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Evaluation of Heavy Metals Contamination of Soil and Vegetation in the Vicinity of a Cement Factory in the Volta Region, Ghana

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ABSTRACT

Heavy metal mobilization in the biosphere by human activities has become an important process in the geochemical recycling of these metals. In this work, 34 soil samples and 29 *Tephrosia elegans* plants collected in the vicinity of the Diamond Cement Factory, Aflao, Ghana were analyzed for As, Co, Cr, Cu, Mn, Ni, Pb and Zn using energy dispersive XRF. The results of the metal analysis indicated that some metallic levels were in excess of natural background and critical limits for the soil and plants respectively. The results further revealed that the metal distribution were in a fluctuating manner considering various distances and directions from the cement facility. However, it was observed that the mean metal concentrations of the soil and plants decrease as distance from the cement facility increased for most metals. This indicated that the facility which is the only industrial source in the area is the major cause of the pollutants contamination in its vicinity. In an attempt to understand the pattern of metal contamination in the area, useful tools including enrichment factor, geoaccumulation index and pollution load index were employed to indicate the sources of soil contamination were anthropogenic in character. Recommendations for the need for other studies on environmental and human health around the cement and similar facilities to protect human life and the environment are suggested.

Key words: *Heavy metal, Contamination, Geoaccumulation index, Vegetation, Cement facility, Toxicity.*

1. INTRODUCTION

Air pollution has long been recognized as a lethal form of pollution. Much of the problems of societal concern today are the heavy metals associated with air pollution. Heavy metal mobilization in the biosphere by human activities has become an important process in the geochemical cycling of these metals [1]. This is evident in industrial areas where stationery and mobile sources release large quantities of heavy metals into the atmosphere, soil and plants exceeding the natural emission levels [2, 3]. Pollution of the natural environment by heavy metal is a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms, when they exceed a certain concentration [4].

Most heavy metals can be found generally at trace levels in soils and vegetation and in living organisms that need some of them as micro-elements [5]. Metal distribution between soil and vegetation, is a key issue in assessing environmental effect of metals in the environment [6]. Heavy metal toxicity has an inhibitory effect on plants growth, enzymatic activity, stoma functions, photosynthesis activity and accumulation of other nutrient elements, and also damage the root system [7]. On the otherhand, soil is not only a medium for plant growth or pool to dispose of undesirable materials, but also a transmitter of many pollutants to surface water, groundwater, atmosphere and food [8]. Therefore, soil pollution may threaten human health not only through its effects on the hygiene quality of food and drinking water, but also through its effect on air quality especially in enriched trace metal content in airborne particles originating from soil.

The determination of the metals in soils, dusts, plants and sediments are very important in monitoring environmental pollution. The contribution of metals to environmental pollution from industrial, agricultural and mining processes besides automobile emission, have been the main subject of many studies and research in recent years [9]. Botanical materials such as fungi, lichens, tree barks, tree rings, leaves of higher plants and soil samples have been used to detect the deposition, accumulation and distribution of metal pollution [10]. Onder *et al* [5] has observed that the most economical and reasonable method for monitoring heavy metals in the atmosphere is using soil and vegetation samples. Hence, soil and vegetation have been widely used as cumulative matrices of long and short term exposure respectively to environmental pollutants [11, 12, 13, 14].

Atmospheric emissions from industrial establishments are one of the major sources of environmental pollution. One type of industry that causes particle pollution is the cement industry [15]. The main inputs of cement activity on the environment are the broadcasts of dust and gases [16]. Cement dust spreads along large areas through wind rain etc. and are accumulated in and on soils, plants and animals and can affect human health badly [17, 18]. Heavy metals are among the most relevant substances emitted

during the process of cement manufacture [13, 15, 19]. The influence of cement dust as a major cause of heavy metal contamination in plants and soils has been observed by several researchers [13, 14, 15, 16, 20, 21, 22].
Among the metals especially known to have toxic effect in environmental studies are arsenic, cadmium, lead, mercury and thallium [23, 24]. Aluminium, beryllium, chromium, copper, manganese, nickel and zinc, among others, have been identified in the emission from cement plants [13]. The main purpose of the present study was to evaluate the environmental impact caused by dust emissions from a cement factory in the Volta Region of Ghana within a rural area with no other air pollution source in the area. Specifically, the study focuses on the dispersion of heavy metals in soils and vegetation around the cement factory.

