

INDUSTRIAL IMPACT ON SELECTED HEAVY METALS IN SOIL SAMPLES OF NNEWI-NORTH LOCAL GOVERNMENT AREA, ANAMBRA STATE, SOUTHEAST NIGERIA

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Abstract- The impact of industries on selected heavy metals in soil samples of Nnewi-North, Anambra State, Nigeria was studied. The levels of seven heavy metals (Pb, Mn, Zn, Ni, Cr, Cu, and Cd) in top soil (15-20cm), from the area were determined using Flame Atomic Absorption Spectrophotometric technique. The HNO₃-HCl-H₂O₂ method was used in the soil sample extraction. Accuracy of the method was assessed by the determination of a certified reference soil material, CC-141, obtained from European Commission, Joint Research Centre (JRC) Belgium and the results showed agreement with certified values. The soil pH varied from moderately acidic to neutral (6.00-7.11) from the various locations and these are considered as normal for agricultural production. The mean and range concentrations (µg/g), respectively of metals in the soils of the studied area were 38.30±5.54, 13.33-91.67 for Pb, 101.07±16.18, 25.93-190.93 for Mn, 44.04±15.96, 7.33-137.17 for Zn, 2.22±0.50, 0.27-8.60 for Ni, 21.69±8.93, 3.33-136.66 for Cr, 9.57±5.96, 1.17-78.30 for Cu, 1.16±0.17, ND-5.67 for Cd and with the exception of Cd(1.16µg/g), were lower than the threshold values for agricultural soils for most countries and FAO/WHO guidelines. Pollution indices were developed to assess the pollution status of heavy metals in the studied area. The geoaccumulation index (Igeo), pollution index (PI) and the pollution load index (PLI) calculated for the soils of the studied area showed that the area was unpolluted to moderately polluted. In conclusion, the investigated area has been affected by the industrial activities. It is recommended that control measures should be enforced by the relevant authorities in order to avert any adverse effects.

I. INTRODUCTION

Industrialization is essential for economic growth of any nation as it acts as a vehicle for development. Modern life style with increasing population and industrial growth has impacted negatively on the environment at global scale [1]. In order to fulfil the basic requirements of increasing population, different types of industries have been set up in different regions of our country, Nigeria and these include pulp and paper, textile, cement, petrochemical, metal processing, food processing, fertilizer, sugar, pharmaceutical, distilleries among others. The fermentation industry is considered as one of the most polluting industry and has posed serious environmental problems throughout the world while chemical and metallurgical industries are the most important sources of heavy metals in soils [2].

Heavy metals are released into the environment by both natural and anthropogenic sources. The main natural sources of metals in soils are chemical weathering of mineral; the anthropogenic sources are associated mainly with industrial, agricultural, mining, land disposal of waste, waste incineration, mechanic workshop and filling station [3]. Many heavy metals are environmentally stable and non-biodegradable, toxic to the living beings and tend to accumulate in plants and animals, causing chronic adverse effects on human health [4]. Different studies have revealed that the presence of toxic heavy metals like iron (Fe), lead (Pb), mercury (Hg) reduce soil fertility and agricultural output [5]. Also, heavy metals are in various raw materials, such as fossil fuels and metal ores, as well as in industrial products. Some trace metals are emitted entirely or partially from raw materials during the high-temperature production of industrial goods, combustion of fuels, and incineration of municipal and industrial wastes, entering the ambient air with exhaust gases [6]. Atmospheric emissions from industrial complexes are considered as the main source of the environmental pollution. These emissions travel along vast areas by the effect of the meteorological factors and become accumulated in soil, plant and animal whether aquatic or terrestrial and may reach the food chain [7].

Cultivation of crops on polluted soil can adversely affect the health of plants and animals as well as man in the food chain. For instance, cadmium contaminated soil was known to have caused the itai-itai disease as a result of

consumption of rice grown on contaminated soil in Japan in the 1950s [8]. So, increasing the heavy metal content in soil increases the uptake of heavy metals by plants which depends upon the soil type, plant growth stages and plant species. The balancing of agricultural soils for mineral components, organic matter, air and water allow for water retention and drainage, enough oxygen which help to provide physical support and nutrients for plant growth [9].

Nnewi-North Local Government Area is known to be an area with a large number of industries which include petrochemical, metal fabrication, food processing, automobile spare parts industries among others. Apart from meeting the environmental impact assessment (EIA) conditions required for the setting of new industry or factory, most industries in this part of the world never bother on the disposal of their wastes. However, no work has been carried out to holistically evaluate the impact of industries on the heavy metal concentration in soil samples of Nnewi-North Local Government Area of Anambra State, Nigeria. It was against this backdrop that this work was carried out. The aim of this study was to assess the impact of industries on selected heavy metals in soil samples from Nnewi-North Local Government Area. The analysis of heavy metals was conducted using the Flame Atomic Absorption Spectrometry (AAS) situated in Sheda Science and Technology Complex, Abuja.

