DISTRIBUTION OF HEAVY METALS LEVELS IN STREAM WATER AND SEDIMENT AROUND ARUFU COMMUNITY IN WUKARI - NIGERIA

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Abstract: The study was conducted to investigate the impacts of galena mining on heavy metal concentrations in water and sediment from streams around Arufu community after acid digestion using atomic absorption spectrophotometer. The mean concentrations (mg/L) of heavy metals in water were Cd (0.05 ± 0.11), Cu (0.32 ± 0.25), Zn (0.32 ± 0.19), Cr (0.36 ± 0.21), Pb (1.46 ± 1.84), Mn (4.48 ±3.33), Fe (5.01 ± 5.39) while in sediment the mean concentrations (µg/g) were Cd (5.57 ± 15.59), Cu (46.14 ± 25.97), Zn (61.63 ± 27.19), Cr (76.74 ± 34.31), Mn (131.52 ± 86.74), Pb (196.19 ±385.23), Fe (1972 ±1033.82). The concentrations of heavy metals in the sediment samples were generally higher compared to water. The levels of Fe, Mn, Pb and Cd in water were above the NIS and WHO guidelines for water while the concentrations of Cu, Fe, Mn, Pb, Zn and Cd in sediments were above concentration values reported for soil worldwide and upper continental crusts, respectively. This indicates contamination of the two media by heavy metals. The trend of heavy metals concentrations in water were in the following order of decreasing magnitude: Fe >Mn>Pb> Cr > Zn > Cu > Cd, while in sediment the concentrations were in the following order of decreasing magnitude: Fe >Pb>Mn> Cr > Zn > Cu > Cd.

Keywords: Arufu, water, sediment, heavy metals, continental crust

Introduction

Heavy metals are among the most serious environmental pollutants by virtue of their high toxicity, abundance in the environment and ease of accumulation by plants and animals. The presence and elevated level of heavy metals in water, sediments and as well as in plants and animals may be related to their concentrations in effluent from mining fields, power stations, industries, agriculture and waste water treatment plants and other sources released to the environment (Guevara-Riba*et al*., 2004). Measurement of heavy metal levels in different environmental component or compartment among others like sediments, water, plants, dusts, is a good indicators of heavy metal pollution in the environment (Loska*et al*., 2000; Kut*et al*., 2000).

Galena mining in the time past and till now has provided job opportunities and also has served as source of income to individuals as it has found several applications industrially and for beautification by women as eye makeup, reduction of desert sun glare and flies repellant which were potential source of disease in ancient Egypt (James, 2005). Lead – zinc minerals occurs alongside other minerals such as sphalerite, marcasite, barite, pyrite, calcite, and dolomite depending on the geology of the area (Ekeleme*et al*., 2013; Fatoye*et al*., 2014; Onyeobi and Imeokparia, 2014). The ore has served as an important source of lead and silver used in industries as raw material for lead-acid batteries (Lee, 2007). Mining, smelting, weathering and dissolution of the sulphide minerals by acid rain and reduction of lead sulphide in the presence of suitable reducing agent has been reported as major ways of distributing lead and other associated valuable mineral impurities like silver, cadmium, copper among others in the environment (Carolyn, 2004). Lead, among other heavy metals are known for their toxicity at elevated concentrations. The most recent case of heavy metal contamination in global history is the Zamfara lead poisoning that leads to the dead of many citizens and over thousands hospitalized with cases of neurological imbalance among others (Shiloh, 2010; Ogundipe, 2010; Ogabiela*et al*., 2011 Udiba, *et al*., 2013). The aim of this study is to assess and correlate the concentrations of the following heavy metals: Pb, Cr, Cd, Mn, Zn, Fe and Cu in sediment and water samples from streams around Arufu community situated in the Northwestern part of Wukari Local Government Area of Taraba State. The area is rich in galena deposit and is well known for the mining of the important mineral lead-Zn and other sulphide mineral ores.

Materials and Methods

Water and sediment samples were collected and prepared as described by Yebpella (2017), Okoye*et al*. (1991). A representative sediment sample was obtained for each unit by bulking together an average of five samples randomly collected at the base of the stream into a polyethylene bag prewashed in 1:1 nitric acid and placed in portable cooler at 4°C. After drying at less than 30 °C with occasional breaking of aggregated materials with wooden roller, the samples were sorted to eliminate pebbles, coarse materials and sieved with nonmetallic nylon sieve of 2 m mesh hole to remove plant materials and animals debris.

