Assessment of Concentrations of Heavy Metals in Soils around ESPRO Asphalt Production and Quarry Site, Wasinmi, Osun State Southwest Nigeria

O.O. Alabi[1], S.O. Sedara[2] and S.Y. Awowole[3]

[1,3]Department of Mathematical and Physical Sciences, Osun State University, Osogbo. Nigeria
[2]Department of Physics and Electronics, Adekunle Ajasin University, Akungba-Akoko, Ondo State, Nigeria
samuel.sedara@aaua.edu.ng

ABSTRACT

This work examined the concentration of heavy metals in soil samples around ESPRO Asphalt Production and Quarry Site located in Wasinmi, Irewole Local Government Area, Osun State. A total of nine (9) soil samples were collected from three points with distances of 0, 1 and 2km from the quarry site. Atomic Absorption Spectroscopy (AAS) was used to determine the concentrations of heavy metals in the soil samples. The results revealed that the mean values metal contents in the soil samples analyzed were in the order Fe>Zn>Cu>Cr>Mn>Pb>Cd. The concentration of the heavy metals in the soil samples were found to decrease as the soil depths increased from 0-25cm and also as the spatial distances of the sampled locations increased from the quarry plant.

The study also showed that low concentrations of Lead (Pb) had a mean concentration value of 0.87ppm and Cadmium (Cd) with a mean concentration value of 0.29ppm. It was also observed that Iron (Fe) had the highest mean concentration value of 148.8ppm. The study concluded that quarrying activities raised the soil heavy metal contents up to the range of about 2km away from the quarry site. This can be attributed to the number of years of mining and excavation activities in the study area and accumulation of the heavy metal concentrations over time and this could be

dangerous to the site environments, especially for farming and groundwater exploration activities in the area.

1. INTRODUCTION

Quarrying is necessary to provide the materials used in traditional hard flooring such as granite, limestone, marble, sandstone, slate and even clay to make ceramic tiles and other application like alloying [1,3,4,11]. However, like many other man-made activities, quarrying causes a significant impact on the environment which includes air pollution, noise pollution, biodiversity damage, quarry wastes and habitat destruction. This also causes the build-up in soils of persistent toxic compounds, chemicals, salts, radioactive materials or disease causing agents which have adverse effects on plant growth and animal health [13,18].

Due to increasing population growth, agriculture, industries and urban infrastructures in Nigeria, considerable degradation of the environment is occurring. Heavy metals are being released to the soil as a result of human activities, weathering and leaching from waste rocks dumps as a result efforts being made to meet the everyday demand for life [5,7,15,21]. The occurrence of heavy metals in soil can be natural or as a result of human activities. The human activities include mining, smelting, domestic wastes and various industrial activities and they are the major source of soil toxin. The direct activities of extraction, processing for industrial and consumer use contributes to the mobilization of heavy metals into the soil.

According to [24] and [9], heavy metals pollution is more worrisome in the developing countries where research efforts towards monitoring the environment have not been given the desired attention by the stakeholders. Industrial scale mining activity is comparatively low in Nigeria,

yet at this level of mining, the nation is increasingly exposed to the unwanted environmental effects of heavy metals [2,8]. Crushed rock aggregates from quarrying generates considerable volumes of quarry dust which significantly leads to production of considerable amount of wastes harboring a number of Heavy metals [6,14,22]. Interestingly, small amount of these heavy metals are common in our environment and diet which are necessary for good health, but large amount of any of them may cause acute or chronic toxicity and poisoning [10,12,16,17,19,20]. This work was designed to study the concentration of heavy metals in ESPRO Asphalt Production and Quarry Site and assess its impact on the surrounding soil and environment. The distributions and concentration of heavy metals at varying distances (spatial variations) from the quarry site and its environment as well as the variation of heavy metals with soil depth were studied.

2. MATERIALS AND METHODS

2.1 Sample collection and Treatment

Soil Samples were taken at intervals of 0 km, 0-1 km and 1-2 km in Southeast and southwest directions of the quarry site. Two soil samples each were taken from the top layer 0-5cm and two sub-layers of 5-10cm and 10-25cm. Control samples were also taken in the Southeast direction where there is less pollution of heavy metals. The control samples were taken with the same parameters (distance and depth) but one sample was taken at the different points. These Soil samples were air dried and sieved using 2mm mesh size sieve to remove stones and plant roots in order to have soil of uniform particle size. The soil samples were collected and placed in a polythene bag appropriately and kept in dry place until analysis.