2. EXPERIMENTAL

2.1 Study Area

The study area is located in the south eastern part of Ghana in the Aflao area in the Volta region. The Diamond Cement (Ghana) Limited (DIACEM) factory is located 3 km north of the Aflao Township in the Ketu South District (Fig 1). There are no other industrial developments within the area. The cement factory plays a significant role in the local building industry in the economy of Ghana. The Indian-owned factory was established in 2002 and was a major employer in the area. The area lies within the dry equatorial climate of the region. It has two rainy seasons with the major rains in April to June, and the minor rains between September and November. Mean temperatures in the investigated area are 13.5°C and occurs between the months of August and September, and average maximum of 40°C is experienced between February and March. The factory's surrounding area is essentially rural with minor agricultural activities. Settlements are scattered houses at varying distances with the nearest settlement of about 300m. The surrounding vegetation is covered with several shrubs and grasses. The geological formations of the investigated area are rocks of the Dahomeyan series of the Precambrian age. These rocks consist of dense aggregate of essential stable minerals which are banded and have medium to coarse-grained granite texture. The Dahomeyan series are seismically stable and therefore there is no history of earthquake in the area. The soil type is mainly lateritic sandy soils, tropical black clays, tropical grey earths, sodium vleisols and coastal sandy soils [25].

2.2 Sample Collection

The sampling sites were selected in such a manner to cover the entire vicinity of the cement factory. To provide a satisfactory environmental representation of the study area, concentric circles of radii 150m, 300m, 500m, 700m and 1000m around the main stack of the cement facility was taken into consideration. On each circle eight sampling sites representing the north, north-east, east, south-east, south, south-west, west and north-west directions were created on a map (Fig. 1). On the field these pre-determined points were located by means of a GPS. Sampling points which were located within the facility and a water-logged area were ignored. The rejection of these sampling points were that the facility itself perimeter was excluded from the study.
In March, 2011, 34 soil and 29 vegetation plant (*Tephrosia elegans*) samples were collected in the designated sampling points. The *Tephrosia elegans* plant was selected as an important representative species of the annual vegetation of the area and was collected simultaneously with the soil at the same point where the plants occur. Soil specimens were taken with a small plastic shovel from the upper 5 cm of the soil and scrapped into labeled plastic cylindrical containers of approximately 90 cm^3. Any large stones or foreign objects were removed. In the laboratory, the soils were sun-dried in plastic bowls for five continues days and were screened through a 110µm mesh sieve to obtain a more homogeneous distribution. The screening process further enabled the removal of small stones, roots and large organic residues. These oversized materials were discarded and were not included in the analysis. The plant specimens were obtained by cutting at a height 5 cm from the surface of the soil. The samples were immediately packed in aluminum foil and labeled accordingly as the soil samples. Subsequently, they were dried in an oven at a temperature of 60°C for two days after which they were pulverized in a blender and kept in similar plastic containers as the soil samples until analysis.

2.3 Sample Analysis

Both the soil and the plant materials were analyzed using energy dispersive X-Ray Fluorescence (EDXRF) analysis. The EDXRF provides a rapid and non-destructive method for the analysis of trace and major elements in both geologic and biological samples [26]. Before the XRF analysis, 4g of the milled soil and plant samples were made into pellets after which 0.9g of Hoechst wax was added and grounded in a sample cup fitted into a manual press to obtain a homogeneous mixture. Consequently, the concentration of As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the samples were directly measured by XRF. The Compact 3K5 X-ray Generator EDXRF spectrometer which was used for the elemental analysis has a Mo anode and operated at 800 W (40 kV and 20 mA). The irradiation was done using a Mo secondary target arrangement coupled to a liquid- nitrogen-cooled Si (Li) detector with a beryllium window. The detector has a resolution of 160 eV for Mn K" peak. Sample pellets were placed at an angle of 45º to the primary beam and irradiation for 600 sec. Meanwhile, a series of geological and biological Standard Reference Materials (SRM) were used to calibrate the application. The standards used were: Soil 7 SRM and Soil 3 SRM, all

of the International Atomic Energy Agency (IAEA), and Peach Leaves (SRM-1575); and Oyster Tissue SRM, all from the National Institute of Standards and Technology (NIST). To validate the instrumentation, the mean concentrations of the elements obtained from the standard used were compared with the certified values by calculating the ratio of experimental values to certified reference values. The results gave ratios between 6 and 8% indicating that the results of the XRF were in good agreement with the certified values.

