Available online at http://ajol.info/index.php/ijbcs

Int. J. Biol. Chem. Sci. 8(2): 717-726, April 2014

ISSN 1997-342X (Online), ISSN 1991-8631 (Print)

International Journal of Biological and Chemical Sciences

Original Paper

http://indexmedicus.afro.who.int

Assessment of some physicochemical properties and levels of Pb, Cu and Zn in soils of selected dumpsites in Kano Metropolis, North-West, Nigeria

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ABSTRACT

Some physicochemical properties (pH, electrical conductivity (EC), cation exchange capacity (CEC), organic carbon (OC) and particle size analysis) and levels of Pb, Cu and Zn in soil samples collected from particular dumpsites within Kano Metropolis were analyzed with the view to evaluating the impact of solid wastes on the soils. Heavy metal contents were determined using Atomic Absorption Spectrophotometer while conventional analytical methods were employed for the analysis of the physicochemical properties. The results of the physicochemical properties revealed values ranging from 7.84 - 8.26 (pH), 171.3 - 286.1µScm^{-1}(EC), 8.22 - 14.96Cmol/kg (CEC) and 1.35 - 1.86% (OC). The textural class of the soils was mainly sandy loam. The mean concentrations of the metals analyzed from the dumpsite soil samples were in the range of 12.61 - 84.3mgkg^{-1} for Pb, 20.64 - 35.39mgkg^{-1} for Cu and 232.3 - 610.4mgkg^{-1} for Zn, while the mean concentrations of the metals analyzed from the control site soil samples were in the range of 0 - 11.1 mgkg^{-1} for Pb, 5.7 - 11.0 mgkg^{-1} for Cu and 69.03 - 120.8 mgkg^{-1} for Zn. Metal contaminations of the soil dumpsites were in the order of Zn > Pb > Cu. Correlation analysis was used to examine the dependency of heavy metals upon themselves, Pb correlates with Zn in all dumpsites. The results of the analysis of the samples evidently indicate higher contamination of heavy metals, as well as higher values for some physicochemical properties at dumpsites when compared with the control sites; this may pose a serious risk to the environment in which the dumpsites are located.

Keywords: Physiochemical properties, heavy metals, dumpsite, soil, contamination.

INTRODUCTION

Soil is a loose covering of fine rock particles that covers the earth (Birkeland, 1999). It is a natural body which is composed of minerals, organic matter, air and water. Heavy metals occur naturally in soil usually at low concentration as a result of weathering and other pedogenic processes acting on rock fragments from which the soil developed. Soil is a primary recipient of solid wastes (Nyles and Ray, 1999). From a variety of sources such as industrial, domestic and agricultural, millions of tons of wastes find their way into the soil. These wastes end up interacting with the soil system thereby changing the physical and chemical properties (Piccolo and Mbagwu, 1997). Within the terrestrial ecosystem, soil plays a major role in element cycling and accumulates heavy metals in concentration orders of magnitude higher than

DOI : http://dx.doi.org/10.4314/ijbcs.v8i2.29

in water and air (Udensi, 2010). The impact of heavy metals on the environment is a concern to the government regulatory agencies and the public (Tiller, 1992). The concern is the contamination of soil resources by potentially toxic metals from dumpsites located all over the city. These toxic metals constitute serious problems to human beings because they are neither rapidly removed nor readily detoxified through metabolic activities (Udensi, 2010). Solid wastes are sources of environmental pollution through introduction of chemical substances above their threshold limit into the environment. Managing solid wastes have become an environmental challenge in many urban areas in Nigeria because all sorts of wastes are recklessly dumped together; both the toxic and non toxic wastes, as well as the bio-degradable and non bio-degradable ones. The impact of the by-products of waste decomposition to public health and the environment cannot be over emphasized. Apart from the generation of leachate and methane gas, the exposed waste in open dumps can become a breeding ground for potential carriers of communicable diseases. The presence of heavy metals in wastes is as a result of the intended use of heavy metals in industrial products and at the end of their useful life; they end up in dumpsites or as wastes. Heavy metals are included in soil particles by a variety of mechanisms, mainly adsorption, ion exchange, co-precipitation and complexation. Moreover, soil properties such as contents of organic matter, carbonates, oxides as well as soil structure and profile development influence heavy metal mobility (Kabata and Pendias, 2001). Total heavy metal content is a critical measure in assessing risk of a refuse dumpsite to the environment but soil properties such as pH, cation exchange capacity and particle size analysis can give a predictive idea on the extent to which contaminants can leach into the environment. The aim of this study however, is to assess the physicochemical properties and levels of Pb, Cu and Zn of some selected dumpsite soils within Kano metropolitan area in Nigeria, with a view to evaluating the impact wastes could have on the dumpsite soils and its environment.

