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Determination of Copper and Lead in Water Samples from Zamfara State, Nigeria by Linear Sweep Anodic Stripping Voltammetry

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In June 2010, there was a report of a major outbreak of lead poisoning leading to several hundred deaths especially of women and children below five years of age in some parts of Zamfara State, Nigeria. The poisoning was reported to be related to gold mining operations in areas where lead is present in the ores. Medicins Sans Frontiers had reported that lead was implicated in the mortality. The levels of lead and copper in drinking water samples collected from wells, boreholes, stream and ponds in some of the affected areas were determined by linear sweep anodic stripping voltammetry (LSASV), using glassy carbon as working electrode, Ag/AgCl as reference and platinum as the auxiliary electrode. The pre-concentration of lead or copper in the samples was carried out electrolytically. Voltammetric peaks for lead and copper were observed at -495 mV and -19.4mV respectively. The concentrations of lead and copper in the water samples were in the range of 118.46 μg/L−6879.09 μg/L and 61.62 μg/L−1340.18 μg/L respectively. These results are far above the WHO maximum permissible limits in potable water. Other physico-chemical parameters determined include pH, total dissolved solids (TDS), electrical conductivity (EC), temperature, acidity, alkalinity and hardness. The results indicate that in addition to lead poisoning, copper poisoning may have contributed to the mass mortality in the areas.

Keywords: Heavy metal pollution, mining operations, voltammetry, water.

1. INTRODUCTION

Mining and its related operations are the most important anthropogenic sources of heavy metals that affect the environment negatively [1-4]. Heavy metals that can be leached from waste rocks into water bodies include arsenic, cadmium, chromium, mercury, lead and zinc [5].

For decades, illegal miners have operated in the mineral-rich parts of Zamfara State of Nigeria without any consideration for the impact on the environment. Several inhabitants in the rural areas live below the average per capital income and hence illegal mining in the state became a lucrative business in 2007 when gold ores were discovered in Bukkuyum and Anka Local Government Areas (LGAs) of Zamfara State.

Between March and April, 2010, Medicins Sans Frontiers (MSF) observed an increase in the mortality of children aged below five in Anka LGA in Zamfara State. Blood tests of the children in Dareta and Abare villages in Anka LGA showed high levels of lead, with a mean blood lead concentration of 119 µg/dL [6-8] which was above the permissible limit of 10 µg/dL [9]. The high level of lead found in the blood of children in Dareta and Abare villages was attributed to the pollution arising from mining activities by villagers who practiced small scale gold extraction from lead-containing ores. The processing of the ores involves crushing, washing and drying, often inside family huts resulting in soil contamination in the household premises, thereby exposing the children to the risk of lead poisoning [6]. Over 300 deaths were reported in July 2010. It was estimated that the entire population of 10,000 in seven contaminated villages in Zamfara State might have been exposed to lead poisoning while about 2,000 children under five years of age were in acute danger of death.

Lead pollution is of great concern because of the high toxicity of its compounds and bioaccumulation in several organs of exposed subjects [10]. Thus a sensitive, convenient, and cost effective analytical method for the determination of lead in water is highly desirable. Electrochemical methods have found important applications in sample analysis and in organic and inorganic synthesis [11-14]. The determination of lead and cadmium in water samples by adsorptive stripping voltammetry was recently reported [15].

LSASV is a useful electrochemical technique which can be employed for the accurate measurement of low concentrations of metals at the ppb levels with rapid analysis time and low cost instrumentation. Therefore when lead poisoning was reported in Zamfara State, arrangements were made by some members of our research group to collect water samples from wells, boreholes, ponds and streams at locations close to the mining sites as well as the homes of the processors in Abare and Dareta. The aim of the study was to determine the concentrations of lead, copper as well as other physicochemical parameters such as pH, total dissolved solids, electrical conductivity, temperature, acidity, alkalinity, hardness of the water samples.

2. MATERIALS AND METHODS

2.1. Collection of Samples and Preservation

Water samples were collected in July 2010 from Abare and Dareta both in Anka Local Government Area of Zamfara State, Northern Nigeria. Two samples each of 500 cm^3 were collected in two pre-cleaned plastic bottles with screw caps from various sampling locations including 19 wells, 3 ponds, 2 boreholes and a stream. One sample from each location was acidified with 2 cm^3 concentrated nitric acid. Both acidified and raw water samples were filled to the brim, securely stoppered and placed in black polythene bags. They were preserved at 4^0C before transporting to University of Lagos, Lagos, Nigeria, for analysis. The coordinates of the sampling stations were recorded using a Garmin 38 global positioning system (GPS) device.

2.2. Voltammetric Measurements

A Basi-Epsilon potentiostat/galvanostat was used in the determination. Glassy carbon (3.0 mm) was used as the working electrode, Ag/AgCl as reference while platinum electrode (1.6 mm) served as the auxiliary electrode. The working electrode was polished with alumina powder, washed with de-ionized water and dried.

2.3. Calibration Curve

Stock standard solution of each metal salt was prepared by dissolving weighed amount of the salt (0.1598 g of Pb $(NO_3)_2$ and 0.3929 g of $CuSO_4.5H_2O$) separately in 100 cm^3 of deionized water to give 1000 ppm of lead and copper respectively. From the stock solutions serial dilutions were made with 0.1M acetate buffer, pH 4.50 containing 80 ppm $(HgNO_3)_2$ and 0.2 M KNO_3 to give working concentrations of 250 ppb, 500 ppb, 1000 ppb, 2000 ppb and 2500 ppb of the metal. These solutions were used to obtain the calibration curve.

10 cm^3 each of the standard solutions of each metal salt was transferred to the electrochemical cell and purged with nitrogen for 10 min. The pre-concentration of the metal in the standard solution 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 using a scan rate of 20 mV/s. Peak currents for lead and copper were observed at -495 mV and -19.4mV respectively.

2.4. Digestion of Samples

100 cm^3 of each acidified water sample was evaporated until the volume reduced to 25 cm^3. It was filtered and transferred to a 50 cm^3 standard flask and the volume made up to the mark with de-ionized water.

