



HEAVY METALS IN WATER, FISH AND SEDIMENT FROM A GOLD MINE POLLUTED RIVER, NIGERIA

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ABSTRACT

Excessive bioaccumulation of heavy metals in surface water body affect the quality of water and as a result such water is said to be polluted. Bioaccumulation of heavy metals is the presence of these metals above their biological permissible level. It is therefore necessary for the heavy metal in this area to be investigated to ascertain the safety level. Water, sediment and fish samples collected were investigated for their varying concentrations. Eight (8) known heavy metal pollutants investigated include Fe, Cd, Cu, Co, Cr, Pb, Zn and Ni. Water Samples from River Manyera were digested with HNO₃, dry powdered fish samples were digested with a mixture of HNO₃ and HClO₄ (4:1) and dry powdered soil samples with HF-HClO₄ acid mixture (5:1). Digested samples in triplicates were analyzed using Atomic Absorption Spectroscopic method. Results revealed that in water samples, Fe (2.09 mg/g), Cd (0.3 mg/g), Pb (0.29 mg/g) and Ni (0.25 mg/g) exceeded their maximum permissible limit. While, in sediment samples Fe (29.77 mg/g) exceeded the recommended maximum permissible levels. High concentration levels of Fe (166.50 mg/g) and Pb (38.10 mg/g) were recorded in fish sample. However, it was evident that the fish sampled from the River Manyera contained heavy metals concentration levels above their biological permissible limit. Although High concentration levels of heavy metals observed in water samples is an indication that the water is polluted and this may be attributed to heavy metals deposited from anthropogenic activities or natural weathering of rocks around the studied area.

Keywords: mining, contamination, heavy metals, bioaccumulation, pollution and tailing.

Introduction

It is not out of context that both anthropogenic and natural activities contribute heavily to aquatic environmental pollution. The stress conditions that could pose negative effect on aquatic life had been reported (Mason 1991). Discharges of untreated waste such as industrial effluent and run off from agricultural fields have been equally reported to be sources of freshwater pollution (Zhang *et al.*, 2011)

Availability of good quality of water and the sustainability as discussed by Sanchez (2007) cannot be over emphasized because of

benefits human derived from good quality of water. Development of human communities and increase irresponsible use of water resources and unwanted discharges contributes a lot to the deterioration of rivers and lake water qualities (Sanchez, 2007). The hazard and associated toxic effects involved in the process of gold mining are enormous and as such, river Manyera need urgent attention to assess presence and levels of heavy metals in water, soil, sediment and even in fish organ. Toxicity and bioaccumulation of metals in biotic organism have been reported (Sajwan, 2008; Anup *et al.*, 2013).



Among the environmental pollutants, metals are of particular concern, due to their potential toxic effect and ability to bioaccumulation in aquatic ecosystems (Censi *et al.*, 2006). Studies have shown that heavy metals enters aquatic environment through natural or anthropogenic activities and then accumulates in water, soil, sediment and organs of aquatic organisms (Burger *et al.*, 2002., Vutukuru, 2005). Many researchers such as Javed (2005), Sajwan *et al.* (2008) and Vinodhinni and Narayanan (2008) have documented the presence and bioaccumulation of heavy metal such as copper (Cu), lead (Pb), Zinc (Zn), cadmium (Cd), Nickel (Ni), arsenic (As), iron (Fe), and mercury (Hg) in different parts of fish in water. This implies that periodical investigation of fresh surface and ground water for heavy metals is important and required needful attention is crucial.

In aquatic ecosystem heavy metal need considerable attention due to the toxicity and accumulation in biotic organisms such as fish (Sajwan, 2008; Anup, *et al.*, 2013). Heavy metals are normally constituent of marine environment that occur as a result of pollution principally due to discharge of untreated wastes into rivers by many industries. River Manyera is the main source of water for domestic use and even farm irrigation practices in these two populated areas (Sabo and Nassarawa). Thus a constant seasonal discharged of agricultural run - off and all time washing of gold mining residues into this river could be threat factors to the water organisms, the plants and people of the communities.

