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DETERMINATION OF SOME TOTAL AND BIOAVAILABLE HEAVY METALS IN FARMLAND SOIL AROUND RIVERS NIGER AND BENUE IN LOKOJA, NIGERIA

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ABSTRACT
The work assessed the distribution of Cd, Cu, Mn, Ni, Pb and Zn in the farmland soils around Rivers Niger and Benue and beyond the confluence in Lokoja, Nigeria. The samples were collected in the dry and rainy seasons of 2013 and 2014, digested with aqua regia and analysed for heavy metals using atomic absorption spectrophotometry. The soil pH ranged from 6.4 to 7.2 for the farmland soils collected 50 m away from the bank of the rivers and each point 10 m apart (n=72). There was no significant difference in the mean values of the organic matter, organic carbon and moisture contents of the soils across the seasons. Cd concentration (mg/kg)in the soil samples collected in March 2013, June 2013, January 2014 and May 2014 at 0 – 15 cm depth ranged from 3.95 - 8.4; Cu 11.6 - 20.2 ; Mn 150.3 - 211.5; Ni 177.0 - 281.0 ; Pb 20.3 - 34.2 and Zn 40.5 - 77.8. The levels of the metals in the soil follow the ranking: Ni > Mn > Zn > Pb > Cu > Cd; with Cd and Ni being above European Union permissible limits. The order of the percentage of extracted metal by EDTA to the total metal content was Pb>Zn>Cu>Ni>Mn>Cd. I-geo pollution index showed that the farmland soils were moderately contaminated with Ni and Cd. Hence, there is the need to enforce environmental laws that borders on proper solid waste and effluent disposals.
Key Words: Heavy Metals– Pollution index – River Niger and Benue – Soils – Season

INTRODUCTION

About ninety natural elements exist in the environment and are distributed through the environment in the geochemical and bio-chemical cycles (Kaim and Schwederski, 1994). In recent years, with the development of global industrialization, both the type and content of heavy metals in the soil caused by human activities have gradually increased, resulting in the deterioration of the environment (Chao *et al.,* 2014). Heavy metals are metallic chemical elements that have a relatively high density precisely greater than $5gcm^{-3}$. This classification includes transition metals and higher atomic weight metals of group IIIA to VA of the periodic table (Ademoroti, 1996). Some of these metals have been implicated for their toxic and hazardous effects (Ademoroti, 1996; Budnova *et al.,* 1994).

As heavy metals get into the ecosystem they get enriched through the food chain. Once the soil accumulates heavy metal and is contaminated, it is difficult to get it remediated. In the past, soil contamination was not given the desired attention compared to air and water pollution, this is because soil contamination seldom happens and it is more difficult to control. However, in recent years soil contamination in developed countries has become an environmental concern worldwide due to its toxicity and accumulative behaviour (Purves, 1985; Omgbu, 1997; Ganogaiya *et al*., 2001; Chao *et al.,* 2014).

The range and mean concentrations (mg/kg) of some heavy metals in the sediments collected from River Niger via Ajaokuta Steel Company, North Central, Nigeria between 2004 and 2005 were Zn 36.64 – 96.23 (70.70 ± 10.68); Mn 4.97 to 21.77 (13.24 ± 2.04); Pb 8.84 to 17.52 (12.35 ± 1.14); Ni 2.65 to 18.61 (9.67 ± 2.91); Cu 0.89 to 8.21 (3.58 ± 1.32); and Cr 0.48 to 13.08 (3.38 ± 0.76) and Cd 0.07 to 0.62 (0.27 ± 0.07) (Olatunde and Oladele, 2003).Thermal neutrons activation analysis technique (TNAA) indicated that some farmland soil in Lokoja contained Mg, K, Ca in large concentration; Na, Mn and V were present in minor concentration in all the samples; Al and Ti were present in minor concentration while Dy was present in relatively low concentration (Oladipo*et al.,*2012).

Irrigation on river side soil of River Niger and Benue help to provide vegetable crops for the people of Lokoja and the environs during the dry season and early part of the rainy season; and also serves for rainy season farming. This study is aimed at assessing some heavy metals in farmland soils around Rivers Niger and Benue, following the flooding of 2012 in most parts along the rivers; the determination of the total Cd, Cu, Mn, Ni, Pd and Zn and the EDTA-extractable amounts in the farmland soils collected beside River Niger, River Benue and beyond the confluence point, post-flooding becomes imperative.

