Journal of Applied Life Sciences International
10(1): XX-XX, 2017; Article no.JALSI.28671
ISSN: 2394-1103

SCIENCEDOMAIN *international*
www.sciencedomain.org

Assessment of Some Heavy Metal Contamination and analysis of Physicochemical Parameters of Surface Soil within the Vicinity of Minna Railway Station, Niger State, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AA and YAI designed the study, performed the analysis and wrote the draft of the manuscript. Authors JTM and AI collected the samples and performed the statistical analysis. Author HOE managed the literature search. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JALSI/2017/28671
Editor(s):
(1)
(2)
Reviewers:
(1)
(2)
(3)
Complete Peer review History:

Original Research Article

Received 30th July 2016
Accepted 21st November 2016
Published 6th January 2017

ABSTRACT

The main aim of this study is to determine the levels of soil pollution with heavy metals in the vicinity of a railway station in Minna, Niger state, Nigeria. In this study, 15 soil samples were collected at a depth of 0-15 cm from the vicinity of Minna railway station, Niger State, Nigeria, and analyzed at the chemistry department, Federal University of Technology Minna, Nigeria between May 2009 and November, 2009. The soil samples were acid digested using a mixture of three acids namely, perchloric acid, nitric acid and sulphuric acid in the ratio 2:10:1. The heavy metal (Cu, Zn, Pb) levels in the digested soils were analysed using Atomic Absorption Spectrophotometer. The soil pH was determined by glass electrode pH meter using soil water suspension (1:1). Particle size

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distribution was determined using hydrometer method. The pH of the soil samples generally ranged from moderately acidic pH (5.54) to neutral pH (7.01). The particles size distribution ranged from 3.04% to 12.48%, 5.28% to 38.56% and 54.40% to 88.40% for clay, silt and sand respectively. The concentrations of the investigated heavy metals ranged from 18.01 mg/kg to 467.50 mg/kg, 54.47 mg/kg to 417.14 mg/kg, and 3.85 mg/kg to106.78 mg/kg for copper, zinc and lead respectively. There is a significant correlation among the analyzed heavy metals; hence the metals may have the same or similar source of input. Heavy metals pollution indices reveal that various sites within the railway station are moderately polluted with copper, zinc and lead according to USEPA and Nigeria DRP guideline for soil quality. Furthermore, I-geo index reveals that the sites are either unpolluted (grade 0) or moderately polluted (grade 1) by copper, zinc and lead. Similarly contamination factor indicates that the sites are moderately contaminated. However, the PLI result reveals that sites R1, R4, R5, R6 and R9 are polluted with copper, zinc and lead, while the other sites are not polluted. Although railway operation has not been previously reported as a major source of heavy metals pollution, this study however suggests that railway operation could be responsible for moderate heavy metal contamination of soil in railway stations or immediate vicinity.

Keywords: Heavy metal; railway; soil; plant; environment; pollution.

1. INTRODUCTION

Soil is a vital component of the ecosystem; a very important resource for sustaining basic human needs including quality food, water supply and a livable environment [1]. Soil also serves as the major reservoir of contaminants because it possesses the ability to bind various chemicals [2], therefore soil management is key to water and food quality, and sound health for mankind. Researchers have identified heavy metals as common and prevalent soil pollutants [3]; second only to pesticides in terms of environmental impact. These heavy metals are released into the environment by both natural and anthropogenic sources. Environmental pollution by heavy metals is usually as a result of activities related to mining, smelting, industrialization and fuel combustion [4]. Soil around industries and roadside are usually contaminated with heavy metals like Pb, Cd, Zn, Ni, and Cu, which are present in fuel and engine oil as additives and are released into the atmosphere due to combustion of the fuel or other temperature driven reactions associated with vehicular performances [4,5]. These heavy metals are then carried to the soil through rain, wind and fallout, and accumulate in the soil over time [6].