A portion of 0.5 g soil sample and a mixture of 5 ml HF acid and 5 ml aqua regia(1:3 HNO_3/HCl V/V) in a ratio of 1:1 was used for total extractable metals. The acid–soil mixture contained in a screw-capped Teflon bottle was heated in a water bath for 3 h at 60°C. The digest was allowed to cool and the residual HF which would otherwise attack the glassware was complexed with 20 mL boric acid. The digests were decanted into 50 mL standard flask with rinses added and finally made up to mark with deionized water. Water samples from the stream were collected into a 2 liters polyethylene bottle by dipping below the surface. The water samples were filtered then preserved by addition of 5 mL concentrated nitric acid and kept in a dark cupboard prior to analysis. A volume of 100 mL water sample in a 250 mL beaker was heated on a hot plate at 80°C after addition of 5 mL nitric acid until the volume was reduced by half. The digest was later transferred into a 100 mL standard flask and made to mark with distilled deionized water.

Metals analysis was carried out after acid digestion using Atomic Absorption Spectrophotometer model SOLAARM ICE 3000 AA02134104Vi.30 equipped with continuum background correction at Sheda Science and Technology Complex (SHESTCO), Abuja-Nigeria. Apart from calibration before use, replicate analysis of samples, combined standard together with blank after five samples runs were carried out for quality assurance. Analysis of variance (ANOVA) and Duncan's multiple range tests were used to find out statistical differences among various parameters.

Results and Discussion

Heavy metals discharged from man-made sources can accumulate in the surface soil and consequently enter underground and surface water through leaching and surface runoff to a toxic level. When incorporated into food chain, they alter physiological processes in humans, plant and animals because of their persistence and inability to be degraded by biological or chemical processes (Yebpella, 2017). Copper like iron, manganese and zinc are essential minerals, yet potentially toxic to humans and animals at elevated concentrations. Lead and cadmium are the most toxic heavy metals with no known biological importance.

The distribution of heavy metals concentrations in the stream sediment and water samples were in the following order of decreasing magnitude: Fe >Pb>Mn> Cr > Zn > Cu > Cd. The mean and standard deviations of the respective metals in the sediments were: Cd (5.57 ± 15.59), Cu (46.14 ± 25.97), Zn (61.63 ± 27.19), Cr (76.74 ± 34.31), Mn (131.52 ± 86.74), Pb (196.19 ±385.23), Fe (1972 ±1033.82). Iron has the highest concentration in the sediments followed by lead while cadmium has the least concentration. From Table 1, Sample A1 present highest concentrations of Cu and lowest concentrations of Fe, Mn and Pb while F1 gave minimum level of Cd and maximum levels of Fe and Mn. Sample B1 gave highest level of Pb and lowest level of Zn. Sample G1, E1, D2 present maximum levels of Cr, Zn, Cd in that order while sample G2 and C1 has lowest levels of Cr and Cu, respectively.

Table 1: Concentrations (µg/g) of heavy metals in sediments from streams around Arufu area

Sample	Cr	Cu	Fe	Mn	Pb	Zn	Cd
A_1	62.63	85.07	1125.96	82.52	70.17	63.59	BDL
A_2	70.81	88.77	16.5998	1.043	0.59	73.81	BDL
B_1	45.73	78.18	1362.4	93.56	1528.65	0.55	BDL
B_2	77.77	58.47	863.5	125.28	105.14	60.69	1.20
C_1	17.00	64.93	1875.88	148.51	131.95	74.33	0.24
C_2	89.72	52.04	2018.86	109.31	129.85	79.59	0.60
D_1	43.07	26.33	1219.86	69.16	62.01	42.3	BDL
D_2	47.81	43.60	1526.65	84.12	84.26	BDL	47.14
E_1	86.32	47.98	2442.37	183.51	112.6	112.44	BDL
E_2	104.64	26.56	2688.62	138.36	89.93	40.91	0.22
F_1	103.81	21.33	3720.47	376.42	99.61	61.70	0.12
F_2	130.9	19.09	3472.18	210.68	93.32	37.95	0.13
G_1	136.03	19.98	2778.09	112.53	85.58	83.92	0.24
G_2	58.18	13.68	2507.37	106.3	153.04	69.39	0.24
Mean	76.74	46.14	1972.77	131.52	196.19	61.63	5.57
Std.	34.31	25.97	1033.82	86.74	385.23	27.19	15.59
Min	17.00	13.68	16.60	1.043	0.59	0.55	0.12
Max	136.03	88.77	3720.47	376.42	1528.65	112.44	47.14

The presence of lead, zinc and other associative metals like copper, cadmium and chromium in the sediment samples may be attributed to impact of galena mining on aquatic environment.A significant positive correlation was observed between Cu/Cr ($p < 0.05$) and between Fe/Cu, Pb/ Cr, Pb/Cu, Pb/Zn ($p < 0.01$) level of significance. This predicts strong relationship among the metals in the sediment and hence they may originate from the same source.

