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Evaluation of Some Heavy Metals in Wetland Soils of Uguru, Yobe State, Nigeria

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ABSTRACT: Some physicochemical properties and concentrations of Pb, Fe, Cd and Zn in wetland soils of Uguru, Yobe State, Nigeria were evaluated at different locations in the study area using standard methods. Results (mean ± SD) for the soil physicochemical properties showed that pH ranged from 6.10 – 8.85, electrical conductivity (EC) ranged from 0.060 to 0.875 $mScm^{-1}$, organic carbon (OC) ranged from 1.131 – 9.428 mg/100g , Exchangeable base ranged from 2.47 – 12.80 mg/l for Ca, 0.688 – 2.416 mg/l for Na, 0.100 – 3.285mg/l for K and 0.316 – 0.849mg/l for Mg, total nitrogen (TN) ranged from 0.070 to 0.140 mg/l and available phosphorus (AP) ranged from 1.131 – 9.428 mg/100g. The concentrations of Pb, Fe, Cd and Zn ranged 0.53 – 84.95 mg/kg for Pb, 1.95 – 29.90 mg/kg for Fe, 0.13 – 24.95 mg/kg for Cd and 1.63 – 24.95mg/kg for Zn. Generally, the profile of heavy metal followed this order: Pb> Zn > Fe > Cd. Pb. However, the levels of all metals presented with exception of Cd across the sites were found within the permissible levels recommended for agricultural soils. High concentrations of Cd in some of the sites suggested a possible contamination of the farmlands.

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According to Ramsar (1994), wetland is defined as areas of marsh, fen, peatland, or water, whether natural or artificial, permanent ortemporary, with water that is static or flowing, fresh, brackish, or salt, including areas of marine water with depth of which at low tide does not exceed six meters. They are among the Earth's most productive ecosystem (Barbier *et al*., 1997).The life support systems that are inherent within the wetlands ecosystems can provide a wide range of valuable functions to society provided the primary users are incorporate in the management of the wetlands within the context of societal livelihoods and local institutions (Folke, 1991).The occurrence of wetland in Nigeria according to Okusami and Rust (1992) has been associated with three landform types, which are inland depression, alluvial plains, and coastal plains. They are used by peasant farmers in sub-Sahara Africa for agricultural production and water sources for domestic consumption as well as dump sites for urban domestic wastes (Binns *et al*., 2003; Mbabazi *et al*., 2010; Adelana *et al*., 2016).However, the introduction of harmful substances into the environment has been shown to have many adverse effects on human health, agricultural productivity and the natural ecosystems. Heavy metals pollution of the environment, even at low levels and the resulting long-term cumulative health effects are among the leading health concerns all over the world today. In wetlands, heavy metals exist mainly in water, in sediment and in plants and accumulate more easily in soils as a result of changes in natural environment and dominating influence of anthropogenic activities (Ita and Anwana, 2017; May and Edwards, 2001; Mitsch and Gosselink, 2000).

Also, in wetlands, soil, not only serves as source of essential nutrients for crops but also functions as sink for heavy metal pollutants. This ecological function of soil is most pronounced in wetlands (Ita and Anwana, 2017). Their distribution cause changes among the different compartments of each system. The accumulations of heavy metals in wetlands have deleterious effect on human health, as wetlands are the important sources of food and water for human beings. Therefore, as the importance and problems of wetlands in Nigeria cannot be over emphasized as it serve as important sources of food and water for human beings and also constitute health hazard due to heavy metal deposits. It is therefore pertinent to protect soil resources while studies are carried out on the levels of the heavy metals in the soils to ascertain their risk to human. Based on the importance of wetlands as describe in several literatures (Rafferty, 1994; Nwankwoala, 2012; Kar, 2013; Verones *et al*., 2013) coupled with paucity of data in literature on the concentration of heavy metals in soils in the wetlands of Nguru wetlands. Therefore, the objective of the study was to determine the levels of Pb, Fe, Cd and Zn and the soil physicochemical parameters as results of agricultural and other activities carried out within the lands.