2.2 Sample Analysis

The soil samples were analyzed using Atomic Absorption Spectrophotometer (1g of soil) was

weighed into a digestion flask, 10mL of Nitric per Chloric acid (2:1) was added to the sample and digested at 150°C for 1.5hours, 5mL of HCl distilled water (1:1) was added. The temperature was increased to 230°C and further digested for another 30minutes. It was removed from heat and allowed to cool. It was washed into a standard 100mL volumetric flask and made up to the mark with distilled water. The amount of heavy metals in the sample was determined by Atomic Absorption Spectrophotometer (PG.:990). The concentration of heavy metals was extrapolated from the calibration graph prepared.

2.3 Calculation of Metals Concentration

From the laboratory results, the elemental concentrations in parts per million (ppm) were determined by:

$$mc = \frac{c * df}{w} \quad \text{...1}$$

where mc= Metals Concentration; c= Concentration; df= Dilution Factor; w= Weight taken

3. RESULTS AND DISCUSSION

3.1. Results

The concentration of heavy metals in soil and their spatial variation with distance in the study area is presented in Tables 1 and 2. The concentration of heavy metals in soil at a depth of 0-25cm varied with distances (0km, 1km and 2km) to the quarry site.

TABLE 1: HEAVY METALS CONTAMINATION IN SOIL SAMPLES AROUND THE QUARRY SITE

S/N	Sample No.	Distance From the Factory (km)	Depth (cm)	Concentration of heavy metals (ppm)						
				Cu^{2+} (ppm)	Mn^{2+} (ppm)	Fe^{2+} (ppm)	Zn^{2+} (ppm)	Cd^{2+} (ppm)	Pb^{4+} (ppm)	Cr^{3+} (ppm)
1	A	0	0-5	5.20	2.44	323.2	7.35	1.50	4.43	5.23
2	B	0	5-10	4.34	1.67	275.2	7.15	1.10	3.41	3.42
3	C	0	10-25	2.36	0.83	142.6	6.36	ND	ND	1.05
4	D	1	0-5	2.10	0.81	136.4	5.44	ND	ND	0.78
5	E	1	5-10	1.23	0.80	121.5	4.26	ND	ND	0.66
6	F	1	10-25	0.97	0.79	100.4	2.25	ND	ND	0.57
7	G	2	0-5	0.86	0.76	99.4	1.05	ND	ND	0.03
8	H	2	5-10	0.75	0.60	84.5	0.25	ND	ND	ND
9	I	2	10-25	0.67	0.22	56.4	0.04	ND	ND	ND

Note: ND=Not Detected, Cd= Cadmium, Cr= Chromium, Fe= Iron, Cu= Copper, Mn= Manganese, Zn= Zinc, Pb= Lead

In Table 1, the heavy metals concentrations in the soil samples at a depth of 0-5cm ranged from 1.50ppm Cd to 323.2ppm Fe. At depth 5-10cm, the heavy metal concentrations values ranged from 1.10ppm Cd to 275.2ppm Fe, also at the depth of 10-25cm, the heavy metals concentration values ranged from 0.83ppm Mn to 142.6ppm Fe. The results revealed that as the depth increases, the heavy metals concentration values decrease and contamination occurs as a result of the quarry activities. Here, the order of contamination of the heavy metals in all depth in the

quarry site with distance 0 km is Fe>Zn>Cu>Cr>Pb>Mn>Cd.

Considering the spatial variation (distance) of about 1km from the quarry site, the heavy metal concentration values in the soil sample at a depth of 0-5cm ranged from 0.81ppm Mn to 136.4ppm Fe. At 5-10cm, the heavy metal concentration values ranged from 0.66ppm Cr to 121.5ppm Fe, also the depth 10-25cm, the heavy metals ranged from 0.57ppm Cr to 100.4ppm Fe. The results obtained revealed that the trend of decreasing level of contamination was observed as the soil depth increases. The order of contamination in the heavy metals in all depth is Fe>Zn>Cu>Mn>Cr. The heavy metals not detected are Cd and Pb. The experimental results computed in the analysis of the spatial variation (distance) of about 2km from the quarry site follows the regular pattern as the 0km and 1km distances from the quarry site. At depth 5-10cm, the heavy metal concentrations values ranged from 0.25ppm Zn to 84.5ppm Fe and also at depth 10-25cm, the heavy metal levels ranged from 0.04ppm Zn to 56.4ppm Fe. The results revealed that as the soil depth increases, the concentration of heavy metals decreases at 2km distance from the quarry site. The order of contamination of heavy metals at 2km distance from the site is Fe>Cu>Mn>Zn>Cr. Though the concentration of Cr detected was insignificant whereas Cd and Pb were not detected.

