International Journal of Mathematics and Physical Sciences Research ISSN 2348-5736 (Online)
Vol. 8, Issue 1, pp: (22-28), Month: April 2020 - September 2020, Available at: www.researchpublish.com

Ecological risk assessment of heavy metals in road side soils of Onitsha South Local Government Area, Anambra Nigeria

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Abstract: **The concentrations of heavy metals (Mn, Ni, Cr, Cu, Zn, Pb and Fe) in the soils of Onitsha South Local Government area of Anambra Nigeria were investigated and the potential ecological risk of heavy metals pollution evaluated. Atomic Absorption Spectrophotometer (AAS) was employed to analyze the heavy metals concentrations in the studied area. Lars Hakanson's potential ecological hazards index method was used to evaluate the heavy metals potential ecological risk in soils. The results from heavy metal concentration revealed that average concentrations of the metals investigated were as follows: Mn 1.39 mgkg^{-1}, Ni 1.24 mgkg^{-1}, Zn 1.24mgkg^{-1}, Cr 9.08 mgkg^{-1} , Cu 0.80mgkg^{-1}, Pb 0.52mgkg^{-1}and Fe 96.37mgkg^{-1} in the wet season while the following average values were recorded in dry season: Mn 1.60mgkg^{-1}, Ni 1.83mgkg^{-1}, Zn 2.45mgkg^{-1}, Cr 11.54mgkg^{-1}, Cu 1.22mgkg^{-1}, Pb 0.50mgkg^{-1} and Fe 143.54mgkg^{-1}. The concentrations of Fe in the soils were relatively high (96.368- 143.54 mgkg^{-1}) for both seasons. The values obtained from the heavy metals concentrations with the exception of Cr and Fe revealed that the soils were not heavily contaminated by these heavy metals. Based on Lars Hakanson's potential ecological index method, Cr had considerable ecological risk in soils in the wet season with location 8 had highest risk while in the dry season Cr moderately polluted the area with location 7 having considerable ecological risk. The other heavy metals had slight ecological risk. Ecological risk of total heavy metals pollution was moderate. Correlation analysis suggest that heavy metals pollution source for Mn, Ni, Pb, Cr, Cu, and Zn may be mainly derived from metal processing, electroplating industries, industrial wastewater, agricultural activities and domestic sewage.**

Keywords: **Heavy metal, Potential ecological risk, Pollution source, Onitsha South L.G. A.**

1. INTRODUCTION

Increased growth of industrial activities, especially in urban cities, is one of the main sources of toxic substances in Nigeria (Tesleem *et al*., 2018). Heavy metal is one of the important pollutants in the environment as a result of both natural and anthropogenic activities that go on in such industrialized cities. Such activities that form the major sources of soil contamination with heavy metals include solid waste disposal, sludge applications, vehicular exhaust and agricultural and industrial activities such could cause an increased heavy metal uptake by food crops grown on such contaminated soils (Beibei *et al.*, 2017). Heavy metals have a potential to contaminate soil, which can be dispersed and accumulated in plants and animals, and taken in by humans through consumption (Wang, 2012). So heavy metals contamination has been a worldwide environmental concern with its potential ecological effect (Liu *et al.*, 2009).

Onitsha South Local Government Area (hence forth referred to as Onitsha South L.G.A) is located in the East part of Nigeria housing one of the foremost markets in West Africa, which has led to her being one of the most urbanized areas of Nigeria. This part of country is characterized by great intensity of industrialization, commercialization, great accumulation of domestic sewages, heavy industry and transportation, which cause high environmental contamination by heavy metals. Therefore, the chemical composition of soils in this area depends mainly on the degree of human impact

(Baran *et al*., 2016). Within Onitsha South LGA, a lot of industrial plants, commercial activities, human population etc., are located. It is important to note that properties of toxic elements, that is, their concentrations, non-biodegradability and toxicity are the major reason for their monitoring in such environment. Strong attention should be, therefore, put to ecological state of contaminated soils which is one of the main reasons for this research.

2. MATERIALS AND METHODS

2.1 Description of the Study Area

Onitsha South Local Government Area is located between latitudes 06^{o} 07'12' N and 06^{o} 9' 36'N and longitude 06^{o} 45'54'E and 06^{o} 47' 42'E covering an area of 36.12Km^{2}. It is bounded by Onitsha North local government area and in the east Ogbaru L.G.A in the south and in the west by River Niger (Fig 1). Onitsha is the largest urban city in Anambra state with a population of about 561 066 according to 2006 census. It is also a major commercial town east of the Niger (Ejikeme *et al*., 2014). The climate is classified as tropical region. The climate here is classified as Aw by the Köppen-Geiger system. The average annual temperature in Onitsha is 27.0 °C with rainfall averaging 1828 mm with monthly relative humidity being at least 86%. The area stands on a low-lying terrain with altitude ranging from 57m to 59 m above sea level. The area is characterized by medium annual temperature, high rainfall, high evapo-transpiration and high relative humidity, which makes it to be classified as humid tropical region (Akanni, 1992). The soil type of Onitsha south L.G.A is hydromorphic (Ejikeme *et al*., 2014).