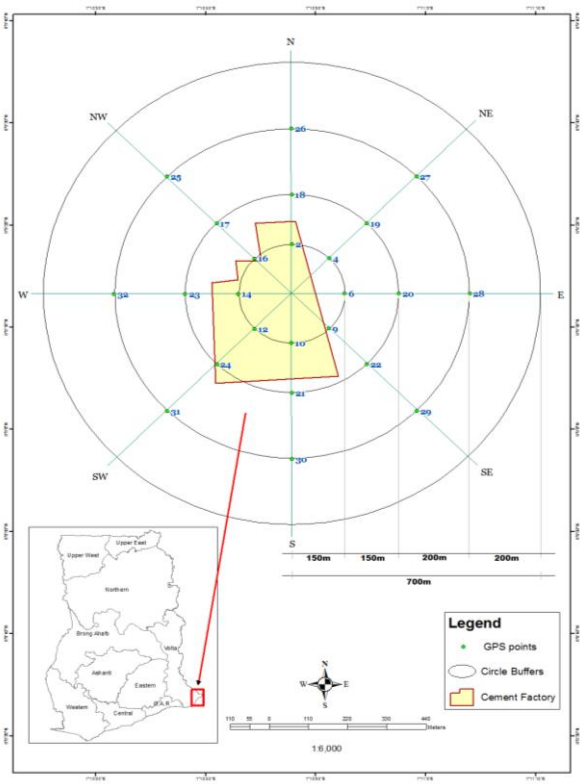

Figure1. Study area showing sampling points around current facility

3. Results and Discussion

Tables 1 and 2 summarize the concentrations of eight heavy metals, respectively, in 34 soil and 29 vegetation (*Tephrosia elegans* plant) samples collected in the vicinity of the Diamond Cement (DIACEM) plant. All the eight elements display their presence in all the soil and vegetation samples used for the study.

Table 1. Heavy metal concentration in soil samples collected in the neighbourhood of a cement factory.

Metal	Heavy metal concentration, µg/g				
	Min	Max	Mean	Median	Std
As	0.4	11.9	**2.55**	1.80	0.38
Co	8.0	582.0	**54.54**	19.95	21.71
Cr	190.0	1721.0	**961.24**	994.50	69.28
Cu	12.0	44.90	**27.97**	27.6	1.58
Mn	155.0	3410.85	**544.92**	426.36	94.32
Ni	12.20	510.0	**245.26**	251.25	18.59
Pb	0.80	45.70	**13.13**	4.75	1.92
Zn	11.70	139.50	**35.02**	31.15	3.79

For the soil samples, the highest level corresponded to Cr and Mn followed by Ni. The lowest level of metal were recorded for As and Pb. The levels of Cr, Ni, Co and Mn is of a significant interest as they are far higher than what Schumacher *et al* [13] recorded in a similar study in the vicinity of a fully fledged cement plant in Spain which has operated for over 50 years as against the nine year period of the current cement facility. Furthermore, studies on soil have implicated these metals as reaching or exceeding toxicity levels. For example, Bergmann [27] has shown that the toxic levels of Cr in soil is around 2-50 µg/g and this in comparison with Cr measurement in the current situation is too high. The critical level for Ni in soil have been investigated by many researchers [7, 27, 28, 29,] and estimated to be in the range of 2-50 µg/g. According to the present study, the range for Ni (12.2-510 µg/g) is alarming suggesting that Ni pollution is critical in the investigated area. Generally, 62.5% of the metals (As, Co, Cr, Ni and Pb) under the current study are higher than their average abundance in the continental crust [30]. Meanwhile, the elemental concentrations in soil samples are in the decreasing order of Cr>Mn>Ni>Co>Zn>Cu>Pb>As.

Metal levels in the vegetation samples collected in the neighbourhood of the cement plant are shown in Table 2. The highest level corresponded to Cr and Mn, followed by Zn. Here again, the lowest level corresponded to As and Pb. The levels of all metal concentration in the plant samples were again much higher than what Schumacher *et al* [13] observed for herbage plant samples in the vicinity of the same cement facility seven years later after the previous study. A close look at Table 2 shows that the variability in the range of all the metal distribution in the plant samples as compared to their means respectively is an indication of over contamination with the metal ions. The issue of over contamination is supported by the fact that most metals exceeded their critical value in the plant samples. For instance, the critical levels of Cr for plants are 5-10 µg/g [31] and 0.06-18 µg/g [32], indicating that the results in the investigated area runs a risk of Cr pollution in the plant samples. Mobility of Co element has been found to be slow in plants [33] and the toxic level is about 0.05 µg/g [34]. The present mean level of 10.02 µg/g is a clear indication of potential pollution. Meanwhile, Kabata-Pendias and Piotrowska [34] have reported that the normal content of Cu in plants ranges from 2 to 20 µg/g, but in most normal plants Cu content is in a narrower range of 4-12 µg/g. Robson and Reuter [35] explained that there are different tolerance ranges for

