Analysis of Pollution Levels of Heavy Elements Using Fractionation Pattern of Street Soils of Langtang North, Plateau State, Nigeria

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Authors’ contributions
This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information
DOI: 10.9734/AJOCS/2021/v10i419
Editors:
(1) Dr. SungCheal Moon, Korea Institute of Materials Science, Korea.
Reviewers:
(1) Theo Davies, Mangosuthu University of Technology, South Africa.
(2) Dodo Juliet Dingtsen, University Of Jos, Nigeria.
Complete Peer review History: http://www.sciarticle4.com/review-history/76432

Received 21 August 2021
Accepted 31 October 2021
Published 02 November 2021

ABSTRACT

Soil Pollution is a serious environmental challenge around the world today. Anthropogenic activities and population explosion have continued to pose great danger to our environment most especially land resources which are fixed. It is against this backdrop that this study assessed the levels of some selected heavy elements (As, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn). To achieve this, various fractions of exchangeable bound metals, carbonate bound metals, manganese oxide bound metals, iron/manganese bound metals, organic/sulphide bound metals and residual bound metals in soils of Bala, Gantang, She–for, Walang and Yangang Streets as well as Intorok Street which serves as control, Langtang North, Plateau State, Nigeria were assayed using Atomic Absorption Spectrophotometry. The results show that the bioavailable/soluble fractions ranges in (mg/kg) are for: As (BDL – 34.00), Cd (3.00 - 45.00), Co (BDL – 70.00), Cr (42.00 – 155.00), Cu (47.00 – 73.00), Fe (48.00 – 116.00), Mn (46.00 – 119.00), Ni (42.00 – 108.00), Pb (30.00 – 292.00) and Zn (45.00 – 207.00) in all the Streets investigated. The residual/ insoluble fraction ranges in (mg/kg) are for: As

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INTRODUCTION

Pollution is a global environmental problem which various countries around the world are suffering from. The problem is ranked among the most significant environmental challenges worldwide which requires evaluation and urgent solution to overcoming the negative impacts [1-2]. Soil is a heterogeneous mixture of organic and inorganic substances in which the binding mechanism of metals varies with the composition of the soil. Accumulation of heavy elements in soils is of great concern due to the probability of food contamination through soil root interface. Soil, water and atmosphere represent a growing environmental problem affecting food quality and human health, [3]. Though heavy elements cadmium, chromium, cobalt and lead are not essential elements, they are readily taken up accumulated in plants in toxic forms. The ecological effects of heavy elements in soil are closely related to the distribution of species in the solid and liquid phase of the soil. The presence of heavy elements in soil is of great ecological significance owing to their toxicity at certain concentrations [4]. Heavy Element pollution in soil has become serious with rapid industrialization and urbanization over the first two decades [5-6]. The toxic heavy elements entering the ecosystem may lead to geo-accumulation and bio-accumulation [7].

Pollution is the cause of many diseases, which affect not only the old, but also the young and energetic as well as all animals and plants [8]. Surface soil may act as carriers and possible sources of pollution, since the mobility of these elements is such that they remain in the upper layers without regard to type of soil. The elements are not permanently fixed and can therefore be released by changes in climatic or environmental conditions such as rainfall and soil pH [9]. WHO report pointed out that twenty million children worldwide suffer from pollution which has become critical because of over-population [10]. The presence of heavy elements at trace level and essential elements at elevated concentration causes toxic effects if exposed to human population [11]. The most important source of heavy elements in the environment are the anthropogenic activities such as road construction, mining, smelting procedures, steel and iron industries, chemical industries, traffic, agriculture as well as domestic activities [12].

1.1 Evaluation of Heavy Elements in Roadside Soils

Abechi et al. [13], studied the Evaluation of Heavy Elements in Roadside Soils of Major Streets in Jos Metropolis. Results indicate the decreasing order of the average total metal content for the studied elements: Fe > Zn > Mn > Pb > Cd > Cu. Except for Cd, all metals are lower than the levels of those reported in other studies. The absence of Co and Ni indicate no pollution due to these elements. Correlation analysis between elements and the traffic volume (V) indicates significant positive correlation (p < 0.05) between Pb, Cd and Mn, and V.

