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ABSTRACT

The main objective of this work is to evaluate the level of some selected heavy metals in soil and water around the vicinity of Mayo Kam, Mayo Dim, Kwano, Roadside steams, Mayo Gamgam, Gashaka village, and Gashaka River of Gashaka Gumti-National Park of Taraba State, Nigeria. The samples of soil and water were analyzed using the Atomic Absorption Spectrophotometer (AAS). The results for the analysis for the soil and water samples revealed that the heavy metals found in the water samples were in the decreasing order of Fe>Zn>Cu>Ni>Cr>Cd>Pb. Cadmium, lead, iron in water samples were found to be above the permissible limit set by WHO. Also the result for the soil samples shows that all the heavy metals determined was found in the decreasing order of Fe>Zn>Cu> Ni>Cd>Cr>Pb. Generally the heavy metal concentration was higher in the soil than in water samples. From the results we draw a conclusion even reserved can be contaminated with heavy metals due some activities that go on at the selected studied location. Similarly the result indicate that the concentration of this heavy metals was that too high, though some locations had concentration beyond the permissible limit set by WHO. Therefore serious awareness need to be carried out to the villages living in the park on the effects of these metals to the environment, animal's plants and human beings.

Keywords: Soil, Water, Heavy Metals, Gashaka Gumti-National Park, Nigeria

BACKGROUND OF THE STUDY

Developmental management and utilization of natural resources should be largely promoted and supported by all the states in the country as a strategy for socio-economic development of their states because every state has specific comparable advantage in natural resources availability (Onwuala, 2010). Considering the undergoing global recession affecting the world which started in 2008 has affected the income generated from crude oil export by Nigeria. This is joined with the crises in the Niger Delta in which the impatient militant's youth continue to attack installations of the multinational oil companies operating in the area. Having critically evaluated the potential danger this situation could position the economy of the country, there is need for an alternative means of sustenance through exploitation of natural resources that the country is largely endowed with, especially in the area of solid minerals such as limestone. barite, gypsum etc., becomes inevitable (Kashim, 2011). As a result for the need for technological advancement, the modern world cannot go forward with meaningfully advancement without utilizing the avaliable solid mineral resources (Ajakaiye, 1985). Also, industrial advancement cannot be raised without the availability of solid minerals. The most important products of solid minerals from the earth's crust are gold, copper, aluminum mercury, zinc, lead, iron, platinum and silicon among others (Ballhaus and Glikson, 1995). According to the economic counsellor of Russian Embassy in Nigeria (2012) discloses that silver is the largest in deposit in the northern part trace of gold and oil which are at a

middle level in the central and northern part of Taraba state.

Also report from TRIP (TarabaInvestment and Properties Limited, 2016) say that Taraba state is endowed with abundant solid mineral resources which if properly harness will transform the economic and social base of the state.

The department of solid mineral, Ministry of Environment and Urban Development in its activities discovered different types of solid mineral deposit around all the sixteen local government of the state. Prominent among them are Azurite, Cassitterite, Chromite, Columbite, Galena, Haematties, Lilmenite, Magnetite, Graphite, Gypsum, Kaolin, Kyanit, Limestone, Quarz, Sapphire Topa etc.

Pollutants are substances or energy introduced into the environment which has an undesired effect or adversely affect the usefulness of a resource. It may cause long or short term damage by changing the growth rate of plant or animal species, or by interfering with human amenities, comfort, and health or property value. (Wikipiedia the free encyclopedia). Pollutants may be classified by various criteria (1) By the origin; where they are natural or man-made, (2) By the effect; on an organ specie or an entire ecosystem (3) By the properties; mobility, persistence, toxicity (4) By the controllability: ease or difficulty of removal (Business Dictionary 2011). Human activities such as industrial production, mining, agriculture and transportation, release considerable amounts of heavy metals into surface and ground water, soil and ultimately to the biosphere. Accumulation of heavy metals in crop plant is of great concern due to the probability of food contamination through the soil root interface. Heavy concentration in the soil plays an important role in controlling metal bioavailability to plant.