MATERIALS AND METHODS

Description of the Study Area and Sampling Sites

Lokoja, the capital of Kogi State, is located in the North Central geopolitical zone of Nigeria on $7^0 30'$ N and $6^0 42'$ E. It is the town where River Niger and River Benue meet. Niger River is the principal river of West Africa, extending about 4,180 km. Its drainage basin is 2,117,700 km^2 in area. Its source is in the Guinea highlands in South eastern Guinea, it runs in a crescent through Mali, Niger, on the border with Benin and then through Nigeria meeting with River Benue. River Benue is the major tributary of the Niger River. The river is approximately 1,400 kilometres long. It rises in the Adamawa Plateau of Northern Cameroon, flows through Garoua and Lagdo Reservoir into Nigeria, south of the Mandara mountains, and through Jimeta, Ibi and Makurdi before meeting the Niger at Lokoja (Areola, 2004).

The soil samples were collected from bank of River Niger and River Benue and beyond the confluence point in Lokoja at a depth of 0 – 15 cm and distance 50 m away from the bank of the river with each point being 10 m away from the other.

Collection of Soil Samples

The river side soils for total metal determination were collected from the bank of River Niger (N1 – N6)and River Benue(B1– B6) and beyond the confluence point(CN1 – CN6, CB1 – CB6) at 0 – 15 cm depth in March 2013, June 2013, January 2014 and May 2014 using a stainless steel soil augar. As presented in Figure 1, the collection sites were 50 m away from the bank of the river and each point of collection was 10 m away from the other (n=72).

