

Heavy Metals Profile and Variations of Soil Properties in a Vicinity of Cement Factory in Obajana in Kogi State of Nigeria

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Abstract: Soils from the vicinity of a cement factory in Obajana in Kogi state of Nigeria were analyzed for their physicochemical and elemental contents in order 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 Rainy seasons. The elemental contents of the soils were determined using the Atomic Absorption Spectroscopy (AAS) technique while the physicochemical parameters were determined using standard analytical techniques. Results indicated that the physicochemical parameter values varied across the study areas. Ten elements (As, Ca, Co, Cr, Cu, Fe, Mg, Ni, Pb and Zn) were analyzed and their concentrations values established. In addition, calculation of Enrichment Factors (EFs), Geo - accumulation Index (I_{geo}), Pollution Indices (PI) and Pearson correlation matrices were performed and the results indicated that across the transects some elements were in the highly pollution class and strongly correlated.

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

1. INTRODUCTION

Soil Physico-chemical properties are affected by the type of parent materials that formed the soil and various human activities such as farming, depositions of industrial wastes materials. Cement materials is one of such industrial wastes that affects the soil Physico-chemical properties. Cement production includes mining and quarrying of raw materials, which are principally oxides and carbonates of metals. It also involves grinding the raw materials into fine particles, such as limestone, shale, sand, clay, iron ore, and fly ash, and mixing them in appropriate proportions. Cement production are among key anthropogenic activities leading to particulate matter emissions in an environment. An inventory of air pollutants in Nigeria classified cement production as the highest source of atmospheric dust emissions as it accounted for about 22.4 million tonnes of emissions for the year 1988 (Adejumo et al., 1994). Based on the chemistry of the cement processes, the emitted particles contain broad spectrum of heavy elements and other pollutants. Soil remains one of the largest sinks of emitted dusts from cement production through direct dumping or atmospheric deposition at distances away from the factories. Deposition of cement generated aerosols could have profound negative impact 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 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 biomagnifications 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 and 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).

Obajana cement plant in Kogi State, Nigeria is the biggest cement plant in sub Saharan Africa and considered one of the biggest cement plants in the world. It is one of several factories owned by Dangote Cement plc. The factory is located in Oworo district in Lokoja local government area of Kogi state, Nigeria. Oworo district is a mountainous terrain that stretches into several cities to the north by Igbira Igu(Egbura), northwest by Kakanda, west by the Abinu and to the south by Ebira land. Obajana is also one of the towns in Oworo land. Obajana with topography of about 100 m above sea level is located within the middle belt of Nigeria and with an average rainfall of about 1,561.86 mm per annum, characterized by distinct Rainy and Dry seasons. Obajana cement factory is the site of the largest cement plant in Africa and currently in the process of increasing its capacity to meet the growing demands of local and exports markets. It therefore becomes imperative to study the physicochemical properties as well as the distributions of heavy metals on soils in the Vicinity and neighborhood of the factory.

The main objective of this research work is to assess the impact of dusts particles emitted from cement industry on the physico-chemical properties and elemental compositions of the soils around cement factory in vicinity of cement factory in Obajana in Kogi state of Nigeria

2. MATERIAL AND METHOD

2.1. Soil Sampling

About thirty sampling points covering the study area were randomly identified and selected in consideration of their distances and group into sample sites (A, B, C, D, and E) from the cement factory. Soil sampling was done systematically 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 a far site from the cement factory were used as control (Asubiojo et al., 1992). A total of seventy-six (76) samples were collected during Dry season (November, December, January and February) and Rainy 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.

2.2. Quality Control and Assurance

For quality control and assurance, the sites were selected because they cut across wide range of land use types as well as key directions from the cement. Prior to laboratory analyses, samples were homogenized, pulverized, air dried for some 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. Calibration of the bulk scientific Atomic Absorption Spectroscopy (AAS) was done using mixed calibration standard solutions prepared from the various element determined (As, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn) and percentage recovery ranged from 90 to 95.

2.3. 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).

2.4. Elemental Analysis

The soil samples were digested using *aqua regia* procedure of USEPA, (1995) and the elemental concentrations of (As, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn) were determined using AAS.