The study has revealed the accumulation of Fe, Mn, Cu and Zn to about 298, 3, 5 and 2 times higher in magnitude than reported for Agbabu stream sediment in Ondo, Nigeria, respectively (Fagbote and Olanipekun, 2010). When compared to the concentrations value reported for Yozgat stream sediments in Turkey (Soylak*et al.*, 2002), Fe, Mn and Cu levels were about 20, 2 and 3 times higher in this study. These elements Fe, Zn, Mn and Cu are basically essential micronutrient in animals and humans with well define role in body metabolism, although at elevated concentration could tend to be toxic. Therefore, aquatic organisms like fish and other sediment feeders may take up the elements at a concentration detrimental to their lives. Human and other animals are not left out through food chain. High consumption of food containing Cu and Zn is linked to liver and kidney damage in animals and humans Zarie*et al.* (2011) and in plants, a case of growth retardation and leaf chlorosis were established (Lewis *et al.*, 2001). Heavy metals like Cu, Fe, Cd and Pb determined in the sediments were found to be about 2, 64, 153 and 14 times higher than their respective maximum allowable concentration in the upper continental crust (Wedepohl, 1999) while Cr and Mn levels were twice lower than the allowable concentration. The above observations indicate pollution of the sediment above the background level.

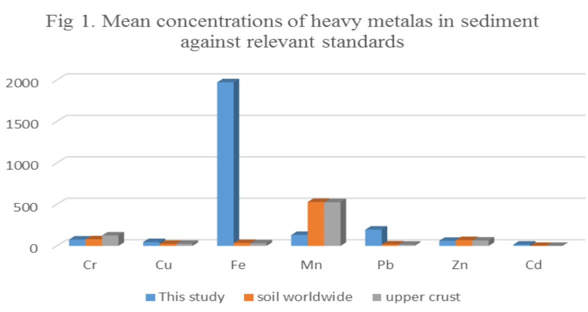

Fig 1: Mean concentrations of heavy metals in sediment against relevant standards

In water, the distribution of heavy metals concentrations in the stream water samples were in the following order of decreasing magnitude: Fe >Mn>Pb> Cr > Zn > Cu > Cd. The mean and standard deviations were: Cd (0.05 ± 0.11), Cu (0.32 ± 0.25), Zn (0.32 ± 0.19), Cr (0.36 ± 0.21), Pb (1.46 ± 1.84), Mn (4.48 ±3.33), Fe (5.01 ± 5.39). Sample Go gave highest concentrations of Cr, Cd and lowest concentration of Pb and Zn. Minimum concentrations of Cu, Fe, Mn were obtained in sample Fo while sample Eo had maximum levels of Fe and minimum level of Cd. Sample Bo had highest level of Pb, Zn and lowest level of Cr while sample Ao and Do each has maximum concentrations of Cu and Mn. Strong positive correlation was seen between Mn/Cu, Zn/Mn, Cd/Cr, Cd/Cu ($p < 0.05$) and Mn/Fe, Zn/Fe ($p < 0.01$) which shows linear relationship in the concentrations of these metals in the sample and they may come from the same source.

Table 2: Concentrations (mg/L) of heavy metals in water from streams around Arufu area

	Cr	Cu	Fe	Mn	Pb	Zn	Cd
A_0	0.22	0.72	4.27	5.85	0.42	0.48	0.01
B_0	0.20	0.40	9.16	5.01	4.15	0.58	0.02
C_0	0.26	0.40	1.37	5.01	4.15	0.36	0.02
D_0	0.30	0.19	4.66	9.85	0.56	0.32	0.01
E_0	0.24	0.15	14.96	0.41	0.41	0.30	0.01
F_0	0.48	0.03	0.16	0.18	0.37	0.20	0.01
G0	0.79	0.00	0.49	5.07	0.15	0.01	0.29
Mean	0.36	0.32	5.01	4.48	1.46	0.32	0.05
Std	0.21	0.25	5.39	3.33	1.84	0.19	0.11
Min	0.20	0.03	0.16	0.18	0.15	0.01	0.01
Max	0.79	0.72	14.96	9.85	4.15	0.58	0.29

