 15), the levels of Pb and Cu were in the range 167.54−3760.96 mg/kg and 48.64−123.08 mg/kg, respectively. Cadmium was found at two mining locations in Dareta (DA 11 and DA 14) in concentrations of 804.50 mg/kg and 1354.25 mg/kg, respectively. At the pond environ sites in Abare (AB 01−AB 05), the levels for Pb and Cu were in the range 390.79−4051.76 mg/kg and 33.71−584.60 mg/kg, respectively, while Cd was found at one site (AB 04) in the concentration of 1216.25 mg/kg. The levels of Pb and Cu at grinding sites of residential areas in Abare (AB 06−AB 10) were detected in the range of 38.16−1615.79 mg/kg and 10.86−49.10 mg/kg, respectively. Cadmium was not detected in these samples. At the ore washing sites in Abare (AB 11−AB 15) at the bank of a stream, the levels of Pb and Cu were detected in the range 51.59−1323.68 mg/kg and 23.55−204.52 mg/kg, respectively. Cadmium in the concentration of 8.03 mg/kg was found at only one site in Abare (AB 11).

The permissible level of Pb in soil of residential areas in the US is 400 mg/kg [16,17]. This value is exceeded in a home in Dareta (DA 01) and grinding sites in Dareta (DA 06−09), and is probably due to the volume of ore being processed over time. The concentration values for Pb, Cu and Cd are comparable for the residential grinding sites DA 01−05 and DA 07−10 in Dareta and AB 06−10 (36.16−1615.79 mg/kg) in Abare. DA 06 appears to be an isolated case. It is pertinent to note that even though there is no mine in Abare, the inhabitants of the two villages appear to be processing about similar quantities of ores. With the exception of site DA 13, the levels of Pb at the mining sites in Dareta (DA 11−15) exceeded the USEPA limit. It should be noted that the site DA 14 is located at the entrance of the main mining site. The mining activities have severely polluted this site and are responsible for the very high level of Pb observed in DA 14 (3760.96 mg/kg). In the pond environment in Abare (AB 01−05), the Pb levels in the soil were very high, with 4051.76 mg/kg and 3720.62 mg/kg detected at sites AB 02 and AB 04, respectively. This may be due to the gathering of processors at these sites. The levels of Pb were moderately high at AB 01 and AB 03 showing values of 900.40 mg/kg and 606.14 mg/kg, respectively. At powdered ore washing sites in Abare (AB 11−15), high levels of Pb were found at AB 12 (1323.68 mg/kg) and AB 15 (51.586 mg/kg). It is significant that these values were recorded in Abare where there are no mines. However, the stream and pond in Abare are both used by the two communities for the washing of the ores. The high concentration value of Pb found at AB 15 maybe due to several processors who converge at this site.

The permissible limit for Cu in the soil of residential areas is 190 mg/kg [18]. Data in Table 1 show that Cu levels in the soil samples from Dareta were under the permissible limit except for DA 14 located at the mining site, where 213.8 mg/kg was detected. In Abare, this permissible limit was highly exceeded at pond sites (AB 02 and AB 04) with the values of 458.37 and 584.60 mg/kg, respectively and marginally exceeded in the residential processing site (AB 12) where 204.52 mg/kg of Cu was detected.

The permissible limit of Cd in the soil is 12 mg/kg [18]. Cadmium was not detected in soil samples taken from the residences in Dareta (DA 01−10), but two sites in the mining areas (DA 11 and DA 14) showed Cd levels of 804 and 1354 mg/kg, respectively. These concentrations of Cd were 67 and 113 times higher than the permissible limit. Cadmium was also detected at two locations in Abare (AB 04 and AB 11). High level of 1216.25 mg/kg found in AB 04 is 101 times higher than the permissible limit, while the level of Cd in AB 11 is under the limit. It is pertinent to note here that all sites where Cd was detected (DA 11, DA 14 and AB 04), exhibited high levels of Pb too.