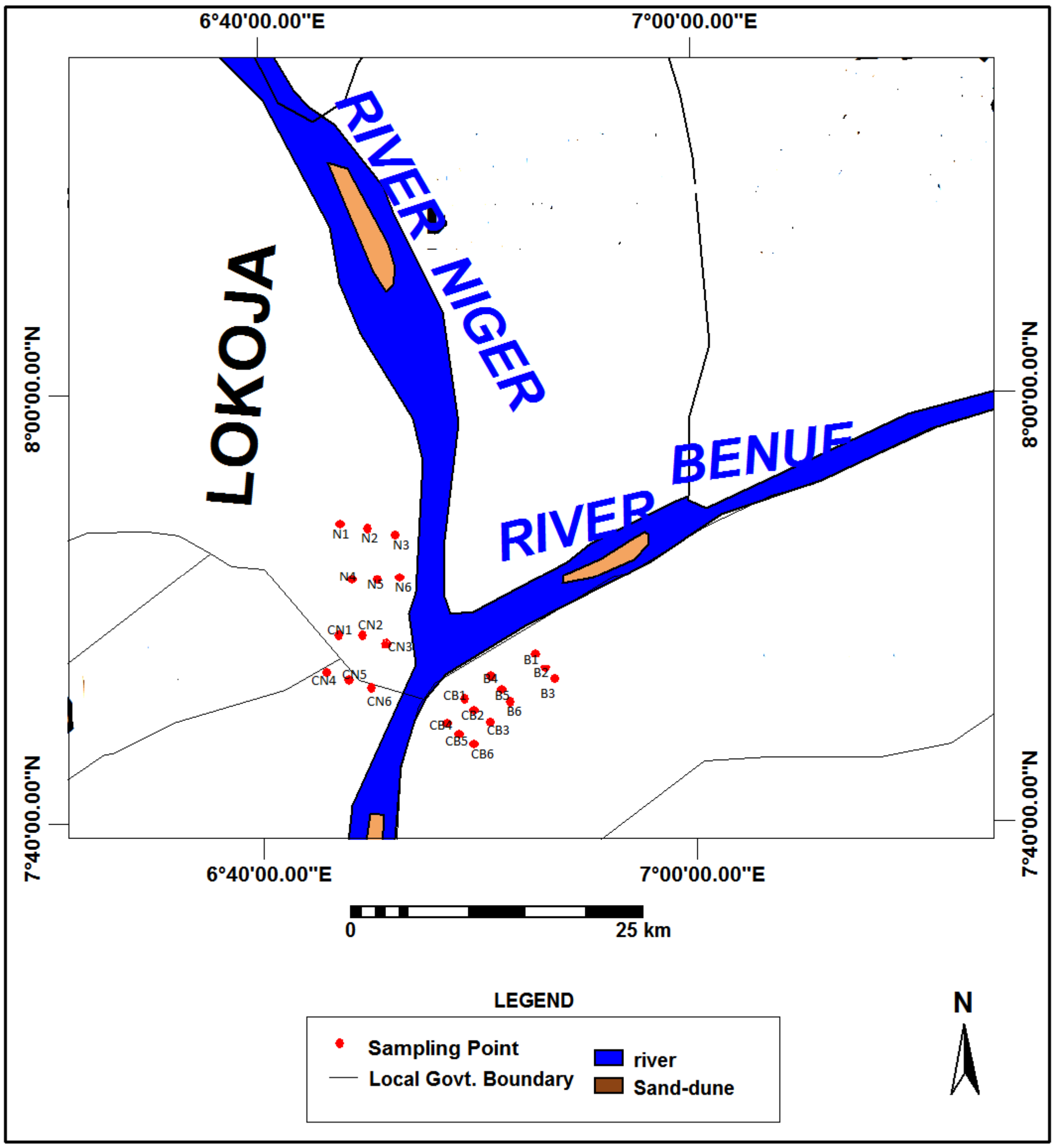

Figure 1: Map Showing the Sampling Points

Key

N = R. Niger riverside soil, B = R. Benue riverside soil, CN = R. Niger riverside soil after confluence, CB = R. Benue riverside soil after confluence

Samples Pre - Treatment

Soil samples from each point was collected in triplicate and then homogenized in an agate mortar and pestle; each was then air-dried overnight in circulating air in an oven at 30°C. It was then sieved through a 2 mm sieve (Onianwa *et al*., 2001).

Determination of the Soil Physico-chemical Properties

The soil pH in the suspension was determined using the method of Black (1965), textural class as adopted by Ogunfowakan (2009); organic carbon, organic matter and moisture contents were determined using the standard method adopted by Walkley and Black (1997).

Digestion of Soil Samples

In order to determine the total levels of Cd, Cu, Mn, Ni, Pb and Zn, the method of Ogunfowokan*et al*. (2009) was employed. In which each 1.0 g amount of the sieved sample was digested using 30 cm^3 aqua-regia ($HCl:HNO_3$, 3:1), followed by 5 cm^3 HF after about 2 h of digestion. The levels of each element in 50 cm^3 of the filtrate were determined using an atomic absorption spectrophotometer (model TAS990, Intec Co. Ltd., Rome); air acetylene flame was used, with the specific hollow cathode lamp required for each elemental determination at the Multi-user Laboratory of Ahmadu Bello University, Zaria, Nigeria. The quality assurance for the analyses was conducted through the spiking method, to evaluate the sample digestion process and effectiveness of the atomic absorption spectrophotometer (Uwumarongie and Okieimen, 2008; Lori *et al*., 2009; Amit *et al*., 2010).

Determination of the EDTA-Extractable Heavy Metals in the Soil Samples

In order to determine the phytoavailbale amounts of Cd, Cu, Mn, Ni, Pd and Zn in the farmland soil, the EDTA-extractableamount wasdetermined by putting 20 g of the sieved soil sample into twenty different 100 cm^3 plastic bottles. Then 40 cm^3 of 0.05M ethylenediaminetetraacetic acid (EDTA) solutions was added to each bottle and screw-capped tightly. The mixture was then shaken on a mechanical shaker at 120 r.p.m. for 2 h. The suspension was then filtered using a Whatmann no. 2 filter paper. The concentrations of the heavy metals were then determined using atomic absorption spectrophotometer (AAS), with the use of the appropriate standards in the EDTA matrix (Guptal and Mittal, 1981)

Determination oftheGeoaccumulation Indices (Igeo) for the soil samples

Geoaccumulation Index (I_{geo})allows for the assessment of metal contamination through a comparison of the metal concentration in the contaminated soil with its concentration prior to contamination (Loska *et al*., 1997). Given as:

$$Igeo = \log_2\left(\frac{C_n}{1.5Bn}\right)$$

Where Cn is the measured mass fraction of the metal (mg/kg^{-1}). Bn is the background mass fraction of the metal (mg/kg^{-1}).

The Chinese Environmental Protection Administration (CEPA) environmental background value was used to calculate the Igeo in accordance to Wang *et al*. (2007). Muller's evaluation method (Muller, 1979) was used to evaluate the level of heavy metal contamination in the farmland soils collected from Lokoja in 2013 and 2014. The classification of the level of contamination is presented in Table 1.

