ASSESSMENT OF THE LEVELS OF HEAVY METALS IN WATER, SOIL, PLANT AND FISH SAMPLES FROM MATARA-UKU WETLAND

Supported by tetfund

S. Yusuf[1], A. Busari[1], A. A. Audu[2], L. Abdullahi[1], M. Aliyu[1] and A. Samanu[1]
[1]Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria
[3]Department of Pure & Industrial Chemistry, Bayero University, PMB 3011, Kano, Nigeria
*Corresponding author: sayzay37@yahoo.com

Received: June 25, 2019 **Accepted:** October 16, 2019

Abstract: The aim of this study was to determine the levels of heavy metals in soil, water, plants and fish samples from Matara-Uku in Hadejia-Nguru wetlands. Twenty (20) samples of soil, water, two plants samples (*Moringa oliefera* and *Paulliria pinnata*) and six Tilapia fishes were collected from the four sites and digested using a mixture of hydrochloric acid and trioxonitrate (V) acid in the ratio 3:1. The plant samples were digested for 4 h at 90^0C. The heavy metals (Pb, Ni, and Cd) levels in the digested samples were analyzed using Atomic Absorption Spectrophotometer. The mean concentration of the heavy metals analyzed for the water samples ranged between 0.127 to 0.273 mg/L for Pb, 0.00260 to 0.00530 mg/L for Cd, and 0.0705 to 0.141 mg/L for Ni, respectively. The Concentration of Pb exceeded the maximum permissible limit of 0.01 mg/L for surface water. The heavy metals concentration in plants ranged between 3.0±0.026 to 14.7±0.084 mg/kg for Pb, 0.056±0.001 to 3.089±0.002 mg/kg for Cd and 1.96±0.003 to 6.87±0.005 mg/kg for Ni. The mean nickel (Ni) concentration in fish liver was 0.010633, muscle was 0.01075 mg/kg and the average nickel (Ni) concentration in gills was 0.0111 mg/kg. The mean concentration of Pb in muscles was 0.01015 mg/kg, in gills it was 0.0043 mg/kg and lead (Pb) was not detected in the liver. While cadmium, (Cd), was not detected in all fish samples. The concentrations of all heavy metals which were analyzed in the muscles, gills and liver of tilapia fish (*Oreochromis niloticus*) were lower than the maximum permitted concentrations recommended by FAO and WHO. The fish of that wetland is good for human consumption.

Keywords: Water, soil, fish, plant, heavy metals

Introduction

The importance of soil cannot be over emphasized, as it is the top layer of earth's crust which supports plant growth. A number of studies have revealed that closeness to industrial areas and urbanization has significantly increased the contamination of the soil and areas used for agriculture (Wan Ngah and Hanafiah, 2007; Mmolawa *et al.*, 2011; Omotoso and Tijani, 2011). Wetland soils are formed as a result of periodic to continuous inundation and soil saturation leads to anaerobic soil conditions and reduced decomposition, which results in the buildup of organic matter.

Natural water bodies are threatened by hazard of pollution due to release of untreated effluents and waste materials from agricultural activities and industries located around rivers (Wang *et al.*, 2014). Yusuf *et al.*, (2018), analyzed the levels of Pb, Cd, Ni, Zn, Cu and Cr in Matara-Uku wetlands ponds and observed that the water is contaminated with respect to Pb, Cd and Ni. They suggested that the use of organic waste from refuse dump sites as the major source of these heavy metals.

Heavy metals are non-biodegradable as such persist for long period of time in aquatic and terrestrial environments. They might be transported from soil to ground waters or may be taken up by plants. Several studies have drawn attention to the heavy metal accumulation in plants (Jamali *et al.*, 2009). These metals can reach unacceptable levels and thus pose a serious problem to society and human health (Stigliani *et al.*, 2008).

Fish is a major source of protein for human beings (Rasheed, 2001). Heavy metals enter our body through the consumption of contaminated aquatic food. Most studies have been concentrated on the accumulation of heavy metals in muscle, because it is the main fish part that is consumed by people (keskin *et al.*, 2007). Muscle is not a good indicator of the contamination of the entire body of fish and therefore, it is necessary to analyze the gills and liver.

