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VARIATIONS IN PHYSICO-CHEMICAL PROPERTIES AND HEAVY METAL CONTENTS OF SOIL AROUND A CEMENT FACTORY IN SOUTH-WESTERN NIGERIA

C.A. Onwudiegwu[1], G.C. Ezeh[2]* and I.B. Obioh[2]
[1]African Institute for Science Policy and Innovations, Obafemi Awolowo University Ile-Ife, Osun State, Nigeria
[2]Centre for Energy Research and Development (CERD), Obafemi Awolowo University Ile-Ife, Osun State, Nigeria
*Corresponding author: goddyich@yahoo.com, gcezeh@cerd.gov.ng

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Abstract: Soils around a cement factory in Sagamu, South West Nigeria were analyzed for their physicochemical (pH, texture, exchangeable cations and organic matter) parameters and elemental contents to assess the contamination level of the soils. Samples were collected at twenty-two identified transects of the soils near the cement factory using standard analytical procedures during dry and rain seasons. Elemental contents of the soils were determined using the bulk scientific Atomic Absorption Spectroscopy (AAS) technique while the physicochemical parameters were determined using standard analytical techniques. In addition, calculation of Enrichment Factors (EFs), Geoaccumulation Index (I_{geo}), Pollution Indices (PI) and Pearson correlation matrices were performed on the elemental concentration data. Results indicated that the physicochemical parameter values varied across the transects as well as in the seasons. Average soil pH ranged from 5.8 to 7.2 (dry season) and 4.6 to 6.8 (rain season) while organic matter contents were from 9.4 to 39.6 g/kg (dry) and 12.8 to 30.9 g/kg (rain). Soil texture of the transects was dominated by sandy structure with an average of 68 % (dry) and 57 % (rain). Ten elements (Ca, Pb, Zn, Mg, Fe, Cu, Co, As, Ni and Cr) were analyzed and their concentrations values established. Average total elemental concentrations were in the order of 2332 µg g^{-1} (0.3 km) > 1870 µg g^{-1} (0.3 km to 1 km) > 1048 µg g^{-1} (1 km to 5 km) > 671 µg g^{-1} (5 km to 10 km) > 322 µg g^{-1} (10 km to 20 km) > 406 µg g^{-1} (20km) and 509 µg g^{-1} (0.3 km to 1 km) > 596 µg g^{-1} (1 km to 5 km) > 319 µg g^{-1} (5 km to 10 km) > 460 µg g^{-1} (10 km to 20 km) > 119 µg g^{-1} (≥20 km) for dry and rain seasons respectively. The elements were majorly in the low EFs class while Igeo, PIs and Pearson correlation results revealed that some elements were in the highly pollution class and strongly correlated. The study concluded that anthropogenic emissions from the cement factory posed great hazard to nearby agricultural soils.

Keywords: Chemical, concentrations, enrichment, geo-accumulation, heavy metal, pollution

Introduction

Cement production is among key anthropogenic activities leading to particulate matter emissions in Nigeria. An inventory of air pollutants in Nigeria classified cement production as the highest source of atmospheric dust emissions as it accounted for ≈22.4 million tonnes (Mt) of emissions for the year 1988 (Adejumo *et al.*, 1994). The chemistry of cement production involves emission of particulate matter which could contain broad spectrum of toxic elements and other gasous pollutants that may have deleterious effect on human health and ecosystem. Soil is a major sink for emitted dusts from cement production through direct dumping or atmospheric deposition or precipitation by rain (Ahiamadjie *et al.*, 2011). Deposition of cement generated aerosols could have profound negative impacts on soil properties and could inevitably be transferred to food chain. Therefore, it becomes important to study the role and impact of dusts generated from cement production on the physico-chemical properties and elemental compositions of nearby agricultural soils.

Heavy metals contamination in soil is a major concern due to its toxicity and threat to human life as well as to the environment (Begum *et al.*, 2009). Heavy metals and other pollutants such as polycyclic aromatic hydrocarbons are major components of cement dusts. Heavy metals in the soil could lead to geo-accumulation, bioaccumulation and bio-magnifications and could have negative influence on physiological activities of plants such as photosynthesis, gaseous exchange and nutrient absorption (Suciu *et al.*, 2008). Heavy metals get into plants via adsorption which refers to binding of materials onto the surface or absorption which implies penetration of metals into the inner matrix. However, both mechanisms can occur (Alloway & Aryes, 1997). In small concentrations, the traces of heavy metals in plants and animals are not toxic (De-vries *et al.*, 2007). Conversely, Pb, Cd and Hg are exceptions as they are toxic even at low concentrations (Galas-Gorcher, 1991).