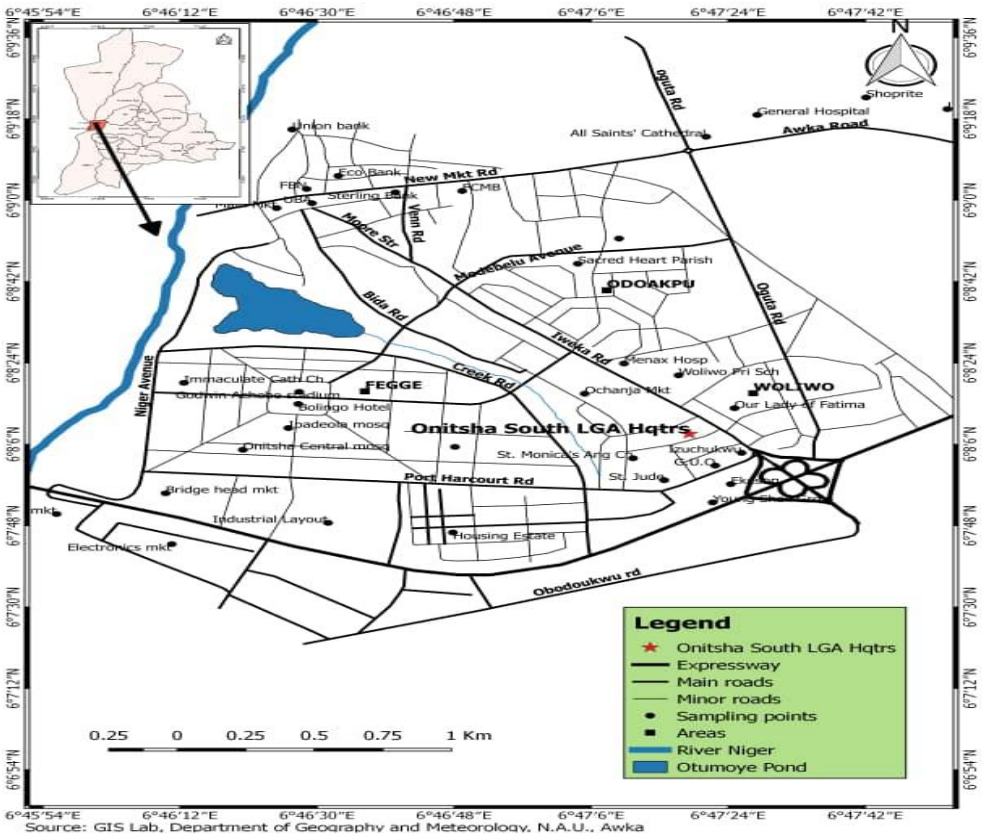

Figure 1: Map of Onitsha South Local Government Area of Anambra State

2.2 Soil sampling:

Soil samples from roadside in eleven streets (Odoakpu, woliwo and Fegge areas) were covered. For this study, a total of 55 soil sampling sites were selected in each season; rainy season (from June to August) and dry season from December to February). Each topsoil sample was collected from the top layer (0 - 10 cm) of the 11 chosen streets. These 11 locations were chosen based on areas which are heavily loaded with activities both commercial and industrial. Approximately 1 kg of soil was collected from 5 different points in each location maintaining at least 500m distance for the two seasons. The collected samples were then mixed, using the quartering method. All soil samples were air-dried, sieved to <650µm, homogenized, and stored in a well labeled polythene bags prior to laboratory analysis and processing.

2.3 Soil samples analysis:

Soil samples were analyzed for pH values,, moisture content and the concentrations of main heavy metal pollutants, such as Mn, Ni, Cu, Pb, Zn, Cr and Fe were analyzed.

