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Assessment of Heavy Metals in Soils and Sugarcane around Cement Factories of Ewekoro Area, South West Nigeria

BY

***Smart M.O., *Fawole O.A., *Adesida O.A.,**Olunloyo A.A**

ABSTRACT

The concentration of heavy metals in soils and sugarcane around cement factories of Ewekoro area were assessed to determine the rate of contamination and pollution (if any), on soil and sugarcane on the study area. Nine bulked soil samples and six sugarcane crop samples were collected transversely and randomly in the sugarcane plantation. The soil and sugarcane samples were prepared and taken to the laboratory for elemental constituents' analysis using Atomic Absorption Spectrometer (AAS). Data were analyzed using environment assessments indices and correlation analysis. Elemental composition result of soils showed that the mean concentrations of zinc (Zn) 72.81±14.8 mg/kg, lead (Pb) 17.68±5.44mg/kg and cobalt (Co)

33.19±8.22mg/kg are the metals with significant effects on the soils while the elemental composition result of plants showed that the mean concentration of manganese (Mn) is 37833.33±37499.1mg/kg, zinc (Zn) 89.48±45.66mg/kg, lead (Pb)72.95±28.24mg/kg are the metals with significant effects on the sugarcane. The calculated contamination factor of the soil revealed that zinc (Zn) 1.04, lead (Pb) 1.26, cobalt (Co) 1.32 are the only metals that can be said to have reasonably contaminated the soil of the study area while manganese (Mn) 39.38, zinc (Zn) 1.28, lead (Pb) 5.21 are the only metals that can be said to have contaminated the sugarcane crop of the study area. The Geochemical accumulation index (Igeo) was used to detect the pollution rate of heavy metals in the soil and sugarcane crop. From calculated Igeo, it was revealed that in the soil, Zn (<0-1), Pb (<0-1), Co (<0-1) are the metals that can be said to have got to pollution rate, while in sugarcane crop Mn (<0-6), Zn (<0-1), Pb (>0-3) are the metals that can be said to have got to pollution rate in the area. The Pollution Load Index (PLI), showed that the general quality of the pollution of the study area with reference to the sugarcane plantation was tending towards deterioration (PLI=0.6108) indicating that sugarcane stem would soon be unfit for consumption with continuous activities of these cements factories. Consequently, the farm land close to this cements factories should be located farther away from these factories.

Keywords: Heavy metals, Geochemical accumulation, Contamination, Pollution, Sugarcane, Soils, Analysis

INTRODUCTION

There is no widely agreed criterion base definition of heavy metals, different meaning may be attached to the term, depending on the context; In metallurgy for example a heavy metal may be define on basis of density whereas in physics the distinguishing criterion might be atomic number and chemist would likely be more concern with chemical behaviors (Pourret, 2018). Heavy metals are naturally present in the soil even though heavy metals contamination comes from local source mostly cement factory industries, power plant and some other metal industries as well. The natural sources of heavy metals in soils are influenced by the parent materials, the chemical and physical soil properties, weathering, the metal speciation and the climatic conditions. Soils are the major sink for heavy metals release into the environments by anthropogenic activities unlike contaminant which are oxidized to carbon (iv) oxide by microbial or chemical degradation (Wuana and Okieimen, 2011). Their total concentration in the soil persists for a long time after their introduction (Kiipichtchkova *et al.,* 2006).

Heavy metals may be found generally at trace levels in soil and vegetation, the presence of toxic metals in soil can severely inhibit the biodegradation of organic contamination of soil which pose risk and hazard to human and the eco system through direct ingestion or contact with contaminated soil through the food chain (soil-plant-human or soil- plant–animal-human), reduction in food quality (safety and marketability) drinking of contaminated ground water, e.t.c (Guo *et al.,* 1996). Uptake of heavy metal by plants and subsequence accumulation along the food chain is a potential threat to animal and human health (Chen *et al.,* 1997). It has been report that metals such as cobalt (Co), copper (Cu), Chromium (Cr), Iron (Fe), magnesium (Mg) Zinc (Zn) are essential nutrient that are required for various biochemical and physiological functions, Inadequate supply of these micro nutrients results in varieties of deficiency disease or syndromes (WHO, FAO, 2007).