2.5. Enrichment Factor Assessment of Soil Samples from the Study Area

The assessment of soil enrichment can be carried out in many ways. In this work, the EF, I_{geo} and PLI were applied to assess the distribution and contamination in surface soils in the vicinity of the Obajana cement factory. 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:

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

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.

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:

$$PLI = \sqrt[n]{(CF_1 \times CF_2} \times CF_3 \times \dots \dots CF_n)$$

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.

| Sites | Α | В | С | D | Е | Control |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| Element | | | | | | |
| Ca | 0.22/0.21 | 0.18/0.61 | 0.15/0.71 | 0.33/0.79 | 0.31/0.30 | 0.84/0.14 |
| Cr | 1.84/0.21 | 0.24/0.54 | 0.16/0.22 | 0.26/0.54 | 0.14/0.13 | N.D/N.D |
| Cu | 0.13/0.08 | 0.09/N.D | 0.08/0.02 | 0.01/0.08 | 0.05/0.04 | 0.13/N.D |
| Fe | 1.00/1.00 | 1.00/1.00 | 1.00/1.00 | 1.00/1.00 | 1.00/1.00 | 1.00/1.00 |
| Mg | 1.72/1.32 | 1.67/2.20 | 2.91/2.15 | 3.60/4.29 | 1.43/2.14 | 4.47/0.68 |
| Ni | 0.11/0.09 | 0.14/0.21 | 0.12/0.04 | 1.15/0.46 | 0.11/0.02 | N.D/0.04 |
| Pb | 0.02/0.01 | 0.18/0.07 | 0.15/0.02 | 0.33/0.03 | 0.31/0.02 | 0.05/0.01 |
| Zn | 0.02/0.01 | 0.01/0.02 | 0.02/0.02 | 0.01/0.08 | 0.01/0.04 | 0.04/0.01 |

Table5. Enrichment Factor of the Analyzed data (Dry/Rain season)

| Sites | Α | В | С | D | Ε | Control |
|---------|-------------|-------------|-------------|-------------|-------------|-------------|
| Element | | | | | | |
| Ca | -1.40/-3.62 | -1.74/-4.24 | -2.29/-5.19 | -3.41/-4.60 | -4.53/-5.72 | -5.17/-5.92 |
| Cr | -4.32/-3.64 | -2.18/-4.06 | -2.42/-3.53 | -3.06/-0.06 | -3.42/-2.56 | N.D/N.D |
| Cu | -0.62/-2.20 | -0.67/N.D | -1.37/-0.08 | -1.63/-1.28 | -1.97/-1.09 | -2.46/-2.56 |
| Fe | -3.47/-5.87 | -4.32/-4.95 | -5.07/-4.95 | -5.02/-4.34 | -6.23/-5.63 | -5.42/-8.76 |
| Mg | -4.32/-6.27 | -5.06/-6.09 | -6.61/-6.79 | -6.75/-7.05 | -6.87/-7.23 | -7.58/-8.21 |
| Ni | -0.42/-2.42 | -0.21/2.73 | -2.01/-0.93 | -5.23/-3.81 | -3.01/-2.23 | N.D/-4.23 |
| Pb | 1.82/0.36 | 1.36/-1.06 | 0.82/-0.14 | 1.68/0.29 | 0.36/-0.23 | -1.23/-1.91 |
| Zn | 2.37/1.08 | 2.01/0.83 | 0.81/-0.24 | 0.24/-1.32 | -0.11/-0.32 | -0.71/-1.91 |

 Table6. Geo-Chemical Indices of the Analyzed data (Dry/Rain Season)

2.6. Statistical Pearson Correlation Analyses

The elemental concentrations of the samples were also subjected to statistical analysis in-order to determine the 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.