TABLE 2: MEAN CONCENTRATIONS OF HEAVY METALS IN SOIL SAMPLES AROUND THE QUARRY SITE

S/N	Heavy Metals	Mean Concentrations (ppm)	WHO (2008) (ppm)
1	Cu	2.11	30
2	Mn	0.99	0.2
3	Fe	148.84	20
4	Zn	3.79	50
5	Cd	0.29	0.3
6	Pb	0.87	85
7	Cr	1.30	2.3

From Table 1, Cu decreases throughout the entire soil profile at all three locations A, B and C. It was found in highest concentration at location A (quarry site), 0-5cm depth where it reaches 5.20ppm and the lowest concentration of 2.36ppm in the sub-soil region in the location A. It can be deduced in the other two locations B and C, follow the same pattern as shown in the statistical approach which explains the decrease in the concentration of Copper as the depth of the soil samples increases. Likewise, locations A and C have the concentration of Mn decreasing with increasing soil depth while location B which is 2km away from the quarry site has relatively stable values with slight variation ranging from 0.79-0.81 ppm. Location B also follows the same pattern with depth of soil samples increasing.

Also from Table 1, the quarry site being the location A is highly concentrated with Fe at the topsoil (0-5cm) with a high concentration value of 323.2 ppm. The lowest values are present at location C which is 2km away from the quarry site. Fe decreases throughout the entire soil profile at the three (3) sampled locations. At close distances (locations B and C) from the quarry site, the soil exhibits higher Fe values than further away from the quarry site, which can be

attributed to the fact that Fe concentration was found to be above 2008 World Health Organization (WHO) limits, which may be due to the deposition of quarry dusts on the soil. The effect of quarry dust pollution on the available Fe in the soil is statistically significant as it decreases with the depth and an increase in the distance or the spatial variation.

However, the concentration of Zn ranged from 7.35ppm to 0.04ppm with an average concentration value of 34.15ppm. The high content of Zn may be attributed to the deposition of accumulated dust. In the absence of any major metal smelting operations, the primary source of Zn in urban street is probably the attrition of vehicle tire rubber. Sewage sludge soils show higher concentration of Zn and addition of fertilizers to the soil such as nitrate, phosphate and ammonium nitrate increases the concentration of Zn. The result revealed that the soil samples taken at locations A and B were highly polluted but the analyzed samples taken at location C showed that the soil samples were slightly polluted by Zn. This could be attributed to the absence of minor smelting operation at location C which is about 2km away from the quarry site. Cadmium, Cd was rarely observed with the highest concentration level of 1.50ppm at the topsoil layer (0-5cm) and also has a concentration value of 1.10ppm at the sub-soil layer (5-10cm) in the soil samples taken from location A. There was no detectable quantity of Cd in the analyzed soil samples from the other two locations (B and C). The composition of Fe, Zn, Cu, Cr, Mn sampled at various distances decreased with increase in distances from the quarry site as shown in Figures 1 to 4 and Figure 7. Though Pb and Cd from the experimental analysis were infinitesimal but still follow the regular pattern of decrease in concentrations as the spatial variation (distance) increases (Figures 5 and 6). Table 1 also shows that the concentration values of Pb in the soil samples indicated that Pb was concentrated in the pollution source environment (location A) at the top soil layer (0-5cm) and sub-soil layer (5-10cm) with 4.43ppm and 3.41ppm concentration values respectively (Figure 6). It was observable that the assessment of Pb follows

the same pattern as Cd with respect to the non-detectable level of contaminants in locations B and C. The concentration of Cr decreased with increase in distance to the quarry site, with the least value (0.03ppm) at location C which is 2km away from the quarry site while the highest value (5.23ppm) was observed in location A at 0-5cm depth level. It was observed that at location C, the sub-soil layers (5-10cm) and (10-25cm) indicated the absence of chromium in the soil samples analyzed and this can be attributed to the distance to the quarry site which makes it less polluted at the top layer (0-5cm) with 0.03ppm concentration value (Figure 7).