Table 1: Classification of Geoaccumulation Index

Geoaccumulation index	Classification	Level of contamination
$5 < I\ geo \leq 10$	6	Extremely serious
$4 < I\ geo \leq 5$	5	Strong to extremely serious
$3 < I\ geo \leq 4$	4	Strong
$2 < I\ geo \leq 3$	3	Moderate to strong
$1 < I\ geo \leq 2$	2	Moderate
$0 < I\ geo \leq 1$	1	Light to moderate
$I\ geo \leq 0$	0	Non contamination

Statistical Analysis

The variation in the levels of the metals accumulated in the soil with respect to the time of the year when the samples were collected was assessed using Analysis of Varience (ANOVA) at $P < 0.05$.

RESULTS AND DISCUSSION

Physicochemical Parameters of the Farmland Soils near River Niger, River Benue and Beyond Confluence Point

The physicochemical properties of the farmland soils in the dry and wet seasons of 2013 and 2014 are presented in Tables 2a-d. The soil pH ranged from 6.4 to 7.2 for the farmland soils of River Niger, River Benue and beyond the confluence in the dry season of 2013 (March 2013). The River Benue side (B) had the highest pH of 7.1 while the River Niger side (N) had the least (6.7) (Table 2a). However, in the wet season of 2013 (June 2013), B had the highest (6.9) and the sample beyond confluence on River Niger side (CN) had the least (6.6) (Table 2b); however in the dry season of 2014 (January 2014) samples collected beyond the confluence on River Benue side (CB) had the highest pH of 7.2 and N had the least (6.5) (Table 2c). In the wet season of 2014 (May 2014), N had the highest (6.7) and CB the least (6.4) (Table 2d). The pH range obtained is close to 6.41 – 6.73 obtained for some farmland soils of Lokoja by Oladipo *et al*. (2012). The pH values for the soil is suitable and could not facilitate solubility of the metals for bioavailability to plants (Oluyemi *et al*., 2008).

The lowest organic matter content in the dry season of 2013 was recorded at N soil sample (0.413 gkg^{-1}) and the highest at B (1.652 gkg^{-1}) (Table 2a) while in the wet season of 2013 the organic matter content ranged from 0.406 gkg^{-1} at N to 1.673 gkg^{-1} at B (Table 2b). The highest organic matter content in the dry season of 2014 (January 2014) was in B (1.602 gkg^{-1}) (Table 2c). On the other hand, in the wet season of 2014 organic matter ranged from 0.533gkg^{-1} at N to 1.859gkg^{-1} at B. The higher organic matter contents of the farmland soil in the dry season compared to wet season could be due to the lower soil moisture contents during the dry season which enables microbial activities needed organic matter decomposition. The organic matter contents of soil plays an important role in absorption reaction in the soil, hence preventing pollutants from reaching ground water sources (Alloway, 1995).

Moisture content of the soil samples ranged from 64.1 to 85.4% (Table 2a to 2d), soil from N in the wet season of 2013 (June 2013) had the highest value (85.4%) while the one from CN in the dry season (February 2013) had the least(64.1%). There was no significant difference in the mean values of most of the parameters across the seasons.

Table 2a: Physicochemical Parameters and Heavy Metal Contents of Farmland Soil near River Niger and River Benue in the Dry Season of 2013 (March 2013)

Soil property	N soil (mg/kg)	B soil (mg/kg)	CNsoil(mg/kg)	CBsoil(mg/kg)
pH	6.7	7.1	6.9	6.9
% sand	84	50	62	76
% clay	6	34	26	10
%silt	10	16	12	14
Textural Class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)	0.239	0.958	0.563	0.852
Organic Matter (%)	0.413	1.652	0.821	1.364
Moisture Content(%)	78.20 ± 0.01	71.20 ± 0.10	64.10 ± 0.12	68.00 ± 0.03
Total Cd (mg/kg)	4.50 ± 0.001	4.15 ± 0.001	4.25 ± 0.000	3.95 ± 0.001
Total Cu (mg/kg)	18.80 ± 0.000	12.00 ± 0.001	17.20 ± 0.000	12.80 ± 0.001
Total Mn (mg/kg)	172.30 ± 0.004	176.20 ± 0.004	163.40 ± 0.003	150.30 ± 0.003
Total Ni (mg/kg)	187.50 ± 0.001	177.00 ± 0.001	187.50 ± 0.001	185.00 ± 0.001
Total Pb (mg/kg)	34.20 ± 0.000	29.00 ± 0.000	33.30 ± 0.001	21.10 ± 0.000
Total Zn (mg/kg)	58.80 ± 0.003	50.70 ± 0.001	40.50 ± 0.002	44.50 ± 0.003