The soil pH was determined using a 1:5 soil weight/deionized water volume ratio by a pH meter model S399590. The pH meter was standardized using buffer pH 4.0 and 7.0. The moisture content was estimated using an electric oven at a temperature of 105^0c using weight difference method. The digestion for the total metal determination was carried out in polytetrafluoroethylene (PTFE) beaker. The dried soil sample (1g) was accurately weighed into a clean and dry Teflon beaker. A mixture of 5mL HF and 5mL aqua-regia (all analar grades) were added and the acids-soil mixtures digested in a water bath at 100^0C for 1.5h with subsequent addition of second sets of 5mL HF and 5mL aqua-regia and this lasted for another 1.5h for complete digestion. The resulting solutions were cooled at room temperature, followed by careful addition of saturated boric acid (H_3BO_3). The boric acid was to form complex with any residual HF, which would otherwise attack glass wares. The digested solutions were filtered into 100ml standard flasks using Whatman No. 1 filter paper. The solutions were made up to mark of 100ml with deionized water in the container after rinsing with deionized water (Sastre *et al.*, 2002). This was then stored for the AAS analysis. The digestion processes were repeated for all the other samples three times each. The blank was also prepared. Both the digested solutions and the blank were analyzed for the presence of the following metals, Fe, Mn, Cr, Cu, Ni, Zn and Pb using BUCK 211 FAAS.

2.4 Potential ecological risk assessment method

The potential ecological risk index (PEI) method, established by Hakanson (1980), is based on the principles of sedimentology. It is widely used by scholars to assess the pollution and potential ecological risk of heavy metal in soil. This method not only accounts for the content of heavy metals in soil, but also connects the ecological and environmental effects of heavy metals to environment toxicology (Li, *et al.*, 2003; Lin *et al.*, 2016). According to Lars Hakanson, The potential ecological risk index is related to the individual pollution coefficient, the heavy metal toxicity response coefficient, and the potential ecological risk individual coefficient, and is expressed as follows (Beibei *et al.*, 2017);

$$E^i_r = T^I_r * C^i_f \quad (1)$$

$$C^i_f = C_A{}^i / C_o{}^i \quad (2)$$

$$R = \sum_{i=1}^{m} E^i_r = \sum_{i=1}^{m} T^i_r \bullet C^i_f = \sum_{i=1}^{m} T^i_r \frac{C^i}{C^i_n} \quad (3)$$

Where E^i_r is potential risk of individual heavy metal. T^I_r is toxic-response factor for a given heavy metal, which reflects toxic level and environmental sensitivity of the heavy metal. C^i_f is contamination factor. $C_A{}^i$ is actually measured concentration of the heavy metal in the sediment. $C_o{}^i$ is reference value of heavy metal concentration in sediment.

For T^I_r, the Hakanson recommended values of Mn, Ni, Cr, Cu, Zn, Pb and Cd are 1, 5, 2, 5, 1, 5 and 30, respectively (Hakanson, 1980). For *Ci*0, soil background values for Onitsha South were used as a reference, for both wet and dry seasons respectively. Five levels of E^i_r are defined by Hakanson, as shown in Table 1.

Table 1: Ecological risk levels of a single metal pollution (Hakanson, 1980).

E^i_r	*Grades of ecological risk of single metal*	R_i	*Grades of potential ecological risk of the environment*
$E^i_r<40$	*Light*	$R_i<150$	*Light*
$40\leq E^i_r<80$	*Moderate*	$150\leq R_i<300$	*Moderate*
$80\leq E^i_r<160$	*Heavy*	$300\leq R_i<600$	*Heavy*
$160\leq E^i_r<320$	*Severe*	$R_i\geq 600$	*Severe*
$320\geq$	*Very severe*		

2.5 Correlation analysis

The correlation analysis was selected to identify the possible pollution sources (Guo *et al.*, 2005) and the data in this work were performed with SPSS 12.0 for Windows (Liao *et al.*, 2008).

3. RESULTS AND DISCUSSION

3.1 Moisture content and pH of metals

The moisture contents and the pH of the soil samples for the study are shown in Table 2.

Table 2: Moisture Content and the pH of the soil samples for rainy and dry seasons respectively.

Location	Moisture content		pH	
	Rainy season	Dry season	Rainy season	Dry season
1	1.350	0.030	6.5	6.9
2	1.110	0.400	6.3	6.0
3	1.350	0.300	6.3	6.7
4	0.810	0.100	6.4	7.0
5	1.100	0.100	6.4	6.7
6	1.610	0.600	6.4	6.7
7	1.060	0.700	6.3	6.1
8	1.200	0.800	6.4	6.6
9	1.220	0.220	6.2	6.7
10	1.710	0.120	6.4	6.6
11	1.400	0.900	7.0	6.9

The results as presented on Table 2 showed no significant difference in the pH of the soil samples for both rainy and dry seasons though the soil is slightly acidic ranging between 6.0 and 7.0 which is the pH considered suitable for plant growth and development (Yi-Yan *et al*., 1980). The average pH during the rainy season is 6.4 while the average in dry season is relatively lower (6.6), this might be due to less intake of dissolved ions from flood rain water. The moisture content was in accordance with the seasons, with rainy season having relatively higher values than dry season (as for this research, dry season is between December to February while rainy season is between May and June). There was no observable trend between pH and the soil moisture content for both wet and dry seasons.