2.5. Analysis of Water Samples

5 cm^3 of the digested water sample was transferred into the electrochemical cell and 5 cm^3 of 0.1 M acetate buffer, pH 4.50, containing 160 ppm $(HgNO_3)_2$ and 0.2 M KNO_3 was added and mixed thoroughly. The solution was purged with nitrogen for 10 min and pre-concentration and stripping were carried out as described for the standard solutions. The peak current obtained at -495 mV or -19.4mV was used to obtain the concentrations of lead or copper in the samples.

2.6. Determination of Physico-chemical Parameters of the Water Samples

The temperature, pH, total dissolved solids and electrical conductivities were determined using a multiprobe meter (Hanna HI 98129 Combo waterproof). The determinations were carried out on site.

The acidity, alkalinity and total hardness were carried out on filtered raw water samples using the methods of the American Public Health Association [16].

3. RESULTS

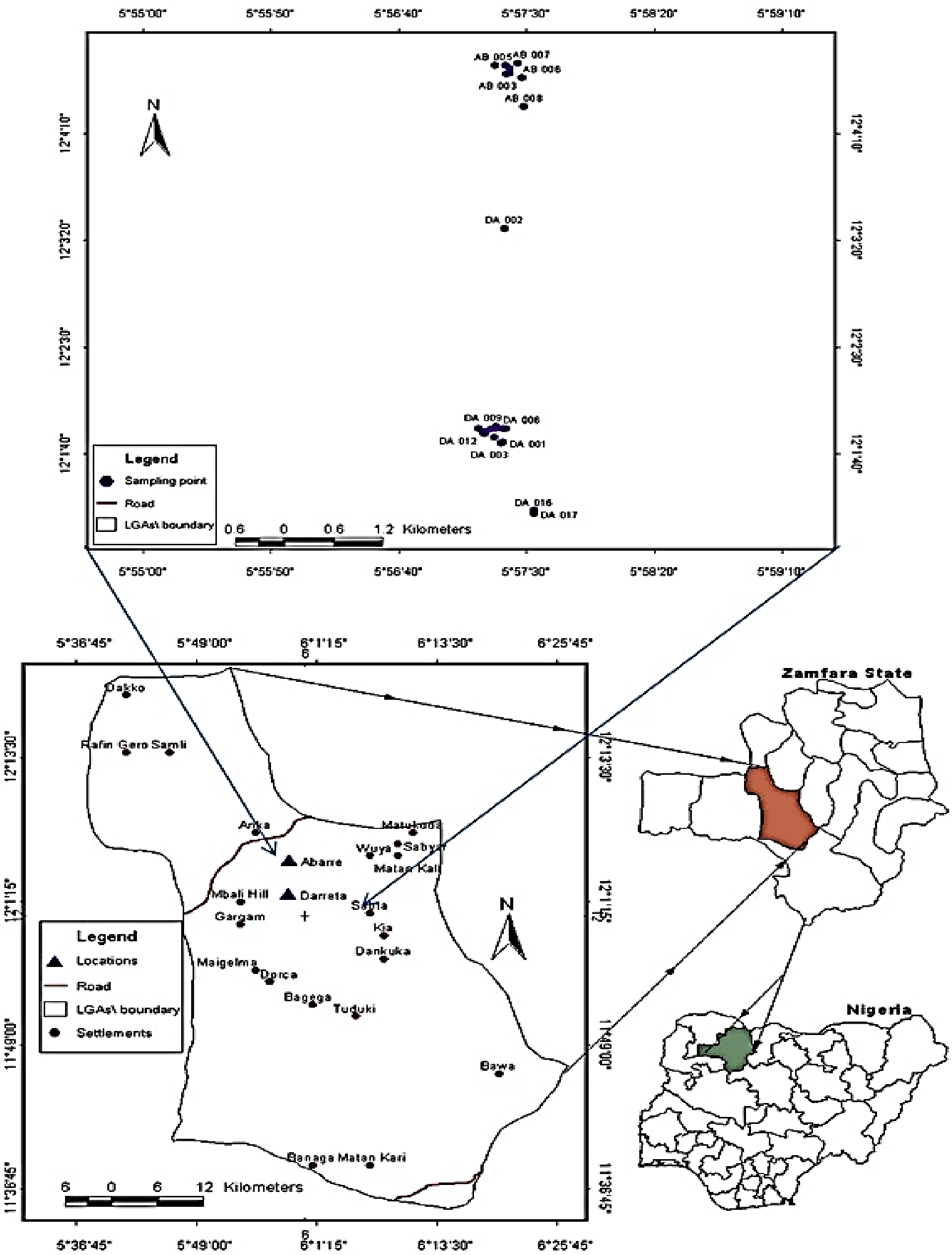

Figure 1. Composite map of Nigeria, Zamfara State and some sampling points.

Fig. 1 shows the location of Zamfara State and the sampling stations. Fig. 2 and 4 show the overlay of the voltammograms obtained for different concentrations of lead and copper respectively using standard solutions. Plots of values of peak current (obtained for the standard solution) against different concentrations of lead and copper are presented respectively in Fig. 3 and 5. A typical result is shown in figure 6 in which sample AB 008 was used.

The coordinates of the sampling sites in Dareta and Abare, the concentrations of lead and copper as well as the physico-chemical parameters of the water samples are presented in Table 1.

Table 1. Coordinates of sampling sites, concentrations of Pb and Cu and physico-chemical parameters of water samples from Dareta and Abare.