MATERIALS AND METHODS

AnalaR grade chemicals and deionized water were used throughout the study. All glassware and plastic containers used were washed with detergent, rinsed with distilled water and soaked in 10% $HN0_3$ for 24 hrs. The lab wares were finally rinsed thoroughly with deionized water. Tools and work surfaces were thoroughly cleaned for each sample during grinding to avoid cross contamination. Reagent blanks were used in all analysis to check reagent impurities and other possible environmental contaminations that could occur during the analysis. Analytical precision was also confirmed with triplicates throughout the study.

Study area

Kano State is located on latitude $11^0$59’18.3sN and between longitudes $08^0$31’E and $08^0$51’E and 418 meters above the sea level (Figure 1). It is known as the economic centre of Northern Nigeria. It is one of the developed industrial cities in Nigeria, with over 350 industrial establishments comprising of chemical industries, tanneries, textile and food processing factories (Olanrewaju, 2001). Due to the huge population, municipal wastes generation is also on the increase. The study areas comprises of four major dumpsites selected from three local government areas within the metropolis. These areas include Nassarawa, Tarauni and Faggae local government area, as shown in Figure 1. The dumpsites selected and their codes were Badawa (BD), Court Road (CR), Mai-malari Dakata (MD) and Hajj Camp (HC). All studied dumpsites are made up of domestic wastes except for Mai-malari Dakata dumpsite which has more of industrial

wastes, due to the industrial activities going on in the area. Control sample areas were also located 50 m away from each dumpsite.

Sample collection

Ten points were randomly identified at each dumpsite as sample collection points. At each point, solid wastes were removed at the surface and the soil subsurface was dug to a depth of 0-20 cm with the aid of an auger. Control samples were also collected from reserve areas within the local government area for each dumpsite (50 m away from each dumpsite). A total of eighty samples were collected and placed in clean polyethylene bags, labeled appropriately and taken to the laboratory. The samples were collected at the end of rainy season in 2012.

Sample preparation

The collected soil samples were air-dried for two weeks to remove moisture. Large soil clods were broken up to facilitate drying of the samples. The dried soil samples were crushed in a porcelain mortar with a pestle. The crushed soil samples were sieved through a 2 mm sieve made of stainless steel (Dikko and Ibrahim, 1999). The soil samples were then stored in labeled polyethylene bags ready for analysis (Ayodele and Gaya, 1998).

Physicochemical analysis of samples

Physicochemical properties such as pH, electrical conductivity (EC), particle size, cation exchange capacity (CEC) and organic carbon content (OC) were analyzed. The pH and EC of the soils were determined using soil sample to distilled water 1:2 (w/v), by digital pH and conductivity meter. The particle size analysis was carried out, using the Bouyoucos hydrometer method as described by Gee and Bauder (1986). Cation exchange capacity (CEC) was determined by the ammonium acetate (1M at pH 7) method, as outlined by Van (1993), while the soil organic carbon was determined by Walkley Black method, as outlined by Van et al. (1999). Same procedures were followed for the analysis of control soil samples for each site.