Although at low concentration some heavy metals are essential for normal healthy growth and reproduction of plants, other animals and human, all heavy metals are toxic to plants and animals at excessive concentration. The poisoning effects of heavy metals in man are due to their interference with the normal body biochemistry in the normal metabolic processes. When ingested, into the acidic medium of the stomach, they are converted to their stable oxidation states (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, As^{3+}, Hg^{2+} and Ag^{+}) and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds [7]. Heavy metals Co, Cu, Mn, Mo, Ni, Se and Zn are essential minerals, in fact their deficiency in plant and animals can lead to diseases, however Ag, As, Ba, Cd, Hg, Pb, Sb and Th have no known essential function even at very low concentration [8]. Diverse amount of heavy metals may be found everywhere in soil, water, plants and sediment [2].

Plants have the ability to absorb water, nutrients and heavy metals from soils. The unique and selective uptake capabilities of plants root systems, translocation and bioaccumulation abilities, makes it possible for plants to accumulate heavy metals in their tissues. Consequently the toxic metals are introduced into the food chain [9]. The accumulation of heavy metals by plants depends highly on the availability of the heavy metals in the soil [10]. Mining, transportation, domestic and industrial waste are reported to cause elevation in heavy metal content in soil [5].

Therefore, continuous monitoring of the level of heavy metal in soil is very important. The main aim of this study is to determine the level of soil pollution with heavy metals in the vicinity of a railway station in Minna, Niger state, Nigeria.

2. METHODOLOGY

2.1 Sampling Method

The soil samples were collected from different points within the vicinity of the railway station in

Minna, Niger state, using a soil auger. Minna lies on latitude 8ºto 11º 30' North and Longitude 03º 30' to 07º 40' East in Niger state north central Nigeria. The control sample was collected from adjoining uncontaminated area far away from any form of anthropogenic activity. A total of fifteen (15) composite soil samples were collected. At each sampling point, three (3) sub-samples were taken at a depth of 0-15 cm and about 1 m apart. The sub samples were mixed together thoroughly in order to ensure a representative sample from each sampling location. The control was also collected in the same manner. The soil samples were packed in clean polyethylene bags labeled and transported to the laboratory where they were allowed to air-dry at room temperature for two weeks.

2.2 Sample Pre-treatment

The dry soil samples were pulverized with the aid of ceramic mortar and pestle to reduce the particle size of the soil and to obtain a homogeneous mixture of the soil. The pulverized soils were sieved using a 2 mm sieve initially, and then further pulverized and sieved with a 0.5 mm sieve.

2.3 Determination of Physicochemical Properties

Part of the soil (2 mm), were analyzed for soil pH and particle size distribution. The soil pH was determined using soil water suspension (1:1) [11]. Particle size distribution was determined using hydrometer method. The soil sample (2 mm) was treated with 5% solution of sodium hexametaphosphate to complex Ca^{2+}, Al^{3+}, Fe^{3+}, and other cations that bind clay and silt particles into aggregates. The organic matter in the soil form suspension with the solution, therefore the density of the soil suspension is determined with a hydrometer calibrated to read in grams of solids per liter after the sand settles out and again after the silt settles. Corrections are made for the density and temperature of the dispersing solution.

2.4 Heavy Metals Determination

About 1 g of each soil sample (0.5 mm) was digested using 13 ml of the triacid mixture ($HClO_4$, HNO_3 and H_2SO_4) in the ratio of (2:10:1). This was then filtered into 100 cm^3 volumetric flask and made to the mark with distilled water. The filtrate was quantitatively analyzed to determine metal levels using Buck Scientific VGP 210 Flame Atomic Absorption Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of the Soil

The physicochemical properties of the soil samples are presented in Table 1. The soil pH ranges from moderately acidic (5.54) to neutral (7.01). Soil pH is a major parameter that influences the sorption/ desorption, precipitation, dissolution, complex formation, availability and oxidation-reduction of heavy metals [12]. The solubility of metal cations generally increases with a decrease in pH. Therefore the maximum retention of cationic metallic species occurs at pH greater than 7 [13]. Zinc is desorbed at a higher pH than copper which again is desorbed at a higher pH than lead [5]. The solubility of zinc, copper and lead in soil decreases when soil pH increases [14]. The pH of the soil investigated in this study is generally around moderately acidic to neutral and may probably responsible for the relative immobility of the heavy metals in the soil.