II. MATERIALS AND METHODS

Study Area

Nnewi is the second largest city in Anambra state, southeastern Nigeria (Figure 1). Nnewi-North Local Government Area is commonly referred to as Nnewi central, and comprises four autonomous quarters: Otolo, Uruagu, Umudim, and Nnewichi [10]. Its geographical coordinates are $6^{\circ}1'0''$ North and $6^{\circ}55'0''$ East. The city is located east of the Niger River, and about 22 kilometers south east of Onitsha in Anambra state, Nigeria [11]. Nnewi is home to many major indigenous manufacturing industries. Nnewi is part of eastern Nigeria's industrial axis and acts as sophisticated networks expanded to include an international dimension through trading relations with exporters from Asia [10]. Infact, Nnewi is usually referred to as the Japan of Nigeria because of its high industrialization and has about thirty giant manufacturing plants and over a hundred cottage industries [12]. By 1940, Nnewi residents were at the center of an international trading network that dominated the supply of motor parts in Nigeria. The town subsequently became a center for commerce and industry, and is known to have one of the largest automotive spare parts markets in Africa today [13].

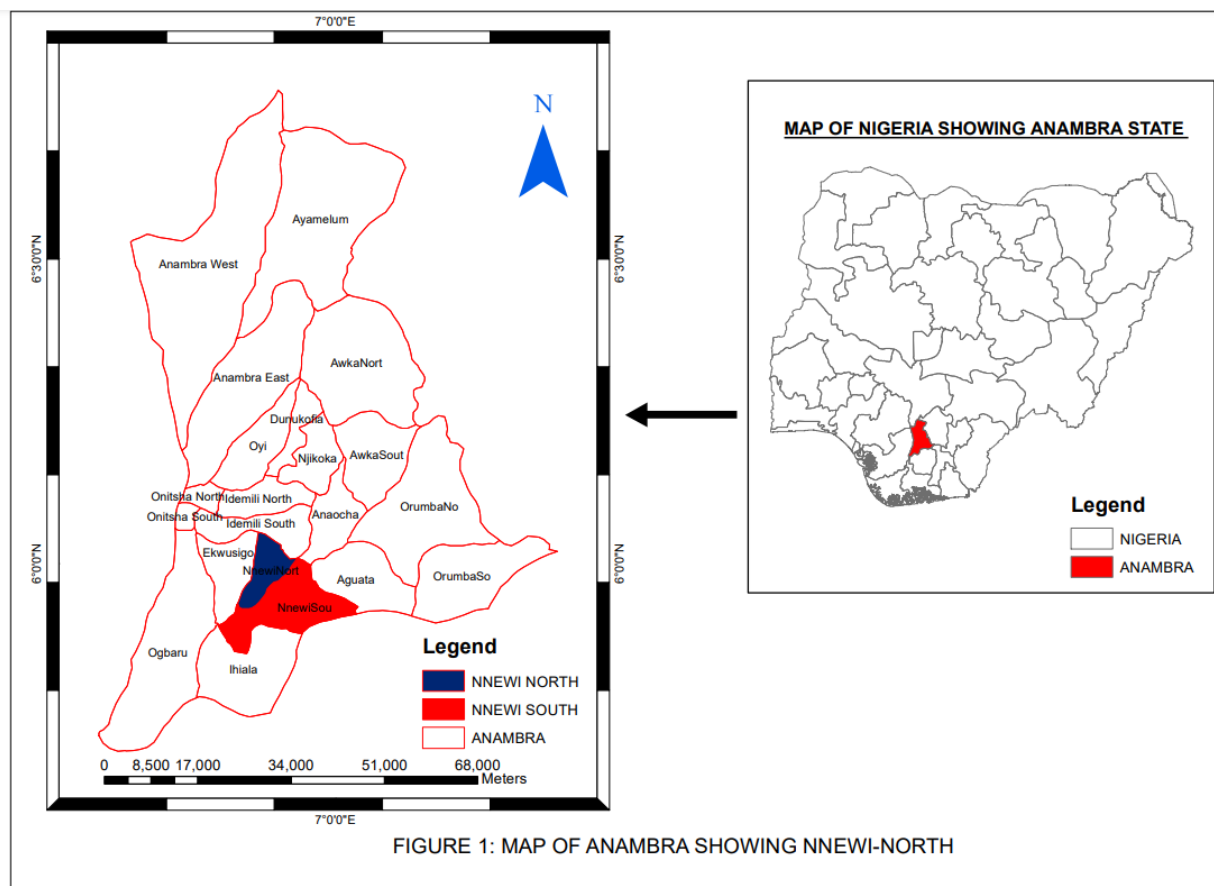
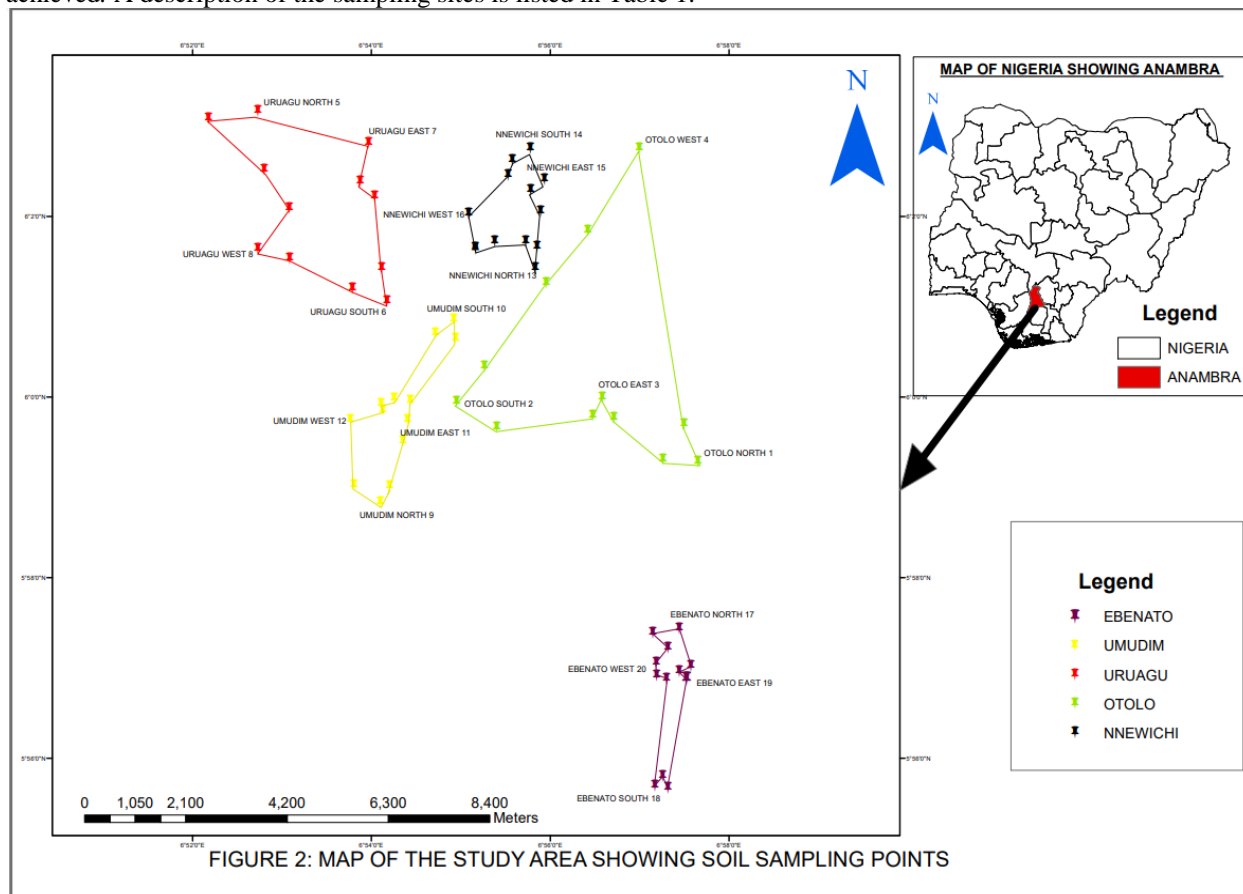