Thus, it is therefore necessary to study the increasing level of heavy metals contamination in soil, water, plant and fish samples in order to protect the environment and human health. The aim of this research work is to assess the levels of heavy metals in soil, water, plants and fish from Matara-Uku wetland.

Materials and Methods

Digestion of soil samples for heavy metals

Two (2) g of the soil samples were weighed into 250 cm^3 beaker. The soil sample was digested by the addition of 20 cm^3 of aqua regia (mixture of HCl and HNO_3 ratio 3:1) and 10 cm^3 of 30% H_2O_2. The H_2O_2 was added in small portions to avoid any possible overflow leading to loss of material from the beaker. The beakers were covered with a watch glass, and heated over a hot plate at 90^oC for two hours. The samples were filtered and each was transferred into a 100 cm^3 volumetric flask and made up to the mark with deionized water. Blank solutions were treated as described for the samples EPA-ROC (1994).

Digestion of water samples for heavy metals analysis

Exactly 500 cm^3 of the filtered water sample in a 1000 cm^3 beaker was placed on a hot plate and evaporated to about 50 cm^3. It was allowed to cool and transferred into a 250 cm^3 beaker. 5 cm^3 of concentrated HNO_3 was added and the resulting solution was heated at 85^0C until a clear solution was obtained (APHA, 1995). The digested sample was allowed to cool, then transferred into a 100 cm^3 volumetric flask and made up to mark with more deionized water. This solution was then used for the heavy metals analysis using Agilent, varian AA240FS Atomic Absorption Spectrophotometer (AAS).

Digestion of fish samples for heavy metals analysis

Fish sample (1.0 g) was placed in a 25 cm^3 beaker and 10 cm^3 of concentrated HNO_3 was added. It was covered with a watch glass and placed on a hot plate set at 40^0C for 1 hour. The temperature was then raised to 110^0C and maintained for 3 hours at this temperature. As the digest was completely dissolved in the acid, the mixture was cooled to the ambient temperature. The sample was filtered by filter paper (Whatman No. 1 grade) and the filtrates was transferred into a 100 cm^3 volumetric flask and made up to mark with more deionized water (Plessis, 2012).

Digestion of plant samples for heavy metals analysis

The method reported by George *et al*., (2013), was adopted.

Study area

The Matara-Uku wetland is located within the Hadejia-Nguru wetlands between latitudes 12º15'N and 12º55'N, and between longitudes 10ºE and 11ºE (Fig. 1) in the Sudan savanna of Nigeria. The area contains large amount of potassium deposit which are used as food additive and also sell them. Most of the people living around the area are engaged in cultivation of cassava, beans, rice and maize.

Five samples each of soil, water, two plants samples (*Moringa oliefera* and *Paulliria pinnata*) and six samples of Tilapia fish were collected from sites A, B, C and D in Matara-Uku wetland.