A study of heavy element concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria by Opaluwa. [4] using digestion and Atomic Absorption Spectrophotometer methods (AAS)
showed the concentration of metals in soil samples in mg/kg from site ‘A’ determined were As = 0.66, Cd = 0.48, Co = 0.58, Cu = 0.91, Fe = 0.63, Ni = 0.31, Pb = 0.49, and Zn = 0.38 while that of site ‘B’ were As = 0.55, Cd = 0.84, Co = 0.63, Cu = 0.82, Fe = 0.64, Ni = 0.42, Pb = 0.53, and Zn = 0.40. The metal concentrations in plant leaves and crops showed high level of Co = 0.33 and Fe = 0.32 in roselle leaves; Cu = 0.71 and As = 0.37 in groundnut; Cu = 0.48 and As = 0.28 in maize grains; As = 0.36 and Co = 0.32 in spinach leaves; and Cu = 0.36 and Co = 0.32 mg/kg in okra. The values of all the metals analyzed for samples from dumpsites were higher than those from the control site suggesting possible mobility of metals from dumpsites to farmlands through leaching and runoffs, but were below values recommended by the World Health Organization (WHO). Abechi et al. [13].

Level of heavy elements in soil Samples from farmlands along highways in parts of Owerri, Nigeria was evaluated by Okereke et al. [14]. The research was designed to ascertain the concentrations of heavy elements (Cu, Pb, Zn, Ni, Cd) in soil samples from farmlands along highways in parts of Owerri. Soil samples were collected from cassava farms along three major roads with high traffic density and a rural road that served as control location. The results revealed that the mean concentrations of metals in soil samples in mg/kg ranged from 3.00 – 6.31 for Cu; Pb, 0.09 – 4.00; Zn, 3.97 – 8.59; Ni, 0.001 – 0.96; and Cd, 0.31 – 0.79. The overall results showed evidence of some heavy element pollution on the soils with possible cumulative effect over time.

Heavy element concentrations in plants and soil along heavy traffic roads in North Central Nigeria was studied by [15]. Plant and soil samples were analyzed to determine the heavy elements (Cd, Zn, Cu, Cr, Pb and Ni) along major roads in Kwara State, Nigeria. Control plant and soil samples were obtained from Kwara State University (KWASU). Eight soil and plant samples were collected. One sample each of soil and plant was collected from Kwara State University as the control sample. Three plant species (Kyllingapumilamichx, Kyllingasquamulatathanm ex vahl, Cenchrus biflorusroxrb) on which animals feed were collected along major roadsides. The samples were digested using wet method and heavy elements were analyzed using Atomic Absorption Spectrophotometry Technique. Lead concentration in plants from the sites was found between 24-142 mg/kg and 24-157.667 mg/kg in soil samples. Copper was found between the ranges of 28.55-115.2 mg/kg and 7.70-80.13 mg/kg in plant and soil samples respectively. Zinc ranges from 13.00-120.45 mg/kg and 30.8219.23 mg/kg in plants and soil respectively. Cadmium was between BDL-0.400 mg/kg and BDL-0.366 mg/kg in plants and soil. Chromium was detected between BDL-53.65 mg/kg and 10.57-77.10 mg/kg in plants and soil respectively. Nickel was between 1.65-11.85 mg/kg and 1.83-14.87 mg/kg in soil and plants samples. Heavy elements (Cd, Zn, Cu, Cr, Pb and Ni) in the control samples were found to be 0.35, 40.00, 88.55, 0.65, 238 and 0.65 mg/kg for Cd, Zn, Cu, Cr, Pb and Ni in plants respectively. The soil samples were between 0.066, 9.50, 4.83, 55.63, 33.667, 4.33 mg/kg, Zn, Cu, Cr, Pb and Ni respectively. Based on this study, plant and soil along road sides were found with high concentration of heavy elements [15].

The ecological risk assessment of some heavy elements in roadside soils at traffic circles in Gombe, Northern Nigeria was reported by Sulaiman. (2018). This study evaluated the levels of some heavy elements in the roadside soils at different traffic circles using geo-accumulation index, ecological risk and Hakanson method to assess the overall ecological risk and identify ecological potential risk of heavy elements pollution. The metals concentrations were found to be higher in the soil samples from edge due to high traffic volume and human activities, and there was significantly decrease in concentration with increase in roadside distance.

Evaluation of some Heavy Elements in Soils along a Major Road in Ogbomoso, South West Nigeria was reported by Taofeek. [16]. Evaluation of the concentration of soil elements (Pb, Cd, Cr, Zn, Mn, Cu, Fe, and Ni) from selected sites (Odo Oba, Sabo and General Areas) along a major road in Ogbomoso was made in comparison with control site, LAUTECH Campus (LC) based on contamination factor and pollution indices. The metal levels in the sites revealed that: General > Sabo > Odo Oba > LC for the analyzed metals except Fe of which highest value was obtained in the control site. Further investigation is highly necessary to study the concentrations and health implications of these metals in residents of the linear settlements along this major road in Ogbomoso.
2. DESCRIPTION OF STUDY AREA

This study was carried out in Langtang North Local Government Area of Plateau State, Nigeria. (Fig. 1). The study area is located at 9°08'00"N 9°47'00"E/9.13333°N 9.78333°E. It has an area of 1,188 km² and a population of 140,643 based on 2006 Census (Wikipedia, 2019).

