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Metal concentration in soil and plants in abandoned cement factory

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Abstract. This study determined the concentration of five heavy metals zinc (Zn), iron (Fe), manganese (Mn), chromium (Cr), and cadmium (Cd) in soil and woody plants species (*Azadiractha indica, Mangifera indica, Andropogon gayanus, Uvarea chamae* and *Gmelina arborea*) at NIGERCEM, Nigeria. Soil samples were collected at 40, 80, 120, 160 and 500 m sampling positions. The highest soil concentrations of Zn (212.40 mg/kg), Fe (186.30 mg/kg), and Mn (68.10 mg/kg) in soil were obtained at 40m while Cd (3.02 and 2.96 mg/kg) and Cr (26.0 and24.68 mg/kg) concentrations in soil was statistically equal ($P > 0.05$) at 40 and 80 m. In plants, the highest concentrations of Zn (18.48 mg/kg) and Fe (33.61 mg/kg) were observed in *Andropogon gayanus*; Cd (0.13 mg/kg) was in *Mangifera indica*; while Cr (2.152 mg/kg) and Mn (7.27 mg/kg) was in *Azadiractha indica*. The concentrations of heavy metals in soil and plants were below toxicity level except for Cd in soil. There were significantly positive correlations between heavy metals in soils and plants.

Keywords: Toxic metals, cement factory, soil, vegetation

1. Introduction

Cement is produced world-wide in large amounts as an important binding agent for the construction industry. There are seven cement producing companies in Nigeria operating eight works; the West African Portland Cement Company is currently the leader in the industry with installed capacity of 1.6 million tons of cement per annum (Tijani *et al*., 2005). Portland cement contains 3-8% aluminium oxide, 0.5-0.6% iron oxide, 60-70% calcium oxide, 17-25% silicon oxide, 0.1-4% magnesium oxide and 1-3% sulphur trioxide (Lea, 1970; Ade-Ademilua and Umebese, 2007).

The ecological components of the terrestrial ecosystem which include the soil, vegetation, micro and macro-organisms exist in a balanced inter-relationship that provides stability, undisrupted succession development and productivity (Nzegbule and Onyema, 2006). Cement factory through the release of air pollutants such as heavy metals (HM), generated in the process of crushing limestone, bagging, and transportation of cement are carried by wind and deposited on soil, plants and water bodies. Globally, the problem of environmental pollution due to heavy metals has begun to cause concern in most cities since this may lead to geoaccumulation, bioaccumulation and biomagnifications in ecosystem. Several studies have been carried out on effect of cement and stone dust on stomatal clogging of *Iphonia grantioides* Boiss leaves (Abdullah and Igbal, 1991), groundnut (Prasad and Inamdar, 1990), chlorophyll contents of selected plants (Shah *et al.,* 1989), periodical effect on growth of some plant species in Karachi, Pakistan (Iqbal and Shafig, 2001). However, very limited studies have been carried out on cement site, including production externalities and profitability of crop (Tijani *et al*., 2005) and growth of *Phaseolus vulgaris* L. cv. (Ade-Ademilua and Umebese, 2007) in Nigeria. Extensive literature search showed that no apparent studies were undertaken on heavy metal concentration in soil and woody plants in cement factory locations in Nigeria. The study, therefore, is aimed at determination of heavy metal levels in soil and plants in abandoned cement factory site in Nigeria.

2. Study area

This study was carried out at Nigeria Cement Company (NIGERCEM) site Nkalagu in Ishielu local government of Ebonyi State, Nigeria. It lies on latitudes 6^o10^1 and 6^o40^1N and longitudes 7^o35^1E and 7^o50^1E. Nkalagu belongs to southern equatorial climate zone, characterized by very heavy rainfall and short dry seasons. The mean annual rainfall is 150-186 cm while annual relative humidity is over 80% and means annual temperature exceeds 21^{o}C (Phillips *et al.,* 2009).