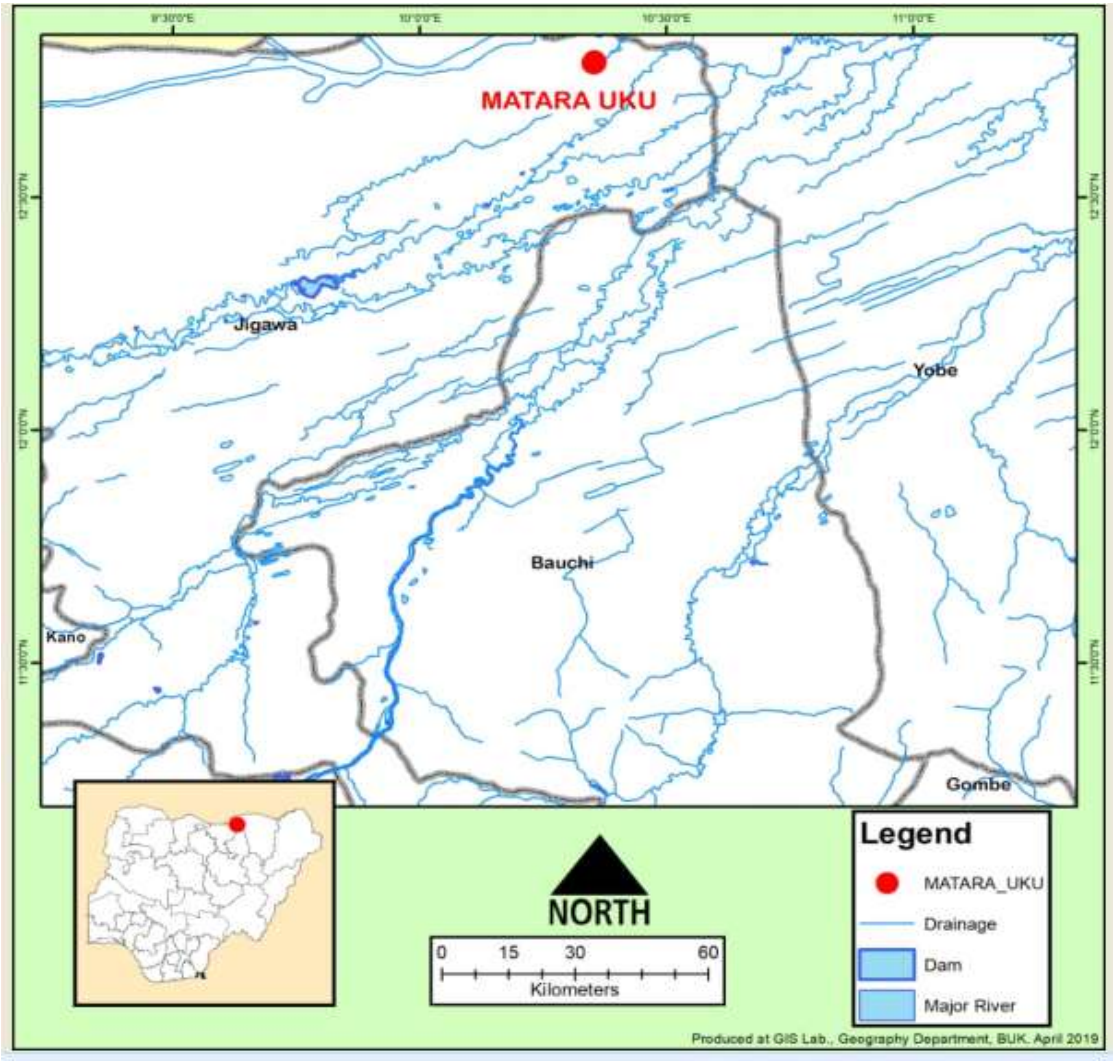

Fig. 1: Map of Matara-Uku wetland

Results and Discussion

Heavy metals levels in soil

Lead (Pb): The mean concentrations of lead obtained from the 20 sampling sites are (85.58±0.198 mg/kg), (35.86±1.70 mg/kg), (63.33±0.18 mg/kg) and (60.61±2.95 mg/kg) in suite A, B, C and D respectively (Fig. 2). It can be seen from (Table 1) that, sites A and D, and sites B and site D have strong negative correlation, while the others have weak correlation except site A and site C which have strong positive correlation, which mean that they have similar source of pollutant. There is no significant difference between the Pb levels from the four sampling sites at $p<0.05$ (Table 1). It should however be noted that the major sources of lead pollution are pesticides, fertilizer impurities, emission from mining and smelting operation and atmospheric fallout from the combustion of fossil fuels (Hong *et al.*, 2009). Lead in all the site were above the permissible limit recommended by WHO (2013) and it has been reported that the use of chemical fertilizer, pesticides and fungicide were the potential source of lead pollution in soil (Wei *et al.*, 2011).