In summarizing the results given in Table 1, it can be said that more than 50 % of the soil samples collected from Dareta and Abare were contaminated by Pb, 20 % by Cu and 12 % by Cd. This is in agreement with the Joint United Nations Environment Programme–Office for the Coordination of Human Affairs (UNEP/OCHA) Environmental Unit (JEU) report [19] on lead pollution and poisoning crisis in Zamfara State. This report showed that the top soil collected from various locations in Dareta and Abare were heavily polluted by Pb. At a processing site near a mosque in Abare, the Pb level in the soil was reported as 1210 mg/kg, while for the top soil from a near site close to a private well, the Pb level of 27000 mg/kg was reported. The UNEP/OCHA study has also reported Pb levels of 23600 mg/kg in top soil from a grinding site in Abare and 37500 mg/kg in top soil from a processing site near a well in Dareta [19]. However, the UNEP/OCHA study did not report any pollution of the soil by Cu and/or Cd.

A study on the assessment of lead, mercury and arsenic levels in soils of Dareta, Bagega, Sunke, Abare and Yargalma villages in North−Western Nigeria was reported in 2014 [20]. Lead concentrations in soil samples were found to be in the range of 6.91−4157 mg/kg. The average concentration of Pb in farmlands in Abare was reported to be 515 mg/kg [21].

The results of all these studies, as well as those presented in this report show that top soil in several parts of Abare and Dareta residences are heavily polluted by Pb as a result of mining activities. In a household survey carried out by Blacksmith Institute, 2011 in two villages, Dareta and Yargalma in Anka area, it was reported that 66 % of the population in the villages undertook at least one mining activity within their residences [22]. These mining activities include crushing of the ore, grinding, washing, drying, extracting gold with mercury and/or melting gold. The results of the study show the impact of anthropogenic activities on abundance of potentially harmful elements in the soils of the area. The mining activities exposed the women and children to high levels of Pb in the soil and this may be responsible for the mean blood lead concentration of 119 µg/dL found in children from these villages. Blood levels as low as 10 µg/dL are associated with impaired neurological development in young children [23].

In the present paper, the levels of Cu were generally found under the limit at most of the sites. However, prolonged exposure to these metals could lead to bioaccumulation. Some of the most commonly reported adverse health effects of Cu are gastrointestinal distress, nausea, vomiting, abdominal pain irritation of the respiratory tract, coughing, sneezing and pulmonary fibrosis [24]. The levels of Cd found at two sites in Dareta (DA 11 and DA 14) and one site in Abare (AB 04) are excessively high and pose a health risk to the processors in these sites. The kidney is the main organ affected by the chronic Cd exposure and toxicity. Cadmium accumulates in the kidney which may result in renal failure [25].

In a study carried out in 2014, on discharges of potentially harmful elements (PHEs) in soils from various sites in Anka Local Government Area where artisanal mining for gold was carried out, concentrations of Pb equal to 2637, 1960, 3920, 290 and 3326 mg/kg were reported for mine site, ore processing site and village square, respectively [26]. The corresponding values for Cu at the same places were reported as 159, 159, 117, 29 and 223 mg/kg, while the corresponding values for Cd were reported as 4.5, 8.7, 3.6, 0 and 6.9 mg/kg.

In our study, the corresponding values for Pb shown in Table 1 for the mining sites (DA 11–DA 15) and residential processing sites (DA 01–DA 10 and AB 06–AB 10) ranged between 167−3761 and 19−1615 mg/kg, respectively. Here, the highest value of 26088 mg/kg was observed at only one location (DA 06). The corresponding values for Cu ranged between 49−214 mg/kg at the mining sites and between 3−49 mg/kg for the residential sites, respectively. It should be noted that 79 mg/kg of Cu was detected at DA 06. The corresponding values for Cd ranged between 0−1354 mg/kg and are detected at the mining sites only.