The average concentrations of lead in water samples (Table 2) and the mean level of 1.455 mg/L obtained were higher than 0.409 and 0.42 mg/L reported for River Nile in Sudan (Hamed*et al*., 2015) and River Benue in Nigeria (Akahaan*et* *al*., 2015). The concentrations obtained were also found to be far above 0.01 mg/L WHO and NIS guidelines on water. Pb showed a positive correlation with Cd and a negative correlation with Cr ($P \leq 0.05$). Cadmium is one of the toxic metals and it enters the body through eating contaminated food or drinking contaminated water. Mean concentration of cadmium in this study was observed to be lower than 0.19 mg/L determined in River Benue (Akahaan*et al*., 2015) but higher than the maximum acceptable limits of 0.01 mg/L (WHO, 2008) and 0.003 mg/L (NIS, 2007) in water. Cd correlates positively with Cr and Pb while negatively with Zn ($P \leq 0.05$). The presence Cd and Pb in water may adversely affects water quality and other aquatic organisms. Health implications resulting from cadmium exposure include kidney disease, pulmonary infections, skeletal infections, testicular system and increase renal failure due to the sensitive nature of the kidneys (Malakootian*et al*., 2009). Copper and chromium contents in Arufu stream water were 0.32 and 0.36 mg/L in that order. These values are less than 1.0 mg/L Nigerian Institute of Standard maximum acceptable level as well as 1.58 mg/L measured in River Benue respectively (Akaahan*et al*., 2015). Copper correlates negatively with Cr and Cd while positively with Zn ($P \leq 0.05$). The concentration of zinc in Arufu stream water is 10 times lower than the 3.0 mg/kg WHO water guideline. This shows that the water is not contaminated by zinc but subsequent accumulation of the metal in water over time due to contribution from the surrounding soils may adversely affects water quality and other aquatic organisms. This observation may be supported by a study which confirmed increase acidity of the water, high accumulation of Zn in fish and the surrounding plants to a detrimental level (Olayinka*et al*., 2009). Iron showed a mean concentration of 5.01 in this study which is about three times higher than 2.00 mg/L NIS acceptable levels. Chromium concentration showed a negative correlation with Cu, Fe, Zn and Pb ($P \leq 0.05$); implying that the Cr content of the water increases with decreasing concentrations of the stated heavy metals and may not have originated from the same source.

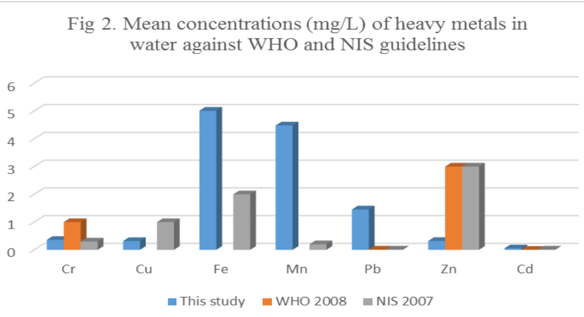

Fig 2: Mean concentrations (mg/L) of heavy metals in water against WHO and NIS guidelines

The mean concentrations of heavy metals in the sample matrices were compared (Fig. 3). The result shows significantly higher concentrations of the metals in sediment than in water. A significant positive correlation ($p < 0.01$) was observed between lead, zinc, manganese and iron in water and sediment while copper in water correlated positively with copper in sediment at $p < 0.05$ level of significance. Source of heavy metals exposure in man is through ingestion of food and water, accidental ingestion of soil, sediment and inhalation of dust. High heavy metal concentration may cause kidney damage (Ako*et al.*, 2014).

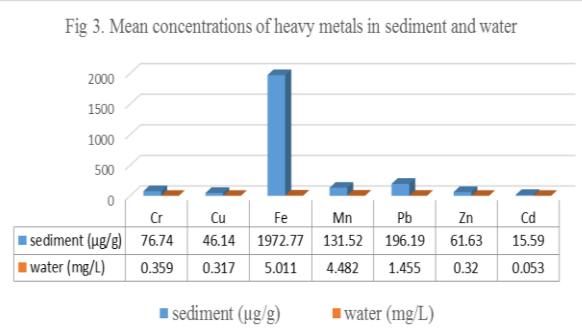

Fig 3: Mean concentrations of heavy metals in sediment and water

Conclusion

Analysis of sediments and water from Arufu stream has been conducted and the study has satisfied its aim by determining the heavy metals contents of the samples. Base on the results, the concentrations of heavy metals in the sediment samples were generally higher compared to that of water. The concentrations of Fe, Mn, Pb and Cd were above the NIS and WHO guidelines for water while the concentrations of Cu, Fe, Mn, Pb, Zn and Cd were above the maximum concentrations of metals in Upper Continental Crust and soil worldwide indicating contamination in both water and sediment respectively. Heavy metals concentrations in water and sediments were in the order: Fe >Mn>Pb> Cr > Zn > Cu > Cd and Fe >Pb>Mn> Cr > Zn > Cu > Cd, respectively.

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