In general, the result indicated that Fe is the dominant heavy metal with a mean concentration of 148.84ppm while Cd has the lowest mean concentration of 0.29 ppm in the sampled soils in all depth and spatial variations (distances). It was observed from the vicinity of quarrying area soil that the mean concentration values of the assessed heavy metals followed the sequence Fe>Zn>Cu>Cr>Mn>Pb>Cd as shown in Figure 8. Although, Pb and Cd were rarely detected as the distance increased, the distributions of the assessed heavy metals with their deep soil profile ranging from 0-25cm for the locations A, B and C are statistically illustrated in Figures 1 to 7.
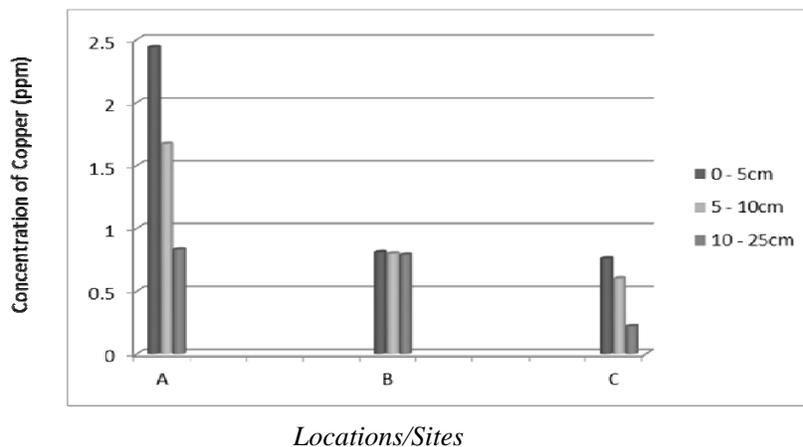

Locations/Sites

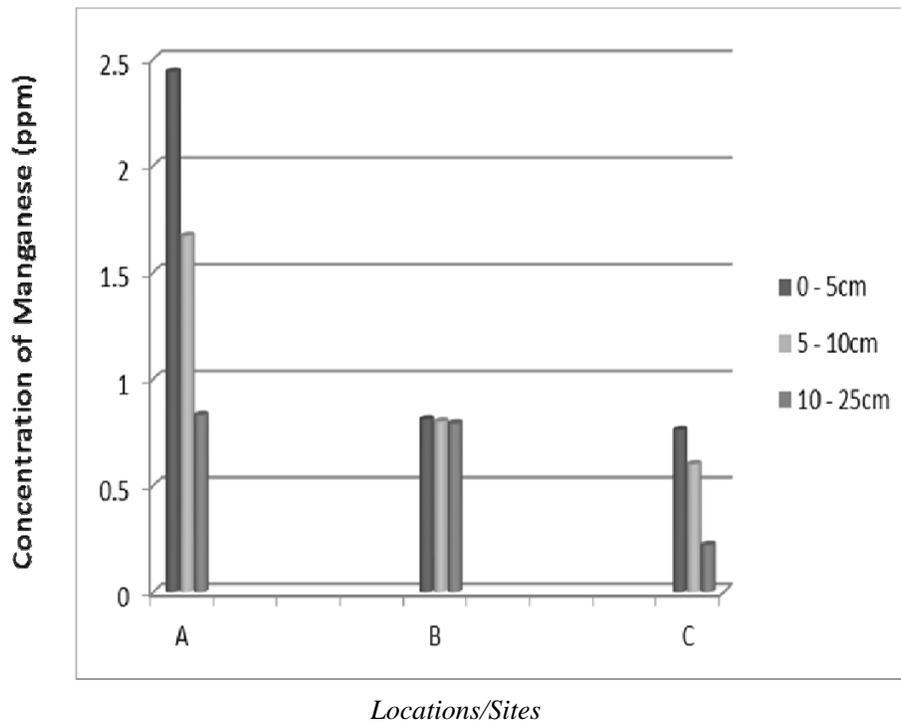**Figure 1: Copper concentrations at varying depth in the soil samples**