FIGURE 1: MAP OF ANAMBRA SHOWING NNEWI-NORTH

Sample Collection and Preservation

Soil samples were collected from four areas in Nnewi-North Local Government Area. The four areas include Otololo, Uruagu, Umudim, and Nnewichi (Figure 2). Control soil samples were collected from Ebonato. Triplicate samples (15-20cm depth), from each study site and control site were collected ten meters apart in a straight form using a stainless steel knife and pooled into polythene bags labelled with site locations. The soil samples were collected twice in rainy and dry seasons. In the laboratory, the soil samples were mixed thoroughly to obtain a composite sample for each site. The composite samples were air-dried for seventy-two hours at room temperature, ground in a glass mortar with pestle and sieved through 2.0mm sieve, further pulverized to a fine powder and passed through 0.5mm sieve for the total metal content determination [14]. This ensured that the analyte is not lost and good results were achieved. A description of the sampling sites is listed in Table 1.



Preparation of Samples for Metal Determination

5.0g of soil sample was digested with 10cm³ of hydrogen peroxide for 10–15 min to oxidize any organic matter. After cooling, 15ml mixture of aqua regia was added and boiled gently on hot plate in a fume chamber for about 40mins [15]. After digestion, the digest was filtered into 50ml volumetric flask and diluted to volume with distilled water.

Analysis of Certified Reference Material (ERM –CC 141)

Accuracy was assessed by analyzing three (3) replicates of certified reference materials, soil samples CC-141, obtained from European Commission, Joint Research Centre(JRC) Belgium.