Research has shown that the use of waste water contaminated with heavy metals use for irrigation over long time increases the uptake of heavy metals by plants depending upon the soil type, plant growth stages and plant species (Maitera*et al.*, 2011). The determination of metal in environmental samples such as soils and plants and water is very necessary for monitoring environmental pollution (Zhou *et al.*, 1997; Tuzen, 2003; Al-Khashman, 2007). Metals are classified as heavy metals if their standard state has a specific gravity of more than 5g/cm3. The bio-accumulation of heavy metals presents a problem both from the start point of how the metals migrate in the environment and how these metals can be effectively removed from contaminated sites. Unlike many substances. metals are not biodegradable, and thus they accumulate in the environment. The most important sources of heavy metal in the environment are the anthropogenic activities such as mining, smelting procedure, steel and iron industry, chemical industry, traffic, agriculture as well as domestic activities (Sucic et al., 2008). Contamination of soils by Heavy Metals is the most serious environmental problem and has significant implications for human health (Moore et al., 2009). Soil to plant transfer is one of the key processes of human exposure to heavy metal through the food chain. Heavy metal uptake through the roots from contaminated soils and direct deposition of contaminants from the air onto plant surfaces can lead to plant contamination by Heavy metal (Zhuang et al., 2009). The presence of heavy metal in soil can affect the wildlife, plant growth etc. (Ene, et al., 2009) These heavy metals can adversely affect soil ecology, agricultural production or product quality and ground water quality which ultimately affect or harm the health of living organism. The determination of these free metal ions in soil, water, and plant becomes very important (Rugia et al., 2015). Pollution of heavy metals in aquatic environment is a growing problem worldwide and currently it has reached an alarming rate. Pollution of fresh water bodies, especially the rivers is no longer within safe limit for human consumption as well as aquatic fauna. Studies on the geological history of the planet require the indepth knowledge of solid mineral and their sources (Aigbedion and Lyayi, 2007). To the best of my knowledge no geological survey has given information on the availability level of heavy metals has been done in the area of study as the park is reserved area where there is no activities that may encourage pollution. Nigeria is a country that has enormous social and economic problems and with exploding population. A general exodus from rural to overcrowding urban area, therefore there is a pressing need for change (Glanville, 1995). These include things like improvement of our economy and social life which can be harness through job creation to enhance better living condition even in our rural areas.

MATERIALS AND METHODS

The Study Area

The areas of study were located at Mayo kam, Gashaka River, Mayo gamagam, Mayo Dim,

Gashaka Village, Roadside streams and Kwano of the Gashaka-Gumti National Park of Taraba State. Gashaska-Gumti National Park is located in the mountain north east region of Nigeria, the park boundaries fall within Adamawa and Taraba State of Nigeria and also shares borders with Republic of Cameroon to the east adjacent to Faro National Park. It is the largest national park in Nigeria. The park is divided into five ecological zones, which range from scrub to lowland forest. These diverse and rich ecosystem support a vast array of both plant life and wildlife (See Figure 1)



Fig1. Map of Taraba State showing Gashaka Park

The Sampling Locations

The rocks, soil, and water to be studied were collected from different location of Mayo Kam, Gashaka River, Mayo Gamagam, Gashaka Village, Kwano, Roadside streams, and Mayo Dim of Gashaka-Gumti National Pack of Taraba State as shown in Figure 1. Sampling point was space about two meters (2m) apart for a possible variation in their constituents. Small pieces of rock were chiseled and hammered out. Sampling were randomly collected from eigth (8) sample site at the distance of two meters from each other, which was mixed together to give a representative sample.

Sample Collection and Treatment

The soil and water were collected randomly from Mayo kam, Gashaka River, Mayo gamgam, Mayo dim, Gashaka Village, Kwano, and small streams by roadside. The water samples were collected in plastic bottles, while the soil samples were collected in polyethylene bags. The samples were continuously dried and then crushed and ground to fine powder. The obtained powder was sieved to achieve particle size homogeneity.

Determination of Heavy Metals in Soil and Water Samples

The samples were analyzed of heavy metals using a Bulk Scientific model NO.210 VGP, Atomic Absorption Spectrophotometer (AAS). An Atomic Absorption Spectrophotometer method was adopted for the determination for the presence of heavy metal in the soil samples as reported by Maigil et al., (2012). 2.0 g each of the powdered soil was digested in 6.5ml of acid solution (HNO3, H2SO4, HClO4 in ratio of 5:1:0.5). The corresponding solution was heated on a hot plat in the fume cupboard until white fumes had appeared. The clear solution was diluted up to 250 ml with distilled water. It was then allow standing for fifteen hours then filtered with Watt man filter paper no.1. The water samples were also digested with acid a method described by (Radojevic and Bashkin, 1999). A 100ml of water sample was transfer into a beaker and 5mls of concentrated nitric acid was added. The beakers with the content were heated on a hot and evaporate down to 20mls. The beaker was allowed to cool and another 5mls of concentrated nitric acid was added. The content in the beaker was transfer to the hot plat and continue heating. These processes continue until the solution appears light color and clear. The clear solution was allowed to cool and after which it was filtered to remove any insoluble materials that could clog the atomizer. The volume was adjusted to 100mls with distilled water. The standard working solutions of elements of interest was prepared to make the standard calibration curve. Absorption for the sample solution uses the calibration curves determine the to concentration of particular element in that sample. A Bulk Scientific model NO.210 VGP,