It must be noted here that the values of Pb in the mine and processing sites in two studies are comparable, except for the high value of 26,088 detected at DA 06. Also, the values for Cu in the mine sites in the two studies are not far apart, but the values for the processing site in our study are significantly lower than those reported in 2014 [26]. The values for Cd for some mine sites in our study are significantly higher, while those for Cu are lower than the values reported in 2014 [26]. However, no GPS values were provided in the study carried out in 2014 [26].

*Plants/food analysis*

Concentrations of metals in the samples of plants and food presented in Table II show that concentrations of Pb in the cereals; guinea corn, maize and millet seeds from Abare were in the range of 5.70−24.56 mg/kg. The value for beans was 10.64 mg/kg, while the value for the elephant grass was 24.63 mg/kg. In Dareta, the values of Pb in guinea corn and millet seeds were 79.91 and 22.29 mg/kg, while the corresponding values found in guinea corn and millet leaves were 36.86 and 22.76 mg/kg, respectively. The concentrations of Cu in the cereals in Abare were in the range of 11.17−14.84 mg/kg, while the corresponding value for beans was 30.41 mg/kg and the value for elephant grass was 27.37 mg/kg. In Dareta, the values of copper in guinea corn and millet seeds were 41.21 mg/kg and 11.53 mg/kg, respectively, while the levels of Cu in guinea corn leaves and millet leaves were 19.05 and 40.58 mg/kg respectively. Cadmium was not detected in guinea corn, millet, beans and elephant grass in Abare, but the maize from Abare was found to contain 5.74 mg/kg of Cd. In Dareta, Cd was not detected in the cereals, but the level found in millet leaves was 5.34 mg/kg.

Guinea corn, maize and millet are the main food in this sub region, and therefore the concentrations of heavy metals in the food samples grown in the contaminated soils are pertinent to health. It is shown in Table II that the levels of Pb in guinea corn and millet seeds in Abare were 15.60 and 7.50 mg/kg, respectively, while the corresponding values for these samples in Dareta were 79.91 mg/kg and 22.29 mg/kg, respectively. The values for Dareta samples were understandably higher than the values for Abare samples because the tonnage of gold ore processed in Dareta is much higher than that of Abare. The permissible limit of Pb in cereals is 0.1 mg/kg [27]. This value is highly exceeded by factors in the range 156−799 for guinea corn seeds and 57−223 for millet seeds. The level of Pb in the maize sample from Abare exceeds the permissible level by a factor of 245. The corresponding factor in beans is 106. Thus, all the cereals in Abare and Dareta are not good for human consumption because of the high level of Pb. Elephant grass, guinea corn leaves and millet leaves that are consumed by cattle also showed very high levels of Pb. Thus, Pb can enter the food chain and will be transferred to humans who consume meat from such cattle. The permissible limit for Cu in cereals is 2 mg/kg [27]. The value for millet seeds was 14.84 mg/kg and 11.17 mg/kg in guinea corn seeds in Abare while in Dareta, the value for millet seeds was 11.53 mg/kg and that for guinea corn seeds was 41.21 mg/kg. The values for millet seeds in Abare and Dareta were comparable but the value for guinea corn seeds in Dareta of 41.21 mg/kg, is more than double the values for guinea corn and millet seeds in Abare and the millet seeds in Dareta. The value of 30.41 mg/kg for beans obtained in Dareta was also much higher than those for the other food items except for guinea corn seeds. The values for the elephant grass in Abare and the guinea corn and millet leaves from Dareta also exceeded the permissible level by factors ranging from 10−20, if the permissible value of 2 mg/kg for cereal is adopted. Cadmium was detected in the maize from Abare and millet leaves in Dareta, and both values exceeded the permissible limit of 0.1 mg/kg for Cd by a factor of about 50.