Determination of pH in Soil (H₂O)

The pH of the soil samples was determined according to [16] at a ratio of 1:2.5. Ten grams (10.0g) of the air dried sample were weighed into 100cm³ beaker and 25cm³ of distilled water was added and stirred. The suspension was allowed to stand for 30mins with occasional stirring with glass rod. The pH of the supernatant suspension was then determined using a pH meter.

Table 1 Description/Identification of Sampling Sites

S/N	Areas	Code	Sample site address	The Coordinates	Number of samples
1	Otolo	OTN	Otolo North	05°59.282 ¹ N/06°57.656 ¹ E	9
2	Otolo	OTS	Otolo South	06°00.342 ¹ N/06°55.264 ¹ E	9
3	Otolo	OTE	Otolo East	05°59.768 ¹ N/06°56.716 ¹ E	9
4	Otolo	OTW	Otolo West	06°01.258 ¹ N/06°55.958 ¹ E	9
5	Uruagu	URN	Uruagu North	06°02.512 ¹ N/06°52.800 ¹ E	9
6	Uruagu	URS	Uruagu South	06°01.059 ¹ N/06°54.175 ¹ E	9
7	Uruagu	URE	Uruagu East	06°02.225 ¹ N/06°54.038 ¹ E	9
8	Uruagu	URW	Uruagu West	06°01.575 ¹ N/06°56.032 ¹ E	9
9	Umudim	UMN	Umudim North	05°59.009 ¹ N/06°54.209 ¹ E	9
10	Umudim	UMS	Umudim South	06°00.860 ¹ N/06°54.927 ¹ E	9
11	Umudim	UME	Umudim East	05°59.662 ¹ N/06°53.915 ¹ E	9
12	Umudim	UMW	Umudim West	05°59.928 ¹ N/06°54.594 ¹ E	9
13	Nnewichi	NNN	Nnewichi North	06°01.647 ¹ N/06°55.738 ¹ E	9
14	Nnewichi	NNS	Nnewichi South	06°02.462 ¹ N/06°55.530 ¹ E	9
15	Nnewichi	NNE	Nnewichi East	06°01.654 ¹ N/06°55.165 ¹ E	9
16	Nnewichi	NNW	Nnewichi West	06°02.210 ¹ N/06°55.823 ¹ E	9
17	Ebenato	EBN	Ebenato North	05°57.440 ¹ N/06°57.446 ¹ E	9
18	Ebenato	EBS	Ebenato South	05°55.675 ¹ N/06°57.318 ¹ E	9
19	Ebenato	EBE	Ebenato East	05°56.962 ¹ N/06°57.446 ¹ E	9
20	Ebenato	EBW	Ebenato West	05°56.886 ¹ N/06°57.305 ¹ E	9

III. RESULTS AND DISCUSSIONS

The results of the analysis of the ERM-CC141 reference materials are listed in Table 2. The results showed good agreement with certified values indicating that the sample preparation method adopted for this work is reliable and accurate.

The pH of the soil ranged from 6.00-7.11 with the mean value of 6.52±0.39, moving from moderately acidic (6.24±0.19) to neutral (6.80±0.20) (Table 3 and 4). Generally, the soil pH during the dry season were slightly acidic with the soil pH of Uruagu being the highest with a value of 6.46±0.64 across the study sites (Table 4) whereas Otolo with a soil pH of 6.00±0.50 was the lowest during the dry season. The trend in this result showed that acidity increases with decrease in soil moisture. The soils were acidic during the dry season and as the rainy season increases, pH values also increased even reaching to moderately alkaline. This trend can be attributed to the fact that increased moisture in the soil dissolves more soluble salts for instance, exchangeable Ca²⁺ and Mg²⁺ which has the potential to increase pH to a neutral value (6.00-7.11) thus, reducing acidity [17].

Table 2 Result of the Analysis of the Certified Reference Material (ERM –CC 141) based on Aqua Regia Extractable Content

METAL	CERTIFIED VALUE(µg/g)	EXPERIMENTAL VALUE±sd(µg/g)
Zn	50.00	47.50±2.16
Pb	32.20	32.50±3.53
Ni	21.90	21.80±2.82
Cu	12.40	12.15±0.69
Cd	0.25	0.29±0.14

Statistical Summary of Heavy Metals Concentrations ($\mu\text{g/g}$) in the soils during rainy, dry, and the studied area are summarized in Tables 3, 4, and 5 respectively. The concentrations of the metals in the studied area were found to be higher than the concentrations of the metals in control soils (Table 3 and 4) during both the raining and dry season. The mean abundance of the metals in the soils of Nnewi-North is in the order $\text{Mn} > \text{Zn} > \text{Pb} > \text{Cr} > \text{Cu} > \text{Ni} > \text{Cd}$ (Table 5). Lead, Manganese and Nickel were more abundant during the dry season whereas Zinc, Chromium, Copper and Cadmium were more abundant during the rainy season.