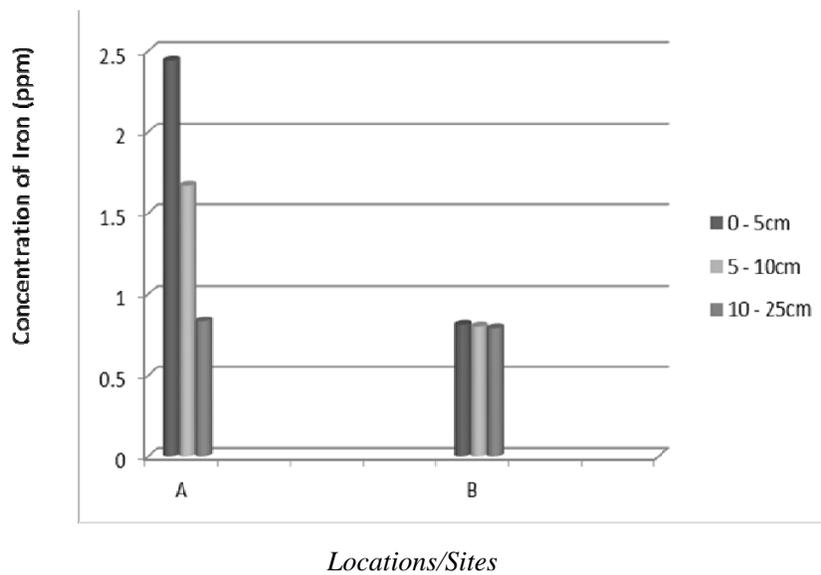**Figure 2: Manganese concentration at varying depth in the soil samples**

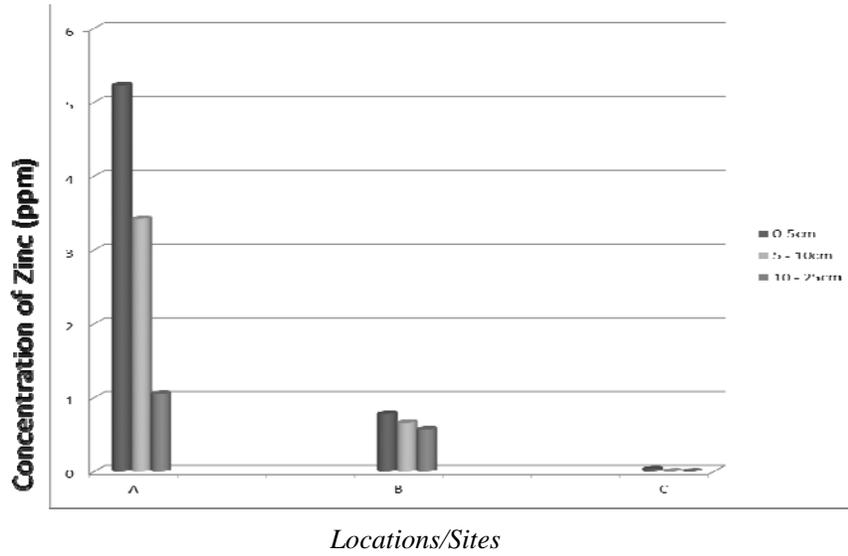**Figure 3: Iron Concentration at varying depth in the soil samples**

Locations/Sites

Figure 4: Zinc concentration at varying depth in the soil samples
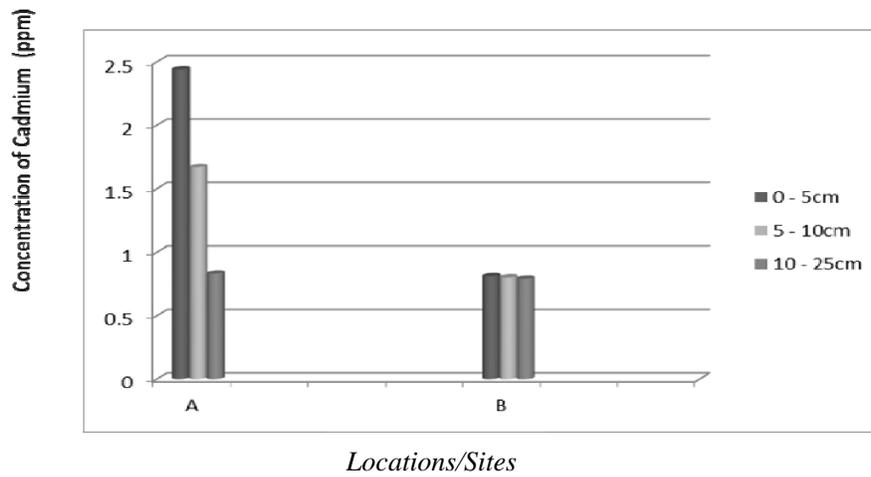

