

Spatial Assessment of Some Heavy Metals in Hadejia Nguru Wetlands, Nigeria

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Abstract: The evaluation of Hadejia- Nguru wetland soil was carried out to monitor some of the soil's heavy metal loading using atomic absorption spectrophotometer. Pb, Cr and Cu levels were within the approved standard levels for heavy metals in soil while Cd and Fe were mostly higher than the approved standards. Analysis of variance (ANOVA) results indicated considerable statistical significance: Cd, Cr, Cu and Fe and Pb gave $F(4, 45) = 18.594$, $p = 0.0001$ at 95% confidence interval. A strong positive correlation was also observed between Pb and Cd (0.756), Cd and Fe (0.464) while moderately negative correlation was recorded for Cr and Fe (-0.450).

Key words: Soil contamination Heavy metals Atomic Absorption Spectroscopy AAS

INTRODUCTION

Heavy metals have been widely used as environmental monitoring factors, and their toxicity in humans, animals, and plants is well known. Most heavy metals are considered priority pollutants due to harm that they are capable of causing when present in even slightly higher than normal threshold concentrations.

The mobility of some of these metals within the environment, from soil to water and to plants is something worthy of investigation in order to monitor their levels in the food chain and ecosystem. Many metals are found in the soil due to their presence in surrounding rocks in the lithosphere or from the activities that take place on the surface of the soil such as dumping of wastes, oil spill, degradation of disposed batteries etc.

Heavy metals, which may result from chemical leaching of bedrock, water drainage, and runoff from banks, as well as discharge of urban industrial and rural agricultural wastewaters, are widely present in rivers and serve as important indicators of environmental water quality (Zhan et al., 2010).

Heavy metals from anthropogenic sources can impact estuarine areas, and they are considered to be one of the most common types of pollutants (Bai et al., 2011a; Bai et al., 2011b; Pan and Wang, 2012; Zhang et al., 2013). Many researchers found that heavy metals could be released to water bodies from sediments, which would increase the potential ecological risk and toxicity to aquatic organisms (Kumar, Solanki, and Kumar, 2013).

Heavy metal pollution has increasingly been an area of concern all over the world due to the toxicity of most

metals and how easily they accumulate in food. The level of these metals in food substances can affect human health at varying degrees and also other living organisms in the ecosystem (Lu et al., 2014; Yu et al., 2014; Maanan et al., 2015).

Most sources of heavy metals in soil are from underlying rocks and anthropogenic activities (Yu et al., 2014). Thus, it is important to assess the potential risk posed by heavy metals in the soil surrounding wetlands to have basic knowledge regarding existence and concentration of these metals in the soil.

Various methods have been used for assessing heavy metal contamination (Xiao et al., 2013). The toxic unit (TU), which is defined as the ratio of the measured concentration to the probable effect level (PEL), is usually employed to evaluate the toxicities of various metals in coastal areas (Lu et al., 2014; Xiao et al., 2012, 2013).

The constant unregulated dumping of refuse into water bodies can lead to retention of heavy metals in high concentration by the soil over time. The constant unregulated dumping of refuse into water bodies can lead to retention of heavy metals in high concentration by the soil over time.

Up till now, a large number of researches on heavy metals in estuarine and coastal wetlands have been conducted in larger deltas such as the Yellow River Delta (Sun et al., 2015; Bai et al., 2012), the Yangtze River Delta (Hu et al., 2015; Hu et al., 2013; Gorenc et al., 2004), the Pearl River Delta (Xiao et al., 2012; Zhang et al., 2010; Li et al., 2007), the Mekong River Delta (Cenci and Martin, 2004), the Amazon River Delta (Vital and Stattegger, 2000) and the Mississippi River Delta (Grabowski et al., 2001) and so on.

Many researches have focused on the bioaccumulation (Sun et al., 2015; Zhang et al., 2010), the spatial and temporal variations (Lu et al., 2014; Hu et al., 2013; Gorenc et al., 2004; Bai et al., 2014), the fate (Cenci and Martin, 2004) and the ecological risks (Long et al., 2000) of heavy metals, and the effects of anthropogenic activities on their enrichment levels (Wang et al., 2014; Hu et al., 2015). However, little information is available on the heavy metal pollution levels in wetland soils situated in North West / North Eastern Nigeria.

Heavy metals have shown an increasing tendency in the YRD in the last decade as a result of intensive human activities, e.g., sediment movements resulting from the flow-sediment regulation of Xiaoliangdi Reservoir, the rapid development of petrol oil industries and irrigated agriculture around this delta (Nie et al., 2010; Bai et al., 2012). Therefore, the YRD become an ideal area to investigate heavy metal levels in wetland soils with different ages.

Wetlands in Nigeria are also used for similar purposes and are increasingly being targeted as sources of water for dry season farming activities.

METHODOLOGY

Preparation of soil samples: Composite soil samples were taken from each site using an auger at 15cm depth and air dried under laboratory conditions to a constant weight by spreading into thin layers, ground, sieved using a 0.5 mm polyethylene sieve and stored in clean, air tight polyethylene containers in preparation for analysis (Tan, 1996).