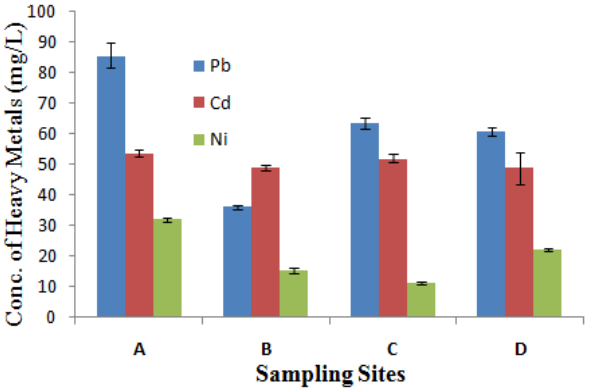

Fig. 2: Concentration of heavy metals in soil samples from four sites in Matara-Uku wetland

Table 1: Pearson correlation of lead (Pb) between the four sampling site

	site A	site B	site C	site D
site A	1			
site B	0.221159	1		
site C	0.968262	0.104042	1	
site D	-0.54189	-0.86826	0.48492	1

Table 2: Pearson correlation of nickel (Ni) between the four sampling sites

	Site A	site B	site C	site D
Site A	1			
Site B	-0.97336	1		
Site C	0.427398	-0.52466	1	
Site D	0.346455	-0.21532	-0.15391	1

Nickel (Ni): The mean Nickel levels from sites were (31.8±1.45 mg/kg), (15.2±1.61 mg/kg), (11.0±0.836 mg/kg), and (22.0±1.36 mg/kg) in sites A, B, C and site D, respectively (Fig. 2). However, there is strong negative correlation (Table 2) between the samples collected from all sites, except between sites A and D, which have a weak correlation. Hence, they have different source of input. There is no significant difference between the concentration of Ni recorded from all the sampling sites at $p<0.05$. The level of Nickel in all the sites is below permissible limit recommended by WHO (2013) which is set at 35 mg/kg.

Cadmium (Cd): The mean concentrations of cadmium obtained from the sampling sites were (53.51±0.27 mg/kg), (48.7±0.190 mg/kg), (51.82±0.300 mg/kg) and (48.73±0.116 mg/kg) and (48.73±0.116 mg/kg) in sites A, B, C and site D, respectively (Fig. 2). From Table 3, it can be seen that there is weak positive correlation between the samples collected from all sampling sites except sites A and C, and site B and site D which have strong positive correlation, hence, they have similar source of pollutant. There is no significant difference between the concentration of Cd values recorded from all the sampling sites at $p<0.05$. The concentrations of cadmium obtained from the study area, were above the permissible limit set by WHO (2013) and FAO (2007). However, the source of cadmium may be from industrial and agricultural activities. Several compounds of Cadmium are used in chemical industries and in the manufacture of pesticides and herbicides used in agriculture (Alloway and Ayres, 2010).

Table 3: Pearson correlation of cadmium (Cd) between the four sampling site

	site A	site B	site C	site D
site A	1			
site B	0.020643	1		
site C	0.709403	0.05432	1	
site D	0.224304	0.60141	0.158777	1

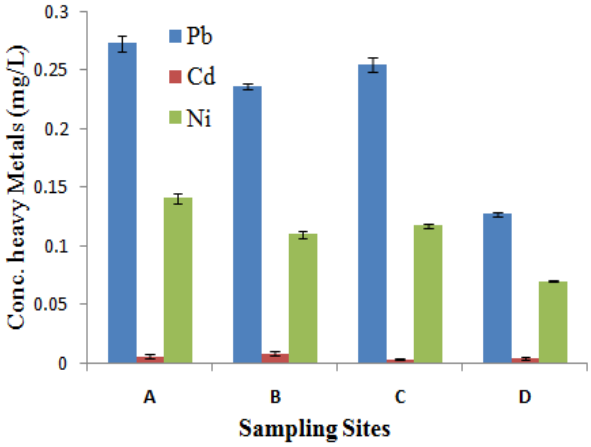

Fig. 3: Mean concentration of heavy metals in water samples

Levels of heavy metals in water samples

Result in Fig. 3 showed the concentrations of heavy metals in surface water of Matara-Uku from various sampling sites. The metal levels ranged between Pb (0.1272 ± 0.0445) to (0.2727 ± 0.029) mg/L, Cd (0.0026 ± 0.001) to (0.0053 ± 0.001) mg/L and Ni (0.071 ± 0.001) to (0.141 ± 0.002) mg/L, respectively. Levels of Cd were generally below the permissible limit set by WHO (2011) which is 0.2 mg/L, whereas the concentrations of Pb exceeded the maximum permissible limit of 0.01 mg/L WHO (2011) for surface water.