Sample Identity	Source	Coordinates	Heavy metal concentrations (µg/L) of water samples		Physico-chemical parameters of water samples						
			Pb	Cu	pH	TDS (mg/L)	EC (µS. cm^{-1})	Temp (^{o}C)	Acidity (mg $CaCO_3$/dm^3)	Alkalinity (mg $CaCO_3$/dm^3)	Total Hardness (mg $CaCO_3$/dm^3)
DA 001	Well	N 12^o 01'45.6'' E 005^o 57'21.1''	ND	72.37± 5.60	7.41± 0.02	207 ± 4.50	419 ±5.10	29.70	39.10± 1.56	363.63± 2.51	1.25 ± 0.01
DA 002	Well	N 12^o 01'45.7'' E 005^o 57'21.5''	ND	ND	7.47± 0.03	247 ± 4.50	493± 4.70	29.30	29.92 ±0.77	464.10± 0.84	1.40 ± 0.01
DA 003	Well	N 12^o 01'45.3'' E 005^o 57'20.3''	ND	ND	7.06± 0.05	249 ± 2.50	498 ±3.60	29.50	27.20± 0.10	383.18± 0.05	0.34 ± 0.02
DA 004	Well	N 12^o 01'47.8'' E 005^o 57'17.6''	ND	117.28 ± 29.79	6.82± 0.01	215 ±6.10	440 ± 7.1	29.00	41.82 ± 3.15	333.88± 15.69	1.40 ± 0.03
DA 005	Well	N 12^o 01'52.0'' E 005^o 57'20.8''	118.46± 65.00	104.34 ±29.79	7.12± 0.05	533 ±7.50	1094 ± 9.20	32.10	54.40 ± 3.20	610.30 ± 1.97	3.62 ± 0.02
DA 006	Well	N 12^o 01'52.1'' E 005^o 57'21.9''	ND	87.78± 14.10	6.93± 0.02	321± 4.30	643± 5.10	31.70	26.50 ± 2.26	311.10 ±4.17	1.42 ± 0.02
DA 007	Well	N 12^o 01'52.1'' E 005^o 57'18.2''	ND	ND	6.88± 0.02	293±5.14	585± 6.10	29.30	35.02 ±5.49	333.90±1.47	1.80 ± 0.04
DA 008	Well	N 12^o 01'52.2'' E 005^o 57'18.5''	154.26± 105.18	455.16 ±11.00	6.96± 0.03	358±5.60	720 ±6.20	29.20	32.30 ± 1.54	403.58± 1.67	2.42 ± 0.19
DA 009	Well	N 12^o 01'53.1'' E 005^o 57'18.1''	ND	62.92± 5.60	7.04± 0.01	537 ±6.50	1073 ±7.10	29.70	41.82 ± 1.13	436.60 ±2.51	3.34 ± 0.02
DA 010	Well	N 12^o 01'51.6'' E 005^o 57'16.3''	ND	ND	6.85± 0.04	435 ±4.20	871± 5.30	29.70	48.62 ± 0.79	352.58 ± 1.67	2.98 ± 0.06
DA 011	Well	N 12^o 01'50.7'' E 005^o 57'14.0''	ND	97.81± 11.40	6.97± 0.05	298 ±6.10	596 ±7.30	29.40	32.30 ± 1.54	307.70 ± 0.83	2.02 ±0.06
DA 012	Well	N 12^o 01'51.8'' E 005^o 57'11.4''	ND	98.09± 10.29	6.97± 0.02	317 ±1.20	635 ± 3.05	29.20	32.30 ± 3.08	367.20± 4.35	2.16 ± 0.06

DA 013	Well	N 12° 01’49.4’’ E 005° 57’13.7’’	ND	149.11 ±15.60	6.84± 0.02	249 ±5.20	499 ± 6.50	29.20	29.20 ± 0.75	267.50± 1.66	1.52± 0.01
DA 014	Well	N 12° 01’49.75” E 005° 57’14.0’’	ND	ND	6.92± 0.01	435 ±4.50	866 ± 5.00	29.70	36.70 ± 1.12	299.90±3.33	3.20 ± 0.04
DA 015	Well	N 12° 01’50.2’’ E 005° 57’13.0’’	ND	98.97 ±11.13	6.98± 0.05	295 ±11.5	592± 12.30	29.50	35.70 ± 3.10	469.20± 2.52	2.24± 0.05
DA 016	Pond	N 12° 01’13.5’’ E 005° 57’33.0’’	404.50± 153	389.18 ± 54	7.72± 0.03	185 ± 1.20	370 ± 3.50	32.80	10.20 ±0.02	20.40 ±0.65	1.60 ±0.02
DA 017	Pond	N 12° 01’12.3’’ E 005° 57’33.3’’	897.23± 98.14	150.56 ±23.13	7.14± 0.01	66 ±3.50	132± 3.50	35.10	6.80 ± 0.03	23.80 ±0.68	0.76 ± 0.08
AB 001	Well	N 12° 04’40.5’’ E 005° 57’23.5’’	ND	ND	6.48± 0.04	225 ±2.50	454± 3.20	29.90	47.60 ± 3.17	247.18 ± 1.66	1.72 ± 0.02
AB 002	Well	N 12° 04’38.1’’ E 005° 57’23.8’’	ND	ND	6.83± 0.04	224 ±6.13	448 ±6.50	29.60	34.00 ± 2.44	276.08±3.14	1.70 ± 0.02
AB 003	Well	N 12° 04’37.7’’ E 005° 57’22.3’’	ND	ND	6.44± 0.02	127 ±2.00	254± 2.00	29.80	34.00 ± 3.09	202.00± 4.93	0.90 ± 0.01
AB 004	Well	N 12° 04’41.8’’ E 005° 57’22.0’’	ND	ND	6.73± 0.03	397 ±4.50	795± 5.00	29.70	54.40 ±0.41	461.38±3.36	2.88 ± 0.06
AB 005	Bore hole	N 12° 04’42.0’’ E 005° 57’17.8’’	ND	61.62 ± 14.50	6.52± 0.03	247 ±6.11	497± 7.60	30.30	53.72 ± 2.40	294.78±3.33	1.96 ±0.06
AB 006	Bore hole	N 12° 04’36.1’’ E 005° 57’28.3’’	ND	70.63 ± 13.50	6.67± 0.05	141 ±5.40	285 ±5.14	31.70	44.00 ± 1.57	257.00± 1.66	1.13 ± 0.02
AB 007	Pond	N 12° 04’42.8’’ E 005° 57’26.8’’	121.24 ±16.45	114.66 ±11.60	9.00± 0.04	43 ±2.50	87 ±2.70	35.30	23.80 ± 2.38	78.88 ±3.16	1.76 ±0.02
AB 008	Stream	N 12°04’22.6’’ E 005°57’29.1’’	6879.09 ±387	1340.18 ±84.50	6.93± 0.01	15 ±3.10	29 ±4.10	29.70	12.92 ± 0.67	24.48 ± 0.14	1.52 ±0.12
WHO Limits (WHO, 2011)			10 μg/L	2000 μg /L	6.5-8.5	500	150		0.00	100-150	30-200

ND=Not detected, TDS= Total dissolved solids, EC= Electrical conductivity.