3. RESULTS AND DISCUSSIONS

3.1. Physico - Chemical Compositions

The mean distribution of the soil properties (pH, particle size, organic matter and exchangeable cations) obtained during the dry and rainy seasons are summarized in Table 1 and Table 2. Soil pH is an important parameter that directly influences sorption/desorption, precipitation/dissolution, complex formation and oxidation reduction reactions (Ovedele et al., 2008). 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 Rainy season. This indicates that the soils were moderately acidic to neutral and strongly acidic to neutral during the dry and rainy seasons respectively. These values were relatively higher compared to the average pH values recorded for the control site. Although, the pH of most soils in the tropics ranged from acidic to slightly neutral (Alloway and Aryes, 1997). Mclean and 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 rainy 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 in the soil solution during the rainy season.

| 0 | Range | | Mean ± Sd | Control |
|------|----------------|---------------------|-----------|---------|
| PH | 5.890 - 7.200 | 6.390 ± 0.360 | | 5.750 |
| Sand | 31.500 - 84.00 | 64.360 ± 11.978 | | 68.000 |
| Silt | 3.000 - 40.000 | 9.940 ± 8.910 | | 7.500 |
| Clay | 7.000 - 56.000 | 25.140 ± 9.980 | | 24.500 |
| O.M | 9.400 - 39.600 | 21.336 ± 6.721 | | 10.100 |
| K | 0.120 - 0.570 | 0.230 ± 0.093 | | 0.170 |
| Na | 0.060 - 0.150 | 0.084 ± 0.023 | | 0.070 |
| Ca | 3.300 - 22.500 | 7.022 ± 5.546 | | 2.500 |
| Mg | 2.030 - 6.080 | 3.744 ± 1.224 | | 2.030 |

Table1. Summary Results of Physic – Chemical properties of soil from the Study area (Dry Season)

| Parameters | Range | | Mean ± Sd | Control |
|------------|-----------------|--------------------|-----------|---------|
| PH | 5.140 - 6.920 | 6.110 ± 0.517 | | 5.750 |
| Sand | 44.000 - 84.000 | 63.700 ± 10.16 | 0 | 56.500 |
| Silt | 5.000 - 40.000 | 10.692 ± 8.595 | | 5.000 |
| Clay | 7.000 - 38.000 | 23.648 ± 8.113 | | 38.000 |
| O.M | 9.400 - 30.900 | 17.924 ± 5.466 | | 22.800 |
| K | 0.050 - 0.570 | 0.169 ± 0.109 | | 0.100 |
| Na | 0.060 - 0.650 | 0.451 ± 0.189 | | 0.440 |
| Са | 0.470 - 20.000 | 3.330 ± 5.561 | | 0.010 |
| Mg | 0.240 - 5.770 | 1.500 ± 1.661 | | 0.730 |

Table2. Summary Results of Physic – Chemical properties of soil from the Study area(Rain Season)

The control site was moderately and strongly acidic during the dry and rainy season respectively, considering the pH status of soils in the study area has conformed to the observation that the impacts of cement dusts reduces with distance away from the plant. 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 content ranged from 9.4 to 39.6 mg/g (Dry season) and 12.8 to 30.9 mg/g (Rainy season) respectively 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 organic matter content in the Dry season could be due to lower soil moisture in the soil during the dry season. Thus, microbial decompositions of organic matter are often retarded during the Dry season. On the other end, soils in the control site revealed low (10.100 mg/g) and moderate (22.800 mg/g) concentrations of organic matter content. The low concentrations of organic matter at the control site indicated that it could support optimum plant growth than those that are closer to the factory.

The soil concentrations of exchangeable bases differed between the seasons and across the sampled sites. The Dry season mean value ranges were K⁺ (0.14 to 0.57 cmol kg⁻¹), Na⁺ (0.06 to 0.15 cmol kg⁻¹), Ca²⁺ (2.50 to 22.50 cmol kg⁻¹) and Mg²+ (2.03 to 6.08 cmol kg⁻¹). The content of cations decreased during the Rainy season in the order: Ca>Mg>Na>K at the exchange sites with a range of K⁺ (0.05 to 0.34 cmol kg⁻¹), Na⁺ (0.40 to 0.65 cmol kg⁻¹), Ca²⁺ (0.47 to 2.15 cmol kg⁻¹) and Mg²+ (0.24 to 1.70 cmol kg⁻¹). Dry season concentrations of exchangeable cations were slightly higher than the wet season concentrations and may be attributed to high rainfall and weathering intensities as well as to 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 organic matter.

