International Journal of Biochemistry Research & Review
4(1): 16-27, 2014

SCIENCEDOMAIN ***international***
www.sciencedomain.org

Evaluation of the Concentration of Selected Heavy Metals and the Effects on Soil Enzymatic Activities in an Abandoned Cement Factory Nigercem Nkalagu and Its Environs

Orinya Onyebuchi Frederick[1*], Akubugwo Emmanuel Iroha[2] and Edeogu Chukwu Oswald[1]

[1]*Department of Medical Biochemistry, Ebonyi State University, Abakaliki, Nigeria.*
[2]*Department of Biochemistry, Abia State University, Uturu, Nigeria.*

Authors' contributions

This work was carried out in collaboration between all authors. Author OOF designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author AEI managed the analyses of the study. Author ECO managed the literature searches. All authors read and approved the final manuscript.

Research Article

Received 25th May 2013
Accepted 21st July 2013
Published 9th October 2013

ABSTRACT

This study investigated the concentrations of heavy metals, the activities of some selected enzymes and the pH of the soil surface (1-10 cm) and depth (11-20 cm) within the vicinity of an abandoned cement factory Nigercem Nkalagu, and further away 1km from the factory centre. The results indicate that the pH and heavy metals gradually decreased with increase in distance from the cement factory centre with the exception of Fe, Zn and Pb which was the reverse. The concentrations were also higher in the depths. The enzymatic activities increased away from cement factory centre and decreased with depth. There was a significant difference ($p \leq 0.05$) between most of the sampling points and the control (1 km) for all the parameters studied, except Cd and Cr. The enzymatic activities correlated positively with Fe, Zn and Pb and negatively with the other parameters. The inverse correlation between most of these heavy metals, the pH, and the activities of the soil enzymes are indicative that pollution caused by cement production still exhibit a

**Corresponding author: Email: orinyafreedman@gmail.com;*

significant effect on the enzymatic activities and this may invariably affect the quality of the soil of this area.

Key words: Cement; pollution; heavy metals; enzymes; soil.

1. INTRODUCTION

The environment is the natural surrounding of an organism which includes air, water and land; they contain certain amount of elements and compounds in a given proportion by nature and are considered polluted when there is an imbalance in the natural composition [1]. The soil plays a vital role in life of organisms, not only for anchorage and source of nutrients but also as a sink to many industrial wastes most of which are hazardous [2]. The biochemical processes of the soil are usually carried out by enzymes which are primarily derived from micro-organisms but can also originate from plants and animals [3]. Enzymes are usually sensitive to changes in soil properties due to presence of pollutants from anthropogenic activities and therefore can be used as measure of soil quality [4]. Cement production is one of the major anthropogenic sources of soil pollution. It is characterized by particulate air pollutants usually dust [5]. Dust from limestone is highly alkaline with pH varying between 6.0 and 12.0 [6]. Cement dust also contains metals that have direct toxic effects on the environment. They include Mg, Al, Si, Pb, Cu, Fe, Cd, Cr etc [7]. Some of these metals at very low concentrations are essential components of enzymes, pigments and structural proteins, but at high concentration alter the soil environment and adversely affect soil biotic properties such as microbial biomass and enzymatic activities [8].

Micro-organisms in the soil are responsible for nitrogen fixation, assimilation and degradation of organic residues to release nutrients. Heavy metals released from cement pollution retained in the soil interfere with these key biochemical processes and affect soil quality. This implies that soil fertility is closely linked to microbial flora and fauna [2,9]. In assessing soil microbial properties, culturable organisms are used. This method is deficient as it estimates culturable organisms only while the unculturable ones are underestimated [10]. Therefore the use of enzyme activities becomes important in the estimation of soil quality since it evaluates both the extracellualr and intracellular activities [11]. The toxic effects of heavy metals and other pollutants from cement production on microbes manifests in numerous ways such as decrease in litter decomposition and nitrogen fixation, less efficient nutrient cycling and impaired enzyme synthesis. Heavy metal toxicity to enzymes is due to their ability to induce oxidative stress, high affinity for the functional groups of protein. They may also displace constituent metals of proteins [12]. It was also believed that an additive or synergistic effect is responsible for enhanced toxicity of metals [13]. Soil pH and type of soil greatly influences the solubility, availability and toxicity of metals. High pH of cement dust also affects the activities of soil microbial enzymes [14]. The aim of this study was to determine the level of heavy metals from cement production in the soil of the abandoned cement industry and the effects on soil enzyme activities and hence estimate the suitability of the soil for plant production.