The inhabitants are synonymous with farming and commerce. It is the administrative capital and the commercial nerve center of the LGA and is the most densely populated area in the Local Government according to the 2006 Nigerian census result. It has the highest number of aging automobiles plying its roads compared to any part of the Local Government Area which contribute greatly to the source of heavy elements in the environment. Six sampling sites of Bala, Gantang, She – For, Walang, Yangang Streets and Intorok Street where selected, with Intorok Street used as control. At each sampling point, 500.00 g of soil was collected over a depth 0-10 cm using a stainless-steel sampler. Soil samples along roads were collected at a distance of 1.00 m away from the road and within an area of 1.00 m². Three (3) samples were collected from each point, thoroughly mixed in a clean plastic container to obtain a representative sample, dried, crushed, sieved with a 2 mm mesh, kept in polyethylene bags and labeled prior to the analyses. The soil samples were labeled according to the regions from which they were obtained.

3. MATERIALS AND METHODOLOGY

The GPS coordinate of each point where soil sample was taken was recorded.

To assess the concentration of each metal in the sampled soil in the laboratory, reagents were used. The reagents used throughout this study are sodium ethanoate solution, hydroxylamine hydrochloride, 25.00 % (v/v) ethanoic acid, mol/dm³ trioxonitrate (V) acid, 30.00 % (v/v) hydrogen peroxide, aqua regia, ammonium ethanoate solution, 20.00 % (v/v) trioxonitrate (V) acid, 10.00 % (v/v) trioxonitrate (V) acid, and oxalate buffer.

3.1 Fractionation of Heavy Elements

The elements were fractionated using the methods of Tessier et al. [17] and Elsokkary [18] adopted by [19] [20]. The elements species were classified into six (6) fractions as shown in Table 1.
Table 1. Classification of element species into six fractions

| Fractions (Soil and Control)                      | Symbols |
|--------------------------------------------------|---------|
| Exchangeable bound metals                        | F1      |
| Carbonate bound metals                           | F2      |
| Manganese oxide bound metals                     | F3      |
| Iron-manganese oxides bound metals               | F4      |
| Organic/sulphide bound metals                    | F5      |
| Residual bound metals                            | F6      |

Table 2. Mean metal concentrations in soils from the study areas

| Fractions | As  | Cd  | Co  | Cr  | Cu  | Fe  | Mn  | Ni  | Pb  | Zn  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Bala      | 0.00| 6.00| 15.83| 35.17| 13.50| 24.00| 21.33| 10.83| 21.50| 20.50|
| Gnagtang  | 2.50| 8.33| 3.50 | 8.67 | 15.33| 11.00| 11.17| 21.50| 60.00| 42.33|
| She-for   | 0.83| 2.83| 2.50 | 9.00 | 9.67 | 10.00| 9.67  | 8.67 | 6.83 | 9.00 |
| Walang    | 6.17| 0.67| 1.50 | 9.83 | 10.00| 22.50| 10.83| 8.50 | 21.83| 15.33|
| Yangang   | 2.33| 8.83| 0.00 | 12.17| 12.67| 22.17| 24.00| 12.67| 42.17| 11.67|

3.1.1 Determination of exchangeable bound metals

Soil sample (1.00 g) was weighed into a 250 cm$^3$ conical flask and 10.00 cm$^3$ of 1.00 mol/dm$^3$ sodium ethanoate solution was added. The pH was adjusted to 8.7 by the addition of 25.00 % ethanoic acid. The mixture was agitated for 2 hours using an orbital Shaker SOI, filtered into a 100 cm$^3$ volumetric flask using Whatman Filter Paper Number 1. The filtrate was made up to mark with water. The metals were determined using (AAS) Model 210 VGP and the residue was reserved for further fractionation [19-20].

3.1.2 Determination of carbonate bound metals

The residue from the exchangeable bound metals was leached for 3 hours with 1.00 mol/dm$^3$ sodium ethanoate solution and the pH adjusted to 5.0 using 25.00 % dilute ethanoic acid. The leachate was filtered into a 100 cm$^3$ volumetric flask and made up to mark with water. The leachate was used to analyze : As, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn using (AAS) Model 210 VGP. The residue was reserved for further analyses [19-20].