3.2. Elemental Characterization

Tables 3 and 4 showed the concentrations of elements in the soil samples during dry and rain season with respect to the site distances away from the cement industry. All the elements considered, As, Ca, Co, Cr, Fe, Mg, Ni, Pb, and Zn were detected. 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 and Voutchkov, 2011).

| Metals | Range | Mean± SD | Control |
|--------|----------------|-------------------|---------|
| As | 0.004 - 0.023 | 0.013 ±0.007 | 0.007 |
| Ca | 1.536 - 13.589 | 7.240 ± 4.525 | 0.985 |
| Со | 0.011 - 0.012 | 0.026 ± 0.012 | 0.009 |
| Cr | 0.007 - 0.023 | 0.020 ± 0.010 | N.D |
| Cu | 0.021 - 0.256 | 0.083 ± 0.089 | 0.015 |
| Fe | 1.122 - 2.239 | 3.002 ± 2.161 | 1.978 |
| Mg | 0.298 - 1.739 | 0.892 ± 0.706 | 0.183 |
| Ni | 0.003 - 0.084 | 0.035 ± 0.029 | N.D |
| Pb | 0.024 - 0.066 | 0.046 ± 0.016 | 0.008 |
| Zn | 0.064 - 0.542 | 0.262 ± 0.192 | 0.064 |

Table3. Summary Results of Heavy metal content (mg/g) of soil from the Study area (Dry season)

| Metals | Range | Mean± SD | Control |
|--------|----------------|-------------------|---------|
| As | 0.002 - 0.017 | 0.007 ± 0.006 | N.D |
| Ca | 0.968 - 13.589 | 4.139 ±4.831 | 0.584 |
| Со | 0.009 - 0.019 | 0.015 ± 0.004 | 0.005 |
| Cr | 0.007 - 0.013 | 0.011 ± 0.002 | N.D |
| Cu | 0.018 - 0.078 | 0.040 ± 0.023 | 0.014 |
| Fe | 1.442 - 7.239 | 3.158 ± 2.154 | 0.195 |
| Mg | 0.264 - 1.739 | 0.649 ± 0.562 | 0.118 |
| Ni | 0.008 - 0.084 | 0.038 ± 0.030 | 0.006 |
| Pb | 0.009 - 0.066 | 0.028 ± 0.020 | 0.005 |
| Zn | 0.042-0.542 | 0.216 ± 0.179 | 0.023 |

Table4. Summary Results of Heavy metal content (mg/g) of soil from the Study area(Rain season)

During the dry season, the concentrations of the elements like (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 and gypsum) used for cement production (Akinlolu et al., 2007). For instance, Ca was the most abundant element; it recorded average concentrations of 13.549 mg/g (Site A), 10.555 mg/g (Site B), 7.254 mg/g (Site C), 3.332 mg/g (Site D), 1.536 mg/g (Site E) and 0.985 mg/g (control). Inadvertently, the concentrations of Fe in the Dry season were in the order 7.239 mg/g (Site A), 4.531 mg/g (Site B), 2.595 mg/g (Site C), 2.521 mg/g (Site D), 1.122 mg/g (Site E), 1.978 mg/g (control).

Trace element concentrations (mg/g) during Dry Season are presented in Table 1. Though, Fe has been found to occur at high concentrations in Nigerian soil (Adefemi et al., 2007). The concentrations

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of Fe obtained in this study were similar to values reported for Fe in soils around a cement factory in other cities in the world, Riyadh city, Saudi Arabia (Al-Oud et al., 2011). The average concentrations of Pb varied along the sampling distances; 0.066 mg/g (Site A), 0.060 mg/g (Site B), 0.048 mg/g (Site C), 0.033 (Site D), 0.024 mg/g (Site E), 0.008 mg/g (control). Similarly, Cu Co, As and Cr average concentrations also varied with sampling sites. For instance, the highest concentrations; 0.256 mg/g (Cu), 0.046 mg/g (Co),0.023 mg/g (As) and 0.033 mg/g (Cr) were observed at site D, site E and control 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; site A > site B > site C > site D > site E > 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 displayed the elemental concentrations obtained during the Rainy season. As expected, 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 is a clearly noticeable at all the sampled sites as the concentrations of all the elements sought for were lower than their corresponding values in the Dry season. For instance, the average concentrations of Ca at sites which were located between site A and B less than site C away from cement industry during the Dry and Rainy seasons were 13.549 and 2.875 mg/g respectively. Similarly, lowest Zn (0.028 mg/g; control site) and Fe (0.195 mg/g; control site) concentrations were recorded against Dry season concentrations of 0.064 mg/g (control site) and 1.122 mg/g (Site E to control Site) respectively. The levels of Pb, Cr, Ni and Co are of a significant interest as they are far 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 in the top soils than in the sub soils, 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 heavy metals analysis implicates cement dust originating from the cement facility for being partly or wholly responsible for metal contamination in the soil around the factory. The decreasing order in the quantitative trend of the metal content could indicate a certain measure of similarity between the different sets of samples.