2. MATERIALS AND METHODS

2.1 Site Description

NIGERCEM Factory is situated at Nkalagu (Fig. 1.) in Ishielu Local Government Area of Ebonyi State, Nigeria. The geographical coordinates are 6º29[1]N and 7º46[1]E. The area is typical of tropical climatic conditions with guinea savannah features. Cement production and limestone quarrying activities was on in this area for about 42 years (between 1959 and 2001). The factory has now been abandoned for close to a decade. The rural dwellers in this area are mainly farmers with cassava, rice and yam as major crops.

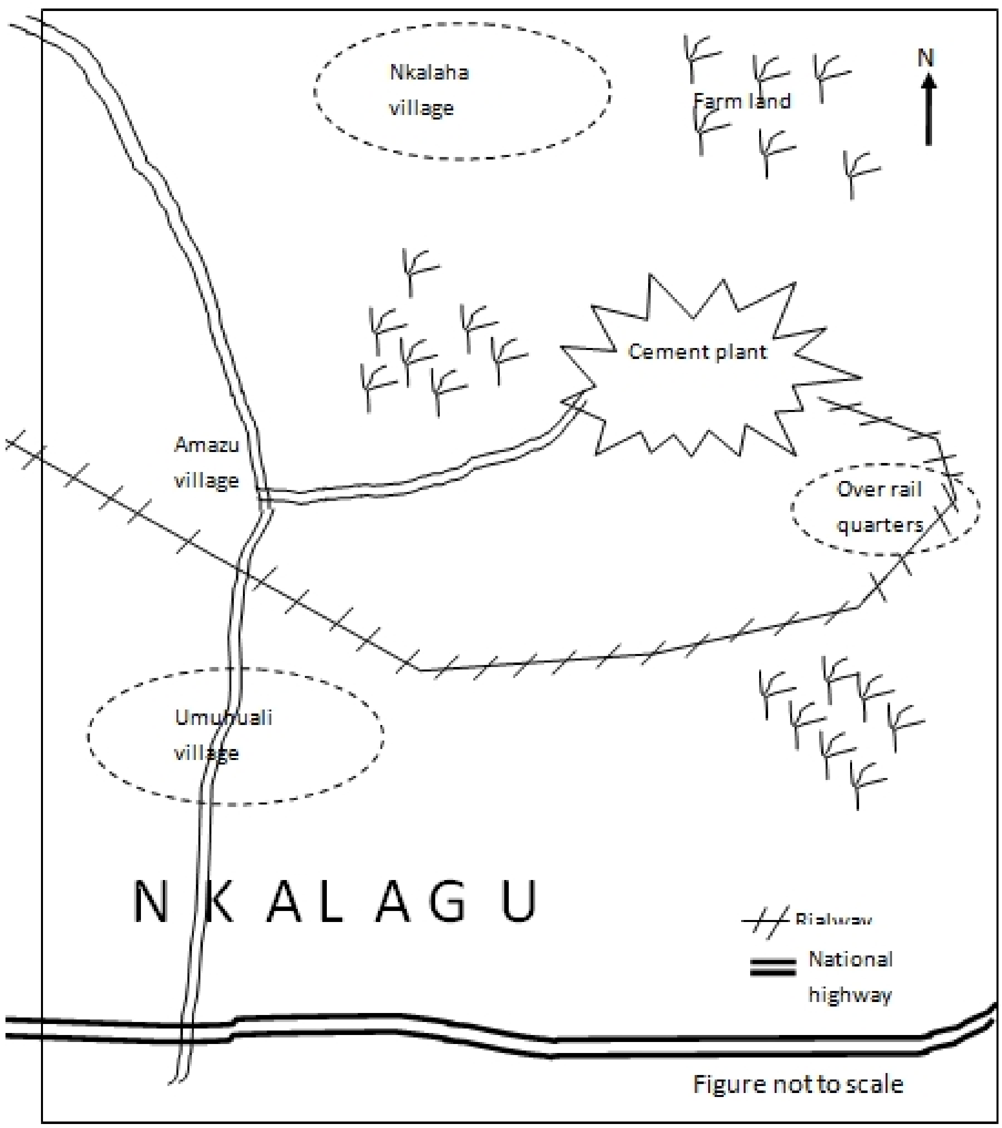

Fig. 1. Location map of Nigercem cement factory, Nkalagu Eastern Nigeria

2.2 Soil Sampling

Soil samples were collected in August, 2011 at different distances from the cement factory: factory centre, factory edge, 100 m from the edge, and 200 m from the edge. The control sample was collected at about 1 km from the cement factory. The collection of samples was done with a plastic soil auger. At each sampling point, three (3) Samples were collected at random at two (2) depths, 1-10 cm (surface) and 11-20 cm (depth), and were pooled together to make one composite sample.