Heavy metal analysis

Total metal concentrations of heavy metals such as Pb, Cu and Zn in the soil samples were also analyzed. Hot plate reflux technique (USEPA, 1996) was used to digest the studied soil samples. One gram (1 g) of air-dried soil sample was accurately weighed into 125 cm^3 conical flask. 10 cm^3 of 1:1 HNO_3 was added and the slurry was mixed and covered with a watch glass. Heating was done on a hot plate at 95 °C for 10-15 minutes, after which sample was cooled. This procedure was repeated with additional 5 cm^3 of concentrated HNO_3 until digestion was completed, and the solution was reduced to about 5 cm^3 without boiling (by only partially covering the beaker). The sample was allowed to cool again and 2 cm^3 of deionized water along with 3 cm^3 of 30% H_2O_2 were added. With the beaker covered, the sample was heated gently to start the peroxide reaction. A continuous addition of 30% H_2O_2 in 1 cm^3 increments was done, followed by gentle heating until reaction with peroxide (effervescence) was minimal or sample appeared unchanged. The digest was further reduced to 5 cm^3 and refluxed in 10 cm^3 concentrated HCl for 15 minutes. The sample was allowed to cool, filtered through a Whatman no. 42 filter paper into a 100 cm^3 volumetric flask and filtrate was made to the volume.

Contamination/pollution index

The contamination/pollution index is as defined by Lacatusu (2000).

C/P Index = Concentration of metal in soil/Target value.

The standard employed for interpreting soil heavy metals contamination/pollution index varies from country to country based on the chosen factors (Lacatusu, 2000). In this

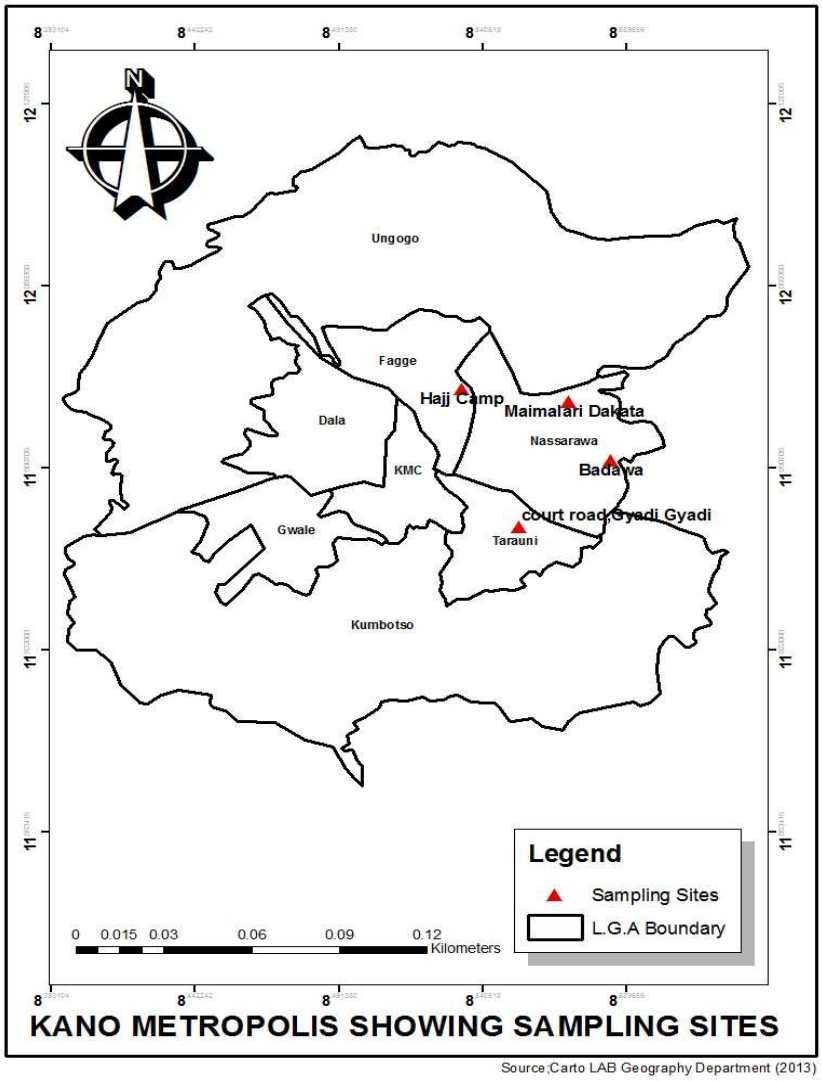

Figure 1: Map of Kano metropolis showing sampling sites.