Table 3 Statistical Summary of Heavy Metals Concentrations ($\mu\text{g/g}$) in the Soils of the Studied Area During Rainy Season

Metal	Location					
	Otolo	Uruagu	Umudim	Nnewichi	Total Mean	Ebenato Control
Pb						
mean\pmsd	32.73 \pm 9.01	34.14 \pm 11.80	34.10 \pm 9.76	36.14 \pm 5.88	34.28 \pm 1.40	11.01 \pm 3.81
Range	24.50-41.60	20.00-45.60	24.50-48.66	28.80-47.83		8.30-14.25
Mn						
mean\pmsd	94.47 \pm 24.50	118.22 \pm 52.14	59.70 \pm 29.45	73.85 \pm 48.30	86.56 \pm 25.48	29.14 \pm 9.07
Range	67.60-160.93	55.93-190.93	25.93-100.93	34.26-139.26		21.06-38.10
Zn						
mean\pmsd	33.73 \pm 4.05	65.40 \pm 0.79	30.00 \pm 1.31	53.54 \pm 3.88	45.67 \pm 16.73	10.82 \pm 3.38
Range	22.83-45.16	28.33-93.50	7.33-48.83	22.50-101.83		6.33-15.77
Ni						
mean\pmsd	1.54 \pm 0.06	2.90 \pm 0.45	1.48 \pm 0.28	1.42 \pm 0.09	1.83 \pm 0.71	1.10 \pm 0.28
Range	0.90-2.20	0.90-8.50	1.10-2.10	1.10-1.85		0.90-1.35
Cr						
mean\pmsd	23.91 \pm 11.45	51.04 \pm 15.61	14.80 \pm 6.78	39.60 \pm 5.90	32.34 \pm 16.14	7.615 \pm 0.97
Range	10.00-46.60	10-136.66	3.33-28.33	16.66-81.66		5.00-8.86
Cu						
mean\pmsd	7.00 \pm 3.88	28.00 \pm 0.40	7.00 \pm 2.86	15.54 \pm 8.28	14.39 \pm 9.93	3.05 \pm 1.13
Range	1.50-25.30	6.80-78.30	2.66-18.16	5.80-34.80		1.50-4.60
Cd						
mean\pmsd	1.73 \pm 0.22	2.10 \pm 0.04	1.91 \pm 0.10	2.03 \pm 0.10	1.94 \pm 0.16	0.925 \pm 0.95
Range	1.50-2.00	1.80-2.50	1.70-2.20	1.80-2.20		0.23-1.70
pH						
(1:2.5)	6.77\pm0.41	7.11 \pm 0.90	6.70 \pm 0.50	6.64 \pm 0.84	6.80 \pm 0.20	8.43 \pm 0.74
Range					6.64-7.11	

Table 4 Statistical Summary of Heavy Metals Concentrations ($\mu\text{g/g}$) in the Soils of the Studied Area During Dry Seasons

Metal	Location					
	Otolo	Uruagu	Umudim	Nnewichi	Total Mean	Ebenato Control
Pb						
mean\pmsd	56.45 \pm 1.45	28.63 \pm 13.63	39.99 \pm 10.62	44.16 \pm 11.78	42.31 \pm 11.48	12.42 \pm 8.13
Range	30.00-81.70	17.70-56.60	13.33-91.67	13.33-70.00		5.00-18.33
Mn						
mean\pmsd	98.42 \pm 21.20	126.78 \pm 6.44	107.52 \pm 2.86	129.59 \pm 23.08	115.58 \pm 15.06	37.83 \pm 7.81
Range	64.26-144.2	70.90-177.60	85.43-135.10	70.43-164.26		29.82-45.70
Zn						
mean\pmsd	34.06 \pm 8.22	56.23 \pm 18.47	24.69 \pm 3.29	54.67 \pm 13.90	42.41 \pm 15.55	23.66 \pm 2.70
Range	11.83-52.33	17.83-89.83	11.83-40.16	26.33-137.17		21.08-30.05
Ni						
mean\pmsd	2.56 \pm 0.88	2.40 \pm 1.08	1.65 \pm 1.66	3.85 \pm 2.94	2.61 \pm 0.89	1.43 \pm 0.60
Range	1.00-5.00	0.77-3.33	0.27-3.50	1.28-8.60		0.50-2.10
Cr						
mean\pmsd	10.41 \pm 3.48	11.95 \pm 2.71	8.56 \pm 0.55	13.30 \pm 0.80	11.06 \pm 2.04	7.36 \pm 0.98
Range	5.16-16.67	6.80-19.80	4.00-5.33	8.30-17.16		3.33-10.00
Cu						
mean\pmsd	3.31 \pm 0.61	7.58 \pm 4.82	3.31 \pm 0.84	4.56 \pm 2.02	4.69 \pm 2.01	2.32 \pm 1.86
Range	2.00-5.50	2.00-78.30	1.17-5.33	1.50-9.00		0.50-4.17
Cd						
mean\pmsd	1.11 \pm 1.32	0.15 \pm 0.02	0.14 \pm 0.04	0.19 \pm 0.06	0.39 \pm 0.44	0.15 \pm 0.00
Range	ND-5.67	ND-0.23	0.09-0.22	0.03-0.34		0.14-0.16
pH (1:2.5)	6.00 \pm 0.50	6.46 \pm 0.64	6.18 \pm 0.66	6.33 \pm 1.03	6.24 \pm 0.19	6.62 \pm 0.26
Range					6.00-6.46	

