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Assessment of Manganese, Nickel and Zinc Pollution in Soils from the Bank of Komadugu River in Gashua, Yobe State, Nigeria

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Abstract: *This study was aimed at assessment of soil contamination by manganese (Mn), nickel (Ni) and zinc (Zn) in four sampling points at the bank of Komadugu River in Gashua, Yobe State. After microwave digestion of the soils, the extracts were analyzed for these heavy metals. Average concentration of nickel and zinc in the soil samples were below the permissible limits set by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA). Manganese was below WHO permissible limit. The contamination factors and geo-accumulation indices indicated that the sampling sites showed no contamination by Mn, Ni and Zn by Hakanson (1980) and Muller (1979) classifications.*

Keywords: *Assessment; Soil; Geo-accumulation indices; Hakanson (1980) scale; Muller (1979) classification*

1. Introduction

The presence of heavy metal contaminants in soil is an indication of global industrialization attributed to large scale inappropriate disposal of untreated solid waste containing heavy metals from anthropogenic sources (Pravin *et al,* 2012). Soil functions as a medium of transport for pollutants which can be damaging to both living organisms and the environment (Rakesh and Raju, 2013). Heavy metals naturally enter humans through ingestion, inhalation and absorption as trace elements. Trace amounts of heavy metals are dangerous because they tend to bio-accumulate and bio-magnify. The damaging effects of heavy metals on both living organisms and the environment have been reported by several workers. According to Addis and Abebaw (2017), bio-accumulation and bio-magnification increase the concentration of heavy metal in a biological organism or targeted organ over time until they become hazardous to health. This can lead to deficiencies in certain nutrients and also result in Parkinson's disease, cancer, skin disorders, respiratory abnormalities, abdominal and intestinal problems, central nervous system damage, blood disorders and reproductive failure. Acute exposure to high concentration of heavy metal can cause nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis (Ogundele *et al,* 2015).

Various reports on impeccable impacts of heavy metal contamination of the environment have been reported. According to Turkdogan *et al.* (2003), soil pollution in Thailand, which was caused by combination of heavy metals and nutrients together with eutrophication, had resulted in degradation of the habitat, particularly mangrove forest and coral reef. For public health, the threats are posed through seafood contamination. Besides that, several economically important activities such as fishery, tourist and agriculture were also directly affected due to deteriorating conditions. For the classical heavy metal disruptive case of Minamata Bay in Japan, methylmercury poisoning effects are still seen today as the impacts are not only widespread and acute but are also chronic (Okoronkwo *et al* 2005). From the perspective of human health, each of the heavy metal imparts different effects and symptoms (Nwaogu, 2014; Sana'a and Alshammari, 2011).

2. Materials and Methods

2.1 The Study Area

The Yobe River, also known as the Komadugu Yobe River is a river in West Africa that flows into Lake Chad through Nigeria and Niger. In Yobe State, it is located on longitud12º52´N and latitude 10º58´E in Gashua, Bade Local Government Area. Its tributaries include River Hadejia , River Jama'are , and the Komadugu Gana River. The river forms a small part of the international border between Niger and Nigeria with 150 km and flows a total of 320km (KYBP, 2006). There are concerns about changes in the river flow, economy and ecology due to upstream dams, the largest at present being the Tiga Dam in Kano State, with plans for the Kafin Zaki dam in Bauchi State (NPC, 2006). The River Yobe provides a means of subsistence for hundreds of thousands of people who work in a variety of commercial and agricultural endeavours along its almost 200 km length in the state's northern region, which spans seven local government areas (LGAs) from Nguru to Yunusari. Notable towns near the river include Gashua, Geidam and Damasak in Nigeria, and Diffa in Niger Republic (Wakawa *et al*, 2017).