2.2.1 Preparation of soil samples for analysis

Soil samples were air dried to a constant weight and crushed with a wooden roller, sieved with 2 mm sieve and stored in a soil sac (plastic bag) for the pH, heavy metals determination and assay of enzymatic activities.

2.3 Chemical and Enzymatic Analysis

he digested samples were spectrophotometrically analyzed for heavy metals (Mn, Si, Pb, Cu, Fe, Zn, Cd, and Cr) according to [15]. The following enzyme activities were assayed: total dehydrogenase according to [16], β-glucosidase according to [17], acid and alkaline phosphatases according to [18], urease according to [19], and arylsuphatase according to [20]., pH was determined according to [21]., moisture content according to [22].

2.4 Statistical Analysis

Statistical analysis was performed using the Analysis of Variance (ANOVA). The data represented means calculated from three replicates. A least significant difference test was employed for comparison of the changes and values at $p \leq 0.05$ are said to be significant.

3. RESULTS

The tables below show the results of the chemical analysis while those of the enzymatic activities are represented in Figs. 2 to 7. It was observed that among the heavy metals, Fe, Pb and Zn increased with increase in distance from the cement factory for both surfaces and 10-20cm depth as shown in Table 1 and 2. Mn, Si and Cu were the reverse. Cd and Cr were slightly higher at the factory center and edge but maintain almost the same concentration in the rest of the samples. In Table 3, the pH and temperature decreased with increase in distance from the factory centre, but slightly higher at the 10-20cm depth, while the moisture content increased in that direction.

The soil enzyme activities generally increased with increase in distance from the centre of the factory with little exception on alkaline phosphatase which was not linear. The enzymatic activities were also significantly higher at the surface when compared to the depth. Total dehydrogenase has the highest activity while the least was recorded for urease. There were significant differences between the level of the parameters in most of the samples and the control except for Cd and Cr as indicated in the result. The enzymatic activities correlated negatively with the pH and most of the heavy metals studied.

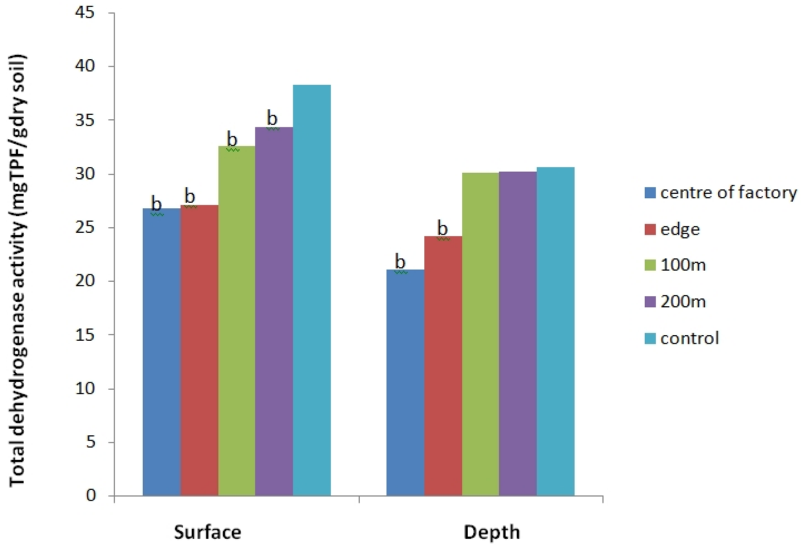

Fig. 2. Total dehydrogenase activity (mgTPF/gdry soil) of the factory
a = significantly higher, b = significantly lower than control (p ≤ 0.05)

Table 1. Heavy Metals Concentrations (mgkg^{-1}) Soil Surface (1-10cm)