Locations/Sites

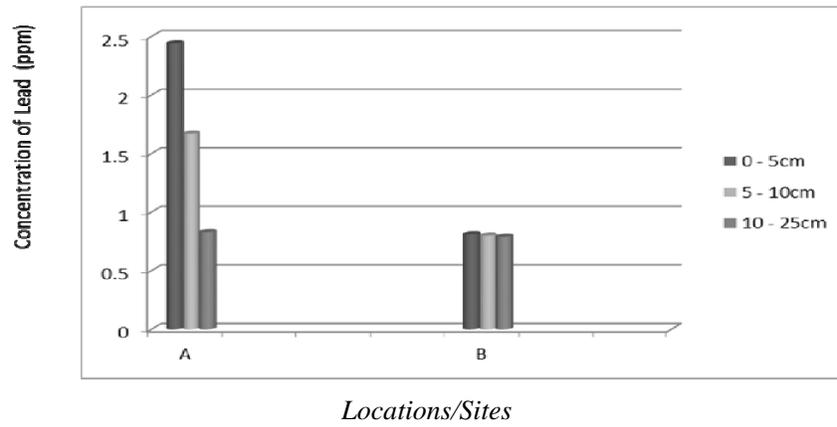**Figure 5: Cadmium concentration at varying depth in the soil samples**

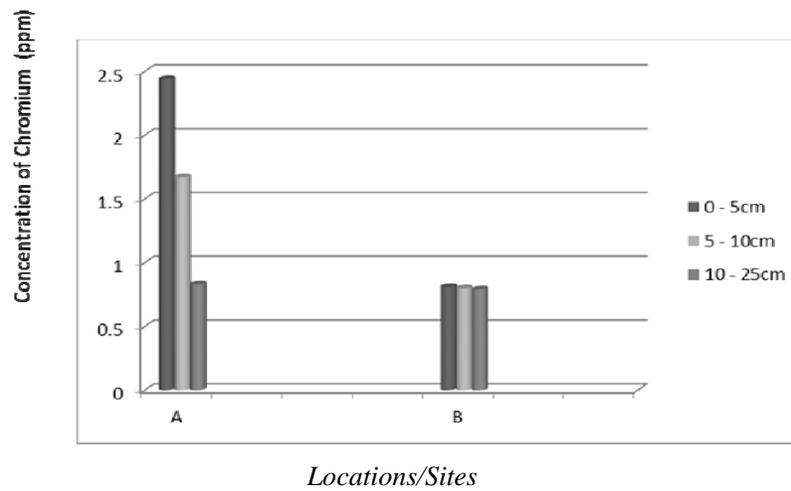**Figure 6: Lead Concentration at varying depth in the soil samples**

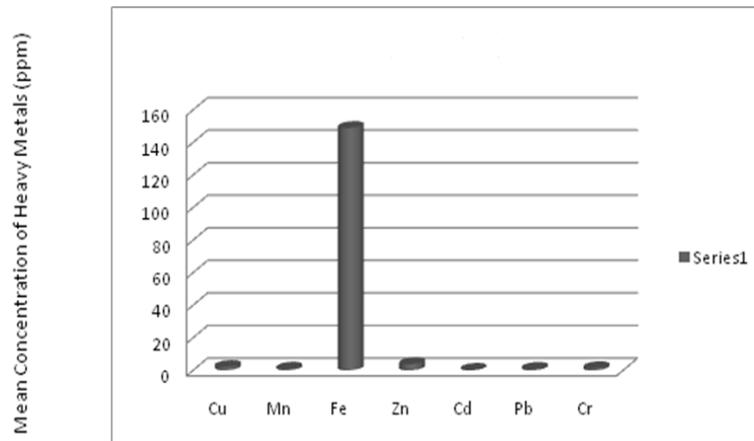**Figure 7: Chromium Concentration at varying depth in the soil samples**