This problem has been noticed in both developing and developed countries (Listori, 1990). Water quality monitoring has a high priority for the determination of current

condition and longtime trends for effective management.

A vast range of chemical pollutants or xenobiotic contaminants, originating from domestic wastewater and various anthropogenic activities has become a pervasive threat to the water resources (Saidi, 2010). The Contamination of River Manyera by accumulation of heavy metal such as mercury (Hg) has been reported (Idowu *et al.*, 2013) hence this research. According to Kumar *et al.* (2007), the main sources of heavy metal pollution are the agriculture, industry and mining activities. This waste generated contaminates the river with a variety of heavy metals acting as point sources (Idowu *et al.*, 2013). Anthropogenic activities such as gold mining, fishing, farming, bathing, washing/laundry, car/motorbike washing, refuse disposal, municipal wastewater and human waste disposal are constantly going on within and around this river, thus this study then assessed and evaluated the presence and levels of some heavy metals in River Manyera.

Materials and Method

Description of study area

Manyera River is located between Sabo village in Magama Local Government Area longitude 10° 28' N and latitude 5°03'E and Nassarawa village in Mashegu Local government Area, longitude 9°57' N and latitude 5°13'E Niger state The River Manyera had been a washing point for the entire people of Nassarawa and Sabo communities. It is also a source of water for illegal gold miners in Borgu Local Government Area for a very long time.

Sampling sites

The method of Memet and Bulent (2012) was adopted. Surface water, sediment at 5 cm and



fish samples were collected from three sites along the Manyera River (Fig 1).

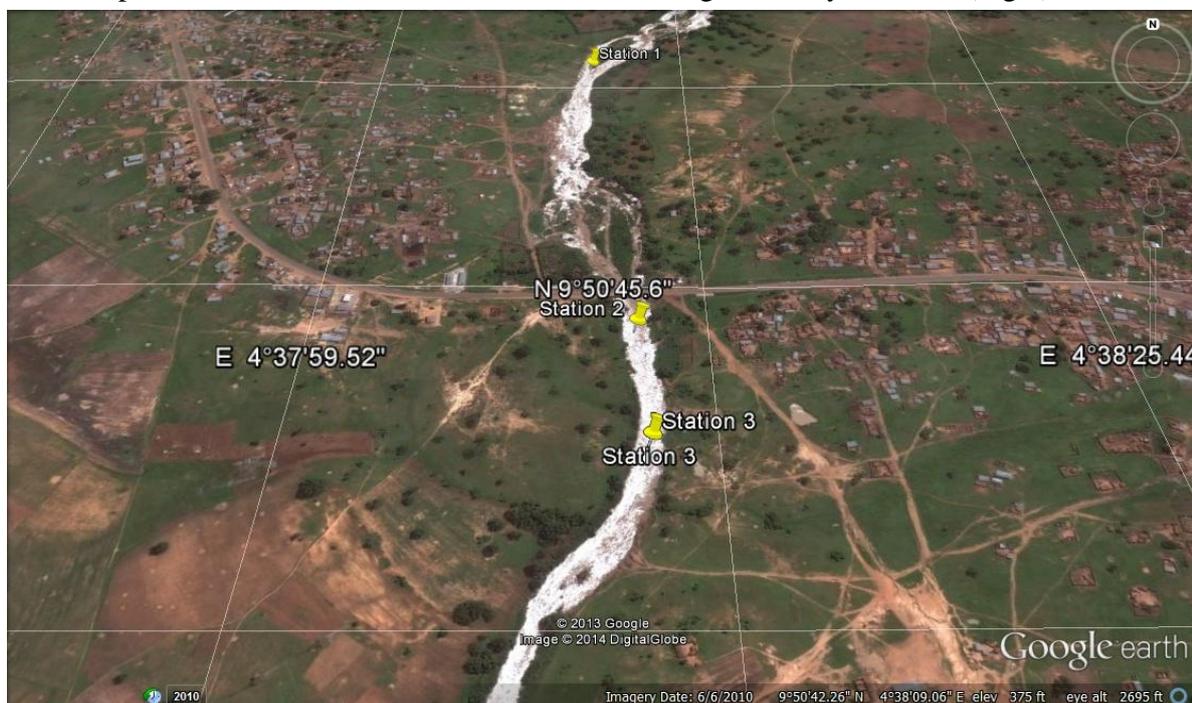


Fig: 1 Area view of Nassarawa village showing Manyera river and sampling stations.