Heavy metals	Centre	Edge	100 m	200 m	Control (1 km)
Mn	0.80±0.36[a]	0.60±0.10[a]	0.05±0.26[a]	0.42±0.02	0.41±0.05
Si	2.40±0.40[a]	3.10±0.00[a]	0.80±0.26[a]	0.30±0.00	0.30±0.17
Pb	8.20±1.60[a]	10.10±0.43[a]	12.90±0.81	13.60±0.35	14.20±0.35
Cd	0.70±0.03	0.70±0.36	0.06±0.03	0.06±0.03	0.60±0.02
Cr	0.70±0.03	0.70±0.36	0.06±0.25	0.06±0.04	0.06±0.03
Fe	10.700.36[b]	10.60±0.53[b]	15.40±0.53[b]	16.30±0.26[b]	17.30±0.10
Zn	12.10±0.46[b]	14.30±0.30[b]	18.30±0.46[b]	20.30±0.26[b]	21.70±0.30
Cu	11.30±0.44[a]	11.00±0.26[a]	10.60±0.40	10.60±0.20	10.40±0.20

Values are mean ± standard deviation of three values. a= significantly higher, b= significantly lower (p≤0.05)

Table 2. Heavy Metals Concentrations (mg/kg^{-1}) Soil Depth (11-20cm)

Heavy metals	Centre	Edge	100 m	200 m	Control (1 km)
Mn	0.80±0.17[a]	0.60±0.00[a]	0.41±0.06[a]	0.43±0.04	0.40±0.20
Si	2.20±0.36[a]	1.80±0.52[a]	0.70±0.28[a]	0.30±0.10	0.30±0.10
Pb	8.30±0.26[b]	10.30±0.30[b]	13.80±0.60	13.80±0.69	14.10±0.53
Cd	0.80±0.53	0.70±0.20	0.06±0.20	0.06±0.00	0.06±0.20
Cr	0.70±0.26	0.70±0.10	0.06±0.05	0.06±0.00	0.06±0.17
Fe	10.60±0.35[b]	11.20±0.42[b]	15.90±0.10	16.70±0.44	17.40±0.61
Zn	13.10±0.26[b]	14.90±0.36[b]	18.80±0.35[b]	20.70±0.61	21.80±0.20
Cu	13.60±0.21[a]	13.40±0.00[a]	13.10±0.26	13.20±0.43	13.10±0.10

Values are mean ± standard deviation of three values. a = significantly higher, b = significantly lower (p≤0.05)

Table 3. Soil physicochemical properties

	Centre		Edge		100 m		200 m		Control(1 km)	
	S	D	S	D	S	D	S	D	S	D
pH	10.30 ±0.10[a]	10.50 ± 0.42[a]	9.80 ±0.20a	9.90 ±0.10[a]	8.40 ±0.32[a]	8.40 ±0.20[a]	7.20 ± 0.20	7.30 ± 0.30[a]	6.80 ± 0.20	6.60 ± 0.20
Temperature ºC	30.30 ±0.26[a]	32.10 ±0.10[a]	30.10 ± 0.01[a]	31.40 ±0.17[a]	29.20 ± 0.17	29.10 ±0.17[a]	29.10 ± 0.10	28.70 ± 0.20[a]	28.50 ± 0.44	27.50 ± 0.26
Moisture %	12.20 ± 0.10[b]	15.20 ± 0.20[b]	13.10 ± 0.10[b]	16.31 ±0.05[b]	16.70 ±0.26[b]	14.70 ±0.30[b]	20.10 ±0.26[b]	19.30 ± 0.17	21.70 ± 0.10	20.40 ± 0.30

Values are mean ± standard deviation of three values. S = surface, D = depth, a = significantly higher, b = significantly lower (p≤0.05).