The particle size distribution of the soil sample ranges from 3.04% to 12.48%, 5.28% to 38.56% and 54.40% to 88.40% for clay, silt and sand respectively. Heavy metal retention by soil is strongly influenced by the size of the soil grain. Clay soils have very fine and compacted particle, therefore heavy metals cannot easily be leached out of clay soils. Tessier et al. [15], observed significant correlation between soil texture component and heavy metal content in soil, and reported further that greater percentage of zinc in polluted soil were readily absorbed by clay minerals. This was in agreement with the finding of [16], that clay proportion and heavy metal content in soil are positively correlated. The investigated soil samples were mainly loamy, therefore it is very easy for heavy metals to leach out of them.

3.2 Heavy Metal Content of the Soil

3.2.1 Zinc

The result of the heavy metal content presented in Table 2 reveals that zinc in the investigated soils has a mean concentration of 200.37 mg/kg and ranges from 58.99 mg/kg to 417.14 mg/kg for control and R6 respectively. However, it is worth noting that the concentration of zinc in about 80% of investigated sites is within the range of zinc in uncontaminated soils at (20 – 300 mg/kg) as reported by [17] although some samples exceeded this limit. The highest concentration of zinc (417.14±1.4 mg/kg) is obtained in the dump site (R6) of the train station's workshop area. The result of this study is in agreement with the report of Jian-Hua, [18] that railway operation leads to elevation in the level of Zn in soils.

Table 1. Physicochemical properties of the surface Soil (0-15 cm) of Minna railway station

Sample	pH	% sand	% clay	% silt
R1	6.25	78.24	10.48	11.28
R2	6.87	74.40	5.04	20.56
R3	6.75	70.40	7.04	22.56
R4	6.83	84.24	5.04	10.56
R5	6.82	74.24	10.48	15.28
R6	6.33	88.24	6.48	5.28
R7	5.72	72.24	4.48	23.28
R8	5.58	76.24	12.48	11.28
R9	5.88	78.40	5.04	16.56
R10	6.39	80.40	6.52	13.08
R11	7.01	82.40	3.04	14.56
R12	6.97	88.40	3.04	8.5
R13	6.91	60.40	9.04	30.56
R14	7.01	54.40	7.04	38.56
R15	6.98	68.24	4.48	27.28
Control	6.95	72.64	3.91	23.45
	Glass electrode pH Meter [11]	Hydrometer method	Hydrometer method	Hydrometer method

R1-R5 was collected at 100 m, 80 m, 60 m, 40 m, 20 m from the railway line. While R6 and R9 are from the railway station dump site. R7, R8, R10-R15 were collected from other location within the station randomly

Table 2. Heavy metal content of soil samples by atomic absorption spectrophotometer in (mg/kg)

Sample	Zn	Cu	Pb
R1	149.61±0.44	140.12±2.21	8.79±0.46
R2	264.93±0.69	18.99±0.76	4.04±1.50
R3	74.90±2.69	100.21±1.02	3.90±1.83
R4	339.29±1.77	338.75±0.72	52.52±1.49
R5	247.30±0.89	228.13±3.22	21.75±1.10
R6	417.14±1.43	467.50±1.13	106.78±1.66
R7	106.19± 1.02	62.01±0.99	4.28±2.21
R8	83.84±0.88	105.21±1.01	3.85±1.37
R9	355.84±2.10	105.00±1.98	4.52±2.7
R10	216.65±1.76	39.98±1.23	6.02±3.34
R11	64.47±3.34	28.75±2.78	9.53±1.97
R12	168.12±4.72	42.68±3.10	8.04±2.54
R13	177.20±2.28	21.99±1.87	9.64±2.11
R14	186.00±2.11	26.70±2.89	7.04±1.12
R15	154.08±0.98	30.89±1.12	11.48±2.30
Mean	200.37±1.14	117.12±1.27	17.48±2.66
Control	58.99±0.99	18.01±0.74	1.77±1.3
Range	58.99-417.14	18.01-467.50	1.77-105.78