In Dareta DA 001−015, the mean concentrations of lead in the well water samples were in the range of 0−154.26 μg/L while the values for copper were in the range of 0−455.16 μg/L. The corresponding values for the water from the two ponds (DA 016 and 017) were 404.5 and 897.23 μg/L respectively for lead and 150.56 and 389.18 μg/L for copper respectively.

Lead and copper were not detected in the water samples from the four wells AB 001−004 in Abare. However, while lead was not detected in the two boreholes AB 005 and 006, copper was present at mean concentrations of 61.62 μg/L and 70.63 μg/L respectively.

The mean concentrations of lead and copper in the water sample obtained from a stream in Abare, AB 008, was found to be 6879. 09 μg/L and 1340.18 μg/L respectively.

The pH values for the well water in Dareta were in the range of 6.82−7.47 while the values for the pond were 7.72 and 7.14. The range for the wells in Abare was 6.44−6.83 while the values for the boreholes were 6.52 and 6.67 and the values for the pond and stream were 9.00 and 6.93 respectively.

In Dareta, the values of TDS obtained were in the range of 207−537 mg/L for well water and 185 and 66 mg/L for the ponds. The range for the well water in Abare was 127−397 mg/L while the values for boreholes were 247 and 141 mg/L, 43 mg/L for the pond and 15 mg/L for the stream.

In Dareta, the electrical conductivities for the well samples were in the range of 419−1094 μS. cm^{-1} while the values for the two ponds were 370 μS. cm^{-1} and 132 μS. cm^{-1} respectively. The range for the samples of well water from Abare was 254−795 μS. cm^{-1}, 497 and 285 μS. cm^{-1} for the two boreholes, 87 μS. cm^{-1} for the pond and 29 μS. cm^{-1} for the stream.

In Dareta, the temperatures of several water samples were in the range 29.20−29.70^{o}C except for well water samples DA005 and 006 which had temperatures of 32.10^{o}C and 31.70^{o}C respectively. The values for the ponds were 32.80 ^{o}C and 35.10 ^{o}C. In Abare, the temperatures of the water samples were in the range 29.60−29.90 ^{o}C for the wells, 30.30 ^{o}C and 31.70 ^{o}C for the boreholes, 35.30 ^{o}C for the pond and 29.70 ^{o}C for the stream.

In Dareta, the values of acidity were in the range 26.50−54.40 mg.$CaCO_3/dm^3$ for well water samples, 10.20 and 6.80 mg.$CaCO_3/dm^3$ for the ponds. In Abare, the corresponding values were in the range 34.00−54.00 for well water samples, 53.72 and 44.00 mg.$CaCO_3/dm^3$ for borehole water, 23.80 mg.$CaCO_3/dm^3$ for pond water and 12.92 mg.$CaCO_3/dm^3$ for water from the stream.

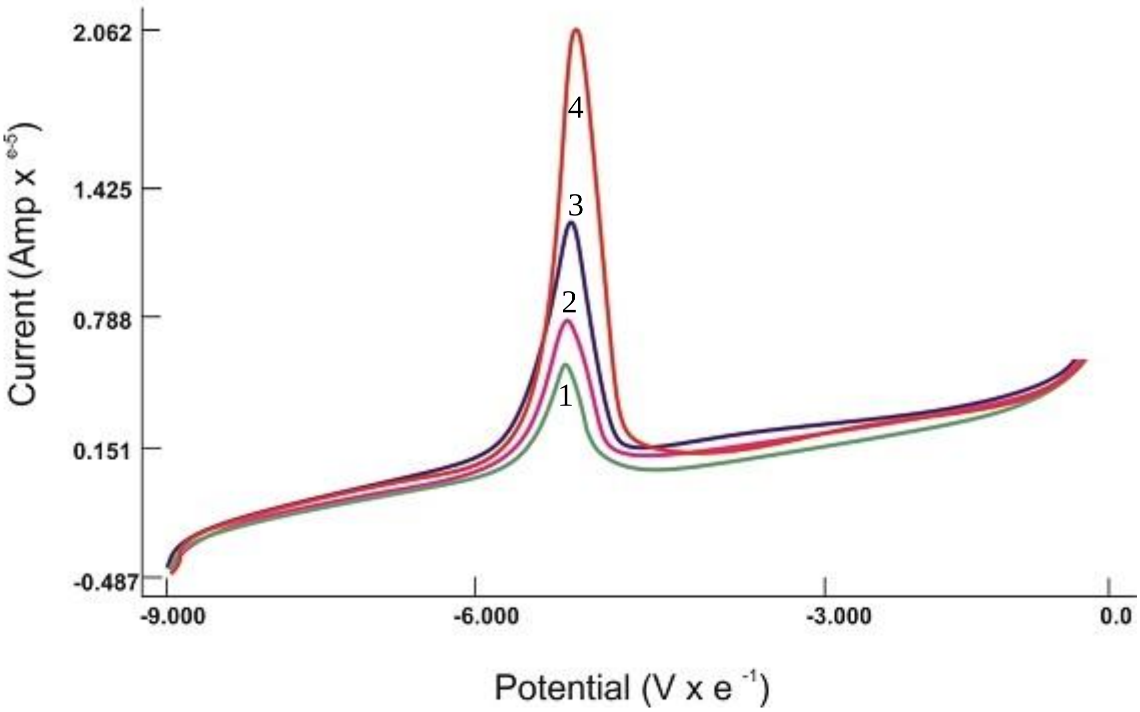

Figure 2. Overlay of the voltammograms obtained for the determination of lead in 0.1M acetate buffer pH 4.5 containing 80 ppm $(HgNO_3)_2$ and 0.2 M KNO_3. (Pb concentration: 1=250 ppb, 2=500 ppb, 3=1000 ppb, 4= 2000 ppb).