plants, but a critical toxic level of Cu is in the range of 20-30 µg/g for most plants. The risk of Cu toxicity in vegetation species is clearly evident by the fact that 23.8 µg/g mean level has been reported by the current study. According to Onder *et al* [5], the acceptable Pb limit level is 3 µg/g for plants; however, 13.13 µg/g average levels was recorded for Pb in vegetation samples for the current study indicating over contamination. The decreasing order of elemental concentrations in the plants is in the order of Cr>Mn>Zn>Cu>Ni>Co>Pb>As.

Table 2. Heavy metal concentration in Tephrosia elegans samples collected in the neighbourhood of a cement factory

Metal	Heavy metal concentration, µg/g				
	Min	Max	Mean	Median	S. E.
As	0.4	8.0	**1.33**	0.7	0.25
Co	4.2	60.1	**10.02**	7.0	2.01
Cr	14.0	775.0	**238.75**	197.0	27.45
Cu	13.1	50.7	**23.8**	20.6	1.82
Mn	72.52	310.08	**182.94**	155.04	10.08
Ni	5.9	22.1	**11.67**	10.59	1.29
Pb	1.0	43.5	**6.02**	3.4	1.54
Zn	40.6	172.0	**66.77**	62.5	4.64

These metals with the exception of Pb were analyzed in Portland limestone cement produced from the cement facility under the current investigation by Kpeglo *et al* [36] using Instrumental Neutron Activation Analysis (INAA). The INAA is not a good method for the analysis of Pb because it does not have easily measurable isotope [37]. However, Pb is an important member of the ^{238}U and ^{232}Th decay series which were included in the Portland cement analyzed by Kpeglo *et al* [36]. The heavy metals analysis in the cement product implicates cement dust originating from the cement facility for being partly or wholly responsible for metal contamination in the soil and plants in the neighbourhood of the factory.

The decreasing order in the quantitative trend of the metal content in both the vegetation and soil samples indicate a certain measure of similarity between the different sets of samples. This similarity is expected since heavy metals from soil enter plants primarily through the root system. The similarities in the trend suggest some level of relationship in the plants uptake of elements from the soil. In general, plant roots are the most important site for uptake chemicals from soil [38]. In an attempt to understand this relationship, the Pearson Correlation Co-efficient, r, was used to establish the relationship between the concentrations of corresponding metals evaluated from the soil and plant samples. As shown in Table 3, the correlation coefficients (r) between soil and vegetation samples, as mean heavy metal content of different places and distances, for each metal separately.

Table 3: Computed Pearson correlation coefficient between heavy metal levels between soil and plant samples in the investigated area

Correlation between metals	**r_c value**
Correlation between soil and plants for As	0.287
Correlation between soil and plants for Co	0.983*
Correlation between soil and plants for Cr	0.505
Correlation between soil and plants for Cu	0.717*
Correlation between soil and plants for Mn	0.783
Correlation between soil and plants for Ni	-0.558
Correlation between soil and plants for Pb	0.253
Correlation between soil and plants for Zn	-0.840

*significant at $p < 0.05$

As seen from Table 3, with the exception of Ni and Zn, there are positive correlation between soil and plants for most of the metals in the investigated area. These relations were only significant for Co and Cu (r=0.983 and r=0.717 respectively), but not significant for the rest of the metals under the current study. The results of positive correlation between soil and plants have been supported by earlier findings [5, 39]. Thus, indicating that plants take nutritional elements from soil through their roots [7]. However, the negative correlation results indicated by the two metals, Ni and Zn, give a strong suspicion to the fact that some elements might be assimilated through other organs of the plants other than their roots or some plants may have high affinity of assimilation of some elements directly from atmospheric deposition. Another good reason may be linked to the fact that only the upper layer (A soil horizon) of soil was sampled [40]. Generally, the mean concentration levels in soil are higher than that of the plant samples (Table 1 and 2). However, Zn was an exception to this observation, indicating that the mean soil concentration of Zn (35.02 µg/g) is lower than mean concentration of 66.77 µg/g for the plants which might have led to the negative correlation result for the metal. Another important observation was that, the mean metal concentration ratio (r_c) of soil to plant ranged from 1.18 to

5.44, Zn (r_c < 1) and Ni (r_c > 21) showed complete departure from this range. On the part of Ni, Güne *et al* [7] in an earlier study had indicated that Ni is absorbed easily and rapidly by plants from the soil, therefore the negative correlation might be due to the over contamination of the metal in the soil.