Cements production is a major source of metal and metalloids in the environment and is one of the key industrial sources of particulate matter. Heavy metals such as lead (Pb) mercury (Hg) cadmium(Cd), arsenic (As), copper (Cu), zinc (Zn) and nickel (Ni) are produced from cement factories wastes which when associated with the surrounding environment can lead to toxic effects in human even at low level of exposure, (Herawati *et al*., 2000). In cement plant the major area of dust elusion are the precipitate exhaust stack and the cement mill stack (NSCEP, 1975) other location of gas emission are linkage through the compressors and transport screw pipe, the quarry, the packing plant, the cements and raw materials grinding pills are other emission source. Dust which is emitted during cement process is eventually deposited on the soil, water and plant. A study by Khashman and Shawabkah in 2006, advocate that soils around cement factories show high concentration of heavy metals especially Pb, Zn, and Cd on the top soil of 0-10 cm deep (Semhi *et al.,* 2010). Also the fine particulate of dust can be inhaled along with air and in cause of time cause health issue such as respiratory problem in people living near and working in the cement factories.

Heavy metals can cause quality deterioration as well as reduction in crop yield and agricultural produce generally which negatively affect ecosystems and life of animals and human (Takasin *et al*., 2014) Since heavy metals accumulate in cash crops growing on polluted land, then they can pose risk to people's health as edible part of crops which are consumed by people may have been contaminated or polluted (Alloway, 1990). The critical load of heavy metal in the soil depend on the acceptable total load from anthropogenic heavy metal source, such as deposition of industrial wastes, fertilizer applications and other anthropogenic sources below which ecosystem damage. Plants take up heavy metals by absorbing the contaminated soil with part of the contamination deposited on part of plants exposed to the air from polluted environments (Suruchi and Pankaj, 2011). Heavy metals therefore serve as significant environmental pollutant and there toxicity is a problem of increasing significant for ecological evolutionary. Sugarcane is a major farm produce in southern Nigeria. Aside the edible stem, other parts like the leaves are usually processed into varieties of form before getting to the consumer. The effect of heavy metal pollutants in the soil on the growth and juice quality of sugarcane varies; phosphatic fertilizer, sewage sluge, sugar mill byproduct, fungicide metal polluted soil lead to contamination of the ecosystem in which sugarcane grow. Hence, analyzing and characterization of the constituents of soils in which the sugarcane plants grow on and the stems being consumed are very important from the health point of view.

METHODOLOGY

The study was carried out around cement factories of Ewekoro environs which fall within the tropical low land rainforest region of Nigeria. Ewekoro is a local government area of Ogun state with a total land mass area of 594km^2 and a population of 55,156 (2006 census). It is on a latitude 6^o 58^{1}N and longitude 3^o 17^{1}E. It is approximately 64 kilometers north of Lagos and 42 kilometers south of Abeokuta.

Materials used for the field work are global positioning system (GPS), soil auger, sample bags, field book, hand glove, pen and nylon, paper tape and markers. The soil samples were taken with the aid of soil auger at a depth ranging from 0-15cm. These samples were collected randomly and along traverse around the cement factories and the sugarcane plantation present in the study area. After collection, the soil samples were dried for two weeks and then taken to the lab for sieving and heavy metal constituents' analysis. Stems of sugarcane plants were collected randomly around the plantation. The samples from each plantation were composite and bagged separately. The bagged samples were also taken to the laboratory for elemental constituent analysis

RESULTS AND DISCUSSIONS

Table 1: Summary of Heavy Metals Concentration in Soils and Sugarcane

SOIL SAMPLES			SUGARCANE SAMPLES		
Metals	Range	Mean±SD	Range	Mean±SD	CA
Mn	112-449.6	282.99±111.76	800-90000	37833.33±37499.1	950
Cu	6-50	19.76±14.8	1-30	9.89±12.18	60
Zn	36.9-99.2	72.81±23.36	70-124.2	89.48±45.66	70
Fe	312-780	51.33±184.53	80-190	140.83±45.6	56300
Pb	9.8-23.8	17.67±5.44	43-125.6	72.95±28.24	14
Ni	0.9-3.3	2.36±0.84	1.5-5	3.6±1.74	84
Co	19.66-44.35	33.19±8.22	0.5-35	10.18±14.78	25

CA- Crustal Abundance of each metals (Jefferson lab 2007)