Sagamu, (latitudes 6°45'N to 7°15'S and longitudes 3°00' E to 4°00' W) with topography of about 100 m above sea level is located within the tropical rainforest belt of Nigeria and with an average rainfall of about 1,561.86 mm per annum, characterized by distinct rain and dry seasons (Akinlolu *et al.*, 2007). The soils in this area are classified as the Ogun soil series which developed from heavy clay alluvial materials and are acidic in nature (Akinlolu *et al.*, 2007). The cement factory at Sagamu was built in 1978 and currently in the process of increasing its capacity to meet the growing demands of local and exports markets. Therefore becomes imperative to study the distributions of heavy metals as well as the physico-chemical properties on agricultural soils around the neigborhood of the factory.

The aim of this work is to assess the impact of dusts particles emitted from cement industry on the physico-chemical properties and elemental compositions of neighbouring agricultural soils around a cement factory in Sagamu, South Western Nigeria.

Materials and Methods

Soil sampling

Twenty-two sampling points (Fig. 1) covering ≈ 30 km^2 land area were randomly identified and selected in consideration of their distances (0.3, 1, 5, 5 to 10, 10 to 20 and ≥ 20 km) from the cement factory. Soil sampling was done randomly on 10 m x 10 m plots using the Dutch stainless steel Auger for top (0-15 cm) and sub (15-30 cm) soils. Soil samples collected at site >20 km from the cement factory were used as control (Asubiojo *et al.*, 1992). During dry season, Sagamu is predominantly influenced by North East (NE) trade wind; therefore sites that are south west of the factory were classified as down-wind while sites in the NE of the industry were up-wind. Conversely, during rain season, South-western (SW) trade wind is predominant thus, sites located North East (NE) of the factory becomes down-wind, while sites located in the South-west is up-wind. A total of seventy-six (76) samples were collected during dry season (November, December, January and February) and rain season (April, May, June, July, August and September) months in order to investigate the seasonal effect of cement dust over the area. Soil samples were prepared using the IAEA-TECDOC (1993) method.

Sample collection, preparation and quantification

The sites were selected because they cut across wide range of land use types as well as key directions from the cement. Fig. 1 displayed the sample locations. The classification of sampling points with respect to Mean Trade Wind (MTW) directions during dry and rain seasons are displayed in Table 1. During rain season, four, nine and six sampling points were classified as down-wind and up-wind directions respectively while the reverse was done during the dry season sampling. Several factors; such as surface temperatures, pressure gradient and friction could influence MTW directions over a city (Adejumo *et al.*, 1994).

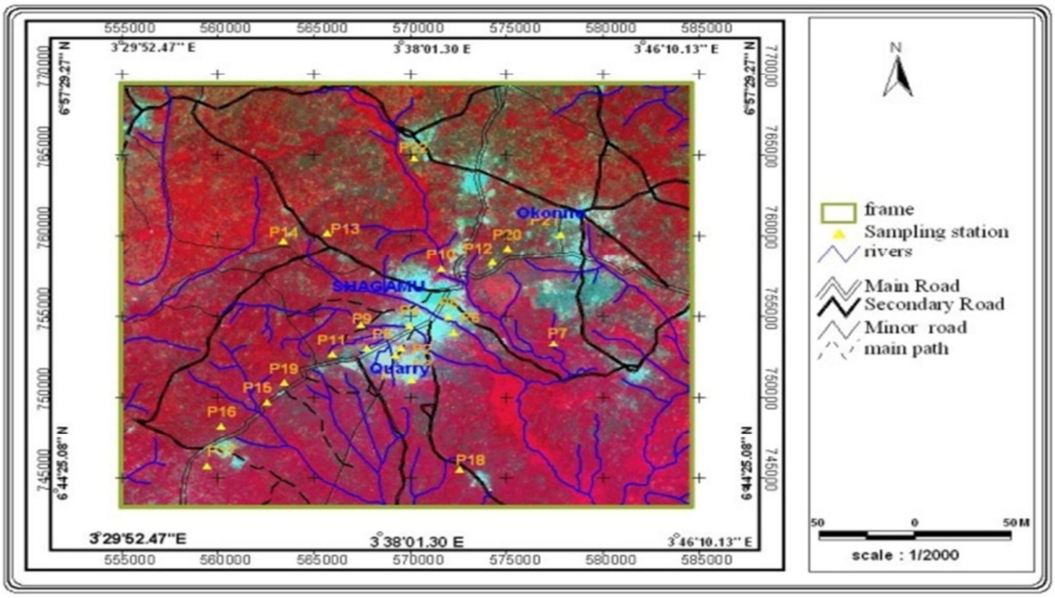

Fig. 1: Map of study sites

Table 1: Classification of sampling points per Mean Trade Wind (MTW) direction

Seasons	Within Factory	Down-wind	Up-wind	Cross-wind	Control
Dry	p1 p2	p12, p13, p14, p15	p3, p4, p5, p6, p7, p8, p9, p10, p11	p16, p17, p18, p19, p20, p21	p22
Rainy	p1 p2	p3, p4, p5, p6, p7, p8, p9, p10, p11	p12, p13, p14, p15	p16, p17, p18, p19, p20, p21	p22

"p" = denotes points

Soil sampling within 0.3 km away from the cement industry were not done during the Rainy seasons due to local challenges. Prior to laboratory analyses, samples were homogenized, pulverized, air dried for 7 days in-order to stop all microbial activities and sieved through a 2 mm stainless steel mesh. Soil fractions with mean size <2 mm were used for the determination of the physico-chemical properties and elemental compositions.