study, the target values of metals were obtained using the standard table formulated by the Department of Petroleum Resources of Nigeria (DPR, 2002) for maximum allowed concentration of metals in the soil. The target values considered here are Cu (36 $mgkg^{-1}$), Pb (85 $mgkg^{-1}$) and Zn (146 $mgkg^{-1}$). C/P Index value greater than unity (1) defines a pollution range while values less than unity define a contamination range (Table 1).

RESULTS

The result of physicochemical properties of the soil samples at different dumpsites including the control sites is presented in Table 2. The pH of the waste soils were close, ranging from 7.84 to 8.26 with dumpsite MD and BD having the lowest and highest pH values, respectively. This suggests alkalinity of all soil samples studied. Results of electrical conductivity (EC) of the soils in the study areas ranged from 171.3 to

286.1 μScm^{-1} with the highest value obtained at dumpsite CR. This indicates a higher amount of soluble (salt) ions. However, the least conductivity value was recorded at dumpsite MD. The organic carbon content of the waste soils ranged from 1.35 to 1.86%. These values obtained are moderate based on the classification of organic carbon adapted from Kparmwang et al. (2000). However, the waste soils have higher organic carbon content than their control sites. This could be attributed to decomposition of the organic components of waste by the action of microorganisms which increases the level of organic carbon (matter) in the dump soils. The sand and clay contents had a mean range of 58.2 to 71.6% and 7.4 to 15% respectively. This implies that all soils have high sand content and their textural classes were sandy loam. All dumpsite soils had low cation exchange capacity (Lancrop Laboratori, 2013). Dumpsite HC had the least CEC (8.22 Cmol/kg) while dumpsite CR had the highest CEC value (14.96 Cmol/kg). This suggests a low capability of the studied soils to hold cations from being leached or washed away. The mean concentrations range of the metals analyzed from the dumpsite soil samples and the control site soils are as follows; Pb (12.61 - 84.3 and ND - 11.1) $mgkg^{-1}$, Cu (20.64 - 35.39 and 5.7 - 11.0) $mgkg^{-1}$, Zn (232.3 - 610.4 and 69.03 - 120.8) $mgkg^{-1}$, respectively (Table 3). These results revealed higher concentrations of the analyzed metals when compared to their corresponding levels at the control sites. This, however, suggests contamination of the dumpsite soils.

Table 4 shows the relationship existing between the heavy metals and among themselves, which was examined by correlation analysis and was computed using Microsoft excel. The analysis revealed that a strong relationship exists between Pb and Zn in all studied dumpsites with the highest correlation at dumpsite MD (r = 0.96) and the lowest at dumpsite BD (r = 0.51). This suggests a common source of Pb and Zn in the studied dumpsites. However, Zn and Cu had a negative correlation in all sites except for dumpsite MD. The contamination/pollution index for heavy metals in soil samples from all studied sites was estimated as shown on Table 5. Using the significance of interval of contamination/pollution index values (Table 1), it can be seen that the C/PI values for the analyzed metals in the dumpsite soils ranged from 0.15 - 4.18 (slight contamination to severe pollution). For the control sites soils, the C/PI values ranged from 0.03 - 0.83 (very slight contamination to very severe contamination) implying that these soils (with a C/PI value less than one) were unpolluted with the analyzed metals.

Table 1: Significance of interval of contamination/pollution (C/P) index values.