From the descriptive statistical table above, it was observed from the soil samples that mean concentrations of Zinc (Zn), Lead (Pb) and Cobalt (Co) are the means having figures (72.81mg/kg, 17.67mg/kg and 33.19mg/kg respectively) greater than their crustal abundance (CA) (70, 14, and 25 respectively). These indicate that there are likely considerable contaminations and/or pollution of these metals in the soil samples analyzed. Lead (Pb) with mean concentration of 17.67mg/kg is said to be greater than the crustal abundance of Pb (14) on the earth but it is lower when compared with Slovakia and China soils which have concentrations of 628mg/kg and 29.41mg/kg respectively (Lenka *et al.*, 2017 and Zhongmin *et al.*, 2018). Zinc with mean concentration of 72.81mg/kg is also said to be greater than the crustal abundance of zinc (70) on the earth surface and also greater than the soils (14.33mg/kg) of Port Harcourt, Nigeria (Edori and Kpee, 2017) but lower when compared with soil (207mg/kg) around Slovakia (Lenka *et al.*, 2017).

Manganese, copper, iron, nickel have mean concentrations lower than their CAs indicating low or no contamination in the soils of the study area. The mean concentrations of the sugarcane samples shows that only Manganese (Mn), Zinc (Zn) and Lead (Pb) have figures (37833.33mg/kg, 89.48mg/kg and 72.95mg/kg respectively) greater than their various CAs (950, 70 and 14) indicating considerable contamination and/or pollution of these metals on the sugarcane samples analyzed, while copper, iron, nickel and cobalt shows figures lower than their various CAs indicating low or no contamination of these metals on the sugarcane plants.

Metals like copper and nickel that have standard deviations close to their means (19.76±14.8 and 2.36±0.84 respectively) in the soil samples indicate that the sources of these metals are likely the same or close to be same. It also indicates closeness in the concentrations of these metals, i.e. they are not widely spread in the area covered. Manganese and cobalt with standard deviations farther from means (282.99±111.76 and 33.19±8.22 respectively) in the soil samples indicate the sources of these metals are different and the concentrations are significantly different i.e. they are widely spread.
In the sugarcane samples, nickel and cobalt have standard deviation close to their various means (3.6±1.74 and 10.18±14.78 respectively) indicating a close or same source and the concentrations are close to each other. Iron and lead have standard deviations farther from their means (140.83±45.6 and 72.95±28.24 respectively) indicating a different source and the concentrations are widely spread.

The likely sources of zinc toxicity in the samples analyzed (both soils and sugarcane) include addition by sewage sludges, cement powered additives which would have mixed with metallic by-products from the industries. Pb contamination in both soil and sugarcane samples can be trace to human activities in the environment such as fossil fuels burning of limestone extraction, addition by sewage sludges, cement powered additives which would have mixed with metallic by-products from the industries, e.t.c. While the likely source of Mn in the area may include emissions from stack in this industries, waste water discharge, sewage combustion probably mechanic work shop activities of the study area. Natural source of cobalt in the environment include, burning of coal, by-products from cement plants and exhaust from vehicles.

Correlation Analysis
Pearson`s coefficient analysis was used to measure the degree of correlation between the logarithms of the metals concentration data, the inter-elemental relationship metals was obtained using Pearson`s correlation coefficient. This is based on the standard of Pearson standard rule of correlation analysis (Pearson, 1895).

TABLE 2 Correlation Matrixes among Metals in the Soil

Metals	Mn	Cu	Zn	Fe	Pb	Ni	Co
Mn	1	0.17	0.56*	0.60	0.43	0.54*	0.73**
Cu		1	0.58*	0.34	0.58*	0.27	0.33
Zn			1	0.68**	0.80**	0.33	0.64*
Fe				1	0.75**	0.70**	0.75**
Pb					1	0.65*	0.77**
Ni						1	0.87**
Co							1

***=<0.05, correlation is significant at 5%. **correlation is significant at 0.01level.**

A strong positive relationship exist between Mn/Zn (0.56), Mn/Fe (0.60), Mn/Ni (0.54), Mn/Co (0.72), Cu/Zn(0.57), Cu/Pb (0.58), Zn/Fe (0.68), Zn/Pb (0.80), Zn/Co (0.64), Fe/Pb (0.75), Fe/Ni (0.70), Fe/Co (0.75), Pb/Ni (0.65), Pb/Co (0.77), and Ni/Co (0.87) because they have a correlation matrix of 0.5-0.99 . These imply simultaneous increment or reduction of concentration of these metals with each other indicating same anthropogenic source of the same or same degree of effect by these sources. Also positive but weak relationship also exists between Mn/Cu (0.17), Mn/Pb (0.43), Cu/Fe (0.34), Cu/Ni (0.28), Cu/Co (0.33), and Zn/Ni (0.33) because they have correlation matrix between 0-0.4. These indicate gradual increments of the concentration simultaneously between the two metals considered. It was observed that negative relationship does not exist between the elements consider in the soil sample.