3.1.3 Determination of manganese oxide bound metals

The residue from the carbonate bound soil was leached with 10.00 cm$^3$ of 0.10 mol/dm$^3$ hydroxyamine hydrochloride and 0.01 mol/dm$^3$ trioxonitrate (V) acid (adjusted to a pH of 2.0 with 25.00 % ethanoic acid) after shaking for 3 hours using an orbital Shaker SOI. The leachate was quantitatively filtered into a 100 cm$^3$ volumetric flask and made up to the mark with water. The leachate was analyzed for: As, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn using (AAS) Model 210 VGP at their respective wavelengths. The residue was reserved for further analyses [19-20].

3.1.4 Determination of iron-manganese oxide bound metals

The residue from the manganese oxide bound soil was extracted using 10.00 cm$^3$ of pH 3.0 oxalate buffer solution after shaking for 12 hours in a water bath. The extract was filtered into a 100 cm$^3$ volumetric flask and water was added to mark. The sample solution was also analyzed for: As, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn using (AAS) Model 210 VGP at their respective wavelengths. The residue was reserved for further analyses [19-20].

3.1.5 Determination of organic matter/sulphide bound metals

The residue from the iron-manganese oxide bound soil was extracted by shaking with 100.00 cm$^3$ of 30.00 % hydrogen peroxide solution. This was adjusted to a pH of 2.0 by the drop-wise addition of 20.00 % trioxonitrate (V) acid and heated for 6 hours at 90$^\circ$C in a water bath. This was re-extracted at room temperature with 10.00 cm$^3$ of 1.00 mol/dm$^3$ ammonium ethanoate solution and the pH was maintained at 2.0. After shaking for three (3) hours, the first extract of the mixture was filtered using Whatman Filter Paper Number 1 into a 100 cm$^3$ volumetric flask and...
The concentrations of Cd ranged from 3.00 mg/kg (found in walang Street) to 45.00 mg/kg (yangang street). This is lower than 75.00 mg/kg assayed by Nduka et al. [22] but is much higher than 0.66 mg/kg found in irrigation farm Railway Quarters, Bauchi [20]. The presence of Cd may be as a result of anthropogenic activities such as the application of artificial phosphate fertilizers that can contribute to the level of Cd in the roadside soil samples within the study area. Cd is toxic at low exposure levels and has acute and chronic effects to health.

Co concentrations in the five streets spread from 0.00 mg/kg (yangang street) to 70.00 mg/kg (bala street). The 70.00 mg/kg agrees with the threshold limit of 100.00 mg/kg [23]. Building materials and hospital waste may act as sources of Co in these streets in the study area. Co is used in chemical industries as drying agents for paints and tiles, using these products in the study area can also contribute to the level of cobalt in the road side soil samples.

The concentration of Cr assayed in the five street soils ranged from 42.00 mg/kg (found gantang) to 155.00 mg/kg (found in bala street). These values are greater than the value (100.00 mg/kg) of Cr reported by Iwegbue et al., [24], as well as 150.00 µg/g (mg/kg). European Union Standard [25]. However, Cr concentration in soils varies up to as high as 350.00 mg/kg [26]. Cr has been identified in at least 1,127 to 1,699 waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) [27]. Most of the Cr in the study area is found naturally in soil and dump sides (bioavailable fractions). Cr is an essential trace element because small amounts of Cr is necessary for human health, it is use for Cr deficiency, diabetes and high cholesterol in form of supplements. Breathing high levels of Cr can cause irritation to the nose and throat, but pure Cr has no adverse effect on humans [28].

The bioavailable Cu in all the streets soil samples assayed ranged from 47.00 mg/kg (shefor) to 73.00 mg/kg (gantang), this is higher than the permissible limits of 36.00 mg/kg [21] and less than 100.00 mg/kg set by FAO/WHO, 2001. The residual Cu spread from 11.00 mg/kg to 19.00 mg/kg as recorded in all the Streets. The Residual fraction is associated with minimal toxicity due to the difficulty in its migration and transformation under general conditions. The soluble fraction is observed to dominate in all the soils assayed in all the Streets, it is usually associated with anthropogenic factors. Cu may be present in the soil through natural sources.
such as windblown dust and anthropogenic sources (phosphate fertilizer production, wood production and metal pollution such as burnt vehicles and electrical appliance along this street because Cu is commonly found in electrical wirings.