Table 5 Statistical Summary of Heavy Metals Concentrations ($\mu\text{g/g}$) in the soils of the Studied Area

Metal	Mean\pmsd	Range
Pb	38.30 \pm 5.54	13.33-91.67
Mn	101.07 \pm 16.18	25.93-190.93
Zn	44.04 \pm 15.96	7.33-137.17
Ni	2.22 \pm 0.50	0.27-8.60
Cr	21.69 \pm 8.93	3.33-136.66
Cu	9.57 \pm 5.96	1.17-78.30
pH (1:2.5)	6.52 \pm 0.39	6.00-7.11

The Pb concentration from the studied area ranged from 13.33-91.67 $\mu\text{g/g}$ dry weight (Table 3 & 4) with a mean value 38.30 \pm 5.54 $\mu\text{g/g}$ dry weight (Table 5). The highest and lowest concentration of 91.67 and 13.33 $\mu\text{g/g}$ dry weight were respectively recorded during the dry season. Pb content was more abundant during the dry season with a mean value of 42.31 \pm 11.48 compared to raining season with a mean value of 34.28 \pm 1.40 (Table 3 & 4). Ebenato, the control site recorded the least mean value of 11.01 \pm 3.81 during the raining season compared to dry season with a mean value of 12.42 \pm 8.13 $\mu\text{g/g}$ dry weight.

The highest lead contents from Umudim East could be attributed to the presence of lead batteries and chemical industries in the area which could affect the level of lead in the soil. The area is close to a clustered mechanical and automobile fitting workshop, where automobile repair and related activities (disposal of used batteries) are carried out. Various authors have identified sources of lead to industrial effluents [18], paint flakes [19], refuse dumps [20] and electronic wastes [21].

Manganese has the highest concentration range for all the heavy metals examined in the soil samples from Nnewi-North; varying considerably from 25.93-190.93 $\mu\text{g/g}$ dry weight (Table 3 & 4). The mean value recorded was 101.07 \pm 16.18 $\mu\text{g/g}$ dry weight and the highest concentration of 190.93 $\mu\text{g/g}$ dry weight was recorded during rainy season in Uruagu (Table 3). The lowest concentration was found during rainy season also but in Umudim with a concentration of 25.93 $\mu\text{g/g}$ dry weight. (Table 3). In all, the control site (Ebenato) had the least Mn values during the rainy and dry seasons (Table 3 & 4). The highest concentrations of 190.93 $\mu\text{g/g}$ dry weight obtained from Uruagu could be attributed to the use of manganese as an alloying constituents in fabrication/welding of industrial machines, as fuel-oil additives, smoke inhibitors, and pigments for paints used in spraying of vehicles along the various sampling points [22]. The highest concentrations of Mn, Cu and Cr were found within Uruagu community, probably because Nkwo Nnewi market where a lot of anthropogenic and commercial activities take place is located in Uruagu community.

Zinc concentration from the studied area ranged from 7.33-137.17 $\mu\text{g/g}$ dry weight (Table 3 & 4). The mean value recorded was 44.04 \pm 15.96 $\mu\text{g/g}$ dry weight and the highest concentration of 137.17 $\mu\text{g/g}$ dry weight was recorded during dry season in Nnewichi (Table 4). The lowest concentration was found during rainy season in Umudim with a concentration of 7.33 $\mu\text{g/g}$ dry weight. (Table 3). Sampling locations in Nnewichi East are mainly cultivated farmlands and highest concentrations recorded here could be attributed to agricultural chemicals or materials such as impurities in fertilizers, pesticides and wastes from poultry production. [23].

The Zn contents of 7.33-137.17 $\mu\text{g/g}$ dry weight obtained in this study were higher than the normal concentration range of 17-125 $\mu\text{g/g}$ dry weight for top surface soils suggested by [24]. A lower ranged value of 10-85 $\mu\text{g/g}$ dry weight than the value obtained in this study have also been reported by [25] in their study of cultivated farmlands in the Bida City. The heavy metals concentrations are below the European Commission and WHO/FAO's recommended threshold values of both 300 $\mu\text{g/g}$ as reported by [26] and within a soil level range of 0-250 $\mu\text{g/g}$ classified as being typical of no contamination by the UK Department of the Environment for the recreational and Agricultural uses [27].