MATERIALS AND METHODS

The Study Area: The Hadejia-Nguru Wetlands is a wide expanse of floodplain wetlands situated in the northeast Nigeria, the location lies in the Sudan Sahelianzone, which is the zone between the Sudanian Savanna in the south and the Sahel in the North. The wetland is found in Yobe state, located in the northern part of Nigeria, which include the Nguru Lake (Elegbede *et al*., 2014). The HadejiaNguru wetland is the first Nigeria wetland to be named as a Ramsar site (Ramsarm 1994). The area is dominated by Hausa, Fulani, Kanuri and the Bede ethnic group with population capacity of 1,000,000 people; these people depend on this wetland for water supply and other daily activities. According to Idris (2008), the Hadejia-Nguru wetlands community benefit from various activities that surround the wetlands, such as income generations and provision of food, from the different activities such as agriculture, land grazing, wood for domestic fueling, other wood products, tourism and mechanisms for protection against drought.

*Sample Collection***:** Soils were collected from ten (10) selected sites at 3 m apart in lateral dimension within the wetlands of Nguru, Yobe State after the rainy season in the month of October, 2016. The soil samples were taken at 0 – 30 cm to the surface layer of the soil. Five samples were drawn from each site to give a give a composite sample for the site using a stainless steel soil auger. The composite soil samples were air dried at room temperature and allowed to pass through a 2-mm nylon sieve to remove gravels. The samples were stored in polythene bags prior to soil analysis.

Determination of Soil Physicochemical Parameters: The pH of soil samples was measured with a soil: water ratio of 1:2 (w/v) using Crison MicropH 2000, pH meter (Herdeershot*et al*., 1993). Electric conductivity (EC) Electrical conductivity (EC) was determined in supernatant of 1:5 soil: water mixtures using Digital Conductivity meter model No PT360 (Herdeershot *et al*., 1993). Soil Particle size distribution was determined by the hydrometer method as described by Bauyocos (1951). Soil organic matter (SOM) was measured using dichromate oxidation (Nelson and Sommers, 1982). The exchange base (Ex-base) was determined by the sum of exchangeable cations (Banerjee *et al*., 2004).

Determination of Heavy Metals: Soil samples were digested according to Sharidah (1990): 0.5g of soil sample was weighed into 250cm^3 conical flask and moistened with few drops of water to prevent sputtering. 3cm^3 of 30% H_2O_2 was then added and was left to stand for 60min until the vigorous reaction ceased. About 75cm^3 of 0.5 mol/dm^3 solution of HC1 was added and the content heated gently at low heat on the hot plate for 2 h. The digest was allowed to cool, and then filtered into 50cm^3 standard flask. The content was then diluted to 50cm^3 mark and blank digestion without the sample was carried out using the same. Duplicate digestion was carried out for each sample. This method has been widely applied and recognized as informative in environmental metallic investigations where metal fractions associated with carbonate, sulphides, soluble salts organic matter held, Fe-Mn oxides are removed (Awofolu *et al*., 2005). The solutions were then stored for heavy metal (Pb, Fe, Cd and Zn) determination using Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer 400 AAS).

All glassware, polythene tubes and Teflon beakers used in the analyses were pre-cleaned by washing with liquid detergent, rinsed with water and distilled-deionized water, and then soaked in 10% HNO_3 for 24hrs and rinsed with distilled – deionized water and in such a manner that no contamination occurred (Adnan *et al*., 2003). Thereafter, the apparatus were oven-dried for 12hrs at a temperature of 80^{0}C. All reagents used were of analytical grade, and the instrument working calibration was made by diluting the commercial Scharlau Japan stock solution (1000ppm) standard with distilled-deionized water. Quality assurance and quality control were assessed using duplicates, method blanks and spiking methods using prepared multi-element standard solution of 1 ppm for all the elements presented for the study (1 blank and 1 standard for each 10 sample runs). The recoveries of samples spiked with standards ranged from 935 to 102%.