Determination of physicochemical parameters

Soil samples were analyzed for the following parameters; pH, particle size, organic matter and exchangeable cations. Soil pH was measured in 1:1 (soil/water) suspension using a glass electrode pH meter (Hendershot *et al.*, 1993) while particle size distribution was determined by the hydrometer method using sodium hexametaphosphate as the dispersant (Bouyoucous, 1962). Soil organic matter was determined using the Walkley and Black, (1934) method. Exchangeable bases in the soils were extracted with ammonium acetate at pH of 7 and the Mg, Ca, Na and K ions of the extracts were determined with a Jenway flame photometer (Oyedele *et al.*, 2008).

Elemental analysis

The soil samples were digested using *aqua regia* procedure of USEPA, (1995) and the elemental concentrations of (Ca, Pb, Zn, Mg, Fe, Cu, Co, As, Ni and Cr) were determined using AAS at International Institute of Tropical Agriculture (IITA), Ibadan Nigeria. Calibration Atomic Absorption Spectroscopy (AAS) facility was done using mixed calibration standard solutions prepared from pure BDH Analar® grade salts with know weights (10 mg kg^{-1}) of each element (Mn, Zn, K, Cu, Fe, Ni, Cr, and Pb). After calibration, percentage recovery of the elements ranged from 90 to 95. All the glassware and sample bottles were cleaned using the procedure reported elsewhere (Laxen and Harrison, 1981).

Statistical analyses

The elemental concentrations of the samples were also subjected to statistical analysis to include Pearson correlation (Szekely *et al.*, 2007) matrix of the elements and show how they are correlated. This was calculated using Statistical Package for Social Scientist (SPSS) and correlation was considered significant at the 0.05 level (two-tailed).

Results and Discussions

Physicochemical Compositions

The mean distribution of the soil properties (pH, particle size, organic matter and exchangeable cations) obtained during the dry and rain seasons are summarized in Table 2. The soil pH differed from one season to the other across the sites. Its average values ranged from 5.8 to 7.2 units during the dry season and from 4.6 to 6.8 units during the rain season. This indicates that the soils were moderately acidic to neutral and strongly acidic to neutral during the dry and rain seasons respectively. These values were relatively higher compared to the pH value (5.75) recorded for the control site. Although, the pH of most soils in the tropics ranged from acidic to slightly neutral (Alloway & Aryes, 1997). Akinlolu *et al.* (2007) had observed that soils of Sagamu are acidic in nature. Mclean & Bledsoe (1992) reported that the optimum soil pH for plant production is one that is slightly acidic. At acidic pH soil plant nutrients are readily available and microorganisms are mostly active. The modification of the soils in some sites from acidic to neutral during the dry season could be attributed to the deposition of liming materials (CaO and Ca (OH) $_2$) which are often used for cement production. An increase in soil pH (from 5.4 to 5.6) could be as a result of soil amendment with low proportions of cement (Oyedele *et al.*, 1990). During the rain season, the soils across the sites were observed to be more acidic than in the dry season. This may be attributed to the fact that there are more hydrogen ions (due to rainfall) in the soil solution during the rain season. The control site was moderately and strongly acidic during the dry and rain season respectively, maintaining the pH status of soils in Sagamu and conformed to the observation that the impacts of cement dusts reduces with distance away from the plant**.** Soil pH is an important parameter that directly influences sorption/desorption, precipitation/dissolution, complex formation and oxidation reduction reactions (Oyedele *et al.*, 2008).