The Chromium contents in the examined soil samples from Nnewi North varied widely between 3.33-136.66 $\mu\text{g/g}$ dry weight (Table 3 & 4) with the highest concentration of 136.66 $\mu\text{g/g}$ dry weight (Table 3) seen in Uruagu during the rainy season while the lowest concentration of 3.33 $\mu\text{g/g}$ was recorded in Uruagu during the raining season also. The highest concentration of 136.66 $\mu\text{g/g}$ dry weight recorded in Uruagu south may probably be ascribed to the industrial waste water from paper and paint industry located along the sampling points. The mean value of 21.69 \pm 8.93 dry weight (Table 5) were higher than the mean value of 4.86 \pm 2.21 $\mu\text{g/g}$ reported by [28] in their study on phytoremediation of contaminated soils from Challawa industrial estate, kano State, Nigeria, but lower than the allowable limit of 65 $\mu\text{g/g}$ set by WHO, 2000.

As explained by [29] with increasing pH their solubility tends to increase. This explains why the Cr values in the soils were relatively much higher during the rainy season (where the pH values were more neutral to alkaline in

concentration). The finding here is similar to the report of [30] whose report showed that Cr in the soils was relatively higher in alkaline soils than in acid solutions in crude oil contaminated soils remediated with mushroom plants. Chromium concentrations range between 1 and 3000mg/kg in soil [31].

The nickel concentration from the study area ranged from 0.27-8.60 $\mu\text{g/g}$ dry weight (Table 3 & 4). The mean value recorded was 2.20 \pm 0.50 $\mu\text{g/g}$ dry weight and the highest concentration of 8.60 $\mu\text{g/g}$ dry weight was recorded during dry season in Nnewichi as against the lowest concentration of 0.27 $\mu\text{g/g}$ dry weight in Umudim (Table 4).

The highest concentrations of 8.60 $\mu\text{g/g}$ dry weight obtained from Nnewichi South could be ascribed to the use of nickel as an alloy in fabrication/welding of industrial machines and as an additive in batteries and plastics littered along the sampling points. A report by [26] had a higher mean range values of 54.03-57.77 $\mu\text{g/g}$ dry weight of nickel than obtained in this study. However, the mean values obtained in this study were higher than the mean values of 1.9 \pm 0.96 $\mu\text{g/g}$ reported by [25] in their study of heavy metal levels around ceramics and pharmaceutical industrial sites in Niger State, Nigeria. The heavy metals concentrations are below the European Commission and WHO/FAO's recommended threshold values of 75 and 50 $\mu\text{g/g}$ as reported by [26].

The copper concentration from the study area ranged from 1.17-78.30 $\mu\text{g/g}$ dry weight (Table 3 & 5). The mean value recorded was 9.57 \pm 5.96 $\mu\text{g/g}$ dry weight and the highest concentration of 78.30 $\mu\text{g/g}$ dry weight was recorded during rainy season in Uruagu (Table 3). The lowest concentration was found during dry season in Umudim with a concentration of 1.17 $\mu\text{g/g}$ dry weight (Table 4). The highest concentrations of 78.30 $\mu\text{g/g}$ dry weight obtained from Uruagu North could be ascribed to the use of copper metal in fabrication/welding or painting of industrial machines, production of various auto parts and passage of industrial/ domestic waste water along the sampling points [32]. The area is known predominantly for industrial activities where repair of car brakes and tyres, car fitting occur. Copper could also be released from brakes of vehicles that ply the road every day [32]. The high concentrations in some locations could be as a result of burnt vehicles along the major roads as copper is commonly found in electrical wirings, engine wear, brake linings [33].

The cadmium concentrations varied considerably across the various seasons with three sites in dry season having cadmium contents that were too low to be detectable. The cadmium concentration from the studied area ranged from ND-5.67 $\mu\text{g/g}$ dry weight Table (3 & 4). The mean value recorded was 1.16 \pm 0.17 $\mu\text{g/g}$ dry weight and the highest concentration of 5.67 $\mu\text{g/g}$ dry weight was recorded during dry season in Otolu South (Table 4). The highest concentrations of 5.67 $\mu\text{g/g}$ dry weight obtained from Otolu South could be as a result of industrial effluent from auto battery and petrochemical products manufacturing plant located along the sampling points.

The trend in the results shown in Tables 3 & 4 shows that the mean value of Cd was lower in the dry season than in raining season. This implied that reducing the soil moisture content also reduced the availability of Cd in the soils. This suggest that in the dry season, Cd does not portend any significant hazard. However, it is important to note that industrial activities have generally increased the concentration of Cd in the soils especially during the rainy season [34].