RESULTS AND DISCUSSION

Heavy Metal Concentrations: The mean concentrations of Pb, Fe, Cd and Zn in the wetland agricultural soils are summarized in figures 1 - 4. The mean concentrations ranged from 0.53 (Site 4) – 84.95 mg/kg (Site 3) for Pb, 1.95 (Site 2) – 29.90 mg/kg (Site

8) for Fe, 0.13 (Site 5) – 24.95 mg/kg (Site 7) and 1.63 (Site 3) – 24.95mg/kg (Site 7). Generally, the heavy metal concentration profile followed this order: Pb> Zn > Fe > Cd. The correlation analysis showed that Cd and Zn are significantly correlated ($p < 0.01$) as shown in Table 1. This indicates similar sources of these metals in the soil and hence, an increase in Zn concentration leads to an increase in Cd concentration. In related studies, Huang *et al*. (2013) found that the correlation coefficients between Cd and Pb and Zn are 0.465 and 0.395, respectively, and Xie *et al*. (2016) reported 0.173 and 0.304, respectively. In this study, the correlations with Cd are similar to those reported by Xie *et al*. (2016).

However, when the levels of these metals in study area were compared with values reported in literature, Pb across the sites were found to be higher than 0.046 and 0.439mgkg^{-1}, respectively reported by Awofolu *et al*. (2005), although below 100mgkg^{-1} permissible levels recommended for agricultural soils (Ewers, 1991).Also, when the levels of these metals in study area were compared with values reported in literature, mean Cd and Zn were found to be higher than the values reported by Awofolu *et al*. (2005), although Zn is below 300mgkg^{-1} permissible levels for soils recommended by MAFF (1992), however, Cd concentrations across the sites showed that Sites 7, 9, 9 and 10 are above the permissible concentration of 3mgkg^{-1}.