Values are mean ± standard deviation; R1-R15 is the point at which samples were collected within the railway station

3.2.2 Copper

Table 2 shows that copper (Cu) have mean concentration of 117.12 mg/kg. It ranged from 18.01 mg/kg to 467.50 mg/kg for control and R6 respectively. The concentration of copper obtained is comparable to the result of [3]. Some of the soil samples have high concentration of copper higher than the range of 80 – 200 mg/kg permissible level of Cu concentration in soil set by EU, UK and USA Standard as reported by [19]. R6 has the highest concentration of copper as well.

3.2.3 Lead

Lead in the soil samples had a mean concentration of 17.48 mg/kg as presented in Table 2. The range of lead in the soils was 3.85 mg/kg to 106.78 mg/kg. The level of lead in all the sites is below the limit of lead in soils which is set at 200 mg/kg – 400 mg/kg by EPA. It should however be noted that the major sources of lead pollution are pesticides, fertilizer impurities, emissions from mining and smelting operations and atmospheric fallout from the combustion of fossil fuels [19]. Although lead in all the site of this study are below permissible limit of lead, Jian-Hua, [18] in a similar study reported that railway operation is a potential source of lead pollution in soils.

3.3 Pearson's Correlation Coefficient Matrix among Copper, Zinc and Lead

Pearson's product moment correlation coefficient matrix among copper, zinc and Lead in the investigated soils as presented in Table 3 show that significant correlation exist between copper and Zinc (r=0.67), copper and lead (r=0.91) and Lead and zinc (r=0.68). This result suggests that these heavy metals have the same or similar source of input.

Table 3. Result of pearson product moment correlation between heavy metals in the soil sample from Minna railway station

	Zn	Cu	Pb
Zn	1		
Cu	0.67*	1	
Pb	0.68*	0.91**	1

**Correlation is significant at the 0.05 level (2 tailed)*
*** Correlation is significant at the 0.01 level (2 tailed)*

3.4 Heavy Metals Pollution Assessment Indices

3.4.1 Assessment according to united states environmental protection agency (USEPA)

The levels of the heavy metals in the soil sample from this study is compared with the soil/sediment quality guideline set out by USEPA, as presented in Table 4. The result showed that the entire sites are not polluted with Pb except R6 (Dump site). While all the sites are either moderately or heavily polluted with Cu and Zn.

3.4.2 Assessment according to department of petroleum resources (DPR) of Nigeria (1991)

In Nigeria, the maximum allowable concentration of heavy metals in soil (Table 5) formulated by the Department of Petroleum Resources of Nigeria, DPR [20] is used as a reference value for comparing the level of copper, zinc and lead in the investigated soils. From Table 5 below, sites R1, R2, R8 and R9 are moderately contaminated with copper while R4-R6 are heavily polluted with copper. R1, R2, R4-R6, R9, R10, R12-R15 are moderately contaminated with zinc. No site is heavily polluted with Zinc. However, only R6 is moderately polluted with lead.

3.4.3 Assessment according to Geo-accumulation index (Igeo)

The Geo-accumulation index proposed by Muller [21] is used to determine metals contamination in soils, by comparing current concentrations of the metals with pre-industrial levels. Geo-accumulation index is a quantitative measure of the degree of pollution of the soils by heavy metals. It generally consists of seven grades ranging from unpolluted to extremely polluted and can be calculated using the following formula:

$$I_{geo} = \mathrm{Log}_2\left[\frac{Cn}{1.5\ Bn}\right]$$

where, Cn is the concentration of element "n" and Bn is the geochemical background value. In this study, the world average concentration of Cu (45 kg/mg), Pb (20 kg/mg), and Zn (95 kg/mg) reported for shale were considered as the background value [22].