C/PI	Significance
<0.1	Very slight contamination
0.10 - 0.25	Slight contamination
0.26 - 0.5	Moderate contamination
0.51 - 0.75	Severe contamination
0.76 - 1.00	Very severe contamination
1.1 - 2	Slight pollution
2.1 - 4	Moderate pollution
4.1 - 8	Severe pollution
8.1 - 16	Very severe pollution
>16	Excessive pollution

Adapted from Lacatusu (2000).

Table 2: Physicochemical parameters of soil samples from all studied dumpsites.

Dumpsite parameters	BD	BD Ctrl	CR	CR Ctrl	MD	MD Ctrl	HC	HC Ctrl
pH (H_2O)	8.26±0.38	8.5±0.19	8.1±0.39	7.8±0.16	7.84±0.4	8.1±0.15	8.07±0.47	7.8±0.16
EC (μScm^{-1})	240.4±187.71	28.0±1.33	286.1±124.4	134.0±10.4	171.3±131.57	20.0±1.63	179.5±109.39	23.0±10.73
CEC (Cmol/kg)	8.73±4.72	6.4±1.63	14.96±4.95	10.8±2.23	13.75±5.39	0.6±0.28	8.22±5.91	1.5±0.80
OC (%)	1.35±0.77	0.06±0.03	1.86±1.31	0.02±0.01	1.43±1.13	0.99±0.67	1.62±1.31	0.47±0.25
Sand (%)	71.6±3.65	78.6±6.49	59.8±4.14	62.8±5.66	58.2±7.91	64.0±4.90	67.8±6.70	73.0±3.06
Silt (%)	21.0±2.35	16.2±6.43	28.2±2.99	27.6±4.11	28.4±6.80	24.0±4.90	22.8±5.98	20.0±0
Clay (%)	7.4±2.15	5.2±1.15	12.0±1.84	9.6±1.89	15.0±4.99	12.0±5.48	9.4±1.65	7.0±3.06

Note: BD- Badawa, CR- Court Road, MD- Maimalari Dakata, HC- Hajj Camp, Ctrl- Control, EC- Electrical conductivity, CEC- Cation exchange capacity, OC- Organic carbon, mean values are based on n=10 for each site.

Table 3: Mean Concentration ($mgkg^{-1}$) of heavy metals in soil samples from all studied dumpsites.

Heavy metals	BD	BD Ctrl	CR	CR Ctrl	MD	MD Ctrl	HC	HC Ctrl
Cu	20.64±11.11	6.45±1.08	35.39±19.59	9.67±3.63	31.1±11.93	11.0±4.03	29.23±13.26	5.7±1.55
Pb	12.6±7.67	ND	19.6±9.3	4.22±1.61	84.3±54.2	11.1±2.98	15.9±7.58	2.11±0.83
Zn	232.37±155.5	69.03±9.56	281.58±152.9	80.0±7.82	523.4±241.69	105.0±14.58	610.42±340.0	120.8±16.55

Note: ND- not detectable, BD- Badawa, CR- Court Road, MD- Maimalari Dakata, HC- Hajj Camp, Ctrl- Control, mean values are based on n=10 for each site.

Table 4: Correlation of heavy metals for all studied dumpsites.

		Dumpsites BD and MD	
	Cu	Pb	Zn
Cu	1	-0.59	-0.08
		(0.88)	(0.88)
Pb	-0.35	1	0.51
	(-0.01)		(0.96)
Zn	-0.5	0.74	1
	(-0.09)	(0.8)	
		Dumpsites CR and HC	

Right top shows correlation for dumpsites BD and MD with MD coefficient in parenthesis.
Left bottom shows correlation for dumpsites CR and HC with HC coefficient in parenthesis.

Table 5: Contamination/pollution index for heavy metals in soil samples from all studied sites.