N = R. Niger riverside soil, B = R. Benue riverside soil, CN = R. Niger riverside soil after confluence, CB = R. Benue riverside soil after confluence

Levels of Total Heavy Metals in Farmland Soil Samples near R. Niger and Benue

The total amounts of Cd, Cu, Mn, Ni, Pd and Zn in the farmland soils collected near River Niger,River Benue and beyond the confluence are presented in Table 2a – 2d.The quality assurance carried out to determine the efficiency of the atomic absorption spectrophotometer through the spiking method revealed that the mean % recovery for the analyses ranged from 82.9 ± 0.15 to 93.3 ± 0.40 mg/kg.

The highest concentration of Cd (8.4 mg/kg) was obtained in both B and CB sampling sites in the wet season of 2014 (May 2014); while the least concentration (3.95 mg/kg) was obtained at N sampling site in the dry season of 2013 (March 2013), though this value was higher than the European Union Standards of 3 mg/kg for soil (EU, 2002). Cadmium is regarded as one of the most toxic trace elements in the environment; its intake in high doses is responsible for kidney failure, damage to testis and liver, softening and rotting of teeth and bones (a disease condition known as Itai-Itai) (Erickson *et al.*, 1994; Prater, 1995; Alloway, 1995).

Table 2b: Physicochemical Parameters and Heavy Metal Contents of Farmland Soil near River Niger and River Benue in the Wet Season 2013 (June 2013)

Soil property	N soil (mg/kg)	B soil (mg/kg)	CN soil(mg/kg)	CB soil (mg/kg)
pH	6.7	6.9	6.6	6.7
% sand	84	50	62	76
% clay	6	34	26	10
%silt	10	16	12	14
Textural Class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)	0.278	0.935	0.547	0.825
Organic Matter (%)	0.406	1.673	0.839	1.350
Moisture Content(%)	85.40 ± 0.01	77.3 ± 0.10	69.2 ± 0.12	73.3 ± 0.03
Total Cd (mg/kg)	5.60 ± 0.001	5.80 ± 0.001	5.80 ± 0.001	5.50 ± 0.001
Total Cu (mg/kg)	14.00 ± 0.001	17.20 ± 0.001	13.90 ± 0.001	15.00 ± 0.001
Total Mn (mg/kg)	192.20 ± 0.004	181.30 ± 0.004	211.50 ± 0.003	150.30 ± 0.003
Total Ni (mg/kg)	250.00 ± 0.001	218.70 ± 0.001	281.00 ± 0.001	250.00 ± 0.001
Total Pb (mg/kg)	26.50 ± 0.000	26.50 ± 0.001	20.30 ± 0.001	20.30 ± 0.000
Total Zn (mg/kg)	66.20 ± 0.003	56.50 ± 0.001	61.60 ± 0.001	50.80 ± 0.003

So awareness should be intensified on proper disposal of wastes. The level of Cd in the site could result from the use of phosphatic fertilizers, wastes from the sediments and the impact of the flooding of year 2012.

The range of Cu is 11.6 $mgkg^{-l}$ in the soil at N to 20.2 $mgkg^{-l}$ in B both obtained in the wet season of 2014. The amount of copper (Table 2a-d) were generally lower than the European Union Standards of 140 mg/kg (EU, 2002). Thus, Cu is in amount that does not raise environmental concern.

Table 2c: Physicochemical Parameters and Heavy Metal Contents of Farmland Soil near River Niger and River Benue in the Dry Season 2014 (January 2014)