Table 4. USEPA guidelines for soil/sediments (mg/Kg dry weights)

Heavy metal	Not polluted	Moderately polluted	Heavily polluted	Present study (Mean)	Present study (Range)
Lead	<40	40-60	>60	17.48±2.66	3.85-106.78
Copper	<25	25-50	>50	117.12±1.27	18.99-467.50
Zinc	<90	90-200	>200	200.37±1.14	74.90-417.14

Table 5. Department of petroleum resources of Nigeria guideline for heavy metals in Nigeria soil (mg/kg dry weight)

Heavy metals	Not polluted	Moderately polluted	Heavily polluted	Present study (Range)
Lead	<85.0	85-530	>530	3.85-106.78
Copper	<36.0	36-190	>190	18.99-467.50
Zinc	<140.0	140-720	>720	74.90-417.14

Table 6. Geo-accumulation index (Igeo) at different sampling sites in Minna railway station by Muller (1979) [21]

Sample	Zn	Cu	Pb
R1	0.07	1.05	-1.77
R2	0.89	-1.83	-2.89
R3	-0.93	0.57	-2.89
R4	1.25	2.33	0.81
R5	0.80	1.76	-0.46
R6	1.55	2.79	1.83
R7	-0.42	-0.12	-2.81
R8	-0.77	0.64	-2.70
R9	1.32	0.63	-2.73
R10	0.60	-0.76	-2.32
R11	-1.14	-1.23	-1.65
R12	0.24	-0.66	-1.90
R13	0.31	-1.61	-1.64
R14	0.38	-1.34	-2.09
R15	0.11	-1.13	-1.39

The result of the geo-accumulation index for the quantification of heavy metal accumulation in the study sites is presented in Table 6. The interpretation of the I-geo grades for the study sites vary from metal to metal and site to site. From Table 7, Apart from site R4, R6 and R9 which are moderately polluted all the other sites are not polluted with zinc. While sites R1, R4, R5 and R6 are moderately polluted with Cooper. The other sites remain in grade 0 (unpolluted) with copper. The I-geo for Pb attain grade 1 in site R6 (moderately polluted), while, in other sites the grade is 0 which indicates that the most of the sites were unpolluted by Cu, Pb and Zn. The I-geo showed that all heavy metals in all the sites are in grade 0 and grade 1 (Table 6). This suggests that the soils in Minna railway station are moderately polluted with copper and zinc.

Table 7. Muller's classification for the geo-accumulation

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 polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly polluted to extremely polluted
>6	6	Extremely polluted

3.4.4 Assessment according to contamination factor (CF) and pollution load index (PLI)

The contamination factor and Pollution Load Index are potent tools in evaluating heavy metal pollution. CF and PLI give proper assessment of the degree of contamination of each site by individual metals. The PLI represents the number of times by which the metal content in the soil exceeds the average natural background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular site. The Pollution Load Index (PLI) is obtained as contamination Factors (CFs) of all the analysed heavy metals. This CF is the quotient obtained by dividing the concentration of each metal in the sample by the background concentration of the metal. The PLI of each site

Table 8. Contamination factor (CF) and pollution load index (PLI) of copper, zinc and lead in surface soil of Minna, railway station