Table 2: Soil physicochemical properties

S/N	Distance (km)	Dry Season									Rain Season								
		pH	Sand	Silt	Clay	OM	K+	Na+	Ca²+	Mg²+	pH	Sand	Silt	Clay	OM	K+	Na+	Ca²+	Mg²+
				(%)		(g kg^{-1})		(c mol kg^{-1})					(%)		(g kg^{-1})		(c mol kg^{-1})		
1	0.3	6.40	44.00	49.00	7.00	9.40	0.31	0.12	16.00	4.05	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC
2		6.92	44.00	37.00	19.00	16.10	0.57	0.15	20.00	4.86	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC
3		6.65	70.00	13.00	17.00	25.20	0.32	0.12	17.50	5.67	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC
4		6.40	84.00	5.00	11.00	12.10	0.16	0.06	3.40	5.27	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC
5		6.25	70.00	7.00	23.00	30.90	0.22	0.06	4.25	2.03	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC	NSC
6	0.3 to 1	6.05	66.50	8.50	25.00	26.80	0.22	0.09	6.10	4.46	5.95	70.00	9.00	21.00	16.80	0.11	0.40	0.99	0.65
7		6.65	31.00	13.00	56.00	22.80	0.27	0.07	5.30	6.08	5.42	58.00	9.00	33.00	16.10	0.15	0.45	0.70	0.89
8		6.05	48.50	7.00	44.50	28.20	0.26	0.08	4.50	2.83	5.04	59.00	7.00	35.00	12.80	0.15	0.58	0.51	0.49
9		6.32	57.00	8.00	35.00	16.10	0.21	0.07	4.80	2.82	6.33	68.00	10.00	22.00	18.10	0.12	0.54	0.88	0.73
10	1 to 5	5.92	63.50	7.50	29.00	26.20	0.16	0.08	4.50	5.67	5.69	69.00	6.00	26.00	21.10	0.13	0.50	0.88	0.24
11		5.89	62.50	5.50	32.00	11.40	0.15	0.08	3.30	3.24	6.11	54.00	8.50	38.00	19.50	0.08	0.47	1.09	0.81
12		7.02	82.00	5.00	13.00	16.80	0.32	0.11	6.30	2.43	6.18	83.00	5.00	12.00	13.40	0.12	0.58	1.29	0.57
13		7.20	68.50	8.50	23.00	24.20	0.26	0.11	22.50	2.43	6.23	70.00	9.30	21.00	13.40	0.34	0.61	1.24	0.66
14	5 to 10	6.25	69.00	4.50	26.50	39.60	0.29	0.07	4.20	4.05	5.14	68.00	6.50	26.00	16.80	0.12	0.58	0.47	1.70
15		6.25	63.00	7.50	29.50	18.10	0.24	0.08	4.50	2.43	5.42	65.00	8.00	27.00	16.50	0.15	0.57	1.88	0.79
16		6.25	72.00	6.00	22.00	16.40	0.19	0.06	3.30	4.86	6.60	58.00	13.00	30.00	26.20	0.17	0.65	2.15	0.65
17		6.40	75.00	3.00	22.00	18.10	0.16	0.07	4.00	2.82	6.80	53.00	9.00	38.00	14.40	0.17	0.60	0.98	0.73
18	10 to 20	6.98	64.00	9.00	27.00	28.20	0.27	0.08	8.50	3.24	5.30	70.00	8.00	23.00	18.80	0.08	0.60	1.19	0.89
19		6.00	70.00	9.00	21.00	17.50	0.15	0.07	4.10	2.43	6.20	71.00	10.00	19.00	19.50	0.13	0.50	1.04	0.89
20		6.54	72.00	8.00	20.00	21.50	0.14	0.07	4.35	2.43	5.40	72.00	9.00	19.00	30.90	0.14	0.48	1.42	0.89
21		6.62	67.50	7.50	25.00	23.50	0.16	0.06	5.50	4.05	6.00	67.00	7.00	27.00	16.50	0.05	0.49	1.28	0.73
22	≥20 (Control)	5.75	68.00	7.50	24.50	10.10	0.17	0.07	2.50	2.03	4.60	57.00	5.00	38.00	22.80	0.10	0.44	0.61	0.73

"NSC" denotes "no sample collected"

The textural composition of the soils did not differ among sites and across the seasons. This is expected as soil texture is mainly inherited from the soil forming parent materials. The average soil organic matter (SOM) content ranged from 9.4 to 39.6 g kg^{-1} (dry season) and 12.8 to 30.9 g kg^{-1} (rain season) were in the low-to-very high and low-to-high soil fertility classes in Nigeria (Federal Ministry of Agriculture and Natural Resources, 1990). The relatively higher SOM content in the dry season could be due to lower soil moisture in the soil. Thus, microbial decompositions of organic matter are often retarded during the dry season. On the other end, soils in the control site revealed low (10.1 g kg^{-1}) and moderate (22.8 g kg^{-1}) concentrations of organic matter content. The low concentrations of SOM at the control site indicated that it could support optimum plant growth than those that are closer to the cement plant.

The soil concentrations of exchangeable bases differed between the seasons and across the sampled sites. During dry season mean value ranged from K$^+$ (0.14 to 0.57 cmol kg^{-1}), Na$^+$ (0.06 to 0.15 cmol kg^{-1}), Ca^{2+} (2.50 to 22.50 cmol kg^{-1}) and Mg^{2}+ (2.03 to 6.08 cmol kg^{-1}). The concentrations of exchangeable cations during the rain season ranged from K$^+$ (0.05 to 0.34 cmolkg^{-1}), Na$^+$ (0.40 to 0.65 cmol kg^{-1}), Ca^{2+} (0.47 to 2.15 cmol kg^{-1}) and Mg^{2}+ (0.24 to 1.70 cmol kg^{-1}). Smyth & Montgomery (1962) reported K$^+$ (0.33 to 2.12 cmol kg^{-1}), Ca^{2+} (2.5 to 12.9 cmol kg^{-1}) and Mg^{2}+ (0.75 to 5.40 cmol kg^{-1}) for Egbeda soil series in

South Western Nigeria. Dry season concentrations of exchangeable cations were slightly higher than the wet season concentrations and may be attributed to high rainfall and weathering as well as leaching and lateral translocations (Adegbenro *et al.*, 2013). It was observed further that the soil content of most of the exchangeable bases correspond to the clay and soil organic matter content. This is probably because the cations are concentrated in exchange sites on the clay colloids and in organic matter which on decomposition provide continuous release of cations. Oyedele *et al.* (2008) had observed that cation and anion exchange in the soil accounted for a great percentage of clay along with SOM.