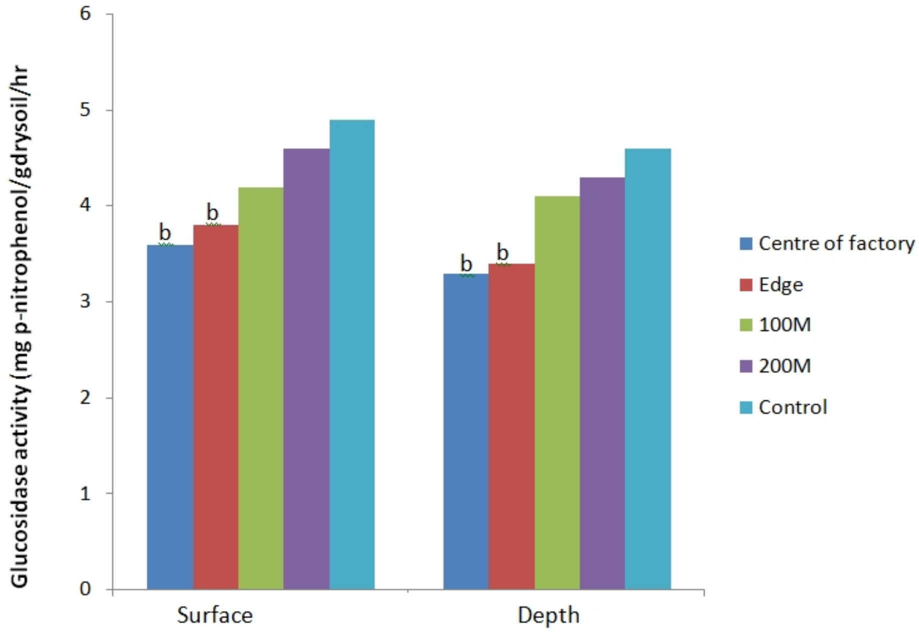

Fig. 3. β-Glucosidase activity mgPNP/gdrysoil/hr
a = significantly higher, b = significantly lower than control (p ≤ 0.05)

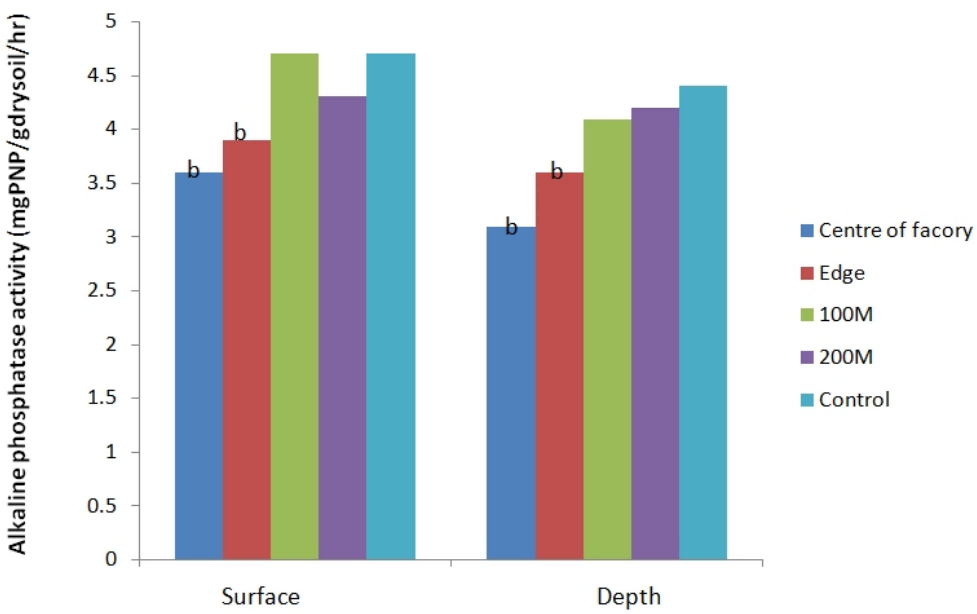

Fig. 4. Alkaline phosphatase activity (mgPNP/gdrysoil/hr)
a = significantly higher, b = significantly lower than control (p ≤ 0.05)