To assess the influence of the cement facility on the area directly within the vicinity, various radii distances (150, 300, 500, 700 and 1000m) as well as different directions (north, north-east, east, south-east, south, south-west, west and north-west) with the facility as the centre were considered. Tables 4 and 5 summarize the mean elemental concentrations of both soil and plants and their distribution with respect to distance and direction from the cement facility. A close observation from the available data reveals a number of irregular distributions in metal concentration in the samples in respect of distance and direction. At one point, the highest levels of some metals occur closer at varying directions from the factory. In another instance, the peak levels of some metals were observed further away in varying directions. For instance, for the soil samples: the highest level of Cr is observed at a radius distance (rd) of 150m at the NW direction; Mn (rd=1000m at easting direction); Ni (rd=150m at southing direction); and Zn (rd=500m at northing direction). However, a close inspection of Table 4 suggests that the mean concentration of the soil and plant specimen decrease as the distance from the facility increased for most metals. The situation can be linked to the cement factory as a major source responsible for this metal distribution pattern.

Table 5. Concentration of heavy metals (µg/g) in soil and plant samples at varying directions from the Diamond Cement Factory

Metals	Geographical directions from cement factory							
	N	NE	E	SE	S	SW	W	NW
As	2.9 (3.27)	2.3 (0.74)	1.6 (0.74)	4.5 (1.17)	2.2 (1.05)	2.2 (0.67)	2.9 (0.85)	1.6 (1.10)
Cr	1000.8 (359.9)	935.4 (119.7)	762 (271.2)	1101.2 (228.0)	1070.3 (285.5)	745.7 (87.3)	795.5 (239.3)	1211.2 (231.5)
Co	159 910.4)	20.8 (5.40)	14.8 (21.7)	35.3 (6.40)	22 (10.3)	44.2 (5.53)	42.7 (7.80)	19 (22.8)
Cu	25.9 (27.9)	24.8 (22.3)	24.7 (21.7)	31.2 (37.1)	27.9 (24.4)	24.5 (20.2)	28.4 (22.48)	36 (25.9)
Mn	562.0 (206.7)	387.6 (180.9)	341.1 (170.5)	573.6 (232.0)	413.4 (155.1)	568.5 (180.9)	1124 (193.8)	465.1 (174.4)
Ni	242.3 (13.2)	228.9 (8.07)	186.4 (9.72)	262.9 (11.0)	328.0 (14.4)	185.4 (11.73)	224.1 (13.25)	308.4 (12.2)
Pb	7.7 (7.40)	4.8 (3.68)	9.0 (3.72)	16.7 (43.5)	7.1 (3.30)	9.8 (3.73)	14.8 (5.45)	3.5 (3.50)
Zn	40.2 (108.9)	32.2 (54.77)	42.1 (57.5)	53.4 (55.3)	28.2 (74.1)	24.5 (59.03)	27.3 (63.6)	24.8 (64.48)

*The values in the parenthesis are the corresponding metal concentration in the plant samples

Likewise, the highest levels of these elements in plants have differing distances and directions which cannot be described even with the understanding of the three main prevailing wind directions (north, north-east and east). These differing discrepancy levels are associated with each metal in the soil and vegetation samples. Several industrial studies, particularly in the cement and Municipal Solid Waste incinerator industrial facilities, involving similar studies had encountered similar phenomena [11, 19, 41, 42, 43].

The relationship between the elemental contents in soil and vegetation samples in relation to distance and direction from the cement factory is rather complicated as indicted earlier and may depend on several factors. Among these factors are: possible variations that occurred in the factors that can affect metal emissions from the facility which resulted in their subsequent deposition on the soil and plant; other potential pollutant sources; metrological conditions of the area; the sampling season; and homogeneity of the samples. Meanwhile, it is important to re-emphasized that no other industrial facility exists in the study area, however, the irregular distribution of metals in samples could be due to traffic of vehicles, and specially trucks, operating within and the proximity of the cement plant. The trucks operating around the cement facility include the facility's own which transport cementitous materials. In the cause of operations of these vehicles, metal distribution into the soil and atmosphere may come about through the spread of cement dust and exhaust fumes.

As a result of the complicated relationship in levels of individual element in the different set of samples, focusing on their distribution in terms of distance and direction will be futile, instead we find a way of discussing contamination status of the sampling sites. Surface soil and vegetation are considered as major sink of airborne metals.