Figure 8: Heavy Metals Concentration in the soil samples

3.2 Discussion

The assessment of the concentration of heavy metals in soils showed significant differences between samples in different distances. Results of this study showed that there was a marked decrease in concentration of Cd, Pb, Mn, Cr, Cu, Zn and Fe in soil as the sampling distance increases (Figures 1-7). The highest value of Zn (7.35ppm) observed at the topsoil layer (0-5cm) from the study site was higher than Zn (1.05ppm) recorded at the topsoil layer (0-5cm) in the soil sample 2km away from the quarry site. Soils at a distance of 300m from the quarry plant site were still contaminated, but the concentration decreased exponentially with the distance. Soil samples collected between 0km and 1km appeared to show higher concentration of most heavy metals than samples farther away probably because of their proximity to the exploration area and leaching of metals from quarry tailing.

However, the concentration of heavy metals in soil during dry and wet seasons could be compared. From the findings of [24], it was detected that the concentration of heavy metals is higher in dry season than in wet season.

In this work we have not compared such but this might be due to the run-off effect that is capable of removing heavy metals from the site and the effect of rainfall which may facilitate the dilution of soil solution during the wet season and intense evaporation in the dry season makes soil

solution more concentrated. A concentration of heavy metals in the soil samples vary considering the topography of the area, atmospheric influence and farmland cultivation in the area of the quarry.

Iron was found to be in high concentrations in most of the soil samples. This can be attributed to the soil in the investigated areas being rich in Fe. The Mn content varies from 0.22-2.44ppm. The concentration of the toxic heavy metal Cd in the results obtained from the analyzed soil samples was too low to be detected by the analytical technique used in this study as the distance from the quarry site increases. The non-detectable level of Cd in the soil samples assessed indicated that the soils around the quarry site were not contaminated with Cd.

The elemental concentration of Cr in the results of the samples assessed ranged from 0.03-5.23ppm. The highest concentration of Cr was recorded for the topsoil sample layer (0-5cm) in the quarry site with a value of 5.23 ppm as shown in Figure 7. Lower values of Cr in soil samples in the quarry site with increase in distance were observed. Also, the results obtained indicated that the concentration of Pb ranged from 3.41-4.43ppm and it was rarely detected as the distance increased from the quarry site as shown in Figure 6.

4. CONCLUSION

The assessment of the concentration of heavy metals in soils around the quarry site showed that the concentrations of heavy metals from soil samples were decreasing with increase in distance from the quarry site. It was also deduced that the concentrations of heavy metals in the soil samples decreased as the soil depth increased from 0-25cm. It was noticeable that metals like Fe, Mn, Cu, Zn and Cr were densely detected while metals like Pb and Cd were rarely detected as the distance from the quarry site significantly increased from 0-2km. This may be due to the landscape topography, soil chemical composition, regional and microclimatic effects on the study area. However, the concentrations of heavy metals in the study area was observed to be lower

than the concentrations of metals in other quarrying/mining industrial sites such as the limestone quarry in southwest (Ibadan), Nigeria. This can be attributed to the number of years the quarry plant in the study area has been in operation.

From the results, the concentration of heavy metals still falls below the [23] limits but accumulation over time could be dangerous, therefore, there is the need to carry out periodic Environmental Inspection Assessment studies on industrial activities and their impact on the environment. This will prevent and minimize the negative effects of quarrying operations on human health including the factory workers and the physical environment thereby protecting the environment from hazardous pollutants.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Ademoroti CMA., (1996). Environmental Chemistry and Toxicology, Folded Press Ltd, Ibadan, 17-24.

2. Ahmed F and Ishiga H, (2006). Trace metal concentrations in street dusts of Dhaka city, Bangladesh. Atmospheric Environment, 40:3835-3844

3. Alguacil FJ., Caravaca C., Combo A. (1994). Hydro metallurgical treatments of steel making flue dusts, Rev. Metal. Madrid 30:173-182

4. Amusan AA., Ige DV and Olawale R., (2003). Characteristics of Soil and Crops Uptake of Metals in Municipal Waste Dump Sites in Nigeria, 21-13

5. Deng WJ., Louie PKK., Liu WK., Bi XH., Fu JM., Wong MH. (2006) Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM 2.5 at an electronic waste recycling site in southeast China, Atmospheric Environment. 40:6945-6955

6. De Gruijter JJ. (2002). Sampling in J. H. Dane and G. C. Topp, Eds. Methods of soil analysis, Part 4--Physical Methods. Soil Science Society of America, Inc., Madison, WI 45-79.