2.1. Collection and digestion of soil samples

Surface soil samples (0-10 cm) were collected at 40 m, 80 m, 120 m and 160 m within the study site while the control sample was taken at 500 m away from the site. Each replicate sample was homogenized and air-dried in circulating air in an oven at 30˚C to a constant weight and passed through a 2 mm sieve. Soil samples were digested according to Alegria *et al* (1991). To 1 g of each soil sample was added 10 ml HNO_3 acid and 3 ml $HClO_4$ and the solution was heated until boiling. The sample solution was obtained by processing the residue with 4 ml of hot 5 M HCl, and the digest was filtered into 50 cm^3 volumetric flask and diluted with deionised water. Triplicate digestion of each sample was carried out together with blank digest without the soil sample. The concentrations of Zn, Cd, Fe, Cr and Mn in the solution were quantified using a flame atomic absorption spectrophotometer (UNICAM 919 model).

2.2. Collection and digestion of plant samples

Old leaves of *Azadiractha indica* (neem, Meliaceae)*, Mangifera indica* L. (mango, Anacardiaceae)*, Andropogon gayanus* (Kunth) (gamba grass, Poaceae)*, Manihot esculenta* . (cassava, Euphorbiaceae)*, Uvarea chamae* (P. Beauv.) (finger-root, Annonaceae), and *Gmelina arborea* Roxb. (gmelina, Verbenaceae) were randomly taken from the sampled area where soil were collected using a well cleaned stainless secateur, placed in envelops, labeled and taken to the laboratory at ambient temperature. The plant samples were washed with distilled water to remove any attached dust and pollen particles, placed in crucibles and oven dried at 105˚C for 48 h. The dried samples were milled with a Thomas Wiley milling machine (Model ED-5). 1 g of each sample was placed in a muffle furnace at 400^{0}C to ash for 5 h. Each ashed sample was dissolved with 10 cm^3 of 1 M HCl and the solution was filtered into 50 cm^3 volumetric flask using Whatman no. 1 filter paper. Triplicate digestion of each sample was carried out together with blank digest without the plant sample. The concentrations of heavy metals in solution were determined using atomic absorption spectrophotometer (UNICAM 919 model).

2.3. Statistical Analysis

The factorial experiment was conducted as a randomized complete block design (RCBD) with three replications. Data were subjected to one-way analysis of variance (ANOVA) and Pearson's correlation analysis using Statistical Package for Social Sciences (SPSS) v. 15 and mean separation according to Steel and Torrie (1980) at $P < 0.05$.

3. Results And Discussion

3.1. Metal concentration in soil

The concentrations of Zn, Cr, Cd, Mn, and Fe in sampled soils from NIGERCEM site are summarized in Table 1. The highest and lowest metal concentrations were observed at the cement factory (NIGERCEM) sites, respectively. The highest concentrations of Zn (212.40 mg/kg), Fe (186.30 mg/kg), and Mn (68.10 mg/kg) in soil was obtained at 40 m, and this may be attributed to the size of the particles vis-à-vis the proximity of this sampling position than the others (80, 120, 160, and 500 m). Metals originating from industrial activities are distributed in soils by the atmosphere within a distance that depends on the size of particles (Mandal and Voutchkov, 2011).

Table 1: Heavy metal content (mg/kg) in soil

Sampling position (m)	Zn	Cd	Fe	Cr	Mn
40	212.40^a	3.02^a	186.30^a	26.00^a	68.10^a
80	180.00^b	2.96^a	161.00^b	24.68^a	65.70^b

120	87.00[c]	1.19[b]	140.00[c]	20.81[b]	24.50[c]
160	73.10[d]	1.21[b]	117.50[d]	18.53[b]	16.40[d]
500	10.04[e]	0.41[c]	5.02[e]	0.07[c]	3.61[e]

The concentration of Zn in soil ranged from 73.10 to 212.40 mg/kg, which is higher than 67.48-259.78 ppm observed in top soil (0-10 cm) samples around cement factory in Rockfort, Jamaica (Mandal and Voutchkov, 2011).