In Dareta, the values of alkalinity were in the range of 267.50−610.30 mg.$CaCO_3/dm^3$ for well samples and 20.40 and 23.80 mg.$CaCO_3/dm^3$ for pond water. In Abare, the corresponding values were in the range 202.00−461.38 mg.$CaCO_3/dm^3$ for well water, 294.78 and 257.00 mg.$CaCO_3/dm^3$ for borehole water, 78.88 mg.$CaCO_3/dm^3$ for the pond water and 24.48 mg.$CaCO_3/dm^3$ for water from the stream.

In Dareta, the values for total hardness were in the range of 0.34−3.62 mg.$CaCO_3/dm^3$ for well water samples and 1.60 and 0.76 mg.$CaCO_3/dm^3$ for pond water. In Abare, the corresponding values were 0.90−2.88 mg.$CaCO_3/dm^3$ for well water, 1.13 and 1.96 mg.$CaCO_3/dm^3$ for the borehole water, 1.76 mg.$CaCO_3/dm^3$ for the pond and 1.52 mg.$CaCO_3/dm^3$ for the stream water.

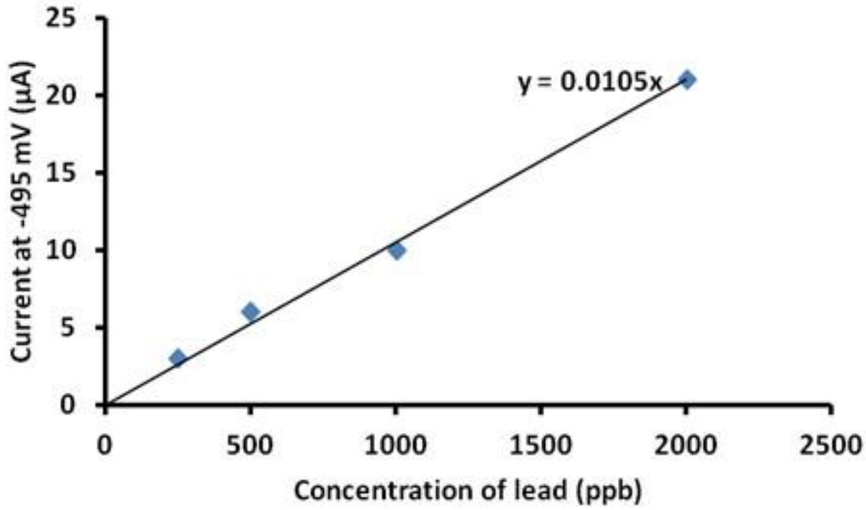

Figure 3. Plot of peak current against Pb concentration in 0.1M acetate buffer pH 4.5 containing 80 ppm $(HgNO_3)_2$ and 0.2 M KNO_3. (Pb concentration: 250 –2000 ppb).

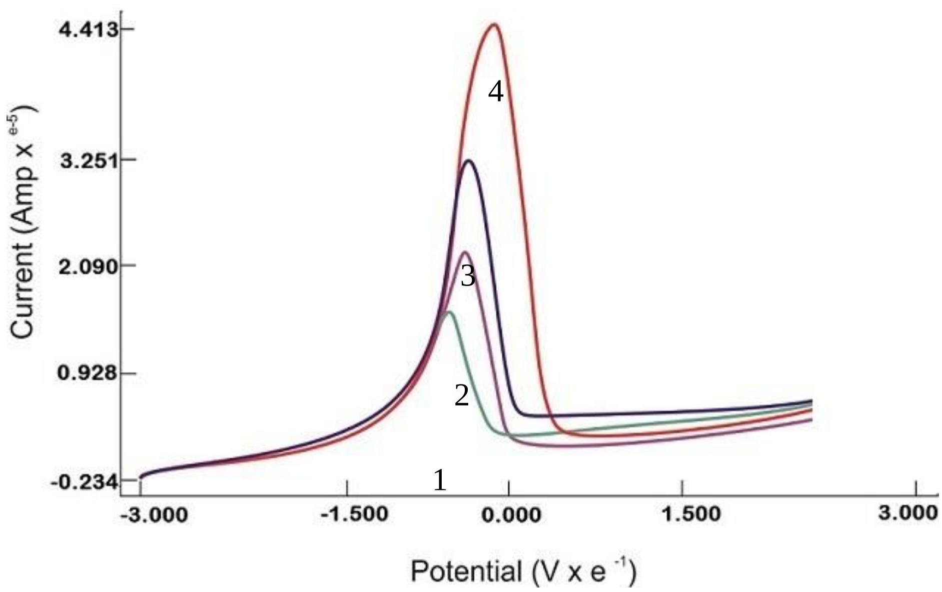

Figure 4. Overlay of the voltamograms obtained for the determination of copper in 0.1M acetate buffer pH 4.5 containing 80 ppm $(HgNO_3)_2$ and 0.2 M KNO_3. (Cu concentration: 1= 250 ppb, 2= 500 ppb, 3= 1000 ppb, 4= 2000 ppb).