7. Escarre J., Lefebvre C., Raboyeau S., Dos Santos A., Gruber W., Marel JC., Frerot H., Noret N., Mahieu S., Collin C., Van Oort F., (2010). Heavy Metals Concentration Survey in Soils and Plants of the Les Malone's Mining District (Southern France): Implications for Soil Restoration, Water and Soil Pollution, 86:13-34.

8. Etim EU and Adie GU. (2012). Assessment of Toxic Heavy Metals Loading in Topsoil Samples Within the Vicinity of a Limestone Quarry in Southwestern Nigeria, African Journal of Environmental Science, 20:710-716.

9. Ezenwa LI., Awotoye OO., and Ogbonna PC. (2014). Spatial Distribution of Heavy

Metals in Soil and Plant in a Quarry Site in Southwestern Nigeria, Research Journal of Chemical Science; 4(8):1-6.

10.   Fifield FW. and Haines PJ. (2000) Environmental Chemistry, Second Ed. Blackwell Science Ltd. Oxford, 364-375.

11.   Goyer RA. (1996) Toxic Effects of metals. The basic science of poisons, 5th Ed.; Klaasen, C. D., Ed; McGraw Hill: New York, NY, USA, 5:691-736

12.   Jarup L., Perrson B., Elinder CG (1995). Decreased glomerular filtration rate in cadmium exposed solderers. Occup Environ Med; 52:818-22

13.   Jha MK., Kumar V., Singh RJ. (2001). Review of hydro metallurgical recovery of Zinc from industrial wastes, Resources, Conservation and Recycling 33:1-22.

14.   Kim JY., Kim KW, Lee JS. and Cook J. (2002). Assessment of As and Heavy Metals Contamination in the Vicinity of Dukum Au-Ag Mine Korea, Environmental Geochemistry and Health, Kluwer Academic Publishers, 24:215-227.

15.   Okoronkwo NE., Odoemalam SA., Ano OA. (2006). Levels of Toxic Elements in Soils of Abandoned Waste Dump Site, African Journal of Biotechnology, 5:1233-1241

16.   Li. H., You L., Sheng G., Fu J., Peng L. (2007) Severe PCDD/F and PBDD/F Pollution in air around an electronic waste dismantling area in China, Environmental Science Technology. 41:5641-5646

17.   Morgan R. (2013). Soil, Heavy Metal and Human Health. In Brevik, E. C. & Burgess, L. C. Soils and Human Health. Boca Raton. FL: CRC Press, 59-80.

18.   Muller, DJ and McBratney AB. (2000). Soil spatial variability. In M.E. Sumner, Ed. Handbook of Soil Science. CRC Press, Boca Raton, FL, A321-A352.

19. Naim S., Ozcan S., Demir G., Nemlioglu S., and Bayat C.(2004),"Determination of Heavy Metals Concentrations in Street Dusts in Instabul E-5 Highway, "Environmental International, 29(7):979-985.

20. Poggio L., Vrscaj B., Schulin R., Happerle E., and Aj-mone-Marsan F., (2009),"Metals Pollution and Human BIOS accessibility of Topsoils in Grugliasco (Italy)", Environmental Pollution, 157(2):680-689.

21. Raikwar MK., Kumar P., Singh M. and Singh A., (2008). Toxic Effects of Heavy Metals in Livestock Health, Vertinary World, 1(1):28-30.

22. Wong SC., Duzgoren-Aydin A., Wong MH. (2007) Evidence of excessive release of metals from primitive e-waste processing in Guiyi, China, Environmental Pollution 148: 62-72.

23. WHO (2008). World Health Organization, Guidelines for drinking water quality, World Health Organization, Geneva

24. Yahaya M I., Mohammad S. and Abdullahi BK.. (2009). Seasonal Variations of Heavy Metals Concentration in Abbatoir Dumping Site Soil in Nigeria, J. Appl. Sci. Environ. Mgt., 13(4):9-13.