Soils around cement factories show high concentrations of metals especially Zn on top soils of 0-10 cm deep (Khashman and Shawabkeh, 2006). Since there were no other sources of contamination in the area, the source of Zn in soil may be attributed to dust particles from NIGERCEM. The concentration of Fe in soil ranged from 117.50 to 186.30 mg/kg and this is significantly higher than 1.92 ± 0.32 mg/kg reported by Sakalauskaite *et al*. (2009) in cement factory in Lithuania probably due to differences in soil parent material and soil chemical composition. Similarly, the concentration of Mn ranged from 16.40 to 68.10 mg/kg, which is substantially higher than 6.5 ± 2.6 mg/kg reported by Sakalauskaite *et al*. (2009). Cement industry plays a vital role in the imbalances of the environment by producing toxic substances such as manganese (Mn), lead (Pb), and beryllium (Sakalauskaite *et al*., 2009), thus, NIGERCEM industry is the source of Mn in soil. The concentration of Cr in soil ranged from 18.53 to 26.0 mg/kg. The range of Cr in this study reflected a significant pollution impact compared to 0.38 ± 0.04mg/kg observed in Lithuania (Sakalauskaite *et al*., 2009). In cement industry the linings for the rotaries contain chromium, which could be liberated by wear and friction (Banat *et al*., 2005). Consequently, the cement factory is implicated as the source of Cr in soil. The concentration of Cd in soil ranged from 1.19 to 3.02 mg/kg, which is significantly lower than 2.51-7.84 mg/kg reported by Mandal and Voutchkov (2011). The source of Cd in the top soils may be associated with emission sources from the cement factory. The process and production of cement industry require a substantial amount of energy supplied by burning fossil fuel and traffic activity in the plant (Banat *et al*., 2005; Ellis and Revitt, 1982). Generally, the concentrations of metals in soil followed a decreasing order: Zn>Fe>Mn>Cr>Cd.

3.2. Metal concentration in plants

The highest concentrations of Zn (18.48 mg/kg) and Fe (33.61 mg/kg) were obtained in *Andropogon gayanus*. The concentration of Zn ranged from 0.23 (*Gmelina arborea*) to 18.48 mg/kg (*Andropogon gayanus*) while Fe was 4.17 (*G. arborea*) to 33.61 mg/kg (*A. gayanus*). In this study, the concentration of Zn in plants is significantly higher than 12.81 ± 3.84-18.00 ± 5.23 µg/g in *Piptatherum* sp. in Vallcarca, Spain (Schuhmacher *et al*., 2009) and 62.899-63.112 ppm in grasses in Konya, Turkey (Onder *et al*., 2007) around cement plant, respectively. Since zinc concentration in soil is high (212.40 mg/kg), the source of Zn in plants may be attributed to the soil. High concentrations of Zn in plants cause poor yield and growth while low levels in plants cause leaf deformation (Bucher and Schenk, 2000; Celik *et al*., 2005; Kashem *et al*., 2007) and reduce photosynthetic processes in plants. The concentration of Fe (4.17 to 33.61mg/kg) is substantially lower than 152.2 ± 32.7 mg/kg reported by Sakalauskaite *et al*. (2009) in apple tree leaves growing in cement factory in Lithuania. Iron aid in energy transfer and chlorophyll development in plants (Briat *et al*., 2001). The concentration of Cd ranged from 0.001 (G. arborea) to 0.130 mg/kg (M. indica) and this is higher than 0.085-0.186 ppm and 0.02 ± 0.02 µg/g in grass and Piptatherum sp. around cement factories in Konya, Turkey (Onder *et al*., 2007) and Vallcarca, Spain (Schuhmacher *et al*., 2009), respectively. Plants absorb Cd from the soil via the roots (Pip 1991; McLaughlin *et al*., 1999) and can become toxic by displacing Zn (Singh *et al*., 2010). The concentration of Cr ranged from 0.001 (G. arborea) to 2.152 mg/kg (A. indica), which is higher than 0.30 ± 0.14-0.87 ± 0.61 µg/g reported by Schuhmacher *et al*. (2009) in *Piptatherum* sp. Cr phytotoxicity can result in inhibition of seed germination, nutrient inbalance and induce oxidative stress in plants (Poschenriender *et al*., 1991; Panda *et al*., 2003).