Heavy metals	**BD**	**BD Ctrl**	**CR**	**CR Ctrl**	**MD**	**MD Ctrl**	**HC**	**HC Ctrl**
Cu	0.57	0.18	0.98	0.27	0.86	0.31	0.81	0.16
Pb	0.15	-	0.23	0.05	0.99	0.13	0.19	0.03
Zn	1.59	0.47	1.93	0.55	3.59	0.72	4.18	0.83

Note: BD- Badawa, CR- Court Road, MD- Maimalari Dakata, HC- Hajj Camp, Ctrl- Control.

DISCUSSION

The pH of the waste soils were close, ranging from 7.84 to 8.26 with dumpsite MD and BD having the lowest and highest pH values, respectively (Table 2). This suggests alkalinity of all soil samples studied. Similar results were reported for dumpsites by other researchers (Sani et al., 2012; Uba et al., 2008). The control sites were also alkaline, ranging from 7.8 to 8.5. Results of electrical conductivity (EC) of the soils in the study areas ranged from 171.3 to 286.1 μScm^{-1} with the highest value obtained at dumpsite CR. These values are comparatively lower than the range of 0.42 to 4.0 $mScm^{-1}$ as reported by Uba et al. (2008) in their study on some dumpsite soils. The low values obtained in this study may be attributed to the high sand percentage of the studied soils (Roberts et al., 2009). However, the least conductivity value was recorded at dumpsite MD. The organic carbon content of the waste soils ranged from 1.35 to 1.86%. The waste soils have higher organic carbon content than their control sites. This could be attributed to decomposition of the organic components of waste by the action of microorganisms which increases the level of organic carbon (matter) in the dump soils. All OC values obtained are moderate based on the classification of organic carbon adapted from Kparmwang et al. (2000). Baize (1993) suggested that the role of silts and sand must be considered when sampled soils contain less than 35% clay. Thus, in this study, the soils were found to have a high percentage of sand with a mean of 58.2 to 71.6% while the clay contents ranged from 7.4 to 15%. High sand content of any soil implies high leaching potentials (Nyles and Ray, 1999). Therefore, it could be deduced that the underground water beneath these dumpsite areas could be threatened by pollutants from the wastes.

The cation exchange capacity (CEC) of the waste soils ranged from 8.22 to 14.96 Cmol/kg with dumpsite CR and HC having the highest and lowest CEC values respectively. A low value of CEC implies that the soil has a low capacity to hold cations in

exchangeable form. In this study, the CEC values obtained may be classified as low (Lancrop Laboratori, 2013) and could be attributed to the low clay content in the soils. Therefore, retention of metal ion is low in all studied dumpsites and this could suggest high leachability of heavy metals from soils underneath the wastes into underground water, thereby posing a health hazard to humans and other animals that drink this water. The EC, CEC and OC values obtained for all control sites were lower than their corresponding dumpsite samples while all control site soils were sandier than their corresponding dumpsite soils (Table 2). The sandier soils observed can be attributed to the absence of wastes in these soils which could have brought about decomposition and then increase in clay content.

Contamination of the studied dumpsites was obviously indicated by the higher concentrations of Pb, Cu, and Zn when compared to their corresponding levels at the control sites. This shows the presence of metal containing wastes, contributing enormously to heavy metal pollution. The range of Pb level in soils from all dumpsites was 12.61 to 84.3 $mgkg^{-1}$. This range falls within the range obtained in a similar study by Leke et al. (2011) but lower than the concentrations obtained in some dumpsite soils within Kaduna metropolis (Abdallah et al., 2012). All Pb levels obtained in this study were lower than the threshold limit of 300 $mgkg^{-1}$ set by USEPA (1986) and also lower than the maximum allowable limit of 85 $mgkg^{-1}$ set by DPR (2002). A probable explanation to the higher Pb concentration at dumpsite MD (Table 3) is the location of this dumpsite which is an industrial area. Lead is used in lead-acid accumulator batteries and cable sheathing as lead shot, rolled and extruded products, alloys pigments in paints and other compounds (Anake et al., 2009). These are all possible sources from which Pb can get into wastes in dumpsites. The mean range for Cu concentration in all dumpsites was from 20.64 to 35.39 $mgkg^{-1}$ with the highest mean concentration recorded at dumpsite CR; this could be from the activities of the mechanic shops located in this study area. However, a similar study by Abdallah et al. (2012) showed much higher contamination levels of Cu. All Cu levels obtained in this study were lower than the USEPA (1986) permissible limit of 250 $mgkg^{-1}$ and the maximum allowable limit of 36 $mgkg^{-1}$ set by DPR (2002). At dumpsites BD, CR and HC, the C/PI value reveals that the soils were slightly contaminated with Pb and were severely contaminated in the soils at MD. At dumpsite CR, MD and HC, the soils were found to be very severely contaminated with Cu and severely contaminated in the BD soils. The contamination/pollution index of Cu obtained in all dumpsites ranged from 0.57 to 0.98 (Table 5).