Table 3 Correlation Matrixes among Metals in the Sugar Cane Sample

Elements	Mn	Cu	Zn	Fe	Pb	Ni	Co
Mn	1	-0.010	0.47	0.66*	0.74**	-0.04	0.90**
Cu		1	0.27	0.04	0.33	0.69*	0.17
Zn			1	0.922**	0.75**	0.63*	0.29
Fe				1	0.76**	0.500	0.47
Pb					1	0.36	0.78**
Ni						1	-0.083
Co							1

***=<0.05, correlation is significant at 5%.**correlation is significant at 0.01level.**

A strong positive relationship exist between Mn/Zn (0.66), Mn/Pb (0.74), Mn/Co (0.90), Cu/Ni (0.69), Zn/Fe (0.92) Zn/Pb (0.76), Zn/Co (0.63), Fe/Pb (0.76) Pb/Co (0.78) because they have correlation matrix of 0.5-0.99. These imply that there is simultaneous increment or reduction of concentration of these metals with each other indicating same anthropogenic source of the same or same degree of effect by these source. Also positive but weak relationship also exist between Mn/Zn (0.46), Cu/Zn (0.26), Cu/Fe (0.03), Cu/Pb (0.32), Cu/Co (0.12), Zn/Co (0.29), Fe/Ni (0.47), Pb/Ni (0.36) because the correlation matrix value is between 0-0.4, these indicating gradual increments of the concentration simultaneously between the two elements considered. Negative relationships exist between Mn/Cu (-0.01), Mn/Ni (-0.04) Ni/Co (-0.08). This implies that there is inverse increments or reduction of concentration between the two elements i,e as one is increasing the other is decreasing and vice-versa, indicating different source of anthropogenic influences and this can be said to have confirm the regression analysis calculated by Pearson (1895).

Environmental Assessment

The quality of the soils and sugarcane plants in the study area were assessed using Contamination Factor (CF), Geochemical Accumulation Index (Igeo) and Pollution Load Index (PLI).

Contamination Factor Analysis.

The contamination factor calculation was used to determine the level of contamination of metals in the soils and sugarcane samples collected around the study area and it is expressed as thus; Contamination factor (CF) =mean concentration/background level (Hakanson *et al.*, 1980; as used by Smart *et al.*, 2017).

The contamination factor classification consist of four classes ranging from low contamination to very high contamination

TABLE 4 Contamination Factor Classification

CLASSES	RANGES	REMARKS
0	< 1	Low Contamination
1	1 < cf < 3	Moderate contamination
2	3 < cf < 6	Considerable contamination
3	Cf > 6	Very High Contamination

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Table 5 Contamination Factor for Soil and Sugarcane Samples

METALS	SOIL CF	SUGARCANE CF	CA
Mn	0.3	39.38	950
Cu	0.329	0.253	60
Zn	1.04	1.28	70
Fe	0.009	0.006	56300
Pb	1.26	5.21	14
Ni	0.028	0.109	84
Co	1.32	0.721	25

CF-Calculated Contamination Factor
CA- Crustal Abundant of each metal

Using the CF classification table 4, it can be deduce that in the soil samples Zinc (Zn), Lead (Pb) and Cobalt (Co) are the metals with noticeable contamination factor in the study area (CF>1), while the other elements can be said to have lowly contaminated in the soil of the area i.e. (CF<1). The three metals have CF>1 but are less than 3 indicating moderate contamination.

In sugarcane samples, zinc (Zn) lead (Pb), and manganese (Mn), can be said to have noticeable contamination in the sugarcane plants. The sugarcane samples collected can be said to have been very highly contaminated with Manganese (39.38), while the lead concentration has considerably contaminated the sugarcane plants (5.21). The zinc concentration can also be said to have moderately contaminated the sugarcane plants (1.28) while the other metals (Co, Ni, Fe, and Cu) have CF less than 1 indicating low contamination of the sugarcane plants as at the time the field work was carried out.