Source: Google earth, 2014

Sample collection

Composite samples of surface water, sediment and fish were collected from the sampling sites in September, 2018. Water samples were collected in acid washed 1 L polyethylene bottles. Composite sediments (top 5 cm of surface) were taken by using a self-made sediment core sampler, with a diameter of 6 cm and a length of 60 cm. The sediment samples were sealed in clean polyethylene bags. Five samples of fish (*Tilapia*) were collected at each sampling sites by professional fishermen using a multifilament, nylon gill net. Samples were washed with clean water at the point of collection, placed on ice, brought to the laboratory on the same day and then frozen at -20°C until dissection. Water and sediment samples collected were placed in a cooler at 4°C ,

and transported to the laboratory immediately for further analysis.

Chemical analysis

Analysis of water samples: A 200 mL aliquot of each water sample was filtered through Whatman No 42 filter paper for analysis of heavy metals. The filtered water samples were digested with HNO_3 , then Iron, Cd, Cu, Co, Cr, Pb, Zn and Ni were analyzed by atomic absorption spectrometry (AAS) equipped with deuterium background correction (AA240FS, Varian).

Analysis of sediment samples:

Sediment samples were air dried; then, stones and plant fragments were removed by passing the dried sample through a 2 mm sieve. The sieved sample was powdered in a mortar and pestle and finally passed through a 500 μm sieve and stored in glass bottles.



Heavy metal content determinations: A 1 g sediment subsamples were digested in Teflon vessel. The sediment extracts were analysed for Fe, Cd, Cu, Co, Cr, Pb, Zn and Ni by AAS. Concentrations in sediment were reported as total recoverable metals on a dry weight basis.

Analysis of fish samples: Frozen fish samples were thawed at room temperature and dissected using stainless steel scalpels. One gram of accurately weighed epaxial muscle on the dorsal surface of the fish samples were transferred to Teflon beaker for acid digestion to prepare the sample for heavy metal analysis (Kenstar closed vessel microwave were digested with 5mL of nitric acid (65%) and after complete digestion the samples were cooled to room temperature and diluted to 25mL with double distilled water. All the digested samples were analyzed three times for metals using AAnalyst 200 model of Atomic Absorption Spectrophotometer (AAS) and the instrument was calibrated with standard solutions prepared from commercially available chemicals.

Quality control: The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, recovery of known additions and analysis of replicates. All analyses were carried out in triplicate, and the results were expressed as the mean.

Statistical analysis: Relationships among the considered variables were tested using correlation analysis with statistical significance set at ($P = 0.05$).

Results

Metal concentration levels in water

Heavy metal concentration levels in the surface water investigated are shown in Table 1. Iron (Fe) concentration levels were significantly higher than other metal levels in all the stations under study as shown in Table 1.

Table 1: Concentration of Heavy Metals in Water Samples from River Manyera

Metals (mg/L)	Station 1	Station 2	Station 3	Permissible. Limit (FEPA, 2003 and WHO, 2011)
Fe	1.27	3.64	1.35	0.30
Cu	0.22	0.25	0.24	<1
Zn	0.03	0.23	0.03	5
Co.	0.05	0.03	0.09	-
Cr.	0.07	0.02	0.01	0.05
Cd	0.05	0.6	0.4	0.01
Pb	0.39	0.13	0.35	0.05
Ni	0.01	0.7	0.04	0.02

The highest iron metal concentration levels was found at station 2 (midstream). The mean value of Fe concentration levels ranged between 1.27 mg/L from location 1 – 3.64 mg/L in station 2 (table 1). The concentrations of copper Cu metal levels

found in water were not significantly different in all the stations studied. Copper Cu concentration levels followed the below trend: Station 1 (0.22 mg/L); Station 2 (0.25 mg/L) Station 3 (0.25 mg/L).