Soil property	N soil (mg/kg)	B soil (mg/kg)	CN soil (mg/kg)	CB soil (mg/kg)
pH	6.5	6.7	6.6	7.2
% sand	84	50	62	76
% clay	6	34	26	10
%silt	10	16	12	14
Textural Class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)	0.239	0.958	0.563	0.852
Organic Matter (%)	0.473	1.602	0.721	1.263
Moisture Content	75.20 ± 0.01	73.20 ± 0.10	62.10 ± 0.12	67.20 ± 0.03
Total Cd (mg/kg)	5.80 ± 0.001	6.40 ± 0.003	6.40 ± 0.000	7.30 ± 0.001
Total Cu (mg/kg)	17.40 ± 0.001	20.00 ± 0.001	18.60 ± 0.000	17.50 ± 0.001
Total Mn (mg/kg)	183.20 ± 0.004	187.70 ± 0.004	209.40 ± 0.003	208.20 ± 0.003
Total Ni (mg/kg)	223.00 ± 0.001	243.70 ± 0.001	209.40 ± 0.001	221.80 ± 0.001
Total Pb (mg/kg)	32.70 ± 0.000	23.50 ± 0.000	32.90 ± 0.001	30.50 ± 0.000
Total Zn (mg/kg)	74.00 ± 0.003	60.20 ± 0.001	61.40 ± 0.001	62.50 ± 0.003

Mn in the soil samples was generally higher than all the other metals studied; though the Mn contents recorded were generally lower than the European Union Standards of about 2000 mg/kg (EU, 2002). The Mn content was highest (211.5 $mgkg^{-l}$) in the soil at CN in the wet season of 2013 (June 2013) and lowest (150.3 $mgkg^{-l}$) at CB in both the dry and wet seasons of 2013. The observed large concentration of Mn in the soil samples might have been due to background concentration of Mn in the soil and sediment of the rivers. The Mn content obtained for this study, however was generally lower than the 354 – 394 $mgkg^{-l}$ reported using neutron activation analysis for some farmland soils from Lokoja metropolis, Nigeria (Oladipo *et al*., 2012). Dara(1993) reported that manganese may be found in most soil since it is one of the key elements in the earth crust.

Table 2d: Physicochemical Parameters and Heavy Metal Contents of Farmland Soil near River Niger and River Benue in the Wet Season 2014 (May 2014)

Soil property	N soil (mg/kg)	B soil (mg/kg)	CN soil (mg/kg)	CB soil (mg/kg)
pH	6.7	6.5	6.5	6.4
% sand	84	50	62	76
% clay	6	34	26	10
%silt	10	16	12	14
Textural Class	Loamy sand	Sandy clay loam	Sandy loam	Sandy loam
Organic Carbon (%)	0.249	0.958	0.563	0.822
Organic Matter (%)	0.533	1.859	1.311	1.034
Moisture Content	81.20 ± 0.01	73.50 ± 0.10	68.10 ± 0.12	73.75 ± 0.03
Total Cd (mg/kg)	7.3 ± 0.001	8.4 ± 0.001	7.6 ± 0.001	8.4 ± 0.001
Total Cu (mg/kg)	11.60 ± 0.001	20.20 ± 0.001	18.30 ± 0.001	18.00 ± 0.001
Total Mn (mg/kg)	179.30 ± .004	205.20 ± 0.004	195.20±0.003	171.00 ± 0.003
Total Ni (mg/kg)	269.40 ± 0.001	267.40 ± 0.001	201.00±0.001	220.80 ± 0.001
Total Pb (mg/kg)	23.5 ± 0.001	33.4 ± 0.001	24.6 ± 0.001	28.1 ± 0.001
Total Zn (mg/kg)	63.10 ± 0.003	77.80 ± 0.001	50.00 ± 0.002	51.60 ± 0.003

Following from the results, Ni in the soil samples of the studied area of River Niger and River Benue was generally higher than the European Union Standards of 75mg/kg (EU 2002). The level of Ni was highest (281 $mgkg^{-l}$) in the sample at CN in the wet season of 2013 (June 2013) and the lowest (177.0 $mgkg^{-l}$) was in the soil obtained at the side of River (B) in the dry season of 2013 (March 2013). Nickel occurs naturally in soils as a result of the weathering of the parent rock (McGrath, 1995). Phosphate fertilizer is a major source of Ni in soil, but it is unlikely to build-up in soil in the long-term from their use (McGrath, 1995).

The concentration of lead in the soil samples (Table 4.1a-d) was highest (34.2 $mgkg^{-l}$) in sample obtained aroundRiver Niger(N) in the dry season 2013 (March 2013) and was lowest (20.3$mgkg^{-l}$) in the samples collected from sites CN and CB in the wet season of 2013 (June 2013).