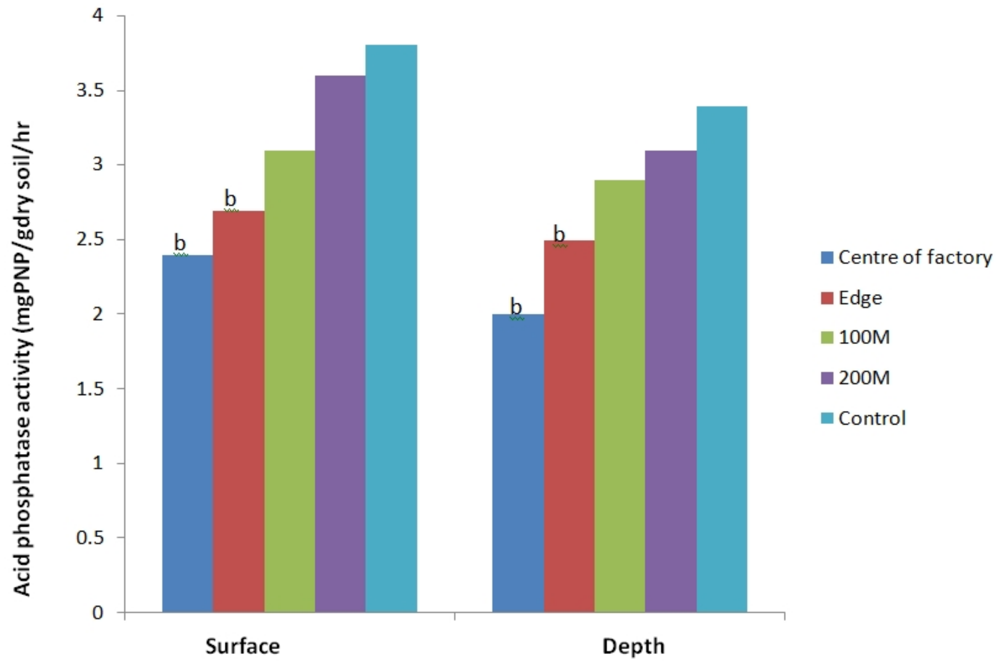

Fig. 5. Acid phosphatase activity (mgPNP/gdrysoil/hr)
a = significantly higher, b = significantly lower than control (p ≤ 0.05)