Atomic Absorption Spectrometer (AAS) was used for the determination of seven metals which are, Cd, Cr, Ni, Fe, Zn, Cu and Pb. Cathode lamps for each element was used as radiation source. Air acetylene gas was used for all the experiments. This method provides both sensitivity and selectivity since other elements in the sample will not generally absorb at the chosen wavelength and thus, will not interfere with the measurement (Sarwoko et al., 2008). Other physic-chemical Working solutions were freshly prepared from these solutions as required by dilution with distilled water. The atomic, absorption spectrometer was set to zero reading while aspirating distilled water as blank. Then seven already prepared standards of Ni, Cu, Cd, Zn, Pb, Cr, and Fe solution were aspirated and their absorbance reading obtained. After which the samples already inform of solutions were aspirated and their absorbance reading obtained. Using the standard calibration curve the concentration of the samples was obtained by extrapolating using the value of absorbance of the samples.

RESULTS AND DISCUSSION

Analysis of some Heavy Metals in Soil and Water

Nickel (Ni)

Nickel has been considered to be an essential trace element for human and animal health (Zigham *et al.*, 2012). The maximum permissible limit for Ni in water is 0.2 mg/l. (Zigham *et al.*, 2012). Nickel in water samples collected was found to be within the ranged 0.04 to 0.17 mg/l which is below the permissible

limit and in the entire soil sample collected the analysis indicated that the concentration of Nickel was within the range of 0.87 to 1.16 mg/kg as shown in the Figure 2 (also see appendix I and II). The concentration of nickel recorded was found to be below the maximum permissible limit set by WHO.

Chromium (Cr)

The maximum acceptable limit for Cr in water by WHO is0.1mg/l (Zigham et al, 2012).The values concentration for Cr in all the collected water samples was found to be within the ranged of 0.08 to 0.14 mg/l .The concentration of Chromium in water recorded was below the permissible limit by WHO. set The concentration of Chromium in all soil samples was found to be between the ranges of 0.32 to 0.95 mg/kg. In all the collected soil samples, the concentration of Chromium was recorded below the permissible limit set by WHO.

Cadmium (Cd)

The maximum permissible limit for Cd in water is 0.01 mg/l set by WHO (Zigham *et al.*, 2012). From the analysis, the concentration of cadmium in all water samples was found to be between the ranged of 0.01 to 0.09 mg/l. Three location of the study area had concentration above the permissible limit while two location had concentration within the permissible limit set by WHO as shown in Figure 6. Concentration of Cadmium in all the collected soil samples was found to be within the range of 0.69 to 1.71 mg/l as shown in Figure 7 which is above the maximum permissible limit of cadmium set by WHO.



Figure2. Mean Heavy Metal Concentration (mg/l) in Water Sample from Gashaka Gumti-National Park Taraba State.

Copper (Cu)

The maximum permissible limit for Cu in water is 2.0 mg/l by WHO. From the analysis of all collected water samples, the concentration of copper was found to be within the range of 0.16 to 0.35 mg/l; which is below the maximum permissible limit set by WHO. Contamination of

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drinking water with high level of copper may lead to chronic anemia (Asma *et al.*, 2011). Copper accumulates in liver and brain. Copper toxicity is a fundamental cause of Wilson's disease (Samuel *et al.*, 2011).

Copper particulates are released into the atmosphere by windblown dust; volcanic eruptions; and anthropogenic sources, primarily copper smelters and ore processing facilities. The fate of elemental Copper in water is complex and is influenced by pH, dissolved oxygen and the presence of oxidizing agents and chelating compounds or ions. The concentration of Copper in all the soil samples collected was found be within the range of 2.02 to 4.04 mg/kg as shown in Figure 7 which is within the maximum permissible limit set by WHO.