Table 3: Permissible limits of heavy metals in soils

Elements	*Threshold concentration in soil (EU, 2002)(mg/kg)	**Background (CEPA, 1995) (mg/kg)
Ni	75	26.9
Cu	140	22.6
Zn	300	74.2
Pb	300	26
Cd	3	0.097
Mn	2000	63.2

The concentrations of Pb in the soil samples were generally low compared to the European Union Standards of about 300mg/kg (EU, 2002). The concentrations of Pb obtained were generally within the limits for agricultural soils.

The amount of Zn in the soils showed that the soil samples in CN during the dry season of 2013 (40.5 $mgkg^{-l}$) was the lowest while the sample from B in the wet season of 2014 (77.8 $mgkg^{-l}$) had the highest Zn concentration. The Zn concentrations in the studied area of River Niger, Benue and beyond the confluence point were lower than the European Union Standards of 300 mg/kg. This might be due to the continuous removal of heavy metals by the food crops grown in this area and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water. Zn is released to the environment from both natural and anthropogenic sources; however the releases from anthropogenic sources (smelter slags and wastes, mine tailings, coal and bottom fly ash, fertilizers) are greater than those from natural sources. Although zinc usually remains adsorbed to soil, leaching has been reported (Prater, 1995; Omgbu, 1997).

The levels of the metals studied in the farmland soils follow the ranking Ni > Mn > Zn > Pb > Cu > Cd. The levels of Cd, Cu and Mn in the soils collected around River Benue side were significantly elevated compared to the soil samples around River Niger (ANOVA at $P < 0.05$).

Geoaccumulation index (Igeo) of the Farmland Soils from River Niger andRiver Benue in Lokoja

The calculations of Igeo values for Cd, Cu, Ni, Mn, Pb and Zn were carried out and referenced to Table 1. The Igeo values for Ni in all the sampling sites were greater 1 but less than 2 (indicating light to moderate contamination). The Igeo values obtained for Cd are greater than 2, this varied with the range 2.163 - 2.649, indicating moderate to strong contamination. Geoaccumulation index showed that Cd and Ni were the major pollutant of the farmland soil near River Niger, Benue and beyond the confluence point in Lokoja, Nigeria. Cadmium virtually polluted all the riverside soils, thus having the highest Igeo in the wet season of 2014 (Igeo = 2.649) and lowest in the dry season of 2013 (Igeo = 2.163). This could be attributed to the possibility of the transportation of Cd containing deposits like phosphatic fertilizers by water run off to the surrounding soil and the discharge of Cd containing effluents into the rivers.

Igeo for Mn was generally above zero in all the riverside soils and across the seasons, an indication of Mn pollution in most of the sites. The highest Igeo value obtained for Mn was in wet season 2013 (Igeo = 1.157) at CN, which showed a relative pollution by Mn, while it was lowest (Igeo = 0.678) at site CB in both the dry and wet season of 2013. These values indicated moderate pollution. However, Cu, Zn and Pbdid not pollute the riverside soils even across the seasons; this could be accounted for by the nature of the solid wastes deposited into the rivers upstream, as there are different kinds of activities around River Niger and River Benue from the source to the different water courses.

The Igeo values indicated that Cu, Zn and Pb were in class 0 (uncontaminated); Mn is in class 1 (except for the soil samples collected from CN in the wet season of 2013 and both the dry and wet season in 2014 that had the Igeo >1) for all the riverside soils. This indicated that the soil in these riverside are uncontaminated to moderate contamination by Cu, Mn, Pb and Zn. Heavy metals extracted by EDTA should be the fraction available for plants. Hence, the amounts of the heavy metals recorded in Table 4 were significantly lower than the total amounts in the soils (Table 2 a-d).

The ranking of the amount of the EDTA extractable metals is the same as obtained for the total metal content.

Table 4: Mean concentration of the EDTA Extractable Fraction of the Heavy Metals in the Riverside Soils of River Niger and River Benue

Metal	N (mg/kg)	B (mg/kg)	CN (mg/kg)	CB (mg/kg)	Control (mg/kg)	% total content
Cd	1.20±0.001	1.70±0.001	1.40±0.001	1.50±0.001	0.92±0.001	15.0
Cu	4.70±0.001	7.00±0.001	4.20±0.001	5.20±0.002	8.30±0.001	31.2
Mn	45.00±0.004	38.80±0.002	40.60±0.004	37.70±0.007	58.00±0.010	21.5
Ni	41.00±0.001	67.00±0.001	64.00±0.001	60.00±0.001	22.30±0.001	24.2
Pb	12.90±0.001	18.70±0.001	14.50±0.001	18.30±0.001	11.20±0.001	58.7
Zn	20.40±0.003	21.30±0.004	24.90±0.003	22.20±0.005	24.70±0.004	36.4