Zinc metal levels 0.23 mg/L was significantly higher in station 2 than station 1 and 3 with same concentration levels of 0.03 mg/L. The concentration levels of cobalt Co ranged from 0.03 mg/L - 0.09 mg/L in the three stations studied with the highest concentration levels at station three (downstream) and the lowest at (midstream) station 2. Cadmium concentration levels of 0.6 mg/L and 0.4 mg/L at station 2 (midstream) and station 3 (downstream) respectively were significantly different from concentration levels of cadmium in station 1 (upper stream).

Chromium, Cr had the least concentration levels of 0.01 mg/L and 0.02 mg/L at Station 2 and Station 3 respectfully. Lead, Pb

concentration levels at station 1, (0.39 mg/L) and Station 3, (0.35 mg/L) were considered not significantly different but differed significantly from concentration levels of 0.13 mg/L at station 2.

Nickel, Ni had lowest concentration of metal levels recorded at Station 1 (0.01 mg/L) followed by Station 2 (0.04 mg/L) the downstream and the highest value of Ni metal concentration levels (0.07 mg/L) at station 2, (the midstream). Metal concentration levels observed for sediment at different locations, the upstream, midstream, downstream and permissible limits values were shown in Table 2 below.

Table 2 Metal concentration levels in sediment in River Manyera

Element (ppm)	Upstream	Midstream	Downstream	Permissible Limit (mg/g) (FEPA, 2003 and WHO, 2011)
Fe	16.18	21.63	51.50	<2
Cu	0.02	0.33	0.25	16
Zn	0.01	0.02	0.02	-
Co	0.002	0.002	0.02	-
Cr	0.03	0.01	0.02	26
Cd	0.01	0.01	0.01	0.60
Pb.	0.01	0.03	0.04	31
Ni	0.01	0.01	0.01	16

In Table 2 above there was variation in the metals concentration levels investigated. At the upstream, metal concentration levels ranged from 0.01 to 16.18 mg/g with iron (Fe) having the highest concentration level of 16.18 mg/g. The metal concentration levels followed the trend below:

Fe (16.18 mg/g) > Cr (0.03 mg/g), > Cu and Co each having concentration levels (0.02 mg/g) > Zn, Cd, Pb and Ni having the same metal concentration levels (0.01 mg/g) each. It is obvious in this study that metal

concentrations recorded from the sediment samples were below their acceptable limit as shown in Table 2 above. Fe and Cu concentrations levels were significantly different at (P = 0.05) in all sample locations. Fe had the following trend: Downstream (51.50 mg/g) > midstream (21.63 mg/g) > upstream (16.18 mg/g). For Cu, midstream (0.33 mg/g) > downstream (0.25 mg/g) > upstream (0.02 mg/g) while other metals (Zn, Co, Cr, Cd and Pb) concentration levels as revealed from the result were not significantly different at (P = 0.05). The concentration



levels for these metals Zn, Co, Cr, Cd and Pb ranged from 0.01 to 0.04 mg/g.

Metals concentration levels in Fish

Result obtained from the fish analyzed for Fe, Cu, Co, Cr, Cd and Ni metal concentration levels revealed high concentration levels in Fe and Ni. This is an indication that bioaccumulation of metal ions which depends on factors such as pH, rate of absorption and adsorption had already occurred in the fish organ or tissue subjected to investigation. It was found that the metal concentration levels

in fish from River Manyera had the following trend: Fe (166.5 mg/g), Ni (38.1 mg/g), Cr (36.85 mg/g), Cu (11.65 mg/g), Zn (10.10 mg/g), and Cd (0.65 mg/g). Table 3

The metal concentration levels for Fe and Ni 166.5 mg/g and 38.10 mg/g respectively were considered higher than the permissible metal concentration levels 100 mg/g and 75 mg/g respectively (FEPA, 2003 and WHO, 2011) in fish. Cobalt Co was not detected in the fish organ investigated.