Consequently, the measurement of metals in these media can be useful to establish trends and abundance and their consequences as a result of natural changes and those caused by man [44]. Of the two environmental matrices, the soil has largely been used to establish metal contamination in relation to natural or anthropogenic influence on the environment. Having established a good correlation between the soil and vegetation samples under the current investigation, the use of the soil data in explaining sources of environmental contamination will provide good judgment in understanding contamination of heavy metals by atmospheric deposition and industrial activities. In this study, three contamination indices have been used to express the extent of soil pollution in the area.

The assessment of soil or sediment enrichment can be carried out in many ways. The most common ones are the index of geoaccumulation and enrichment factors [45]. In this work, the index of geoaccumulation (I_{geo}), Enrichment Factor (EF) and Pollution Load Index (PLI) have been applied to assess heavy metals (As, Co, Cr, Cu, Mn, Ni, Pb and Zn) distribution and contamination in surface soils in the vicinity of the Diamond Cement facility.

The index of geoaccumulation index (I_{geo}) was originally used with bottom sediment by Muller [46]. It is computed by the following equation:

$$I_{geo}=\log_2\left[\frac{C_n}{1.5B_n}\right]$$

Where, C_n is the measured concentration of the element in the tested sediment (surface soils) and B_n is the geochemical background value of the element in fossil argillaceous sediment (continental crusted average or average shale). The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments [45]. Odewande and Abimbola [47] gave the following interpretation for the geoaccumulation index: $I_{geo} < 0$ = practically uncontaminated; $0 < I_{geo} < 1$ = uncontaminated to moderated 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.

Enrichment factor (EF) has been employed for the assessment of contamination in various environmental media by several researchers [45, 48, 49, 50]. Its version adapted to assess the contamination of various environmental media is as follows:

$$EF=\frac{[C_x/C_{ref}]_{Sample}}{[B_x/B_{ref}]_{Background}}$$

Where:
C_x = content of the examined element in the examined environment;
C_{ref} = content of the examined element in the reference environment;
B_x = content of the reference element in the examined environment; and
B_{ref}= content of the reference element in the reference environment;

An element is regarded as a reference element if it is of low occurrence variability and is present in the sample in trace amounts. It is also possible to apply an element of geochemical nature whose substantial amounts occur in the environment but has no characteristic effects i.e. synergism or antagonism towards an examined element.

Five contamination categories are recognized on the basis of the enrichment factor: EF < 2 states deficiency to minimal enrichment; EF = 2-5 moderate enrichment; EF = 5-20 severe enrichment; EF = 20-40 very high enrichment; and EF > 40 extremely high enrichment [48]. Despite certain short comings [51], the enrichment factor, due to its universal formula, is relatively simple and easy tool for assessing enrichment degree and comparing the contamination of different environment.

Each sampling site was evaluated for the extent of metal pollution by employing the method based on the pollution load index (PLI) developed by Thomilson *et al.* [52] as follows:

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

where *n* is the number of metals studied (seven in this study) and *CF* is the contamination factor defined by $CF = C_{metal} / C_{background}$. C_{metal} is the concentration of pollutant in sediment and $C_{background}$ is the background value for the metal. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denote perfection; PLI = 1 present that only baseline levels of pollutants are present and PLI >1 would indicate deterioration of site quality [50].

The EF and I_{geo} of heavy metals under the current study was computed for each element for each radii distance and direction relative to the background value of the element in continental crust average value of the element. In addition, the PLI was calculated for the overall distances and directions. Tables 6 and 7 display a summary of the EF and I_{geo} values for each heavy metal in terms of distance and direction respectively, in addition to PLI of the environments at each distance and direction.

Table 6. Values of the enrichment factor and geoaccumulation index for heavy metals at varying distances from the cement facility

Radius Distance (m)	Index	Heavy metals								PLI
		As	Co	Cr	Cu	Mn	Ni	Pb	Zn	
150	EF	4.81	2.81	43.27	2.41	1.94	16.01	1.38	1.65	1.25
	I_{geo}	-0.08	-0.86	3.09	-1.08	-1.39	1.65	-1.86	-1.62	
300	EF	4.07	2.21	55.81	2.73	2.28	17.2	1.63	2.10	0.94
	I_{geo}	-0.90	-1.21	2.88	-1.45	-1.74	1.18	-2.22	-1.86	
500	EF	6.35	3.31	43.42	2.05	1.42	13.45	1.80	2.55	1.10
	I_{geo}	0.05	-0.89	2.83	-1.58	-2.11	-0.54	-1.77	-1.26	
700	EF	4.54	3.28	39.69	2.22	1.86	14.46	2.27	1.74	1.18
	I_{geo}	-0.30	-0.77	2.83	-1.34	-1.64	1.37	-1.30	-1.69	
1000	EF	10.26	19.25	27.13	1.62	3.16	9.65	8.53	2.56	1.51
	I_{geo}	-1.25	2.16	1.77	-2.30	-0.63	0.28	0.10	-1.64	