Lead (Pb)

According to WHO standards permissible limit of lead in water is 0.05mg/l, and in all the collected water samples the concentration of lead was found to be within the range of 0.02 to 0.06 mg/l. Four locations had concentration which is below the maximum permissible. While one location had concentration above the permissible limit as Shown in Figure 6. The concentration of lead in some of the soil samples was found to be within the range of 0.33 to 0.17 mg/kg which is below the permissible limit set by WHO. In some of the locations Lead was not found or detected. In almost all the collected soil samples concentration of Lead was recorded below the permissible limit set by WHO as shown in Figure 3. Lead as a soil contaminant is a widespread issue; It accumulates with age in bones aorta, and kidney, liver and spleen. It can enter the human body through uptake of food (65%), water (20%) and air (15%).

Iron (Fe)

Iron in drinking water is present as Fe^{2+} or Fe^{3+} in a suspended form. It causes staining in clothes and imparts a bitter taste. It comes into water from natural geological sources, industrial wastes, and domestic discharge and also from by-products. Excess amount of iron (more than 10 mg/kg) causes rapid increase above the permissible limit set by in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness.



Figure 3. Mean Heavy Metal Concentration (mg/l) in Soil Sample from Gashaka Gumti-National Park Taraba State.

The maximum allowed concentration of iron in drinking water is 1.0 mg/L according to WHO report (Gutam *et al.*, 2011). In all the collected water samples concentration of Iron was found to be within the range of 1.50 to 2.75 mg/l which is above the acceptable limit set by WHO. The concentration of iron in all the collected soil samples was found to be within the range of 4.17 to 12.50 mg/kg.

In all the soil samples collected from the six locations of the study area, the concentration of Iron was found to be within the permissible limits set by WHO.

Zinc (Zn)

Zinc is one of the significant trace elements that play a vital role in the physiological and process of many organisms. metabolic Nonetheless, higher concentrations of zinc can be toxic to the organism. It plays a vital role in protein synthesis and is a metal which shows fairly low concentration in surface water due to its constrained mobility from the place of rock weathering or from the natural sources. The range of concentration of zinc in all water samples analyzed was found to be within the range of 0.71 to 1.62 mg/l.

The accepted limit of zinc in water according to WHO standards is 5mg/l. In all the collected water samples, the concentration of zinc was found to be below the permissible limit. The concentration of zinc in all soil samples was found to be within the range of 3.57 to 8.33 mg/kg. In all the soil samples collected from the six locations of the study area, the concentration of zinc was found to be within the permissible limits set by WHO

CONCLUSION

This study was conducted in order to assess the heavy metal contamination of water, and soil in the vicinity of Gashaka Gumti National Park. As water pollution is dangerous for both aquatic and human health hence the need to assess the water quality of rivers in the park which is mostly used for irrigation purpose during the dry season and also some of the river, the water is for domestic work at home. This is a very important issue as it is related to human and environment. Five water samples were collected from the four major river of the park and six soil samples were also collected the study. Water and soil samples were subjected to heavy metal analysis. The Results were presented in the form of Figure 2 and 3.

The result for the water samples analyzed for (Zn, Cu, Fe, Cd, Cr, Ni and Pb) shows that the concentrations of some heavy metals i.e. iron cadmium and lead in some location was beyond the maximum permissible limits set by WHO. Most of the villagers don't know the effect of some of the waste they dispose to the environment and most of these solid wastes dumped into the river are likely to contain toxic materials including heavy metals.

Most of the waste such as sewage, domestic effluents, including automobile garages and car wash, which discharge mixtures of oil is directly discharged into the river. Also the runoff (effluents) of the mountain top especially during the raining seasons directly goes into the river, and most of the villages used these rivers for washing of their cars and motorcycle and this river are used for agricultural purpose in the park. These activities may contribute much to contamination of both the water and the soil which may likely get to the plant through bioaccumulation which eventually enter into the food chain. This is in agreement with the studies (Zaigham et al., 2012) who reported that the level of heavy metals increased in water from the rivers due to discharge of industrial effluents and civic pollution of various kinds. This is in

turn deteriorating the water quality making it unsuitable for both aquatic and human life. Generally the Heavy metal concentration was high in the soil than in water samples.