The percentage of the phytoavailable concentrations of the metals to the total amounts of the metals in the soil samples differ among the elements: lead hadthe highest extractable relative amount (58.7%), followed by zinc (36.4%), copper (31.2%) nickel (24.2%), manganese(21.5%) and the least was for cadmium (15.0%) (Figure 2). However, lead had the extractable absolute amounts (18.70±0.001 - 12.90±0.001mg/kg), and cadmium 1.20±0.001 - 1.70±0.001mg/kg.Similar results were reported for the EDTA extraction in a farmland soil in Croatia, (Lončarić *et al*. 2008) with lead, copper and zinc recording higher percentage extractability than for nickel, cadmium and least for Mn.

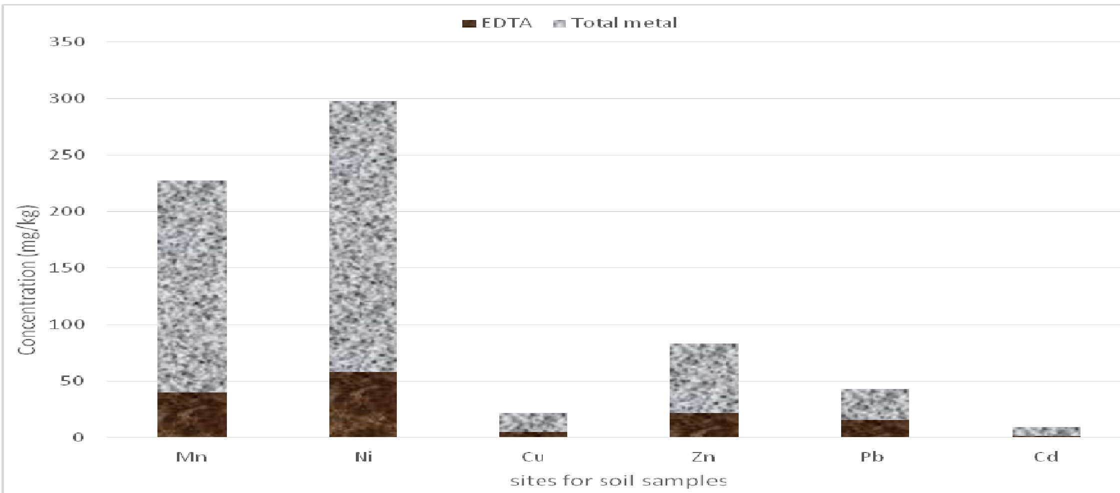

Figure 2: EDTA-Extractable Concentration of the Heavy Metals in Soil versus the Total Metal Content in the Riverside Soils of River Niger and River Benue

CONCLUSION

Almost all the soil samples were found to be enriched with the selected heavy metals but in all the samples the concentrations of nickel and cadmium were in levels above the permissible limits. The heavy metal that recorded the highest total content in the agricultural soils was nickel, followed by manganese, zinc, lead, copper and then cadmium regardless of the soil pH. The order of the amount of the EDTA-extracted metals was almost the same with that of total metal, but the percentage of the metal extracted by EDTA to the total metal content was in a different order: Pb>Zn>Cu>Ni>Mn>Cd. The I-geo pollution index showed that the farmland soils located near River Niger, River Benue and beyond the confluence point in Lokoja, Nigeria are not contaminated and for some cases are moderately contaminated with the studied metals (I-geo grade 0 and grade 1). This suggests that the riverside soils are having background concentrations for Cu, Zn, Pb and Mn and these elements are practically unchanged by anthropogenic influences, while the concentration of Ni and Cd exceeded the average shale value.

RECOMMENDATIONS

It is recommended that research be carried out regularly to ascertain the level of pollution of heavy metals in the farmland soils near River Niger and River Benue. Also, the study of heavy metals in the farmland soils near River Niger and River Benue should be carried out at varying depths. The bio-accumulation of the studied metals by leafy vegetables should be carried out.

In conclusion, there should be enforcement of environmental laws that will minimise the discharge of untreated wastewater to water bodies. Likewise the disposal of wastes into rivers should be avoided to mitigate against flooding.

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CONFLICTS OF INTEREST

The authors have noconflict of interest.

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