According to Zhang and Liu [53], EF values between 0.5 and 1.5 indicate that a metal is entirely from crusted material or natural processes, whereas EF values greater than 1.5 suggests that the source are more likely to be anthropogenic. The result of the present study show that, with the exception of Pb enrichment (at 150m) and Cu at southeast direction, all the metals were over moderately enriched in all the distances and directions considered for the study (Table 6 and 7) since the EF values of the metals are greater than 1.5. This indicates that the environment under the study is moderately to extremely enrich with all the metals. Chromium is the only metal with extremely enrichment (EF>40) status from 150m to 500m in the north, south, west and north-west directions. Nickel show severe enrichment (EF=5-20) at all distances and directions around the investigated area. Zinc and Pb are the least enriched metals which exhibited minimal enrichment up to 700m between south-west and north-west directions. The differences in the EF values may be due to the difference in the magnitude of input for each metal in the soil and/or differences in the removal rate of each metal from the soil [54].

Table 7. Values of the enrichment factor and geoaccumulation index for heavy metals at various directions from the cement facility

Heavy Metals	Indices	Geographical directions around Diamond Cement Factory							
		N	**NE**	**E**	**SE**	**S**	**SW**	**W**	**NW**
As	EF	5.99	8.56	5.00	5.20	6.52	4.79	8.11	4.14
	I_{geo}	0.10	-0.23	-0.76	0.74	-0.30	-0.30	0.10	-0.76
Co	EF	23.65	5.58	3.32	2.93	4.69	6.92	28.78	3.54
	I_{geo}	2.18	-0.85	-1.34	-0.08	-0.77	0.24	1.93	-0.98
Cr	EF	37.22	62.69	42.77	22.89	57.05	29.21	40.05	56.45
	I_{geo}	2.74	2.64	2.36	2.89	2.84	2.31	2.41	3.01
Cu	EF	1.75	3.02	2.53	1.18	2.70	1.74	2.60	3.05
	I_{geo}	-1.67	-1.73	-1.74	-1.40	-1.56	-1.75	-1.54	-1.20
Mn	EF	2.20	2.74	2.02	1.26	2.42	2.34	5.95	2.28
	I_{geo}	-1.34	-1.88	-2.06	-1.31	-1.72	-1.33	-0.34	-1.62
Ni	EF	12.01	20.64	13.95	7.29	23.32	9.68	15.03	19.16
	I_{geo}	1.11	1.03	0.73	1.23	1.54	0.72	0.99	1.46
Pb	EF	2.29	2.57	4.04	2.77	3.03	3.07	5.96	1.31
	I_{geo}	-1.28	-1.97	-1.06	-0.17	-1.40	-0.94	-0.43	-2.42
Zn	EF	2.14	3.08	3.38	1.59	2.15	1.37	1.96	1.65
	I_{geo}	-1.39	-1.71	-1.32	-0.98	-1.90	-2.10	-1.94	-2.08
	PLI	**1.55**	**1.02**	**0.96**	**1.62**	**1.12**	**1.14**	**1.67**	**1.01**

The pollution or the contamination levels in the environment under consideration was further expressed in terms of geoaccumulation index. The index indicated that the environment is uncontaminated in all directions with respect to Cu, Mn. Pb and Zn (Table 7). Chromium is again the only strongly polluted metal according to I_{geo} classification at 150m distance from the cement factory to the north-west. Nickel also shows unpolluted to moderate

polluted characteristics at all distances (except 500m) and directions.