The statistical analysis showed that there is no significant relationship between the levels of metals in the sampling sites. Pearson correlation analysis was conducted between the heavy metals levels in water samples to assess if there are similarities in the sources of these heavy metals as represented in Table 4. Cadmium, Cd, shows negative correlations with Ni at a significance level of 0.01 (2-tailed). Similarly, Pb shows negative correlations with Cd at a significance level of 0.01 (2-tailed). And also Cd shows strongly negative correlation with Ni at a significance level of 0.01 (2-tailed). The sources of these heavy metals displaying negative correlations were considered to be different.

Table 4: Pearson correlation analysis of heavy metals

	Pb	*Cd*	*Ni*
Pb	1		
Cd	-0.12122	1	
Ni	-0.45691	-0.60335	1

Levels of heavy metals in plant samples

The levels of Pb in the stem of *Moringa oliefera* (Fig. 4), is significantly greater than those of the root and leaf. The high concentrations of Pb in the stem may be due to function of the stem primarily for transportation. While the Ni concentration in the leaf is significantly greater than those obtained for the stem. This high Ni, concentration in the leaf compared to the root and stem indicate translocation to above ground tissues. The translocation of Pb from root tissue to aerial tissue causes it to accumulate in the leaves and stems (Wies and Weis, 2004). Nickel, Ni, may be also absorbed directly from the air and other anthropogenic sources through the leaves, resulting in higher amounts of metals in the leaves than in the stems. This result was highly consistent with the result from (Vymazal *et al.*, 2007). It was also in accordance with the result from a study by (Clemens *et al.*, 2002).

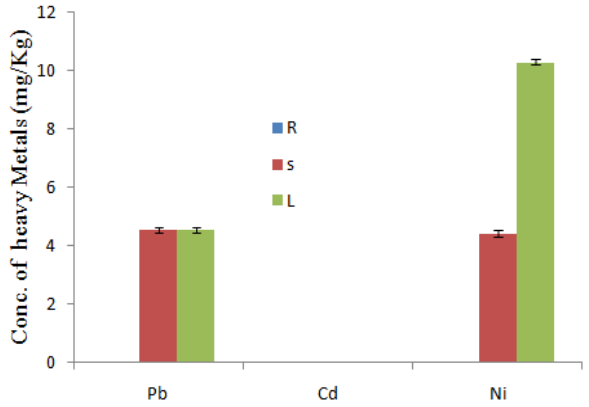

Fig. 4: Level heavy metals concentration in tissues of *Moringa oliefera*

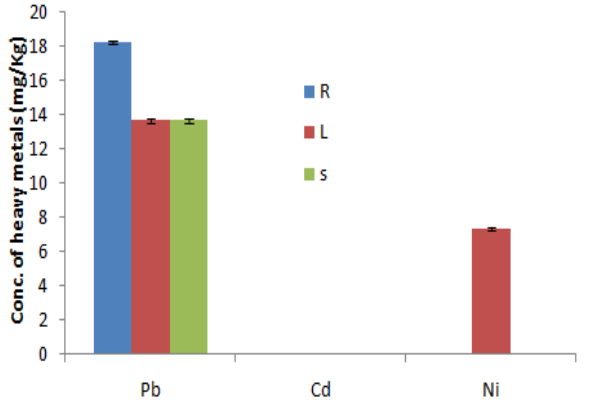

Fig. 5: Level of heavy metals concentration in the tissues of *Paulliria pinnata*

In *Paulliria pinnata*, the level of Pb in the root is higher than those of the stem and leaf. The sequence for the levels of heavy metals in paulliria pinnata is in the following order: root > leaf > stem. This high level of Pb in the root indicates a limiting mobility once absorbed by the root. This result was consistent with those reported by (Hu, *et al.*, 2014). However, only Ni was recorded in the leaf of *Paulliria pinnata* (Fig. 5).

Levels of heavy metals in fish samples

The metal concentration in the gills, livers and muscles of the Tilapia fishes *Oreochromis niloticus* from Matara-Uku in Hadejia-Nguru wetland were shown in Tables 5, 6, 7 and 8, represented.