3.2 Mean metal concentration in rainy and dry season

Table 3: Average concentrations (mg/kg) of heavy metals in soil during wet and dry seasons

heavy metals	dry season	wet season	Average concentration for wet and dry seasons	WHO/FAO Maximum permissible level of heavy metals in the soil (mg/kg)
Mn	1.599	1.391	1.495	2000 (200-3000)
Ni	1.831	1.238	1.535	50 (5-500)
Zn	2.452	1.242	1.847	300 (50-300)
Cr	11.544	9.084	10.314	100 (10-200)
Cu	1.215	0.796	1.006	100 (2-250)
Pb	0.500	0.519	0.510	100(2-20)
Fe	143.543	96.368	119.956	50 000

Table 3 revealed that the order in mean concentrations of the heavy metals in mg/kg in the soil samples for dry season and wet season was in descending order Fe (119.956±3.358) > Cr (10.314±1.739) > Zn (1.847±0.856) > Ni (1.535±0.419) > Mn (1.495±0.147) > Cu (1.006±0.296) > Pb (0.510±0.013) . All the heavy metals investigated showed concentrations that are within the WHO permissible limits (Table 3). All the heavy metals investigated in the soil sample were detected in all the sample locations. Soil sample collected during the wet season recorded lower concentrations of heavy metals in the studied area. The higher concentrations of heavy metals during the dry season could be attributed to low influx of fresh water and higher evaporation rate with the consequent concentration of material in the area of study. The seasonal variations in the concentrations of the heavy metals could also be attributed to differences in individual metal solubility, pH, leaching by acidic rain during the wet season and topography of the area (Iwegbue *et al.*, 2006).

The values of iron ranks the highest compared to other metals in both seasons (Table 3). The high iron content compared with other metals in this study (Table 3) is expected because iron occurs at high levels in Nigerian soil (Adefemi *et al.*,

2007). Similarly, the results of chemical analysis by Myung (2008) indicated that the heavy metals in soils decreased with distance from the source, controlled mainly by water movement and topography.

3.3 Potential ecological risk assessment

The ecological risk assessment results of toxic metals in soils in two seasons are summarized in **Table 4 and 5**. It was found that the risk indices (E_r^i) of metals were ranked in the following order: Cr>Cu>Ni>Mn>Pb>Zn for dry season and Cr>Ni>Mn>Cu>Pb>Zn for wet season.

Table 4: Potentially ecological risk assessment results of toxic metals in soils for wet season

Location	(Mn)	(Ni)	(Zn)	(Cr)	(Cu)	(Pb)
1	28.77	10.07	1.28	96.24	34.17	0.00
2	36.34	35.12	3.83	141.24	20.58	0.00
3	36.34	30.64	3.45	121.68	21.07	0.00
4	37.59	1.73	2.68	110.09	27.90	12.61
5	27.57	13.09	3.24	132.49	8.22	9.34
6	25.60	34.08	3.36	137.59	59.35	25.72
7	18.71	35.27	2.53	147.35	0.00	0.00
8	35.06	54.52	1.78	165.48	53.95	29.85
9	12.97	27.83	4.03	93.02	0.00	0.00
10	24.79	37.36	2.26	90.77	27.49	0.00
11	21.68	27.06	3.48	96.37	0.00	0.00
Mean	27.77	27.89	2.90	121.12	22.98	7.05

E_r^i = ecological risk index

Table 5: Potentially ecological risk assessment results of toxic metals in soils for dry season

Location	(Mn)	(Ni)	(Zn)	(Cr)	(Cu)	(Pb)
1	8.92	19.83	2.79	53.78	45.47	0.00
2	14.82	29.09	5.00	61.83	27.83	0.00
3	14.24	24.79	5.23	57.03	29.41	0.00
4	9.79	3.83	4.36	57.88	26.38	5.76
5	5.85	12.00	3.52	67.01	16.13	4.40
6	7.81	26.65	3.37	57.41	60.14	12.18
7	14.01	25.91	4.17	91.63	0.00	0.00
8	14.85	44.56	4.15	73.43	44.48	13.77
9	15.07	27.40	3.35	41.85	0.00	1.65
10	13.96	34.39	3.51	47.64	36.44	7.82
11	14.54	30.18	4.19	57.09	0.00	2.85
Mean	12.17	25.33	3.97	60.60	26.03	4.40