Comparison of Study Area with soil quality criteria/guidelines for Agriculture

The mean heavy metal contents from this study were compared with criteria from other Countries, European Commission and WHO/FAO upper limit values for soil quality guidelines specified for environmental protection and human health. All metals analyzed in this study were found to be lower than the soil quality guidelines stipulated for some countries except for cadmium whose mean value (1.16 $\mu\text{g/g}$) exceeded the 0.3 $\mu\text{g/g}$ and 0.6 $\mu\text{g/g}$ by [47] and [35] guidelines respectively (Table 6). The toxic effects of these metals on the environment at this level may be regarded as significant. The farmlands are mainly within the vicinity of manufacturing industries and some experience high vehicular emission.

Assessment of Pollution Indices in Soil

The range and mean of the Igeo of the study area were respectively 0.83-1.34 and 1.11 for Pb, 0.74-1.29 and 1.00 for Mn, 0.08-1.23 and 0.69 for Zn, 0.10-0.48 and 0.34 for Ni, 0.06-1.49 and 0.85 for Cr, 0.36-2.14 and 1.04 for Cu, 0.34-0.80 and 0.50 for Cd and these were in the order of Ni<Cd<Zn<Cr<Mn<Cu<Pb (Table 7). The area is categorized uncontaminated to moderately contaminated soils [36]. Pb and Cu are in the class of moderately polluted and this can be due to the release of Pb into the environment from the Pb-acid battery plants in the area as well as several other metal fabrication plants such as welding, painting and automobile fittings and repairs that lead to the discharge of copper into the environment [12, 32].

The mean of the Pollution Index is 3.26, 3.02, 2.56, 1.74, 2.90, 3.54 and 2.15 for Pb, Mn, Zn, Ni, Cr, Cu and Cd respectively and these are in the category of low contamination to considerable contaminated soils [37]. Pb and Cu are in the class of moderately polluted and this can be due to burnt vehicles along the major roads as copper is commonly found in electrical wirings, engine wear, brake linings [33] as well as release from brakes of vehicles that ply the road every day [32]. PLI value ranged from 1.69-3.23(Table 7) with a mean value of 2.61 indicating deterioration of site quality [38].

Table 6 Soil Quality Guidelines for Some Countries Compared to Levels ($\mu\text{g/g}$) Obtained in this Study

Country	Pb	Mn	Zn	Ni	Cr	Cu	Cd	Reference
Kwali, Nigeria	3.98	-	8.39	7.24	-	5.35	0.07	[41]
Republic of Korea, Agriculture	120	-	80	100	-	100	10	[42]
Denmark, Agriculture	40	-	500	30	-	500	5	[43]
Canada, Agriculture	70	-	200	50	-	63	10	[44]
UK, Agriculture	40	-	70	29	-	20.10	1.00	[45]
Canada, Residential	140	200	200	50	-	63	10	[44]
France	100		200	50	-	100	-	[46]
Taiwan	55		200	120	-	150	-	[46]
EU	300		300	75	100	100	-	[47]
FAO/WHO	50		300	50	-	100	0.3	[48]

Table 7 Geoaccumulation Index, Pollution Index and Pollution Load Index

Metal	Geoaccumulation Index		Pollution Index		Pollution Load Index	
	range	mean	range	mean	PLI	mean PLI
Pb	0.83-1.34	1.11	2.67-3.80	3.26	3.23	2.61
Mn	0.74-1.29	1.00	2.50-3.66	3.02	2.99	
Zn	0.08-1.23	0.69	1.59-3.53	2.56	2.42	
Ni	0.10-0.48	0.34	1.22-2.09	1.74	1.69	
Cr	0.06-1.49	0.85	1.56-4.20	2.90	2.69	
Cu	0.36-2.14	1.04	1.92-6.61	3.54	3.08	
Cd	0.34-0.80	0.50	1.90-2.61	2.15	2.12	

IV CONCLUSION

The metal contamination state in farmlands is very important in monitoring heavy metals health of populace as plants can directly take up metals from contaminated soils and accumulate such metals. The levels of Pb, Ni and Mn in soils were higher in dry season whereas that of Zn, Cu, Cr and Cd were higher in raining season. These heavy metals could be attributed to the presence of chemical industries in the area and their use as an alloying constituent in fabrication/welding of industrial machines, fuel-oil additives, and smoke inhibitors, production of various auto parts and passage of industrial / domestic waste water along the sampling points [18], [22] and [32]. All the heavy metals analyzed in this study were found to be within acceptable limits of soil quality criteria/guidelines for agriculture stipulated by some countries except for cadmium whose value exceeded the maximum of $0.3\mu\text{g/g}$ by FAO/WHO guideline [39]. With these levels, the possibility of food crop being contaminated may likely be experienced in the nearest future as plants are known to absorb metals from the soil which have adverse effects on those who consume such food [40]. The toxic effects of these heavy

metals on the environment of the studied area may be regarded as significant and as the area grows industrially, there is need to continuously monitor the place to avoid an outbreak of metal poisoning.

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