Table 5: Concentration of Ni in tilapia fish tissues (mg/kg)

Sample	L	M	G
1.	0.0231	0.0111	0.0037
2.	0.0037	0.0074	0.0037
3.	0.0111	0.0074	0.0074
4.	0.0148	0.0016	0.0111
5.	0.0037	0.0111	0.0222
6.	0.0074	0.0259	0.0185

Table 6: Concentration of Pb in tilapia fish tissues (mg/kg)

Sample	M	G	L
1.	0.0174	0.0043	ND
2.	0.0087	0.0043	ND
3.	0.0087	0.0043	ND
4.	0.0087	0.0043	ND
5.	0.0087	0.0043	ND
6.	0.0087	0.0043	ND

Table 7: Concentration of Cd in tilapia fish tissues (mg/kg)

Sample	M	G	L
1.	ND	ND	ND
2.	ND	ND	ND
3.	ND	ND	ND
4.	ND	ND	ND
5.	ND	ND	ND
6.	ND	ND	ND

The levels of heavy metals varied for the fish species sampled from the different sites of the wetland. Nickel (Ni) concentration in liver ranged between 0.0037 and 0.0231 mg/kg and the average mean concentration was 0.011±0.001 (Table 5), nickel (Ni) concentration in muscle ranged between 0.0016 and 0.0259 mg/kg and the average concentration of Ni in muscle was 0.01075, and the nickel (Ni) concentration in gills ranged between 0.0037 and 0.0222 mg/kg with average concentration of 0.0111±0.001. The concentration of Ni decreases in this sequence in the fish tissues gills>livers>muscles (Fig. 6). The concentration of Pb in muscles ranged between 0.0087 and 0.0174 mg/kg, with an average concentration of 0.010±0.001 (Table 6), concentration of Pb in gills was 0.0043 mg/kg and lead (Pb) was not detected in the liver. The levels of Pb in the fish tissues analyzed follow the order: liver>muscle>gills. Furthermore, Cadmium (Cd) (Table 7) was not detected in all fish samples.

It was observed that gills have the highest concentration of Ni, followed by liver while the muscles have the lowest concentration of Ni. However, the level of Pb is higher in the muscles than in gills whereas Pb was not detected in the liver. The order of heavy metal concentration in different tilapia fish tissue was Pb>Ni>Cd. Tukey test showed that there is no significant difference in the concentration of Ni in liver, muscles and gills of Tilapia fish at $P<0.05$. The differences in the distribution of heavy metal in the fish samples might be due to their feeding habit and metabolism.

The concentrations of the heavy metals analyzed in the muscles, gills and liver of tilapia fish (*Oreochromis niloticus*) were lower than the maximum permitted limit set by WHO (2011), therefore the fish is good for human consumption.

The present study revealed that accumulation of Pb and Ni in muscles, and liver were higher than the concentration found in gills. Gills are consumed by man as such it is used to monitor heavy metal levels. The low heavy metals levels in the gills reflect their lower ability to store these metals. In addition, higher accumulation of heavy metals in livers of fishes does not cause harm directly to human health, since the liver is not consumed by man. However, the predatory animals which feed on the entire fish tend to accumulate these heavy metals in their body (Senarathne *et al.*, 2007). The concentration of heavy metals in the muscle of fish in the present study is similar to the values reported by Abdel-Baki *et al.* (2011) and Lakshmanan *et al.* (2009).

Conclusion

The levels of heavy metals in the fish tissues of Tilapia fish (*Oreochromis niloticus)* did not exceed the, WHO and NAFDAC guidelines. They follow the order Pb>Ni>Cd. However, the leaf of *Moringa oliefera* from Matara-uku is

contaminated with Pb. The roots showed the highest amounts of most heavy metals, possibly because the roots can absorb heavy metals from both the water and sediments.

The results revealed that the surface water of Matara-Uku is contaminated with respect to Pb. But, the concentration of Cd and Ni were below the NAFDAC and WHO (2011) guidelines for surface water which are 0.03 and 0.2 mg/L, respectively.

The result from this study showed that the heavy metal concentration of soil in the studied area were in the order Pb>Cd>Ni in all sites.

Conflict of Interest

Authors declare that there is no conflict of interest.

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