Table: 3 Concentration of Heavy Metals in Fish Samples from River Manyera

Heavy Metals Concentration	Present Study mg/g	Maximum Permissible Limit mg/g (FEPA, 2003 and WHO, 2011)
Iron	166.5	100
Copper	11.65	30
Zinc	10.1	75
Cobalt	0	0
Chromium	36.85	50
Cadmium	0.65	0.5
Lead	38.1	2

Discussion

The mean concentration levels of 0.1 mg/g for metals from sediment samples and surface water samples in this study was considered very low when compared with their worldwide acceptable concentration levels as shown in both Table 1 and 2 (FEPA, 2003; WHO, 2011). Concentration levels of metal recorded from fish samples was high when compared with their respective permissible limits. This high metals concentration levels in fish samples is an indication that the source of metals detected could be attributed to both geochemical and anthropogenic factors because these are the types of metals found in the material used by people. Such anthropogenic factors include bioaccumulation of residues from

agrochemicals and application of fertilizers, gold mining tailing and solid wastes such as cable cover or battery waste that found their ways into the river. Average concentration levels of lead, (Pb) in this research is lower compared to concentration levels 32.0 mg/g and 10 – 30 mg/g in the earth crust (Kabata and Pendias, 2001) (USDHHS, 1999) respectively, though all the concentration exceeded the permissible limit. The toxicities and environmental effects of organo - lead compounds are particularly noteworthy (Raymond and Felix, 2011). Protecting Manyera River from lead toxic metal is necessary, hence a need for public awareness on the danger of toxic heavy metals for proper disposal of waste. Iron, (Fe) concentration



levels (166.50 mg/g) exceeded its permissible limit (100 mg/g) (FEPA, 2003 and WHO, 2011), implies that continuous consumption of fishes or drinking untreated water from river Manyera is unhealthy. Other metals concentration levels detected are still within their permissible limits especially Cu and Zn which some researchers recognized as essentials micronutrients for both man and organisms in water bodies (Osredkar and Sustar, 2011).

Conclusion

It is obvious from this finding that iron and nickel metals were found most abundant in the fish while Cr, Cu, Cd and Zn concentration levels were below their permissible levels. The result also revealed that, only iron concentration level was above the permissible level in the sediment samples analyzed. However, result for the water samples analyzed revealed that Cu and Zn did not exist their permissible limits but Fe, Pb, Cd, Cr concentration levels were above their respective permissible limits. Therefore, this findings implies that the two metals Cu and Zn had no significant pollution while other metals had been exposed to the water body above their respective permissible limits due to the untreated waste discharged from the municipal and anthropogenic activities wastes into the River Manyera by illegal gold miners and probably runoff from agricultural wastes are of great threat to the river Manyera.

Efforts should be intensified so as to ensure that such anthropogenic activities identified around the river be reduced or eradicate completely especially the illegal tailing of mined gold.