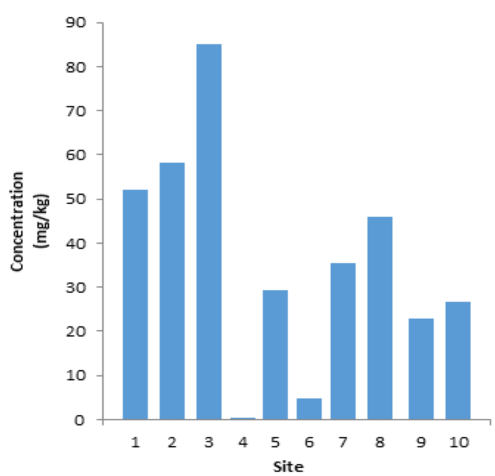

Fig. 1: Concentration of Pb in the wetland soils

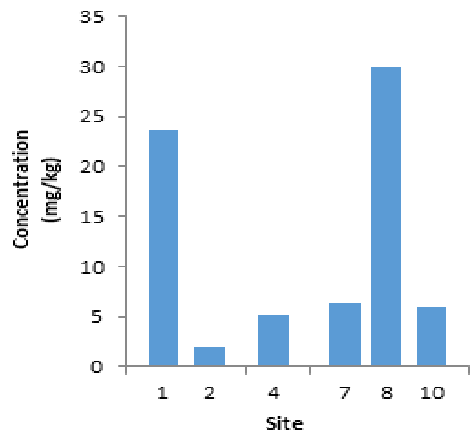

Fig. 2: Concentration of Fe in the wetland soils

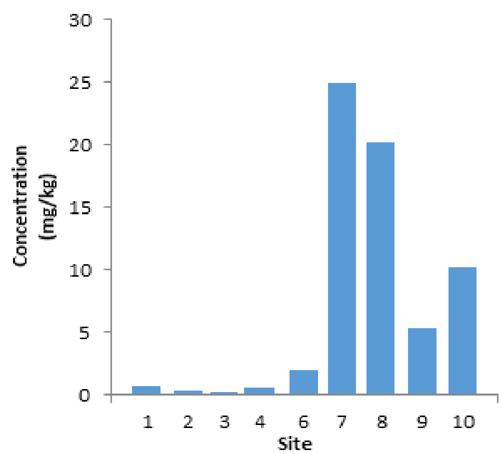

Fig. 3: Concentration of Cd in the wetland soils

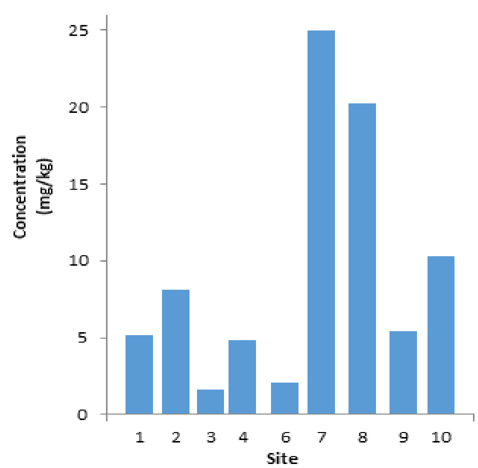

Fig. 4: Concentration of Zn in the wetland soils

Table 1: Correlation matrix among metals in the wetland soils

Parameter	Pb	Fe	Cd	Zn
Pb	1.000			
Fe	0.193	1.000		
Cd	-0.018	0.425	1.000	
Zn	0.065	0.488	0.954**	1.000

**. Correlation is significant at the 0.05 level (2-tailed); **. Correlation is significant at the 0.01 level (2-tailed).*

Physicochemical Parameters: The results of all the physicochemical parameters of the 200 µm sieved air-dried soil samples from the study sites determined are presented in Table 2. The pH_{H2O} and pH_{CaCl2} of the soil samples varied from 7.18 – 8.85 and 6.10 – 7.51, respectively. The low pH in $CaCl_2$ compared to H_2O is due to the hygroscopic nature of $CaCl_2$ thereby increasing the concentration of hydrogen ions. There is no much considerable variation in the pH values across the sites as shown in Table 2.Electrical conductivity (EC) values ranged from 0.060 to 0.875 $mScm^{-1}$ and this suggest non-saline growing conditions across the sites. Also, the organic carbon a measure of organic matter in soil varied from 0.139 – 0.599 %. The values are typically low and characteristic of savanna soils because of rapid decomposition of plant and animal residues added to soil (Jones and Wild, 2005). This indicates that the soil organic matter contains humic materials with low complex functional groups, which have the ability to complex metals thereby retaining them in the topsoil (Evans, 1989). The more organic matter is present in soil, the more functional groups available for complexation with the metals, hence, the more the retention (Okunola *et al*., 2011).The level of available phosphorus (AP) in the soil samples ranged from 1.131 – 9.428 mg/100g. The phosphorus level in Site 3 is very much greater than the level of the phosphate in other sites. Phosphorus is among the nutrient added to the soils through the application of fertilizer, hence, AP content across the sites showed that Site 3 has high level of phosphorus, this suggest possible input of phosphate from other anthropogenic sources. However, the concentration of AP was higher than 0.3 – 0.6 mg/100g reported in related study in Nigeria (Oiganji *et al*., 2015).

Table 2: Physicochemical parameters of wetland agricultural soils

Site	pH_{H2O}	pH_{CaCl2}	EC ($mScm^{-1}$)	OC (%)	AP (mg/100g)	Exchangeable Base (mg/l)				TN (mg/l)
						Ca	Na	K	Mg	
1	7.36	6.94	0.480	0.339	1.886	4.70	0.765	3.285	0.349	0.105
2	7.59	6.94	0.165	0.319	4.526	12.80	1.814	0.780	0.849	0.105
3	7.70	6.10	0.195	0.439	9.428	12.10	1.883	0.440	0.766	0.105
4	8.85	7.51	0.875	0.599	2.263	8.77	2.416	0.485	0.566	0.140
5	7.21	6.93	0.100	0.459	2.639	4.44	0.808	0.225	0.333	0.105
6	7.38	6.79	0.060	0.299	6.034	4.36	0.877	0.230	0.333	0.105
7	7.25	6.61	0.200	0.239	3.771	3.88	0.791	0.125	0.299	0.105
8	7.18	6.41	0.500	0.339	1.131	4.36	0.688	0.215	0.349	0.105
9	7.84	6.70	0.125	0.139	1.886	2.47	0.971	0.100	0.316	0.070
10	8.48	7.28	0.395	0.179	2.639	4.93	1.075	0.300	0.349	0.070