Table 2: Heavy metal content (mg/kg) in plants

Plant species	Zn	Cd	Fe	Cr	Mn
Azadiractha indica	11.030[b]	0.120[b]	21.400[c]	2.152[a]	7.270[a]
Mangifera indica	5.810[d]	0.130[a]	26.000[b]	0.089[c]	4.600[d]

Andropogon gayanus	18.480^{a}	0.060^{c}	33.610^{a}	1.640^{b}	5.780^{c}
Uvarea chamae	8.020^{cd}	0.100^{bc}	25.020^{b}	0.044^{c}	6.080^{c}
Gmelina arborea	0.230^{e}	0.001^{d}	4.170^{e}	0.001^{c}	1.030^{e}

The concentration of Mn ranged from 1.03 (*G. arborea*) to 7.27 mg/kg (*A. indica*), which is relatively higher than 6.5 ± 2.6 mg/kg observed in apple tree leaves in Lithuania (Sakalauskaite *et al*., 2009).

Manganese insufficiency leads to decrease in Ca and Mg in plants, accumulation of nitrates, and disturbance in protein synthesis in plants (Mukhopadhyay and Sharma, 1991). Generally, the concentrations of metal in plants followed an increasing order: Fe>Zn>Mn>Cr>Cd.

3.3. Correlation coefficient between Heavy metals in soils and plants

The correlation coefficient of HMs in soils and plants is summarized in Table 3. Zn in soil was positively correlated with Cd (0.986), Fe (0.895), Cr (0.862), and Mn (0.985) in soil at $P < 0.01$ and with Cd (0.855) and Mn (0.688) in plant at $P < 0.01$. Cd in soil positively correlated with Fe (0.842), Cr (0.819), Mn (0.990) in soil and with Cd (0.869) in plant at $P <0.01$. Similarly, Fe in soil positively correlated with Cr (0.992), Mn (0.833) in soil and with Cd (0.879), Fe (0.780), and Mn (0.892) in plant at $P < 0.01$. Indeed, Cr positively correlated with Mn (0.802) in soil and with Cd (0.899), Fe (0.812) and Mn (0.881) in plant at $P < 0.01$. Significant positive correlation occurred between Zn in plant with Cr (0.741) and Mn (0.725) in plant at $P < 0.05$; while Cd, Fe and Cr in plant positively correlated with Mn in plant at $P < 0.05$. Few non-significant positive correlation occurred between Cd and Fe (0.383), Cd and Cr (0.380) as well as Cd and Mn (0.600) in plant.

Table 3 Pearson correlation coefficient showing the relationship between heavy metal content in soil and plants

	Zn soil	Cd soil	Fe soil	Cr soil	Mn soil	Zn plant	Cd plant	Fe plant	Cr plant	Mn plant
Zn soil	1									
Cd soil	0.986**	1								
Fe soil	0.895**	0.842**	1							
Cr soil	0.862**	0.819**	0.992**	1						
Mn soil	0.985**	0.990**	0.833**	0.802**	1					
Zn plant	0.307	0.180	0.638*	0.629	0.206	1				
Cd plant	0.855**	0.869**	0.879**	0.899**	0.808**	0.283	1			
Fe plant	0.448	0.383	0.780**	0.812**	0.375	0.845**	0.586	1		
Cr plant	0.517	0.380	0.590	0.513	0.438	0.741*	0.208	0.402	1	
Mn plant	0.688*	0.600	0.892**	0.881**	0.561	0.725*	0.763*	0.758*	0.633*	1

** Correlation is significant at the 0.01 level 2-tailed.

* Correlation is significant at the 0.05 level 2-tailed.

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