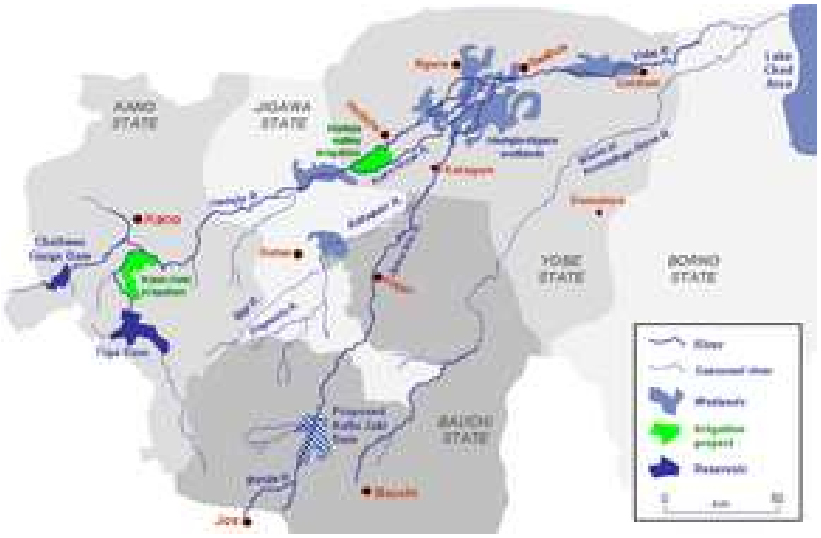


Figure 1: Catchment Area of the Komadugu River

2.2 Instruments, Apparatus and Reagents

All equipment and instruments used in this research were calibrated before conducting the experiments. All glassware used were thoroughly washed with detergents and tap water and then rinsed with deionized water. Suspected contaminants were cleaned with 10% concentrated nitric acid (HNO_3) and metal surfaces rinsed with deionized water. The digestion tubes were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H_2SO_4.

In preparation of reagents, chemicals of analytical grade purity and distilled water were used. All glassware and plastic containers were washed with detergents.

2.3 Digestion of Soil Samples

The soil samples were allowed to dry in a hot oven (Model 30GC). After removing the debris and grinding into fine powder by using a porcelain mortar and pestle, it was sieved through a 2mm mesh. A microwave digester (Master 40 serial No: 40G106M) was used in digesting the soil samples in a digestion tube to which 0.1g of sample was added at a time, followed by 6mL of 65% HNO_3 and 2mL of 30% H_2O_2 and then allowed to stand for a while. The digestion was carried out at 180°C and 1800W in a time of 30 minutes. The digestion was followed by cooling at room temperature in the microwave and the sample was diluted with de-ionized water. Potential presence of selected heavy metals in chemicals used in digestion was determined. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality (SINEO, 2013).

2.4 Atomic Absorption Spectrometric Analysis

The soil extracts were analyzed for manganese (279.5nm), nickel (232.0nm) and zinc (213.9nm) using flame atomic absorption spectrophotometry. Blank determinations were made prior to sample analysis. Heavy metal concentrations in soil extracts were obtained in triplicates from calibration curves and expressed as mg/kg. Metals in chemicals used in digestion were determined. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality (SINEO, 2013).

2.5 Statistical Analysis

The data were analyzed in triplets and expressed as mean and standard deviation. The mean of all treatments was subjected to a One-way analysis of variance (ANOVA) using IBM SPSS Statistics 23 software and mean differences were performed using the Tukey test. All graphs were plotted using Microsoft Excel 2013.

3. Results and Discussion

3.1 Heavy Metals in Soil

Heavy metal exposure is becoming a critical issue especially in developing regions of the world (Adriano, 2001; Jarup, 2003). Heavy metals accumulation in agricultural soil may not only result in contamination of soil but also in increased uptake by food crops which may affect its quality and safety (Muchuweti *et al*., 2006). Quite a number of researches have been carried out on contamination of soil and vegetables by heavy metals (Liu *et al.,* 2005; Mapanda *et al*., 2005; Rattan *et al*., 2005). However, empirical data regarding heavy metals accumulation in soil and the resultant uptake by food crops through peri-urban farming activities are still needed. Therefore, this study was conducted to investigate the health effects of heavy metals in soils at the bank of Komadugu River in Gashua, Yobe State, Nigeria.