E_r^i = Ecological risk index

The average ecological risks of Cr in soils were above 80 in wet season, indicating that Cr posed a considerable ecological risk to the studied area. The values of E_r^i for the other metals were below 40, indicating low risk in the wet season. But in dry season the values are generally lower than what was obtained in wet season. For instance, the average ecological risk of Cr, which was highest amongst other metals studied gave a value lower than 80. Part of the reason for having a lower E_r^i in dry season might be as a result of increase in mobility factor during the wet season

In order to quantify the overall potential ecological risk of observed metals in soils, the value of R (equation 3) was calculated as the sum of the all five risk factors. It ranged from 7.05 to 121.12 in wet season, with an average of 34.95, indicating the low potential ecological risk. The element of Cr accounted most of the total risks, and the average percentage was 57.76% in wet season. For the dry season, it ranged from 4.40 to 60.60, with an average of 22.08, indicating the low potential ecological risk in dry season. The element Cr accounted for most of the total risks in dry season.

3.4 Pollution source of heavy metals

The correlation among heavy metals can be used to speculate their source. For investigation of the relationships between these heavy metals in soils, correlation analysis was conducted, and the correlation matrix is shown in Table 6.

Table 6: Correlation coefficients obtained from Spearman's analysis.

STATS	Mn	Ni	Zn	Cd	Cr	Cu	Pb	Fe
Mn	1.000							
Ni	0.5553 (0.0761)	1.000						
Zn	0.0138 (0.9678)	-0.4884 (0.1274)	1.000					
Cr	-0.1148 (0.7367)	0.0549 (0.8726)	-0.0365 (0.9153)	- (0.0000)	1.000			
Cu	0.1313 (0.7004)	0.0608 (0.8591)	-0.5287 (0.0945)	- (0.0000)	-0.0099 (0.9769)	1.000		
Pb	-0.2041 (0.5473)	0.0856 (0.8024)	-0.4651 (0.1495)	- (0.0000)	0.2667 (0.4279)	0.5657 (0.0697)	1.000	
Fe	0.2865 (0.3930)	0.5174 (0.1031)	0.0582 (0.8649)	- (0.0000)	0.1936 (0.5685)	-0.1220 (0.7208)	0.1922 (0.5713)	1.000

Interpretation clue:

Correlation coefficient of +0.1 to +0.4 shows a weak positive association between the two metals

Correlation coefficient of +0.5 to +0.9 shows a strong positive association between the two metals

Correlation coefficient of -0.1 to -0.4 shows a weak negative association between the two metals

Correlation coefficient of -0.5 to -0.9 shows a strong negative association between the two metals

Correlation coefficient of 1.0 shows a perfect association between two metals.

The values in bracket depicts the p-value of the association and decision rule is that p-value < 0.05 shows the association or correlation is significant; otherwise accept no significant correlation i.e. p-value > 0.05 (provided the level of significance is 5%).

Results obtained revealed that positive correlation existed among Mn, Cu, Pb, Zn, Cr and Ni. The highly positive correlation among soil heavy metals suggested that these heavy metals had similar pollution sources. Therefore, the positive correlation exist among heavy metals in soils of the study area might indicate the combined soil pollution by multi-heavy metals as a result of the rapid development of industry, vehicular emission, as well as human activities, especially sewage disposal.

4. CONCLUSION

Cr was the main pollutant of Onitsha South L. G. A. soils in both wet and dry seasons. However, the soils were not contaminated by other heavy metals, such as Mn, Cu, Pb, Cr and Ni from this research work. The concentrations of heavy metals in soils were influenced partly by the physicochemical properties of the soils such as pH. The pH values of the soils were slightly acidic; this might contribute the bioavailability of these heavy metals in the soils.

The ecological risk assessment results showed that Cr was the only metal posing a potentially heavy risk to the environment especially in wet season while other heavy metals had slightl ecological risk. The overall risk indexes caused by the five toxic metals in soils samples were 151.12, corresponding to moderate risk.

By means of comparison of metal concentrations and correlation analysis, the heavy metals came mainly from anthropogenic activities going on in the area. Therefore, the control of pollution in Onitsha South L.G.A. is vital for the mitigation of toxic metal contamination in study area, especially the activities that release Cr such as combustion processes, metal industries, air conditioning coolants, engine parts, brake fluid emissions. Additionally, a well-managed waste disposal system is necessary for controlling the moderate pollution caused by potentially toxic metals.

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