Elemental analyses

Tables 3 (dry) and 4 (rain) show the elemental concentrations of the soil samples with respect to the site distances away from the cement industry. Higher elemental concentrations were observed in the sites closer to the premises of the cement factory at both dry and rainy seasons probably due to their proximity to cement plant (Mandal & Voutchkov, 2011).

For dry season soil sampling, the concentrations of the crustal elements (Ca and Fe) were more pronounced compared to other elements. This could be as a result of their association with the raw materials (limestone, clay, laterite, sandstone, gypsum and so on) used for cement production (Akinlolu *et al.*, 2007). Ca was the most abundant element; it recorded an average concentrations of 13549 µg g^{-1} (0.3 km), 10555 µg g^{-1} (1 km), 7254 µg g^{-1} (5 km), 3332 µg g^{-1} (5 to 10 km), 1536 µg g^{-1} (10 to 20 km) and 985 µg g^{-1} (>20 km). Ahiamadjie *et al.* (2011) reported 14684 µg g^{-1} for Ca in soils around a cement industry in Aflao Ghana. Inadvertently, the concentrations of Fe in the Dry season were in the order 7239 µg g^{-1} (0.3 km) >4531 µg g^{-1} (1 km) >2595 µg g^{-1} (5 to 10 km) >2521 µg g^{-1} (5 km) >1122 µg g^{-1} (10 to 20 km) >1978 µg g^{-1} (control).

Table 3: Trace element concentrations (µg g^{-1}) during dry season

Elements	0.3 km	0.3 km to 1 km	1 km to 5 km	5 km to 10 km	10 km to 20 km	≥20 km (Control)
Ca	13549 (111)	10555 (34)	7254 (82)	3332 (75)	1536 (42)	985 (28)
Pb	66 (5)	48 (9)	33 (10)	60 (7)	24 (4)	8 (1)
Zn	542 (44)	423 (29)	184 (13)	124 (9)	97 (8)	64 (6)
Mg	1739 (73)	1120 (37)	358 (27)	298 (18)	325 (19)	183 (17)
Fe	7239 (81)	4531 (41)	2521 (71)	2595 (42)	1122 (31)	1978 (53)
Cu	54 (5)	52 (6)	32 (4)	256 (21)	21 (4)	15 (3)
Co	18 (2)	24 (1)	32 (4)	11(3)	46 (5)	9 (2)
As	17 (2)	nd	5 (2)	14 (5)	23 (9)	7 (3)
Ni	84 (15)	44 (8)	28 (4)	3 (1)	14 (4)	nd
Cr	7 (1)	33 (2)	28 (2)	18 (3)	14 (5)	nd

"nd" means "not detected".

Table 4: Trace element concentrations (µg g^{-1}) during rain season

Elements	0.3 km	0.3 km to 1 km	1 km to 5 km	5 km to 10 km	10 km to 20 km	≥20km (Control)
Ca	NSC	2875 (53)	1874 (78)	968 (39)	1458 (78)	584 (25)
Pb	NSC	24 (8)	9 (1)	17 (5)	23 (7)	5 (2)
Zn	NSC	222 (29)	187(20)	89 (13)	42 (6)	28 (8)
Mg	NSC	452 (42)	514 (35)	316 (28)	264 (9)	118 (18)
Fe	NSC	1442 (66)	2733 (74)	1639 (41)	2737(63)	195 (23)
Cu	NSC	18 (5)	nd	78 (6)	34 (9)	14 (3)
Co	NSC	14 (3)	19 (5)	9 (7)	16 (5)	5 (2)
As	NSC	5 (3)	5 (2)	2 (1)	11 (4)	nd
Ni	NSC	21 (11)	17 (7)	59 (8)	8 (3)	6 (5)
Cr	NSC	12 (8)	9 (3)	13 (6)	9 (4)	nd

"NSC" means "no sample was collected"; "nd" means "not detected".