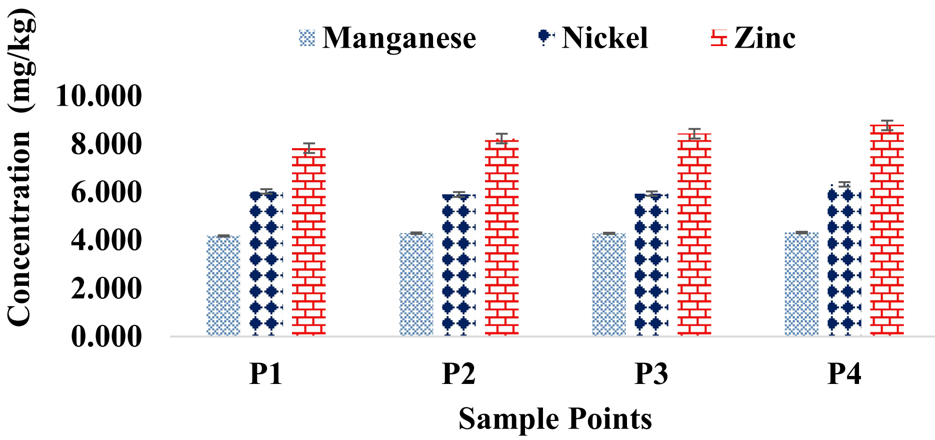
3.2 Abundance of Heavy Metals in Soil

Table 1: Concentrations of Manganese, Nickel and Zinc in Soil

	Mn (mg/kg)		Ni (mg/kg)		Zn (mg/kg)	
Sample Point	**Min.**	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**
P1	3.819	4.612	5.845	6.245	7.393	8.224
P2	3.819	4.841	5.734	6.124	7.854	8.625
P3	3.819	4.765	5.632	6.312	7.658	9.328
P4	3.819	4.863	6.200	6.421	7.626	9.486

Manganese, nickel and zinc were detected in soils collected from the four sample points. The concentrations of Mn, Ni and Zn ranged from 4.185±0.40 to 4.327±0.52 mg/kg, 5.906 ±0.20 to 6.325±0.11 mg/kg and 7.827 ±0.42 to 8.779 ±1.01 mg/kg respectively. **Figure 2** shows the average concentrations of manganese, nickel and zinc in soil samples.

Figure 2: Concentrations of Manganese, Nickel and Zinc in Soil



3.2.1 Manganese

Average concentrations of manganese in soil samples ranged from 4.185±0.40 to 4.327±0.52 mg/kg which are very much below the WHO permissible limit of 200mg/kg. The mean concentration is within the range reported by Al-Huquil *et al*. (2022):1.50±0.09-11.51±0.46mg/kg. P4 has the highest Mn concentration of 4.327±0.52mg/kg, while P1 has the lowest value of 4.185±0.40 mg/kg. Concentrations of Mn in the samples followed the order P4 > P2 > P3 >P1.

Manganese is an important metal for human health, being absolutely necessary for development, metabolism, and the antioxidant system. Nevertheless, excessive exposure or intake may lead to a condition known as manganism, a neurodegenerative disorder that causes dopaminergic neuronal death and parkinsonian-like symptoms.

3.2.2 Nickel

Average concentrations of nickel in soil samples ranged from 5.906±0.20 to 6.325±0.11 mg/kg which are very much below the 70 and 420mg/kg WHO and USEPA permissible limits

respectively. On the contrary, results of Al-Taani *et al*. (2021):32.86-52.12mg/kg and Machender *et al.* (2020):34.3-289 mg/kg were above the mean Ni concentration in this study.P4 has the highest result of 6.325±0.11mg/kg, while P2 has the lowest value of 5.906 ±0.20 mg/kg. Concentrations of Ni in the samples followed the order P4 > P1 > P3 > P2.

Contact with nickel compounds can cause a variety of adverse effects on human health, such as nickel allergy in the form of contact dermatitis, lung fibrosis, cardiovascular and kidney diseases and cancer of the respiratory tract (Oller *et al.* 1997; McGregor *et al*. 2000)). Chronic noncancerous health effects may result from long-term exposure to relatively low concentrations of pollutants. Acute health effects generally result from short-term exposure to high concentrations of pollutants and they manifest as a variety of clinical symptoms (nausea, vomiting, abdominal discomfort, diarrhea, visual disturbance, headache, giddiness and cough). The most common type of reaction to nickel exposure is a skin rash at the site of contact. Skin contact with metallic or soluble nickel compounds can produce allergic dermatitis. This health problem caused by exposure to nickel affects people both at work and away from work. Data indicate that women have greater risk for dermatitis, possibly due to a more frequent contact with nickel-containing items: jewelry, buttons, watches, zippers, coins, certain shampoos and detergents, pigments etc.. About 10% of women and 2% of men in the population are highly sensitive to nickel. Sensitization to the metal is generally caused by direct and prolonged skin contact with items that release nickel ions (Vahter *et al.,* 2002; Szczepaniak and Prokop 2004).