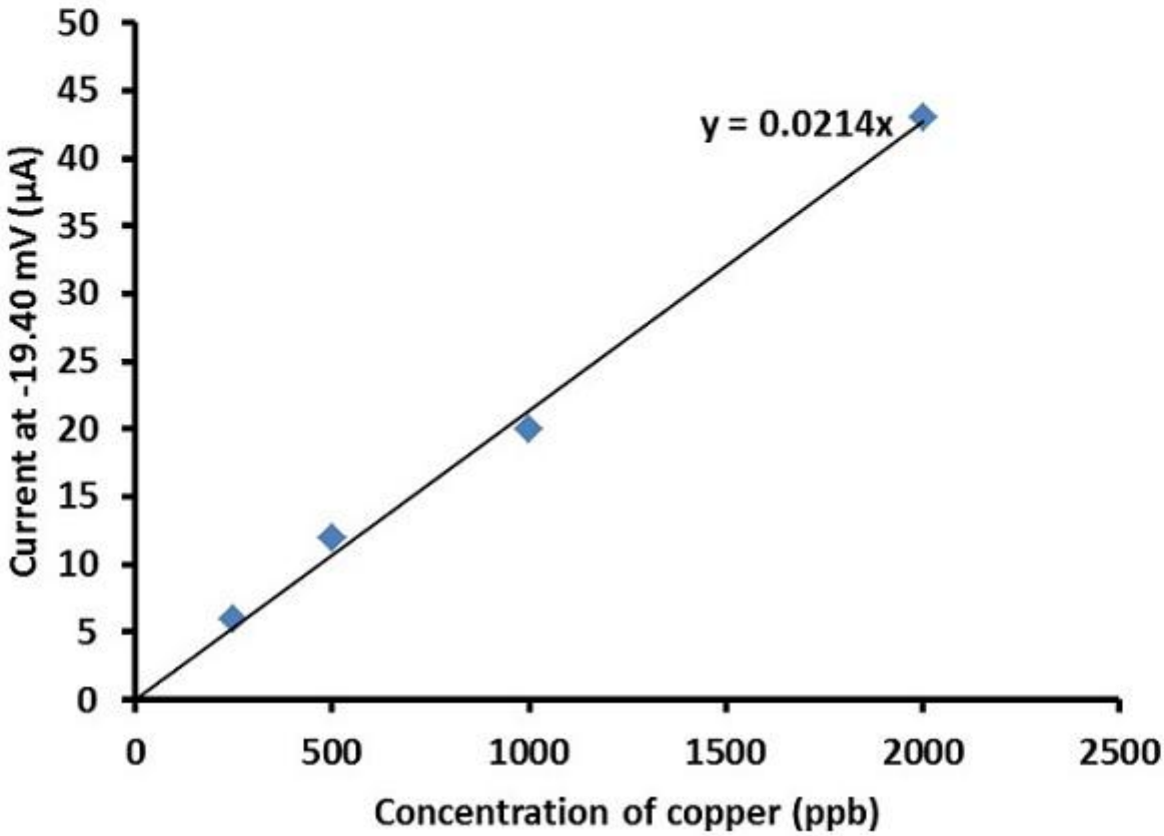

Figure 5. Plot of peak current against Cu concentration in 0.1M acetate buffer pH 4.5 containing 80 ppm $(HgNO_3)_2$ and 0.2 M KNO_3. (Cu concentration: 250 -2000 ppb)

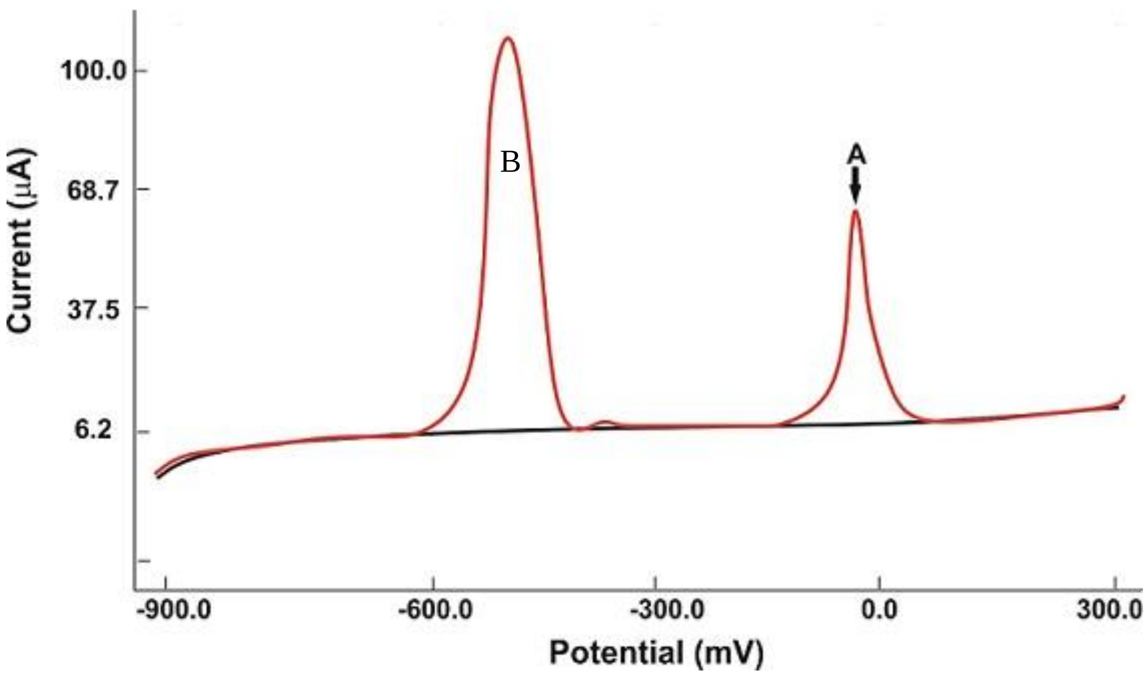

Figure 6. Voltammetric peaks obtained for the determination of metals in water sample (AB 008 from Abare) in 0.1M acetate buffer pH 4.5 containing 80 ppm $(HgNO_3)_2$ and 0.2 M KNO_3. Peak A is for Copper while peak B is for lead.

4. DISCUSSION

The results presented in Table 1 show that water samples from two wells in Dareta, DA 005 and DA 008 had lead concentrations of 118.46 µg/L and 154.26 µg/L respectively. The corresponding values found in the ponds, DA 016 and DA 017 in Dareta were 404.50 µg/L and 897.23 µg/L. These values are above the WHO limit of 10 µg/L [17]. Wells were found to be located in every compound in Dareta. In this study water samples from two wells, DA 005 and 008 were found to contain high levels of lead. The wells in these areas are not covered hence are exposed to dust laden with lead and other pollutants. Contamination of the wells may also arise from the pieces of lead containing rocks thrown into them by children playing in the compounds.