According to data in Table 2, it seems that all the plant samples were polluted by Pb and Cu, while maize in Abare and millet leaves in Dareta were found to contain Cd as a third contaminant. The samples that were collected from the field, namely elephant grass, guinea corn leaves and millet leaves had Pb values in the range 22.76−36.86 mg/kg, while the food items purchased from homes with the exception of guinea corn from Dareta had Pb values in the range 5.70−24.56 mg/kg. The plants obtained from the fields would be contaminated by dusts from ore-processing. It should also be borne in mind that items kept in the residences could also be contaminated by dusts from ore-processing activities in the residential areas. This is probably responsible for the value of 79.91 mg/kg for Pb and 41.21 mg/kg for Cu in guinea corn seeds obtained from Dareta.

The possible sources of heavy metal contamination of the food samples are: direct contact with the ores, uptake from polluted soils, uptake from metal-polluted air, deposition on the surface of plants and exposed food items and contact with polluted water used for irrigation. All these are potential sources of contamination in Abare and Dareta. However, irrigation was not observed in Dareta. Crops and vegetables grown in soils contaminated with heavy metals have been reported to accumulate higher levels of heavy metals than those grown in uncontaminated soils [28,29].

The consumption of the contaminated cereals, millet, guinea corn and maize seeds as well as beans by the inhabitants of Dareta and Abare will pose a risk to human health. The elephant grass obtained from Dareta with mean Pb concentration of 24.63 mg/kg is also unsafe for the livestock.

In a study carried out on the human health risk characterization of lead pollution in plants harvested from contaminated farmlands of Abare village, Pb concentration of sorghum exceeded the FAO/WHO limit by a factor of 3500 [21]. The time of sampling, however, was not stated.

One of the most widely studied mechanisms of action of toxic metals is oxidative damage due to direct generation of free radical species and depletion of antioxidant reserves [30]. Mercury, cadmium and lead can effectively inhibit glutathione peroxidase thereby reducing the effectiveness of this antioxidant defense system for detoxification [31]. Some heavy metals act as molecular mimics of nutritionally essential trace elements and compete with metallic cofactors for entry into cells and incorporation into enzymes [32]. Cadmium can compete with and displace zinc from proteins while lead and thallium are chemically similar to calcium and potassium [32-34].

Lead toxicity in human adults can lead to poor muscle coordination, nerve damage to the sense organs and nerves controlling the body, increased blood pressure, hearing and vision impairment and decreased sperm count. In children it can lead to damage to the brain, nervous system, liver, kidney and death [35]. Children less than seven years old are largely at risk [16].

The health implication of the results presented in this study is the possible occurrence of Pb, Cu and Cd poisoning in all the people exposed to the ores. Ores are processed in residential areas by women and older children. Children including infants sometimes put unwashed hands in their mouths thus ingesting the ore dust. They also inhale the dust during processing of the ore. They have less tolerance to heavy metal toxicity and hence high mortality of exposed children is inevitable. The women are equally exposed and mortality though not as high as in children, would be expected. All the inhabitants ingest the contaminated foods and thus would be victims of heavy metal toxicity, namely lead and cadmium. Lead toxicity is implicated in abdominal pain, confusion, anemia, seizures, coma and deaths [36] while cadmium toxicity is implicated in lung cancer, kidney and bone damage [37].

All reports on high mortality in Zamfara State have attributed the deaths to the Pb poisoning [38]. The electrochemical method used in this study has made it possible to establish the presence of other heavy metal pollutants, namely copper and cadmium which may also be implicated in the high mortality.

## Conclusions

Linear sweep anodic stripping voltammetry has been found very useful in the identification and determination of heavy metal pollutants, copper, cadmium and lead in the soil and plants/food samples. Presence of very high concentrations of these metals in the samples from several parts of Abare and Dareta regions reported in this study is related to the mining of ores at these locations and may be implicated in the high mortality in Zamfara State. It is obvious that to address this health risk, safe mining practices should be enforced and soil remediation of all these areas should be carried out. Educating the people, especially children, on toxicity of heavy metals and monitoring of these toxic metals in their blood should also be carried out periodically.

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