3.3. Pollution Factor Indicators

EF values between 0.5 and 1.5 indicate that a metal is entirely from crustal material or natural processes, where as EF values greater than 1.5 suggests that the sources are more likely to be anthropogenic Addo et al. (2012),. The result showed that during the Dry season, Mg was enriched virtually in all the sites 1.72 (Site A), 1.67 (Site B), 2.91 (Site C), 1.43 (Site D and E) and 4.47 (control site). Again, Cr was enriched only sites collected within Site A away from the cement factory. Similarly, in the Rainy season, only Mg displayed significant enrichments (Table 6). It recorded EF values of 2.20 (Site B and C); 2.15 (Site C and D) and 4.29 (Site D and E) respectively. 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 or the contamination levels in the environment under consideration was further expressed in terms of geo-accumulation index. For Dry season sampling, the I_{geo} result indicated that the Pb and Zn were the only polluted metals at Site A from the factory. Similarly, Pb and Zn were also moderately contaminated for samples collected within Site A and B from the factory. Interestingly the I_{geo} values of the samples collected at the control site were all negative, thus an indication of unp. Again, in the Rainy season, Zn is the only moderately polluted metal according to I_{geo} classification at Site A to B from the cement factory.

Also to determine the level of pollution around the factory, the PLI 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) in most site classes except at the control site whose PLI is < 1. Copper and Nickel also displayed high average PLI for samples collected at Site A, B and C 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 Rainy season. We observed that the PLI of Zn (3.17, 2.67 and 1.27) was higher than unity at site A, B, C, D respectively. Pb concentrations displayed high PLI; 1.92, 1.36 and 1.84 at all the sites (A,B,C,D,and E) respectively. Similarly, Cu registered high PLI (1.42) at sites C and D. In summary, the low EF, Igeo and PLI respect to distance.

3.4. Correlation Analysis

The metals Ca to Cr in the Dry and Rainy seasons respectively in Tables 7 and 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 from the table of significant values. The critical value r with n = 76, $\alpha = 0.05$ is 0.232. For Dry season sampling (Table 7), Ca correlated strongly with Mg ($r^2 = 0.82$) and Fe ($r^2 = 0.71$) probably due to their association with the earth's crust. Pb correlated strongly weakly with Zn ($r^2 = 0.19$) but displayed strong correlation ($r^2 = 0.19$) 0.87, $r^2 = 0.41$, $r^2 = 0.34$ and $r^2 = 0.65$) with Cu, Co, As and Cr respectively. Again, Zn displayed significant positive correlations ($r^2 = 0.41$, $r^2 = 0.53$, $r^2 = 0.81$, $r^2 = 0.38$ and $r^2 = 0.41$ with Mg, Fe, Cu, Co and As while Fe correlated negatively with Cu ($r^2 = -0.62$) and Co ($r^2 = -0.60$). Similarly, for Rainy 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 Rainy season. For instance, only Ca registered highest strong correlation of up to $r^2 = 0.83$ with Fe. Other elements with significant correlation include; Zn and Ni ($r^2 = 0.58$), Fe and Ni ($r^2 = 0.58$), 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 possess non-chemical similarity (Ezeh et al., 2012).