Sample	Zn	Cu	Pb	PLI	Remark
R1	1.57	3.11	0.44	1.29	Polluted
R2	2.79	0.42	0.20	0.62	Unpolluted
R3	0.79	2.22	0.19	0.69	Unpolluted
R4	3.57	7.53	2.63	4.13	Polluted
R5	2.60	5.07	1.09	2.43	Polluted
R6	4.39	10.39	5.34	6.25	Polluted
R7	1.12	1.38	0.21	0.69	Unpolluted
R8	0.88	2.34	0.19	0.73	Unpolluted
R9	3.75	2.33	0.23	1.26	Polluted
R10	2.23	0.89	0.30	0.84	Unpolluted
R11	0.68	0.64	0.48	0.59	Unpolluted
R12	1.77	0.99	0.40	0.89	Unpolluted
R13	1.87	0.49	0.48	0.76	Unpolluted
R14	1.96	0.59	0.35	0.74	Unpolluted
R15	1.62	0.69	0.57	0.86	Unpolluted

is calculated by obtaining the n-root from the n-CFs that is obtained for all the metals in that particular site. Pollution load index (PLI) was developed by Thomlinson et al. [23], which is as follows:

CF = C metal / C background value

PLI= $(CF1xCF2xCF3x\ldots x\ CFn)^{1/n}$

Where,

CF = contamination factor
n = number of metals
C metal = metal concentration in polluted sediments
C Background value = background value of that metal.

The PLI value of > 1 is polluted, whereas <1 indicates no pollution [24]. While CF values < 1= low contamination factor; 1 ≤ CF < 3: moderate contamination factor; 3 = CF < 6: considerable contamination factor; CF values = 6: very high contamination factor.

In the study, the contamination factor and pollution load index as presented in Table 8 above, shows that Site R1, R2, R5, R7, R10, R12, R13, R14 and R15 are moderately contaminated with Zn while, R4, R6 and R9 are considerably contaminated with Zn. Moderate contamination of copper is seen at site R3, R7, R8 and R9. However, site R1, R5 and R4, R6 are considerably contaminated and very highly contaminated with copper respectively. Lead contamination is noticed in site R4, R5 and R6. However, the PLI result reveals that site R1, R4, R5, R6 and R9 are polluted with copper, zinc and lead, while the other sites are not polluted.

4. CONCLUSION

The main goal of this research is to assess the levels of some heavy metals and determine the physicochemical properties of surface soils of Minna railway station, north central Nigeria, in order to determine the impact of anthropogenic heavy metal pollution arising from railway operations. The result of this study reveals that generally the surface soils of Minna railway station are mainly sandy soil and moderately acidic/neutral. Zinc, copper and lead are present in all the sites and ranges from 64.47 to 417.14 mg/kg, 18.99 to 467.50 mg/kg and 4.04 to 106.78 mg/kg respectively. A significant correlation among the heavy metals analyzed was also observed. In order to facilitate comprehensive interpretation of the extent of heavy metals pollution of the soil, different approaches for evaluating soil metal contaminations/pollution were used. The levels of Zinc, copper and lead in the sample were compared with the soil/sediment quality guideline set out by USEPA and Department of petroleum resources of Nigeria respectively and found that various site within the railway station were moderately/ heavily polluted by copper and moderately polluted by zinc and lead. The Geoaccumulation indices (Igeo) are distinctly variable and suggest that soils in the various part of the railway station range from uncontaminated to moderately contaminated with respect to the analyzed metals. Based on the contamination factors, the soils in various site of the railway station can generally be classified as moderately/highly contaminated by copper, zinc and lead. The pollution index load indicates that some sites (R1, R4, R5, R6, and R9) in the immediate vicinity of the railway station are polluted by Copper, Zinc and Lead. This is a reflection of anthropogenic contribution which might partly result from the use of metal-containing additives in fuel, lubricants and other temperature driven reaction occurring in various components of the train. Hence, the need for consistent monitoring of the level of heavy metal in soils in order to ensure a safe environment is penitent.

ACKNOWLEDGEMENTS

The authors are grateful to Dr (Mrs) F. O. Kunle of the department of medicinal plant research and traditional medicine, National institute for pharmaceutical research and development, Idu Abuja, for editing this work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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ISBN 978-94-007-4440-0
DOI: 10.1007/978-94-007-4441-7
Available:http://www.springer.com/978-94-007-4440-0
(accessed on January, 2016)
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Peer-review history:
The peer review history for this paper can be accessed here:
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