Soil samples for physicochemical and heavy metal analyses were air-dried, sieved through a 0.5 mm polyethylene sieve to remove larger aggregates, transferred into clean glass containers and stored at ambient temperature prior to analysis (Jiamo et al., 2003).

Digestion of soil samples for heavy metal analysis: The air dried sample (2.5 g) was transferred into a pyrex beakers and mixed with 10 cm³ of aqua regia (HCl: HNO₃, 3:1). The solution was separately heated on a hot plate at 95 °C for 1 hr and allowed to cool to room temperature. The resultant solution was diluted to 50 cm³ using double distilled water and allowed to settle (Mwegoha and Kihampa, 2010). The supernatant was filtered through Whatman No. 42 filter paper and stored in glass bottles prior to analysis by Atomic Absorption Spectrometry.

Sample analysis: Atomic Absorption Spectroscopy (AAS)

Instrumentation: There are five basic components of an atomic absorption instrument:

1. The light source (hollow cathode lamp) that emits the spectrum of the element of interest

2. An "absorption cell" in which atoms of the sample are produced (flame, graphite furnace, MHS cell, FIAS cell, FIMS cell)
3. A monochromator for light dispersion
4. A detector, which measures the light intensity and amplifies the signal
5. A display that shows the reading after it has been processed by the instrument electronics.

Principles of AAS: The "ground state" atom absorbs light energy of a specific wavelength as it enters the "excited state." As the number of atoms in the light path increases, the amount of light absorbed also increases. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte can be made. The use of special light sources and careful selection of wavelengths allow the specific determination of individual elements.

Descriptive and inferential statistical analysis carried out on the heavy metals determined in the soils are illustrated in form of figures and tables, a summary of distribution of the heavy metals in soil in terms of column charts, analysis of variance (ANOVA) and multiple regression analysis of the results obtained.

Statistical analysis was done on 95% confidence interval and decision was aided following the hypotheses below:

Analysis of Variance (ANOVA).

- If $p < 0.05$, and $F \text{ value} > F \text{ critical}$, reject null hypothesis and fail to reject the alternative hypothesis:
- If $p > 0.05$, and $F \text{ value} < F \text{ critical}$, accept null hypothesis and fail to accept alternative hypothesis

Correlation Coefficient (r)

- If $r = 0.1$ to 0.3 or -0.1 to -0.3 , then strength of association is weak.
- If $r = 0.3$ to 0.5 or -0.3 to -0.5 , then strength of association is moderate
- If $r = 0.5$ to 1.0 or -0.5 to -1.0 , then strength of association is strong.

Regression Model

$$\mu y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_i X_i + e$$

The model simply describes how the mean response (μy) changes with the explanatory variables (X_1, X_2, \dots, X_i). Hence, the overall significance in variation in the regression model is characterised by the output value of F as individual beta (β) coefficients give the individual variations contributed by each predictor.

Statistical significance of the output was also monitored at alpha level $p < 0.05$.

Multiple linear regression is used to estimate the relationship between two or more independent variable and one dependent variable.

RESULTS

Table 1: Mean concentration of heavy metals in soil (mg/kg)

Sample ID	Cd	Cr	Cu	Fe	Pb
RM	1.4550	2.2118	3.7439	11.4191	0.1913
M.Y	1.7500	1.5041	8.5524	37.7113	0.2563
MK	1.6848	1.4361	7.5671	73.8386	0.2031
HA	1.8696	1.8458	3.7505	68.2549	0.2177
HJ	0.6776	1.6212	6.1216	34.0653	0.2016
MR	1.5543	1.3399	8.0724	24.7064	0.2227
MU	1.0181	1.8163	5.7459	12.4088	0.1722
TK	0.5704	1.5555	9.8639	41.0217	0.1513
DA	0.9095	2.3729	4.5854	9.7181	0.1818
GG	1.0505	1.5204	7.5111	19.1081	0.1868
UNEP, 2013	0.35	70	15	0.16-22.3	12

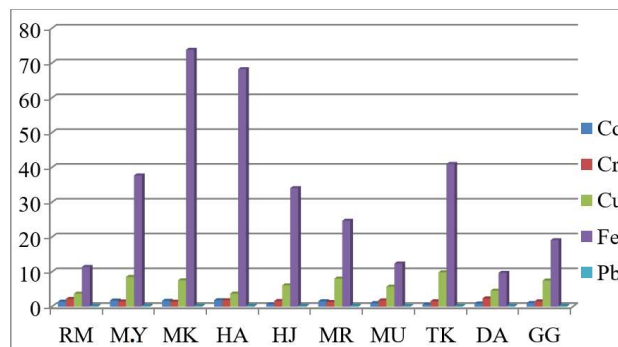


Fig 1.: Graphical distribution of the heavy metals (mg/kg)