Table 3: Correlation matrix among physicochemical parameters in the wetland soils

Parameter	pH_{H2O}	pH_{caCl2}	EC	OC	AP	Ca	Na	K	Mg	TN
pH_{H2O}	1.000									
pH_{CaCl2}	0.651*	1.000								
EC	0.604	0.505	1.000							
OC	0.210	0.182	.0503	1.000						
AP	-0.090	-0.510	-0.440	0.157	1.000					
Ca	0.254	-0.068	0.106	0.486	0.596	1.000				
Na	0.682*	0.274	0.428	0.598	0.366	0.817**	1.000			
K	-0.133	0.151	0.275	0.098	-0.173	0.042	-0.096	1.000		
Mg	0.233	-0.106	0.047	0.409	0.570	0.987**	0.805**	0.018	1.000	
TN	0.074	0.170	0.513	0.879**	0.106	0.414	0.513	0.144	0.339	1.000

**. Correlation is significant at the 0.05 level (2-tailed); **. Correlation is significant at the 0.01 level (2-tailed).*

The exchangeable base of the soil showed ranged of: 2.47 – 12.80 mg/l for Ca, 0.688 – 2.416 mg/l for Na, 0.100 – 3.285mg/l for K and 0.316 – 0.849mg/l for Mg. The content of total nitrogen (TN) in the soil as shown in Tables 2 showed content ranged from 0.070 to 0.140 mg/l. The value in this study is lower than range of 0.2 – 4.62mg/l reported by Oiganji *et al.* (2015). Correlation analysis amongst soil physicochemical parameters as shown in Table 3 showed the presence of significant positive correlations ($p < 0.05$) between parameters especially Na and pH_{H2O}, TN and OC, Na and Ca, Mg and Ca, and Na and Mg. Significant positive or negative correlation could therefore indicate a greater influence of one factor on another. Also, as shown in Table 4, the correlation between heavy metals in soils and the soil physicochemical parameters showed positive and negative correlations between heavy metals and the soil physicochemical parameters. Hence, positive correlation between metal concentration and physicochemical parameter could imply a significant effect on the amount of trace metal in the soil, since the mobility and bioavailability of metal present in soils depend on physico-chemical properties of both the metal and the soil (McEldowney *et al*., 1993).

Table 4: Correlation matrix between physicochemical parameters and metals in the wetland soils

Parameter	Pb	Fe	Cd	Zn
pH_{H2O}	-0.381	-0.274	-0.264	-0.225
pH_{CaCl2}	-0.665*	-0.111	-0.278	-0.196
EC	-0.231	0.499	0.041	0.146
OC	-0.005	-0.001	-0.430	-0.366
AP	0.460	-0.522	-0.298	-0.323
Ca	0.525	-0.267	-0.447	-0.264
Na	0.066	-0.383	-0.476	-0.331
K	0.290	0.494	-0.324	-0.187
Mg	0.536	-0.290	-0.459	-0.272
TN	-0.101	0.118	-0.184	-0.061

**. Correlation is significant at the 0.05 level (2-tailed); *. Correlation is significant at the 0.01 level (2-tailed).*

Conclusion*:* The present study indicates the concentrations of heavy metals in the study areas. Generally, the heavy metals concentration profile showed Pb as the highest and Cd as the least across the sites. Also, Pb, Zn and Fe levels are within the permissible levels in the soils. However, Cd concentrations at some sites are above the permissible level of the metal in soils. The physicochemical parameters determined are generally low with exception of AP, this suggest typical characteristics of savannah soils in Nigeria.

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