Though, Fe has been found to occur at high concentrations in Nigerian soil (Adefemi *et al.*, 2007). The concentrations of Fe obtained in this study were similar to values reported for Fe in soils around a cement factory in Riyadh city, Saudi Arabia (Al-Oud *et al.*, 2011). Lead (Pb) average concentrations varied along the sampling distances; 66 µg g^{-1} (0.3 km) >60 µg g^{-1} (5 to 10 km) >48 µg g^{-1} (0.3 to 1 km) >33 (1 to 5 km) >24 µg g^{-1} (10 to 20 km) >8 µg g^{-1} (≥20 km). Similarly, Cu Co, As and Cr average concentrations also varied with sampling distances. For instance, the highest concentrations; 256 µg g^{-1} (Cu), 46 µg g^{-1} (Co), 23 µg g^{-1} (As) and 33 µg g^{-1} (Cr) were observed at 5 to10 km, 10 to 20 km and 1 to 5 km distances away from the cement industry respectively. In the cement industries, the linings for the rotaries contain Cr, Co and Cu which could be liberated to the environment by wears and frictions (Banat *et al.*, 2005). Interestingly, the average concentrations of Zn and Ni with respect to sampling distances followed similar order: 0.3 km >0.3 to 1 km >1 to 5 km >5 to 10 km >10 to 20 km >Control. The mean concentrations of Ni, Zn and Pb could be attributed to the emissions from fossil fuels and vehicular emissions (tyre abrasions and wears) around the cement factory (Asubiojo *et al.*, 1992).

Table 4 show the elemental concentrations obtained during the rain season. The elemental concentrations were lower than values obtained in the same location during dry season probably due to rain induced heavy metals dilutions and leaching. This was observed in all the sampled sites as the concentrations of all the elements were lower than their corresponding values in the dry season. The average concentrations of Ca at sites located between 0.3 km to 1 km away from cement industry during the dry and Rainy seasons were 13549 and 2875 µg g^{-1} respectively. Similarly, lowest Zn (28 µg g^{-1}; control site) and Fe (195 µg g^{-1}; control site) concentrations were recorded against Dry season concentrations of 64 µg g^{-1} (control site) and 1122 µg g^{-1} (10 to 20 km) respectively. The levels of Pb, Cr, Ni and Co higher than what Al-Oud *et al.*, 2011 recorded in a similar study around a cement factory located at South of Riyadh City central of Saudi Arabia. However, except for Mn and Cr, the concentrations recorded for other elements were similar to the values reported around the soils of Diamond Cement Factory, Ghana (Addo *et al.*, 2012).

Generally, higher mean concentrations of heavy metals were observed, though most of the average concentrations were found to be low when compared to the maximum allowable limits for heavy metals in soils from other countries (Lacatusu, 2000). This may be as a result of the mandatory use of dust precipitators by cement companies which have been enforced by the Federal Ministry of Environment in the last decade. The decrement in the concentration of heavy metals with respect to distance away from the cement factory could responsible for metal contamination in the nearby soils. The decreasing order in the quantitative trend of the metal content could indicate a certain measure of similarity between the different sets of samples.

The assessment of soil enrichment enrichment factor (EF), index of geo-accumulation (I_{geo}) and Pollution Load Index (PLI). Enrichment factors were calculated using Taylor, (1964) values for elemental compositions of crustal rock and using the formula reported in Oluyemi *et al.* (1994). Iron was used as the normalizing element. The use of Fe as a normalizing agent is quite appropriate; it is a crustal element with ubiquitous nature being the fourth most abundance elements in the earth crust.

The I_{geo} values were obtained using the following computation:

$$I_{geo} = \left[\frac{C_n}{1.5B_n} \right]$$

Where, C_n is the measured concentration of the element in the tested soil samples and B_n is the geochemical background value (Taylor, 1964) values for elemental compositions of crustal rock. The constant 1.5 was introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations. Addo *et al.*, (2012) gave the following I_{geo} interpretation; $I_{geo} < 0$ = practically uncontaminated; $0 < I_{geo} < 1$ = uncontaminated to moderate contaminated; $1 < I_{geo} < 2$ = moderately contaminated; $2 < I_{geo} < 3$ = moderately to strongly contaminated; $3 < I_{geo} < 4$ = strongly contaminated; $4 < I_{geo} < 5$ = strongly to extremely contaminated and $I_{geo} > 5$ = extremely contaminated.

Each sampling site was evaluated for the extent of metal pollution by employing the method based of pollution load index (PLI) developed by Thomilson *et al.* (1980) as follows:

$$PLI = \sqrt[n]{(CF_1 \times CF}_{\,2} \times CF_3 . \times ....CF_n)$$

Where n is the number of metals that were analyzed (eight in this study) and CF is the contamination factor defined by $CF = C_{metal} / C_{background}$. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1denote perfection; PLI = 1 present that only baseline levels of pollutants were present and PLI >1 would indicate deterioration of site quality (Addo *et al.*, 2012). The EF, Igeo and PLI of the elements under study were computed for each radii distance and direction relative to the background value of the element in continental crust average value of the element. Tables 5 and 6 displayed a summary of the results of EF, Igeo and PLI values obtained for both seasons.