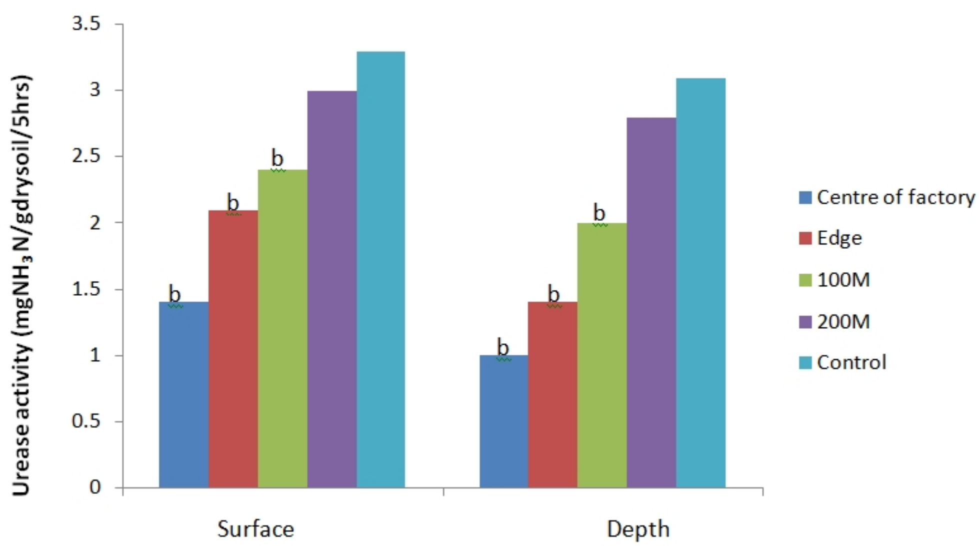

Fig. 6. Urease activities (mgNH3-N/gdry soil/5hrs) of the factory soil

a = significantly higher,

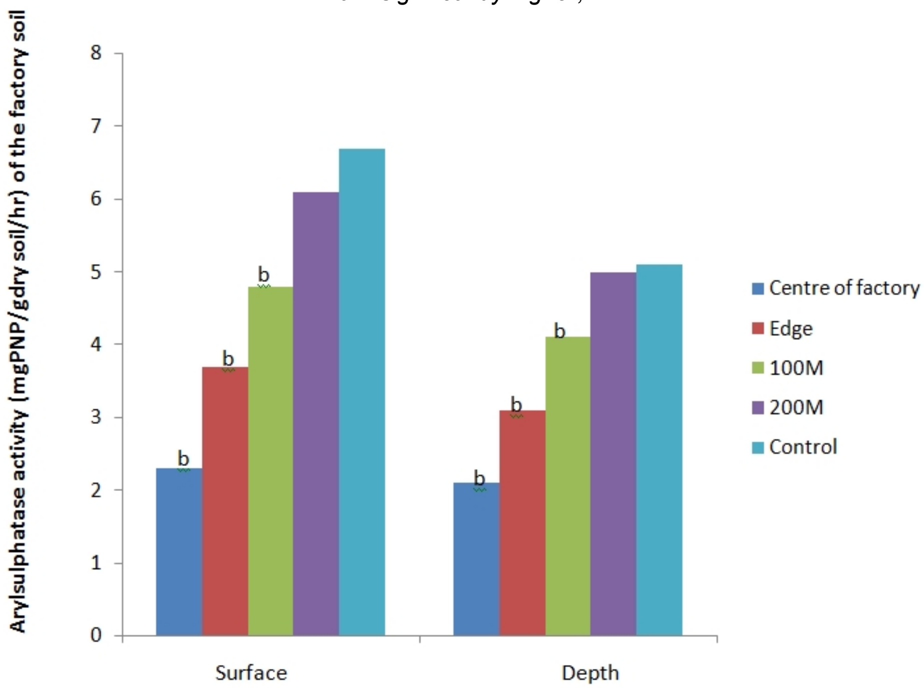

Fig. 7. Arylsulphatase activity (mgPNP/gdry soil/hr) of factory soil
a = significantly higher, b = significant lower than control (p ≤ 0.05)

4. DISCUSSION

The results revealed that Fe, Zn, Pb were significantly p≤0.05 higher in the control than in the other sampling points in the order centre < edge < 100 m < 200 m< control. This suggests that there might be other anthropogenic sources of these metals other than the cement factory. Cd and Cr maintained almost the same concentration at all the distances and control with little exceptions. Si, Cu, Mn Cr and Cd correlated positively which is an indication that they are of the same source. The values of the metals are generally higher at the depths as recorded in our result. This may be attributed to no production activities in the cement factory over a long period and hence factors such as surface run-off, leaching, sedimentation, and bioaccumulation of these metals by some plants come into play thereby making them less available on the top soil.

The pH of the soil ranges between 10.30 ± 0.10 (at centre) to 6.80 ± 0.20 (at control) indicates that the factory soil is still alkaline. It was also observed that enzyme activities increased with increase in distance from the cement factory. This may be due to pollution from cement dust particles and increase in pH as shown in our result. The decrease in enzymatic activities with depth could also be attributed to high pH, heavy metal accumulation in the depth due to sedimentation, or perhaps due to aerobic condition in the surface which supports microbial activities than the underlying soils or the combination of these factors. This is concordant with the works of [23]. Soil enzymes are primarily derived from micro-organisms but can also originate from plants and animals [24]. Hence, factors affecting microbial activities will invariably affect soil microbial enzymes.

Dehydrogenase has the highest enzymatic activity while the lowest value was recorded for urease. This may be as a result of higher sensitivity of urease due to alkaline pH as similarly reported by [25]. Heavy metals have been reported to inhibit enzymes singly or in combination by synergism [25]. Cr, Cd, and Pb, has been shown to inhibit dehydrogenase enzymes in the soil while Cr, Cu, Cd, Zn, Pb strongly inhibit urease. Other enzymes such as the phosphatases, glucosidases, and arysulphatases are also susceptible to heavy metal stress [26]. Zn, Pb, and Fe have positive correlation with the enzymes while others were the reverse. The concentrations of the heavy metals observed were generally low. It seems likely that the concentrations of metals typically found in soil do not generally explain variability of biological activities in the soil. Therefore pH and other soil parameters might have contributed immensely. This is in agreement with the data of [27], who reported that dehydrogenase and phosphatase activities in mining soil which had developed from metal-rich parent materials, were sometimes higher than that detected in corresponding reference soils with low metal concentrations.

5. CONCLUSION

This study showed a high level of heavy metals and alkaline pH within the vicinity of the abandoned cement factory which still exhibits a significant negative effect on the soil enzymes, although, there may be contribution from pedogenic sources. However, it was observed that heavy metals such as Fe, Zn, Pb, have positive correlation with the enzymatic activities, while others were the reverse. Generally, the changes in elemental composition of the soil due to cement production still have significant influence on the soil enzymatic activities. All the heavy metals have higher concentration in the 10 cm depth which is within the reach of plant roots and this may have an effect on the natives who are already using this site as an agricultural farm. We suggest further studies of the chronic toxicity of these heavy metals on human subjects from this area.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Guidelines and standards for environmental pollution control in Nigeria. Federal Environmental Protection Agency. Government Notice, Federal Republic of Nigeria. 1991;1-238.
2. Prescot LM, Klein DA, Harley JP. Microbiology. 5th ed. USA: McGraw Hill; 2001.
3. Paul EA, Clark FE. Soil Microbiology and Biochemistry. San Diego, CA, USA: Academic Press; 1996.
4. Gazso LG. The key microbial processes in the removal of toxic metals and radionuclides from the environment (a review). Central Europ J of occup Environ and Med. 2001;7(3):178-185.
5. El-Daly AF. The status of cement industry environmental pollution and measures. In: Proceedings of the National Conference on Pollution from Industrial installations. Working Force and Training: Alexandria Egypt; 1994.
6. Arslan M, BoyBay M. A study on the characterization of dust fall. Atmos Environ. 1990; 244:267-271.