The concentrations of copper in the water samples from ten wells - DA 001, DA 004, DA 005, DA 006, DA 008, DA 009, DA 011, DA 012, DA 013 and DA 015 were in the range 62.92−455.16 µg/L. These values are below the WHO recommended limit of 2000 µg/L [17]. The values of 389.18 and 150.56 µg/L found in the water samples from two ponds DA 016 and DA 017 were also below the WHO limit for copper.

Lead and copper were not detected in the water samples from the four wells AB 001-004 in Abare. However, while lead was not detected in the two boreholes AB 005 and 006, copper was present at concentrations 61.62 µg/L and 70.63 µg/L respectively. These values are below the WHO limit. The concentrations of lead in water sample from pond AB 007 and a stream AB008 in Abare were 121.24 µg/L and 6879.09 µg/L respectively. These values are above the WHO limit by factors of 12 and 687 respectively. The corresponding values of 114.66 and 1340.18 µg/L for copper in these water samples were below the WHO limit.

In a 2010 Joint United Nations Environment Programme-Office for the Coordination of Human Affairs (UNEP/OCHA) Environmental Unit (JEU) report on lead pollution and poisoning crisis in Zamfara State, six out of the twelve well water samples obtained from Abare had lead concentrations in the range of 11−57 µg/L, one sample had 10 µg/L and five had lead concentrations less than 10 µg/L. In the report, the concentrations of lead in water samples from ponds were in the range 20−320 µg/L [18]. Since the exact locations of the sampling sites are not the same it is not possible to compare the values in this report with those of JEU but it is obvious that about 50% of the wells and the ponds in Abare sampled in the JEU report are contaminated with lead. The values of lead in four well water samples from Dareta were in the range 10−13 µg/L. In a pond close to the processing site in Dareta the lead concentration was found to be 605 µg/L[18].

The results shown in this study as well as those reported by the Joint United Nations Environment Programme-Office for the Coordination of Human Affairs (UNEP/OCHA) Environmental Unit (JEU) report on lead pollution and poisoning crisis in Zamfara State show that water samples from some wells, ponds and streams in Abare and Dareta are polluted by lead. The water from two boreholes AB 005 and 006 sampled in this study did not contain lead which suggests that the pollution most likely remains confined to areas where processing had taken place and has not spread throughout the groundwater aquifer. The high concentrations of lead in the waters from these sites may be attributed to the unsafe processing of the ores in these communities.

It was observed that there were two active mines located 3.5 km on the outskirt of Dareta village. The major mine is 15 meters deep and 3 meters wide while the second mine is 12.4 meters deep and 3 meters wide.

No mines were observed in Abare but inhabitants of this town and surrounding villages travel to Dareta to excavate gold-containing ores. The processing of the excavated ore occurs in three stages. The first stage involves the transportation of the rocks from the mines to the homes where they are crushed into tiny pebbles by women and children. It explains the exposure of women and infants to lead. Infants ingest the ores when they suck their hands or eat with unwashed hands. The crushing generates a lot of dust which contaminates the homes and the environment with lead. The second stage involves further crushing of the pebbles into smaller particles. The third stage involves the washing of the crushed material in ponds, stream or well water during which gold pellets are picked from the mixture.

It is observed that the highest concentrations of lead were found in the ponds and stream. This is understandable because the processed ores are washed in these water bodies. Ponds in sites DA 016 and DA 017 are the closest to the mining site in Dareta. They are located at a distance of 2.5 km from the sites and are 2 meters apart. The washing of the crushed ores by the villagers is carried out there regularly. Pond in site AB 007 located in Abare village is also used for washing the processed ore. This accounts for the high concentration of lead found in the ponds. A villager in Dareta stated that they sometimes drink water from the pond in site DA 016 whenever they are thirsty on site. The water samples from DA 016 and 017 with lead concentrations of 404 μg/L and 897 μg/L respectively are unfit for human consumption.

The lead concentration (121.24 μg/L) in the water from pond AB 007 located in Abare was found to be lower than those in ponds DA 016 and DA 017 which are close to the mining sites in Dareta. This supports the observation that environmental pollution by potentially toxic metals is very prominent in areas of mining and old mine sites and pollution reduces with increasing distance from mining sites [19, 20]. There are no mines in Abare hence the pollution in the pond is expected to be lower than those in Dareta. Furthermore pond AB 007 in Abare, is seasonal and located 50 meters from human settlement. Consequently few villagers use this water for the washing of the ore since processors have ready access to a stream (AB 008) where the bulk of the washing is carried out. The highest concentration of lead (6879.09 μg/L) was found in this stream. It is the only surface water body available all year round and is used for processing of ores by the inhabitants of Abare. The water sample collected from this stream was found to be turbid. There is no evidence that the inhabitants of Abare consume this water since the village is serviced by two boreholes. However, the stream in site AB 008 is used by the villagers to irrigate their crops, an action that can cause pollution of the soil and plants in this environment.

Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders [21]. Lead poisoning symptoms include abdominal pain, confusion, headache, anemia, irritability, and in severe cases seizures, coma, and death as recorded in Abare and Dareta villages in Zamfara State.

The Centers for Disease Control has set the standard elevated blood lead level for adults to be 25 (μg/dL) of the whole blood. For children however, the number is set at a much lower value of 5 (μg/dL) of blood [22]. Children are especially prone to the adverse effects of lead and as a result blood lead levels have been set lower and should be regularly monitored where children are exposed. Lead is dangerous to young children because their bodies and brains are developing. Young bodies also absorb more lead than adults do. The small intestine of a developing child responds to nutritional needs by increasing the absorption of specific nutrients. For example, calcium transport in newborns and infants is about five times the rate in adults. If lead exposure occurs, the lead will compete with the calcium for transport at this high rate. Thus absorption of ingested lead by children may be five times higher than that of adults [23]. Lead absorption affects the development of young children by causing speech delay, hyperactivity, attention deficit disorder, learning disabilities, behavioral disorders, neurological and renal damage, stunted growth, anemia, hearing loss, and sometimes mental retardation.

The WHO permissible limit for copper in water is 2000 μg/L [17] while the EPA permissible limit of copper in water is 1300 μg/L [24].