According to Addo *et al.* (2012), EF values between 0.5 and 1.5 indicate that a metal is entirely from crustal material or natural processes, whereas EF values greater than 1.5 suggests that the sources are more likely to be anthropogenic. The result showed that during the Dry season, Mg was enriched at virtually in all the transects; 1.72 (0.3 km), 1.67 (1 km), 2.91 (5 km), 1.43 (10 to 20 km) and 4.47 (control site). Chromium was enriched at sites within 0.3 km away from the cement factory. Similarly, in the rain season, only Mg displayed significant enrichments (Table 6). It recorded EF values of 2.20 (1 to 5 km); 2.15 (5 to 10 km) and 4.29 (10 to 20 km), respectively.

Table 5: Enrichment factor (EF), geo-accumulation indices (Igeo) and pollution indices (PLI) data during dry season

Ele.	Taylor 1964 (μg g^{-1})	0.3 km			0.3 to 1 km			1 to 5 km			5 to 10 km			10 to 20 km			≥20 km (Control)		
		EF	Igeo	PLI	EF	Igeo	PLI	EF	Igeo	PLI	EF	Igeo	PLI	EF	Igeo	PLI	EF	Igeo	PLI
Ca	23600	0.22	-1.40	0.57	0.18	-1.74	0.45	0.15	-2.29	0.31	0.33	-3.41	0.14	0.31	-4.53	0.07	0.84	-5.17	0.04
Pb	12.5	0.02	1.82	5.28	0.02	1.36	3.84	0.02	0.82	2.64	0.01	1.68	4.80	0.01	0.36	1.92	0.05	-1.23	0.64
Zn	70	0.02	2.37	7.74	0.01	2.01	6.04	0.02	0.81	2.63	0.03	0.24	1.77	0.01	-0.11	1.39	0.04	-0.71	0.91
Mg	23300	1.72	-4.32	0.07	1.67	-5.06	0.05	2.91	-6.61	0.02	3.60	-6.87	0.01	1.43	-6.75	0.01	4.47	-7.58	0.01
Fe	56300	1.00	-3.47	0.13	1.00	-4.32	0.08	1.00	-5.07	0.04	1.00	-5.02	0.05	1.00	-6.23	0.02	1.00	-5.42	0.04
Cu	55	0.13	-0.62	0.98	0.09	-0.67	0.95	0.08	-1.37	0.58	0.01	1.63	4.65	0.05	-1.97	0.38	0.13	-2.46	0.27
Ni	75	0.11	-0.42	1.12	0.14	-0.21	0.59	0.12	-2.01	0.37	1.15	-5.23	0.04	0.11	-3.01	0.19	nd	nd	nd
Cr	100	1.84	-4.32	0.07	0.24	-2.18	0.33	0.16	-2.42	0.28	0.26	-3.06	0.18	0.14	-3.42	0.14	nd	nd	nd

Table 6: Enrichment factor (EF), geo-accumulation indices (Igeo) and pollution indices (PLI) data during rain season

Ele.	Taylor, 1964 (μg/g)	0.3 to 1 km			1 to 5 km			5 to 10 km			10 to 20 km			≥20 km (Control)		
		EF	Igeo	PLI	EF	Igeo	PLI	EF	Igeo	PLI	EF	Igeo	PLI	EF	Igeo	PLI
Ca	23600	0.21	-3.62	0.12	0.61	-4.24	0.08	0.71	-5.19	0.04	0.79	-4.60	0.06	0.14	-5.92	0.02
Pb	12.5	0.01	0.36	1.92	0.07	-1.06	0.72	0.02	-0.14	1.36	0.03	0.29	1.84	0.01	-1.91	0.40
Zn	70	0.01	1.08	3.17	0.02	0.83	2.67	0.02	-0.24	1.27	0.08	-1.32	0.60	0.01	-1.91	0.40
Mg	23300	1.32	-6.27	0.02	2.20	-6.09	0.02	2.15	-6.79	0.01	4.29	-7.05	0.01	0.68	-8.21	0.01
Fe	56300	1.00	-5.87	0.03	1.00	-4.95	0.05	1.00	-5.69	0.03	1.00	-4.95	0.05	1.00	-8.76	0.00
Cu	55	0.08	-2.20	0.33	nd	nd	nd	0.02	-0.08	1.42	0.08	-1.28	0.62	nd	-2.56	0.25
Ni	75	0.09	-2.42	0.28	0.21	-2.73	0.23	0.04	-0.93	0.79	0.46	-3.81	0.11	0.04	-4.23	0.08
Cr	100	0.21	-3.64	0.12	0.54	-4.06	0.09	0.22	-3.53	0.13	0.54	-4.06	0.09	nd	nd	nd

The differences in the EF values may be due to the difference in the magnitude of input for each metal in the soil or differences in the removal rate of each metal from the soil. The pollution levels in the environment under consideration were further expressed in terms of geo-accumulation index. The I_{geo} result indicated that the Pb and Zn were the only polluted metals at 0.3 km from the factory. Similarly, Pb and Zn were also moderately contaminated for samples collected within 0.3 to 1 km from the factory. Interestingly the I_{geo} values of the samples collected at the control site were all negative, thus an indication that the impact of cement is more significant in nearby agricultural soils around the factory. Again, in the Rainy season, Zn is the only moderately polluted metal according to I_{geo} classification at 0.3 to 1 km distance from the cement factory.