Similarly the result indicate that the concentration of this heavy metals was that too high, though some locations had concentration beyond the permissible limit set by WHO. Therefore serious awareness need to be carried out to the villages living in the park on the effects of these metals to the environment, animal's plants and human beings. Another major achievement of this research is that, it has given information on the level of concentration of some selected heavy metals in the locations studied in the park. The research has proven that even the park which is a reserved area contain heavy metals even in high concentration. The result of the research has shown that some selected heavy metals determined was found to have a high concentration which is harm full to the environment, the humans, and animals in the park and this calls for an immediate action by the government to provide a speedy solution to this so that the park can be save to some extant to the wild animals, humans, and the environment

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Location of	Mean conc of	Mean conc of		Mean conc of	Mean conc of		Mean conc of	Mean conc of	Mean conc of Cu
Water	Cd in mg/l	Pb in mg/l		Ni in mg/l	Zn in mg/l		Fe in mg/l	Cr in mg/l	in mg/l±S.D
Samples	±S.D	±S.D		±S.D	±S.D		±S.D	±S.D	
Road side streams	$\begin{array}{c} 0.01 \pm \\ 0.0100 \end{array}$	0.02	$\stackrel{\pm}{0.0200}$	0.04 ± 0.0200	0.71	$\stackrel{\pm}{0.0200}$	$\begin{array}{c} 2.08 \pm \\ 0.0200 \end{array}$	0.08 ± 0.0100	0.16 ± 0.0100
sMayo Kam River	0.05 ± 0.0100	0.04	$\stackrel{\pm}{0.0200}$	0.06 ± 0.0200	1.24	± 0.0140	$\begin{array}{c} 2.25 \pm \\ 0.0200 \end{array}$	0.13 ± 0.0100	0.24 ± 0.0200
Gashaka River	0.09 ± 0.0100	0.03	± 0.0100	0.11 ± 0.0300	1.52	± 0.0300	$\begin{array}{c} 1.50 \pm \\ 0.0200 \end{array}$	0.11 ± 0.0100	0.19 ± 0.0100
Mayo Dimdim River	$\begin{array}{c} 0.07 \pm \\ 0.0100 \end{array}$	0.05	± 0.0200	$\begin{array}{c} 0.15 \pm \\ 0.0100 \end{array}$	1.38	± 0.0140	2.75 ± 0.0300	$\begin{array}{c} 0.09 \pm \\ 0.0200 \end{array}$	0.29 ± 0.0100
Mayo Gamgam River	0.01 ± 0.0200	0.06	±0.0200	0.17 ± 0.0100	1.62	± 0.014	2.50 ± 0.0100	0.14 ± 0.0140	0.35 ± 0.0100

Appendix I. Mean Heavy Metal Concentration (mg/l) in Water Sample

Location of	Mean conc of	Mean conc of	Mean conc of	Mean conc of	Mean conc of	Mean conc of	Mean conc of Cu in mg/kg
Soil	Cd in mg/kg	Cr in mg/kg	Ni in mg/kg	Zn in ±S.D	Fe in mg/kg	Pb in mg/kg	±S.D
Samples	±S.D	±S.D	±S.D	mg/kg	±S.D	±S.D	
Mayo Gamagam river	1.40 ± 0.0132	0.95 ±0.0130	1.16 ±0.0120	3.57 ±0.0123	8.33 ±0.0300	0.17 ±0.0200	3.37 ±0.0200
Mayo Kam River	1.03 ±0.0200s	0.32 ±0.0112	1.16 ±0.0200	5.95 ±0.0200	6.25 ±0.0200	0.17 ±0.0100	2.69 ± 0.0400
Kwano (II) [340 N-E]	0.69 ±0.0124	0.63 ±0.0300	0.89 ±0.0143	8.33 ±0.0400	10.42 ±0.0134	N.D	2.02 ±0.0100
Gsahaka River	0.69 ±0.0300	0.63 ±0.0300	1.45 ±0.0300	7.14 ±0.0500	6.25 ±0.0243	N.D	2.69 ±0.0300
Kwano (I) [272W]	1.71 ±0.0145	0.95 ±0.0231	1.45 ±0.0124	3.57 ±0.0120	4.17 ±0.0246	0.17 ±0.0100	4.04 ±0.0200
Kwano (Compound)	1.03 ±0.0100	0.63 ±0.0200	0.87 ±0.0234	4.76 ±0.0245	12.50 ± 0.0100	0.33 ±0.0300	2.02 ±0.0300

Appendix II. Mean Heavy Metal Concentration (mg/l) in Soil Samples.

Citation: Hitler Louis et al. "Determination of The Level of Some Selected Heavy Metals in Soil and Water Within the Vicinity of Gashaka Gumti-National Park, Taraba State, Nigeria". Open Access Journal of Chemistry, 2(4), pp.27-34

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