Table 2: Analysis of variance (ANOVA) for heavy metals in the soil samples

Source of variation	Sum of Square	Number of groups	df	Mean Square	F	F, critical	P value
Between groups	7824.491	5	4	1956.123	18.594	2.579	0.0001
Within groups	4734.093		45	105.202			
Total	12558.58		49				
Bartlett test			4				0.0001

Regression Equation:

$$Cd = -0.0316(Cr) - 0.0621(Cu) + 0.0062(Fe) + 10.5802(Pb) - 0.5898$$

Best fitting line (actual vs predicted):

$$Actual (Cd) = 1.0 (Predicted (Cd)) - 0.0$$

R squared (actual vs predicted): 0.7023

(P=0.0025)

DISCUSSION

The concentration of cadmium in the soil samples analysed was found to be between 0.57 mg/kg at Tukuikui and 1.87 mg/kg at Hadiyau. These values are much higher than UNEP 2013 limit of 0.35 mg/kg. The lowest value obtained from this research was 0.57 mg/kg which is still higher than the allowed UNEP limit. Hoggang et al., (2010) reported heavy metal concentration in water, soil and plants in the order: soil> plants> water. High concentrations of Cd, Pb, Cr and Cu were reported in the wetland soils studied and this is

similar to the results obtained in this study and with studies of Junhong et al., (2011).

The high cadmium concentrations obtained may be due to its presence in the basement rocks or as part of municipal run offs seeping into the wetland soils. It may also be due to dumping of cadmium containing materials in the soil or as a product of weathering of the surrounding rocks.

Concentration of chromium in the soil had values between 1.34 and 2.37 mg/kg, the lowest value recorded for Makintari and highest for Dabar aro. These values are within the UNEP limit of 70 mg/kg. Chromium has all its concentration in the soil samples to be below the UNEP (2013).

Copper concentration in the soil ranged between 3.74 mg/kg for Ringim and 9.86 mg/kg for Tukuikui. Values for copper concentration obtained across all the sites analysed are within UNEP allowed limit of 15 mg/kg. These values are different from the findings of Nabulo et al., (2008) where a high concentration of 51.20 mg/kg Cu was recorded in Katanga wetland soil, Uganda.

Concentration of iron was between 9.72 mg/kg at Dabar Aro and 73.84 mg/kg at Marke. Values obtained from the study are mostly within the specified UNEP range of 0.16- 22.3 mg/kg. Some of the sites analysed however had higher than standard values: 24.4 mg/kg for Makintari, 34.1 g/kg for Hadejia, 68.3 mg/kg for Hadiyau, 73.8 mg/kg Marke, 41.0 mg/kg for Tukuikui and 37.7 mg/kg for Malamawar Yandutse. The high values obtained may be due to the abundance of the metal in the earth's crust, or the many iron containing materials commonly used by the settlers for their daily activities; or as leachate from the existing rocks.

The concentration of lead in the soil analysed ranged between 0.151 - 0.256 mg/kg. The lowest and highest values were obtained from Tukuikui and Malamawar Yandutse soils respectively. The next highest value in concentration of lead was recorded at Makintari (0.223 mg/ kg) followed by 0.218 mg / kg) for Hadiyau. These values are generally below and therefore within the permissible limit of this metal in the soil (12 mg/kg) as approved by UNEP (2013). High values were however realised when lead was analysed by Nabulo et al., (2008) in wetland soils of Lake Victoria, a basin shared by Uganda, Kenya and Tanzania which differ from the findings of this study. The difference may be attributed to difference in geographical locations and climate.

Pearsons Product Moment Correlation for the heavy metals reveals a strong and positive correlation between Pb and Cd (0.756). Correlation coefficients were observed to decrease as the concentration of the heavy metals decreased. A moderate, negative relationship was established between Chromium and Iron (-0.450) in soil as observed from the result which means that as one increases the other decreases in the soil.

Honggang et al., (2010) reported the abundance of heavy metals in water, soils and plants of wetlands to be in the order: soil > plants > water and this is similar to the trend observed in this study. Most of the heavy metals such as Pb, Cd, Cr exist in quantities higher than world standards as also reported by Honggang et al., (2010) and this has been partly supported by the findings of this research. Several factors have been hypothesized to influence the bioavailability of metals in soils such as pH, soil organic matter, clay and hydrous oxides, as reported by Xuedong et al., (2012) but they established that pH plays a major role in determining the concentration of the heavy metals in soil which to a reasonable extent seems to be in agreement with the findings of this research.

Pearsons Product Moment Correlation for the heavy metals in soil samples also reveals a strong and positive correlation between cadmium and iron (0.464). Notable is the correlation between cadmium and copper which gave a strong and negative value of -0.791. ANOVA results using the Tukey method showed significance at p value = 0.0001 between Fe and other metals. The multiple linear regression analysis with Cd as dependent variable revealed an R squared value of 0.7023 which

indicates a strong dependency of concentration of cadmium in the soil on the concentrations of other metals analysed in this study.

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