To effectively compare whether the vicinity of the factory is contaminated or not, the PLI described earlier was used. The PLI is aimed at providing a measure of the degree of overall contamination at the sampling sites in terms of distance and direction. Based on the results presented in Tables 5 and 6, the overall PLI during the dry season revealed that Pb and Zn were highly polluted (PLI >1) except at the control site whose PLI is < 1. Copper and Nickel also displayed high average PLI for samples collected at 5 to 10 km and 0.3 km from the factory respectively. The deterioration of the soils around the cement factory by Pb and Zn is further noticed in the PLI results obtained during the rain season. As observed that the PLI of Zn (3.17, 2.67 and 1.27) was higher than unity at 0.3 to 1 km, 1 to 5 km and 5 to 10 km, respectively. Pb concentrations displayed high PLI; 1.92, 1.36 and 1.84 for 0.3 to 1 km, 5 to 10 km and 10 to 20 km, respectively. Similarly, Cu registered high PLI (1.42) at 5 to 10 km distance from the factory. The low EF, Igeo and PLI registered for samples collected at the control site could be an indication of the imact of the cement dust with respect to distance.

Correlation analysis

The metals Ca to Cr in the dry season (Table 7) and rain season (Table 8) showed positive and negative correlations. In order to determine which of the correlation is significant in the statistical sense, the critical multiple correlation coefficients (r^2) was obtained at $P \leq 0.05$.

Table 7: Elemental correlation during dry season

Elements	Ca	Pb	Zn	Mg	Fe	Cu	Co	As	Ni	Cr
Ca	1.00									
Pb	0.28	1.00								
Zn	0.28	0.19	1.00							
Mg	0.82	0.24	0.41	1.00						
Fe	0.71	-0.22	0.53	0.65	1.00					
Cu	0.36	0.87	0.81	0.58	-0.62	1.00				
Co	-0.76	0.41	0.38	0.57	-0.60	0.85	1.00			
As	-0.20	0.34	0.41	0.83	-0.58	0.61	0.61	1.00		
Ni	-0.44	-0.49	-0.41	-0.41	0.26	-0.17	-0.09	-0.41	1.00	
Cr	-0.27	0.65	-0.42	-0.37	0.09	0.11	0.28	-0.25	0.33	1.00

Table 8: Elemental correlation during rain season

Elements	Ca	Pb	Zn	Mg	Fe	Cu	Co	As	Ni	Cr
Ca	1.00									
Pb	-0.27	1.00								
Zn	0.09	0.39	1.00							
Mg	0.29	0.15	-0.32	1.00						
Fe	0.83	0.44	0.24	0.26	1.00					
Cu	-0.25	0.07	-0.22	0.58	0.56	1.00				
Co	-0.20	0.12	0.47	-0.12	-0.03	0.14	1.00			
As	-0.68	-0.18	0.47	-0.12	0.03	0.46	-0.08	1.00		
Ni	-0.18	0.36	0.58	0.14	0.58	0.42	0.10	0.03	1.00	
Cr	0.31	-0.14	0.20	0.19	0.21	0.45	0.22	0.61	-0.14	1.00

For dry season (Table 7), Ca correlated strongly with Mg (0.82) and Fe (0.71) probably due to their association with the earth's crust. Pb correlated strongly weakly with Zn (0.19) but displayed strong correlation (0.87, 0.41, 0.34 and 0.65) with Cu, Co, As and Cr, respectively. Again, Zn displayed significant positive correlations (0.41, 0.53, 0.81, 0.38 and 0.41 with Mg, Fe, Cu, Co and As while Fe correlated negatively with Cu (-0.62) and Co (-0.60). Similarly, for rain season sampling (Table 8), the elements showed both weak and strong correlations. However, few elements displayed strong correlations unlike in the dry season. This could be probably due to usual leachates which is prevalent in the rain season. Ca registered highest strong correlation of up to $r^2 = 0.83$ with Fe. Other elements with significant correlation include; Zn and Ni (0.58), Fe and Ni (0.58), As and Cr (0.61). Thus, the positive correlations found between metals could indicate a common source or chemical similarities, whilst the negative correlation could indicate that the metals originated from different sources or different chemical properties (Ezeh *et al.*, 2012).

Conclusion

The physicochemical parameters varied per distance from the factory during dry and rain seasons of which the values were relatively higher compared to the average values for the control site. The levels of metal distributions considering distances and directions from the cement facility were of a complex pattern and many factors such as atmospheric transports and local meteorology could be responsible. EF results showed that the metals were not enriched during both seasons; however, I_{geo} and PLI revealed that some elements were in the high pollution class at most sites. The cement facility together with the vehicular traffic emissions were implicated as responsible for metal pollution in the area as higher concentration of metals were found in the transects closer to the cement factory.

Conflict of Interest

No potential conflict of interest was reported by the authors.

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