7. Gbadebo AM, Bankole OD. Analysis of potential toxic metals in airborne cement dust around Sagamu, Southwestern Nigeria. J of Appl Sci. 2007;7(1):5-40.
8. McCarthy GW, Siebielec G, Stuczynski TI. Response of soil microbiological activities to cadmium, lead, and zinc salt amendments. J of Environ Qual. 2003;32:1346-1355.
9. Mathe-Gaspar G, Mathe P, Szabo L, Orgovanyi B, Uzinger N, Anton A. After effect of heavy metal pollution in a brown forest soil. Acta Biologica Szegediensis 2005;49(1-2):71-72.
10. Li H, Zhang CG, Chen GX. Effect of petroleum containing waste water irrigation on bacterial diversities and enzymatic activities in a paddy soil irrigation area. J of Environ Qual. 2005;34:1073-1080.
11. Wyszkowska J, Kucharski J. Biochemical and physicochemical properties of soil contaminated with heavy metals. Zesz Prob Nauk Rol. In: Polish J of environ Stud. 2003;492:241.
12. Petr B, Carsten IDW, Jiri G, Frantisek N, Frantisek Z. Influence of cadmium and mercury on activities of lignolytic enzymes and degradation of polycyclic aromatic hydrocarbon by Pleurotus ostreatus. Appl and Environ Microbiol. 2000;66(6):2471-2478.
13. Nwuche CO, Ugoji EO. Effects of heavy metal pollution on the soil microbial activity. Int J of Environ Sci and Technol. 2008;5(3):409-414.
14. Utgikar VP, Tabak HH, Haines JR, Govind R. Quantification of toxic inhibitory impact of copper and zinc on mixed cultures of sulphate reducing bacteria. Biotechnol and Bioeng. 2003;82(3):306-312.
15. Official Methods of Analysis. Association of Analytical Chemistry 18th ed. Washington DC; 2005.
16. Alef K. Dehydrogenase activity. Alef K, Nannipieri P, editors. Methods in applied soil microbiology and biochemistry. Academic press, London. 1995;228-231.
17. Eivazi F, Tabatabai MA. Glucosidases and galactosidases in soils. Soil Biol and Biochem.1988; 20:601-606.
18. Tabatabai MA. Soil enzymes. In: Page AL, Methods of soil analysis, Part 2. Agronomy monograph, American Society of Agronomy, Madison WI: 1982; 9:903-904.
19. Kandeler E, Gerber H. Short term assay of soil urease activity using colorimetric determination of ammonia. Biol Fert Soils. 1988;6:68-72.
20. Alef K, Nannipieri P. Methods in Applied Soil Microbiology and Biochemistry. Academic press, New York; 1995.
21. Nayek DC, Sen TK, Chamuah GS, Seghal JCC. Nature of soil acidity in some soils of Mainpur. J Indian Soc of Soil Sci. 1996;44:209-212.
22. Standard Methods for examination of water and waste water. American Public Health Association, American Water Works Association, water pollution control Federation. 20th ed. Washington DC; 1998.
23. Wright AL, Reddy KR. Phosphorus loading effects on extracellular enzyme activity in everglades wetland soils. Soil Sci Soc of America J. 2001;65:588-595.
24. Franzluebbers AJ. Soil Biology. United States Department of Agriculture (USDA), Agricultural Research Service, Watkinsville; 2004.
25. Marzadori C, Ciaviatta C, Montecchio D, Gessa C. Effects of Lead pollution on different soil enzyme activities. Biol Fert Soils. 1996;22:53-58.

26. Parisa S, Hasan SV, Ahmad H. Evaluation of some paddy soil properties on urease enzyme activity. Conference on international Research on Food Security. National Resources Management and Rural Development, Tropentag; 2008.
27. Wyszkowska J, Kurcharski J, Lajszner W. The effects of copper on soil biochemical properties and its i*nteraction* with other heavy metals. Polish J of Environ Studies. 2006;15(6):927-934.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=279&id=3&aid=2218