| Sites | Α | В | С | D | Ε | Control |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| Element | | | | | | |
| Ca | 0.57/0.12 | 0.45/0.08 | 0.31/0.04 | 0.14/0.66 | 0.07/0.03 | 0.04/0.02 |
| Cr | 0.07/0.12 | 0.33/0.09 | 0.28/0.13 | 0.18/0.09 | 0.14/0.11 | N.D/N.D |
| Cu | 0.98/0.33 | 0.95/N.D | 0.58/1.42 | 4.65/0.62 | 0.38/0.62 | 0.27/0.25 |
| Fe | 0.13/0.03 | 0.08/0.05 | 0.04/0.03 | 0.05/0.05 | 0.02/0.02 | 0.04/0.00 |
| Mg | 0.07/0.02 | 0.05/0.02 | 0.02/0.01 | 0.01/0.01 | 0.01/0.01 | 0.01/0.01 |
| Ni | 1.12/0.28 | 0.59/0.23 | 0.37/0.79 | 0.04/0.11 | 0.19/0.02 | N.D/0.08 |
| Pb | 5.28/1.92 | 3.84/0.72 | 2.64/1.36 | 4.80/1.84 | 1.92/2.23 | 0.64/0.04 |
| Zn | 7.74/3.17 | 6.04/2.67 | 2.64/1.27 | 1.77/0.60 | 1.39/0.54 | 0.04/0.91 |

 Table7. Pollution Indices of the

Analyzed data (Dry and Rain Season)

Table8. Elemental Correlation during Dry and Rain season

| As | Ca | Со | Cr | Cu | Fe | Mg | Ni | Pb | Zn |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| _ | -0.410 | 0.283 | -0.868 | 0.048 | -0.143 | -0.292 | -0.070 | -0.069 | -0.272 |
| | | -0.419 | 0.017 | -0.314 | 0.937 | 0.892 | 0.929 | 0.578 | 0.975 |
| | | | 0.063 | -0.729 | -0.563 | -0.338 | -0.229 | -0.934 | -0.398 |
| | | | | -0.099 | -0.271 | 0.010 | -0.290 | -0.314 | -0.074 |
| | | | | | -0.108 | -0.302 | -0.452 | 0.550 | -0.309 |
| | | | | | | 0.880 | 0.930 | 0.770 | 0.959 |
| | | | | | | | 0.857 | 0.543 | 0.961 |
| | | | | | | | | 0.493 | 0.946 |
| | | | | | | | | | 0.603 |
| _ | 0.839 | 0.457 | -0.588 | 0.234 | 0.870 | 0.796 | 0.516 | 0.912 | 0.701 |
| | | 0.411 | -0.482 | 0.294 | 0.950 | 0.993 | 0.779 | 0.965 | 0.963 |

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| | 0.031 | -0.295 | 0.561 | 0.448 | 0.010 | 0.362 | 0.474 |
|--|-------|--------|--------|--------|--------|--------|--------|
| | | 0.142 | -0.471 | -0.420 | -0.139 | -0.453 | -0.319 |
| | | | 0.314 | 0.314 | 0.771 | 0.390 | 0.197 |
| | | | | 0.956 | 0.719 | 0.917 | 0.884 |
| | | | | | 0.801 | 0.943 | 0.973 |
| | | | | | | 0.779 | 0.751 |
| | | | | | | | 0.893 |

4. CONCLUSION

In this study, selected physicochemical parameters (pH, particle size, organic matter and exchangeable cations) and metals (Ca, Pb, Zn, Mg, Fe, Cu, Co, As, Ni and Cr) in soils around cement factory in Obajana were determined seasonally using appropriate analytical techniques. The physicochemical parameters varied per distance from the factory during Dry and Rainy seasons. These values were relatively higher compared to the average pH values recorded for the control site. The levels of metal distributions considering distances from the factory were of a complex pattern and many factors could be responsible. One of the major suggestions was that other pollution sources could be in display during the seasons. To understand the distribution of the metal pollutants, mathematical algorithms; EF, I_{geo} and PLI were employed to explain the distribution dynamics in terms of enrichment, accumulation and overall contamination status of the sampling sites. 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 attendant vehicular traffic emissions were implicated as responsible for metal pollution in the area as higher concentration of metals were found in the sites closer to the cement factory.

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