References

- Anup, Baranwal., Jewvana, Praharsha., Rabindra, Khadka., Ramprasad, Kunchana and Vinod Nagashetti (2013). Bioaccumulation of the heavy and toxic metals by the Novel Micro organisms. *Global Journal of Biology, Agriculture and Health Sciences* Volume 2(3) 106 – 110, Published by: Global institute for Research and Education www.gifre.org
- Burger, J., Gaines, K. F., Boring, C. S., Stephens, W. L., Snogross, J., Dixon, C., McMahan, M., Shukla, S., Shukla, T. and Gochfeld, G (2002). Metal levels in Fish from the Savannah River Potential Hazards to fish and other Receptors. *Environmental Resource*, 89: 85 – 97.
- Censi, P., Spoto, S. E., Saiana, F., Sprovieri, M., Maozzola, S., Nardone, G., Di Geronimo, S. I., Punturo, R., and Ottonello, D (2006). Heavy Metals in Coastal Water Systems: A Case Study from the Northwestern, Gulf of Thailand. *Chemosphere* 64: 1167 – 1176.
- Federal Environmental Protection Agency (2003). Guidelines and Standards for Environmental pollution control in Nigeria. Pp238.
- Idowu, O.S., Adelakun, K.M., Osaguona, P. and Ajayi, J. (2013). Mercury contamination in artisanal gold mining area of Manyera River, Niger State, Nigeria. *E3 Journal of Environmental Research & Management*. Vol. 4(9): 0326-0333.
- Kabata-Pendias, A. and Pendias, H. (2001). Trace metals in soils and plants, CRC press, boca, raton, fla, USA, 3rd edition, 2001. Pp413
- Kumar S. R., Chavan S. L., and Sakpele P. H (2007). Heavy metal concentration in water, sediments, and body tissues of red worm (*Tubifex*spp) collected from natural habitats in Munbai, India. *Environmental Monitoring Assessment*. 129: 471 - 481.



- Listori J. J (1990). Worldwide bank Environmental Health components for water supply, sanitation and urban projects Worldwide Bank Washington Dc. Pp76
- Mason C. F (1991). Biology of Fresh Water Fishes *Longman Scientific and Technical*, New York, USA 351pp.
- Memet, Varol and Sen, Bulent (2012). Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *CATENA* 2012, 92:1-10.
- Osredkar, K. and Sustar, N. (2011). Copper and Zinc, Biological role and significance of copper/Zinc Imbalance. *Journal of Clinical Toxicology*. S3:001. doi: 10.4172/2161-0496. S3-001.
- Raymond A. Wuana and Felix E. Okieimen (2011). Heavy Metals in Contaminated Soils: A Reviewed of Sources, Chemistry, Risk and Best available Strategies for Remediation. *ISRN Ecology Volume 2011*, Article ID402647. <http://dx.doi.org/10.5402/www.hindawi.com>
- Saidi, M (2010). Experimental studies on effect of heavy metals presence in industrial waste water on biological treatment. *International Journal of Environment Sciences* 1(4) 666 – 676.
- Sajwan, K.S., K.K. Senthil, S. Paramasivam, S.S. Compton and J.P. Richardson, (2008). Elemental status in sediment and American oyster collected from Savannah marsh/estuarine ecosystem: A preliminary assessment. *Arch. Environ. Contam. Toxicol.*, 54: 245-258.
- Sanchez, E., Colmenarejo, M.F., Vicente, J., Rubio, A., Garcia, M.G., Travieso, L. and Borja, R. (2007). Use of the water quality index and dissolved oxygen deficit as simple indicator of watersheds pollution. *Ecological Indicators*, 7:315- 328.
- Thomaidis, N.S., Asimakopoulos, A.G., and Bletsou, A.A. (2012). Emerging contaminants: A tutorial mini-review. *Global NEST Journal*, Vol. 14(1): 72-79.
- USDHHS, toxicological profile for lead, united states department of health and human services, Atlanta, Ga, USA, 2003.
- Vinodhini, R. and M. Narayanan, (2008). Bioaccumulation of heavy metals in organs of fresh water fish *Cyprinus carpio* (Common carp). *International Journal Environmental Science Technology*., 5: 179-182.
- Vutukuru. S. S., 2005. Acute effects of Hexavalent chromium on survival, oxygen consumption, hematological parameters and some biochemical profiles of the Indian Major carp, *Labeo rohita*. *Int. J. Environ. Res. Public Health*., 2 (3), 456-462.
- WHO (2011). World Health Organization (WHO) guideline for drinking water quality: recommendation., World health Organization, Geneva, Switzerland.
- Zhang, W., Jiang, F and Ou, J. (2011). Global pesticide consumption and pollution with China as focus. *Proceeding of the International Academy of Ecology and Environmental Sciences* 1(2), 125 – 144.