The mean concentration of Zn ranged from 232.3 to 610.4 $mgkg^{-1}$ for all studied dumpsites. The result of accumulated metals in the soils showed that zinc had the highest concentration which is similar to a report by Adelekan and Alawode (2011). However, a report by Akpoveta et al. (2010) showed lower concentrations of Zn when compared to the present study. The contamination/pollution index obtained for Zn in all dumpsites ranges from 1.59 to 4.18 (Table 5) and indicates that samples were polluted with Zn ranging from slight pollution to severe pollution. All the concentration values obtained in the examined dumpsites for Zn were found to exceed the maximum allowable limit of 146 $mgkg^{-1}$ (DPR, 2002). The profile of metal abundance in the study areas was Zn>Pb>Cu and among the three metals investigated; only Zn (at dumpsite HC and MD) exceeded the permissible limit of 300 $mgkg^{-1}$ set by USEPA (1986). The studied dumpsite soils were found to be unpolluted with Pb and Cu but polluted with Zn (Table 5). It was observed that Zn had a contamination/pollution index > 1 in all dumpsites, but < 1 in their corresponding control sites (Table 5). The unpolluted level of Zn in the control sites revealed that the major

anthropogenic source of Zn in the dumpsite soils is from the wastes.

The relationship existing between the heavy metals and among themselves was examined by correlation analysis which was computed using Microsoft excel (Table 4). The analysis revealed a perfect positive correlation value (r = 0.96) between Pb and Zn in dumpsite MD. Also in this dumpsite, a strong relationship was observed between Pb and Cu with Zn (r = 0.88). This suggests that Pb, Cu and Zn could have a common source in dumpsite MD. In all studied dumpsites, Pb and Zn were observed to have a positive correlation, implying a common source of the metals in the respective dumpsites. However, Zn and Cu had a negative correlation in all sites except for dumpsite MD.

Conclusion

The findings of this study revealed that solid wastes contributed to the levels of Pb, Cu and Zn in all studied dumpsite soil. This could be explained by the higher concentrations of these metals observed when compared to their corresponding levels at the control sites. The soils from dumpsites MD and HC were polluted with Zn at levels higher than the USEPA permissible limit. However, soils from dumpsites BD and CR had Zn concentrations lower than the USEPA permissible limit. It is also evident that all studied dumpsites contained low concentrations of Pb and Cu. However, continuous use of these study areas as dumpsites may lead to heavy metal build up in soils to toxic levels and eventual leaching of these contaminants due to the sandy texture of the soils. The physicochemical properties of the soils indicate that the sand fraction in this study is generally high and according to Nyle and Ray (1999), soil samples that have high sand and low clay content have high pollutant leaching potentials. Therefore, it could be deduced that the heavy metals content in the investigated dumpsite soils may pose a great threat to the environment where these dumpsites are located. Thus, open dumping of waste should be discouraged and proper monitoring/management and remediation plan is needed to reduce the chances of ground water pollution by leaching of these contaminants. It is therefore necessary to undertake regular environmental impact study to assess waste dumpsites.

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