3.2.3 Zinc

The average concentrations of zinc in this study, which ranged from 7.827±0.42-8.779±1.01mg/kg are below the 300 and 2800mg/kg permissible limits set by WHO and USEPA respectively. Also, the value for Zn in soil reported by Al-Taani *et.al*, (2021):42.39-66.92mg/kg was above the mean Zn concentration in this study. P4 has the highest Zn concentration of 8.779 ±1.01 mg/kg, while P1 has the lowest value of 7.827±0.42 mg/kg. Concentrations of Zn in the samples followed the order P4 > P3 > P2 > P1.

Many foodstuffs contain certain concentrations of Zn. Drinking water also contains certain amounts of Zn, which may be higher when is stored in metal tanks. Industrial sources or toxic waste sites may cause the concentrations of Zn in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health. Zinc shortages can cause birth defects. The world's Zn production is still on the rise which means that more and more Zn ends up in the environment. Water is polluted with Zn, due to the presence of large quantities present in the wastewater of industrial plants. A consequence is that Zn polluted sludge is continually being deposited by rivers on their banks. Zinc may also increase the acidity of waters. Some fish can accumulate Zn in their bodies, when they live in Zn-contaminated waterways. When Zn enters the bodies of these fish, it is able to biomagnify up the food chain. Water - soluble zinc that is located in soils can contaminate groundwater. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Finally, Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter. Zinc occurs naturally in soil (about 70 mg kg^{-1} in crustal rocks) (Davies and Jones 1988).

3.3 Pollution Indices of Heavy Metals in Soils

The two most commonly used criteria to evaluate the heavy metal pollution in soils are the geo-accumulation index (I_{geo}) and contamination factor C_f (Saha and Hossain 2011).

3.3.1 Contamination Factor

Contamination factor (Cf) is a ratio of the measured concentration of a metal in a sediment to its background concentration;

$$C_f = \frac{Measured\ Concentration}{Bacground\ Concentration} \text{.....................(1)}$$

The degree of contamination is the sum of all contamination factors

$$DC = \sum_{i=1}^{n} C_{f_i} = C_{f_1} + C_{f_2} + \text{...............} + C_{f_n} \text{............(2)}$$

Table 2: Background Values of Heavy Metals in Soil (WHO)

Heavy Metal	Background Value	Heavy Metal	Background Value
Manganese	300-500	Cadmium	0.1 – 1
Cobalt	10-30	Iron	20,000 – 40,000
Chromium	50 – 150	Zinc	50 – 300
Copper	10 – 50	Nickel	20 – 40
Lead	10 – 50		

Table 3: Contamination Factor and Level of Contamination (Hakanson, 1980)

Contamination Factor (C_f)	Level of Contamination
$C_f < 1$	Low contamination
$1 \leq C_f < 3$	Moderate contamination
$3 \leq C_f < 6$	Considerable contamination
$C_f > 6$	Very high contamination

3.3.2 Geo-accumulation Factor (Igeo)

Geo-accumulation factor (I_{geo}) which was originally defined by Muller (1979) to determine metals contamination in soils, by comparing current concentrations with pre-industrial levels and can be calculated by the following equation;

$$I_{geo} \log_2 \left(\frac{C_n}{1.5 B_n} \right) \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

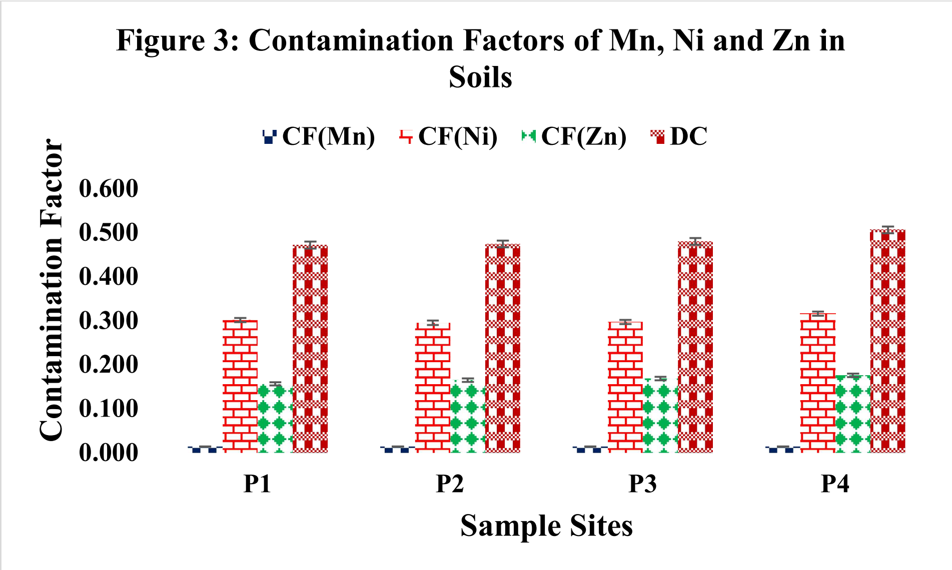
Where, Cn is the concentration of element 'n' and Bn is the geochemical background value. The geo-accumulation index (Igeo) scale consists of seven grades (0-6) ranging from unpolluted to extremely polluted as shown in table 1.2