Geochemical Accumulation Index

The geochemical accumulation index or geo-accumulation index (Igeo) calculation was used to assess the level of pollution in the soil and sugarcane samples collected around the study area. It was calculated using the equation developed by Muller in 1969 as used by Olatunji *et al.*, (2014) and it is expressed as; $Igeo = \log_2 (C_n/1.5 * B_n)$

Where Igeo is the geo-accumulation index, Cn is the observed concentration of each metal in the soil or sugarcane samples B_n the background value obtain from each metals while 1.5 is the multiplication constant. The geo-accumulation index classification consists of seven classes (0-6) ranging from unpolluted to extremely pollute.

TABLE 6 Geo-accumulation Index Classification

CLASSES	RANGES	REMARKS
0	≤ 0	Unpolluted
1	0-1	Unpolluted to moderately polluted
2	1-2	Moderately polluted
3	2-3	Moderately polluted to strongly polluted
4	3-4	Strongly polluted
5	4-5	Strongly polluted to extremely polluted
6	>5	Extremely polluted

Table 7 Summary of Igeo for Soils and Sugarcane Samples

METALS	SOIL	SUGARCANE	CA
Mn	<0,	<0-6	950
Cu	<0	<0	60
Zn	<0-1	<0-1	70
Fe	<0	<0	56,300
Pb	≤0-1	>0-3	14
Ni	<0	<0	84
Co	<0-1	<0	25

Using the Igeo classification table, it can be deduced from the above table (table 7) that the metals (Pb, Zn and Co) that have contaminated the soils have also polluted it with a range of 0-1 signifying unpolluted to moderate pollution. For the sugarcane plants, it can be deduced that manganese has extremely polluted the sugarcane plants in the area (<0-6). This can be said to be due to some anthropogenic sources like by-products from cement industries, welding activities, waste water discharge and sewage sludges which are present in the area. Zn can be said to have moderately pollute (<0-1) the plants while Pb has moderately-strongly polluted (>0-3) the area.

Pollution Load Index

The pollution load index (PLI) was used to measure the general pollution quality of the study area in terms of pollution. The soils and sugarcane plantations of the area was generalized and the quality was measured using the contamination factor and the number of metals studied. The equation for PLI is thus express as;

$(CF1 * CF2* \ldots\ldots\ldots\ldots CFn)^{1/n}$, where n is the number of metals studied and CF is the contamination factors.

TABLE 8 Pollution Load Index Classification

PLI value	**Qualification (Geometric mean)**
PLI < 1	Perfection
PLI =1	Only baseline level of pollutant are present
PLI > 1	Deterioration of the size quality

Using the PLI classification in table 3, it can be concluded that some individual soil samples had been contaminated and polluted by some metals but overall the degree of pollution of the soils of the area covered is not yet polluted (0.2378). In the sugarcane plants analyzed, it can be said that the sugarcane plantations where the sugarcane samples are selected is tending towards deterioration (pollution) because the PLI is close to 1 (0.6108), with continued activities of these cement industries

CONCLUSION AND RECOMMENDATION

The result analyzed show that Zinc (Zn), lead (Pb), cobalt (Co) are the metals contaminating the soils of the study area and also from the pollution factor calculation, these same metals are the metals polluting the soils of the study area. Manganese (Mn), lead (Pb) and Zinc (Zn) are the metals contaminating the sugarcane plants sampled. The pollution load index indicates that the soils of the area are not polluted but the sugarcane plants are tending toward pollution and deterioration of the entire plantation. The major sources of these heavy metals in the area study are the anthropogenic sources which include waste from cement industries, additives used in burning limestone in these cement industries, sewage disposals and mechanical activities.

The increase in the activities of these cement industries are definitely raising the heavy metal contamination rate of this environment thereby leading to increasing rate of pollution both in soils and sugarcane plants in the area. It is thus recommended that an environmental awareness need to be done to create or develop ways to reducing the impact of these industrial activities on the habitants. Farms should be located at a very far distance from these cement industries so as to reduce the level of contamination and pollution in both soil, sugarcane and other crops planted in the area.

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Authors details:* Lecturer II Federal College of Forestry, Jericho, Ibadan.
**Lecturer I Federal College of Forestry, Jericho, Ibadan.