The cumulative sum of soluble Mn determined in the five street soils spread from 46.00 mg/kg assayed in she-for Street to 119.00 mg/kg carried out in yangang Street. The insoluble Mn spread from 10.00 mg/kg to 25.00 mg/kg as conducted in all the Streets. The insoluble fraction is related with minimal toxicity due to the difficulty in its movement and transformation under general conditions. The soluble fraction is observed to dominate in all the soils assayed in all the Streets, it is usually associated with anthropogenic factors. The observed values carried out are below the threshold limit of 850.00 mg/kg of soils set by DPR [21] and 2000.00 mg/kg established by FAO/WHO [29]. Mn may be available in the soil as solids, small particles in water and dust particles in air of fossil fuels [28].

Bioavailable Ni in the five street soils spread from 42.00 mg/kg (she-for) to 108.00 mg/kg (gantang). Residual Ni spread from 10.00 mg/kg to 21.00 mg/kg all the Streets studied. The soluble fraction is observed to be dominant in all the soils analyzed in all the Streets, it is usually associated with anthropogenic factors. The assayed values are within the maximum tolerable level of 75.00 – 150 mg/kg proposed by joint FAO/WHO [30]. However, it is below the intervention value (210 mg/kg) of soil [21]. Small quantities of Ni is essential, but when the uptake is too high it can be a dangerous to human health, it can cause respiratory failure, birth defects, heart disorder and asthma. Atmospheric deposition is the main source of Ni in the soil within the study area.

The soluble Pb obtained in this study spread from 30.00 mg/kg assayed in she-for street to 292.00 mg/kg assayed in gantang street. The soluble Pb ranged from 11.00 mg/kg to 68.00 mg/kg all the Streets assayed. The soluble fraction is observed to be predominant in all the Streets soils analyzed. The values reported for both soluble and insoluble fractions fall between the maximum tolerable level of 250 – 500 mg/kg in dry soil proposed by joint FAO/WHO [30]. However, these values are lower than 530.00 mg/kg [31] and 1000.00 mg/kg [32]. The high concentration of Pb observed could be associated to Pb particle from the combustion of gasoline which settles on street soil around mechanic stands. Domestic waste is one of Pb emission sources, along with superficial drainages and atmospheric deposition. Based on the results obtained in all the fractions it is evident that Pb might pose health risk to the inhabitants of Gantang Street if not checked and controlled.

The concentrations of Zn analyzed in the five streets range from 45.00 mg/kg (she-for) to 207.00 mg/kg (gantang). The residual Zn spread from 9.00 mg/kg to 47.00 mg/kg as recorded in all the Streets. The Residual fraction is associated with minimal toxicity due to the difficulty in its migration and transformation under general conditions. The soluble fraction is observed to dominate in all the soil sediments assayed in all the Streets, it is usually associated with anthropogenic factors. The values obtained are higher than the permissible limit of 50.00 mg/kg ([30]. However, this is much lower than the level of Zn (832.00 mg/kg) determined in soil of locality in the former mining area of rudnany, [33], 600.00 mg/kg [32], 500.00 mg/kg [34], 720.00 mg/kg [35] and 1100.00 mg/kg [31]. Low Zn levels can increase a person’s risk of disease and illness, Zn plays an important role in maintaining healthy skin, people with long-term wounds often have low Zn levels, Zn has antioxidant properties, some researchers have suggested that maintaining adequate Zn levels could possibly offer some protection against COVID-19. Zn is naturally present in all soils in typical background concentrations 10.00 – 100.00 mg/kg [36]. Human activities have enriched the top soils with Zn through the applications of manure or inorganic fertilizers and sewage sludge in the study area.

5. CONCLUSION

The presence of heavy elements (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were observed in the soil sediments in all the streets. Higher heavy element concentrations in these streets were recorded in points where there are evidences of organic load discharge and domestic effluents as in the case of Gantang, Yangang and Bala streets. The results found in this study show that heavy elements levels in the streets are relatively low compared to the referenced permissible limit values reported by WHO. [29] DPR. [21] WHO/FAO. [30] USEPA. [31] EPAA [32] EPMC. [37] CME. [34] EEA. [35] as well as Adagunodo et al. [23,38-39]. This study showed the northern
(hill) part of Langtang North has no potential risk of contamination. However, the plain or southern part of the study area showed high potential risk that if not monitored will result into serious contamination. It is therefore evident that topography plays an important role in the risk factor of heavy elements contamination. The overall results showed evidence of some heavy elements pollution in all the Street soils assayed with possible cumulative effect with time.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
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http://www.sdiarticle4.com/review-history/76432