Table 4: Muller's Classification for Geo- accumulation Index

I_{geo} Value	Class	Soil Quality
≤ 0	0	Unpolluted
0 -1	1	From unpolluted to moderately polluted
1 -2	2	Moderately polluted
2 -3	3	From moderately to strongly polluted
3 -4	4	Strongly polluted
4 – 5	5	From strongly to extremely polluted
> 6	6	Extremely polluted

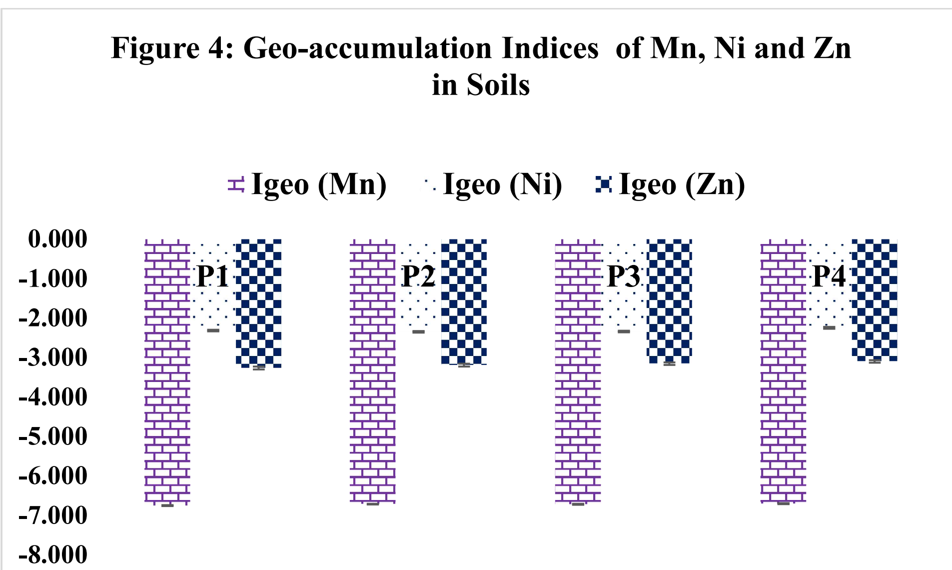
3.4 Assessment of Heavy Metal Pollution in Soils

The contamination factors of Mn, Ni and Zn in the sampling sites are shown on **figure 3.**



The contamination factors ranged from 0.0140 to 0.0144 for Mn, 0.295 to 0.316 for Ni and 0.157 to 0.176 for Zn. The degree of contamination of the metals ranged from 0.472 to 0.506, indicating that the sampling sites are unpolluted with these metals by Hakanson (1980) classification. The level of contamination by the metals was in the order Ni > Zn > Mn.

Figure 4 shows the geo-accumulation indices of Mn, Ni and Zn in the sampling sites.



The geo-chemical indices of Mn, Ni and Zn were in the range -6.749 to-6.701, -2.345 to -2.315 and -3.260 to -3.095 respectively. All geo-chemical indices of the elements were negative, indicating that the sample sites were practically uncontaminated with Mn, Ni and Zn by Muller (1979) classification. For all sample sites the geo-chemical indices decreased in the order Mn > Zn > Ni.

4. Conclusion

Investigation of pollution status of soils collected at the bank of Komadugu River in Gashua, Yobe State revealed that the average concentrations of nickel and zinc were below the permissible limits set by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA). Manganese was below WHO permissible limit. The contamination factors and geo-accumulation indices indicated that the sampling sites showed no contamination by Mn, Ni and Zn by Hakanson (1980) scale and Muller (1979) classification.

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Authors' Contributions
Dagari M.S.: Conceptualization, design and supervision of the research work; Editing of the write-up
Sa'eed B. M.: Undertaking the research work, write-up and data analysis.

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