Our results also show that copper was detected in water samples from several sites in Dareta DA 001, 004, 005, 006, 008, 009, 011, 012, 013,015, 016 and 017 but the values are below the WHO and EPA limits. In Abare copper was not detected in water samples from the wells but the water from two boreholes, AB 005 and 006 had copper concentrations of 61.62 and 70.63 μg/L respectively. The corresponding values found in the pond AB 007 and stream AB 008 were 114.66 and 1340.18 μg/L respectively. The value obtained for the water sample from AB 008 exceeded the EPA permissible limit though marginally. However, further increases may result in health risk to the population in Abare where several deaths were recorded. Copper may not pose a health risk in the water samples from Dareta as the concentrations of copper in these waters were found to be within the WHO and EPA limits. Although the values obtained for the concentrations of copper in the water samples are lower than the WHO and EPA limits, however, the villagers in Dareta and Abare are at risk of copper poisoning when they consume the contaminated water for a prolonged period of time as the copper could bioaccumulate in the body. The water from the stream AB 008 is also unsuitable for livestock watering and irrigation. Acute symptoms of copper poisoning include vomiting, hematemesis (vomiting of blood), hypotension, melena (black "tarry" feces), coma, jaundice and gastrointestinal distress [25]. Chronic effects of copper exposure can damage the liver and kidneys which can lead to death. The impression from the news media was that many of the villagers died as result of lead poisoning but our results show that copper may bioaccumulate and also contribute to the mortality observed in Zamfara State.

In a report on the concentrations of lead and copper in surface waters from Kutcheri, Zamfara State, the values obtained were 0.014 and 1.028 ppm respectively [26]. The value of lead was just above the quoted WHO permissible level, while that of copper was well above the maximum permissible limit. The dates for collection were not stated and the sample points were stated to be within longitude 11.48-11.53^{o} North and latitude 7.00-7.05^{o} East. The exact locations of the sampling points were not stated.

In a report on the lead content of water samples from various sources in Abare village, Zamfara State, the values for three wells were in the range 4.3-9.6 mg/L, 7.0-10.1 for three streams, 4.0 for a river and 6 mg/L for a borehole [27]. There is no information on the sampling period but it is between 2011 and 2013. The exact sampling positions are also not indicated. The values translate to 4,300-9,600 μg/L for well, 7,000-10,100 for streams, 4,000 for river and 6,000 for borehole. All these are several times in excess of the WHO permissible limits. There was no detectable lead in the four wells and two boreholes in our report. However, a value of 6,879 was obtained in one stream AB 008, which may be among the three sampled in the report cited [27].

The concentrations of several metals were determined in well water samples collected in January 2011 in Dareta [28]. The values for lead and copper were in the range 148-445 and 2-55 ppm respectively. However, the exact sites in Dareta were not stated. The values reported translate to 148,000-445,000 μg/L for lead and 2,000-55,000 μg/L for copper which are far above the values in our report. In our well water samples from Dareta, the range for copper was 75-455 μg/L where copper was detected. It is observed that the reports in the literature that are far from the region where we sampled did not state exact geographical positions. This makes it difficult to make comparisons. These pollutants have been introduced as a result of human activity and thus the concentrations of the metals being screened will not follow any particular trend.

The pH values of the water samples collected from the sampling sites in Dareta were in the range 6.82−7.72 and all fall within the WHO recommended limit of 6.5−8.5 [17]. Therefore pH values of the water from these sites are not of health concern. However, samples AB 001 and AB 003 collected from wells in Abare are marginally below the recommended WHO limit and sample AB 007 collected from a shallow pond in Abare was above the limit. The pH values of well water samples in a similar study in Dareta were reported to be in the range 6.7-7.1 which are comparable to our values of 6.82-7.47 [28].

The values for TDS of well water from Dareta are in the range of 207-537 mg/L and the values for the samples from sites DA 005 and DA 009 are above the WHO limits of 500 μg/L while the samples from all the sites in Abare fall within the WHO limit for TDS. The corresponding values for the water from some hand-dug wells in Dareta are in the range 12-380 mg/L [29]. It is difficult to draw any comparison since the positions in the later report are not identified. However, the two sets of results compare within a reasonable range.

The electrical conductivity values of all the water samples collected from wells in Dareta were in the range of 419−1094 $\mu S.cm^{-1}$ and exceeded the WHO recommended limit of 150 $\mu S.cm^{-1}$. The water sample from pond DA 016 also had conductivity value that was above limit. However, the value for the water sample from pond DA 017 was within limit. The corresponding values obtained in the well water samples collected from Abare sites AB 001-004 were in the range of 254-795 $\mu S.cm^{-1}$ which are above the WHO recommended limit. The conductivity values of 497 $\mu S.cm^{-1}$ and 285 $\mu S.cm^{-1}$ for the water samples from the boreholes AB 005 and AB 006 are also above the limit. Conductivity is affected by the presence of ions thus the high conductivity values observed for the wells in Dareta and Abare indicate that these waters contain high levels of anions and cations. In a report on the values of electrical conductivities of water samples from hand-dug wells in Dareta, a range of 100-700 $\mu S.cm^{-1}$ was obtained [29]. In our report, fifteen wells were sampled and this number has made it possible to obtain samples with higher values.

5. CONCLUSION

The results show that water samples collected from some wells and pond in Dareta and pond and stream in Abare villages in Anka Local Government Area of Zamfara State contain very high concentrations of lead. These are probably responsible for the mortality of women and infants under five years in these localities. Our results show that copper was found in water samples from several wells in Dareta as well as in boreholes, pond and stream in Abare. Although the concentrations of copper in the water from these sites are below the WHO limit, prolonged consumption could lead to bioaccumulation of the copper which could result in copper poisoning. Thus copper may have been implicated in the mortality observed in Zamfara State. Some of these water bodies when used for irrigation would cause environmental pollution of the farmland and crops.

The regulatory bodies should endeavor to eliminate illegal mining and establish safe mining procedures. Remediation of soils in the affected areas should be carried out and potable water provided for the community. Information units should be set up to educate the inhabitants of the hazards of lead poisoning.

Awareness activities directed at informing the miners about the hazards of lead poisoning and how to prevent lead exposure should be carried out.

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