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 Table 6, the overall degree of contamination by the eight metals in distance terms is of the order 1000m>150m>700m>500m>300m. Likewise, Table 7 provides information which indicated that the order of contamination is W>SE>N>SW>S>NE>NW>E in terms of directions from the cement facility. The analysis of the direction and distance results indicate that the most contaminated area may be experienced in the western direction at I km distance from the factory. The result may be supported with the explanation that excess cement materials awaiting processing in the factory are stored at the western side of the factory in addition to the fact that vehicular traffic activity is more pronounced at that same direction. This situation may contribute to the distribution of dust from processed cement and cement materials as well as vehicular emission in that direction. The result also supported a position that 300m at the easting direction of the factory is least contaminated. This position is validated in the sense that the sampling site is overshadowed with thick vegetation which makes atmospheric dust or particulate matter deposition on to the soil of the area very minimal. The distribution of the metal concentration of the soil in the study area indicated that this area has been affected by anthropogenic activity, in particular the cement factory, leading to a high accumulation of some heavy metals (As, Co, Cr and Ni) compared with the natural background level. The high accumulation of these metals in the soil has affected normal levels of metals in the *Tephrosia elegans* plant used for the study. A clear indication that vegetable crops like cassava and corn which are the mainstay agricultural crops in the area may suffer metal contamination. This is because bioavailable metal content in soil exerts a decisive impact on soil quality and its eventual uptake by plants and eventually by humans [46]. Most heavy metals in high concentration have adverse effect on human health; they accumulate in the body causing metal poisoning which is a co-factor in many other diseases [55, 56, 57, 58].

The identification and quantification of heavy metal sources, as well as the contamination status of those heavy metals, are important environmental scientific issues. The present study presents useful tools for the evaluation of soil contamination, in relation to how the soil quality may affect useful vegetation. The methods used, including correlation analysis, enrichment factor and geoaccumulation index provided important tools for better understanding the complex dynamics of the pollutants among the sampling sites in relation to the environmental matrices employed for the study. The relatively high concentrations of the studied metals clearly indicate that the main source of pollution comes from the activities of the cement factory.

4. CONCLUSION

In this study, 34 soil and 29 *Tephrosia elegans* plants (representing the annual vegetation of the study area) have been analyzed by energy dispersive XRF technique for eight heavy metals (As, Co, Cr, Mn, Ni, Pb and Zn). Sampling points were chosen in such a manner as to cover the entire vicinity of the Diamond Cement Factory (DIACEM) at Aflao, in the Volta Region of Ghana. The sampling points represent five radii distances (150m, 300m, 500m, 700m and 1000m) and the eight geographical directions.

The results indicated that levels of most metals are above background and critical limits in soil and vegetation respectively. Initially, Cr, Co, Ni and Mn were implicated in that respect. Correlation analysis of the corresponding metal levels in soil and plants suggested a positive correlation (Ni and Zn were exceptional) between the soil and plant samples. The level of metal distribution considering distance and direction from the cement facility were of a complex pattern and many factors were suggested to account for that. One of the major suggestions was that other pollution sources might be in display. To understand the complexity of the distribution of the pollutants, three mathematical models, enrichment factor, geoaccumulation index and pollution load index were employed to explain the distribution dynamics in terms of enrichment, contamination and overall contamination status of the sampling sites. The mathematical models revealed that majority of the sampling points were enriched or contaminated with heavy metals and that the source of pollution was anthropogenic. The cement facility together with the attendant vehicular traffic and emissions were implicated as responsible for metal pollution in the area, as in general the highest metal level were found close to the cement facility.

Until the current investigation, data on metal levels in the two environmental matrices (soil and vegetation) from the area under the potential influence of the emissions of these pollutants by the cement facility here evaluated were scarce. Therefore, the current results should be of a special interest as reference values in future evaluations of the facility, which we deemed very necessary. From the results of the current investigation, we recommend that future cement production facilities must be set away from settlements and that our environmental regulations must be strengthened so as to prompt current industrial operators to take precautions and new techniques to protect the environment from hazardous pollutants. The reason being that the human body is of a complex structure, therefore, the accumulation of metals can cause many toxic effects, which can influence different mechanisms on the body [15]. By way of monitoring the operational influence of the cement facility on the environment, this study underlines the need for replicating periodic studies (two

years duration) on the facility on the environment in addition to the evaluation of the facility on human health.

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REFERENCES

[1] **Chen, T., Zheng, Y., Lei, M., Huang, Z., Wu, H., Chen, H. Fan, K., Yu, K. Wu, X. and Tian, Q**. (2005). "Assessment of heavy metal pollution of urban parks in Beijing, China". Chemosphere 60, 542-551

[2] **Nriagu, J. O.** (1989). "A global assessment of natural sources of atmospheric trace metals". Nature 338, 47-49

[3] **Bilos, C., Colombo, J. C., Skorupka, C. N. and Presa, M. J. P**. (2001). "Source, distribution and variability of airborne trace metals in La Plate City area, Argentina". Environmental Pollution 111, 149-159

[4] **Ghrefat, H. and Yusuf, N.** (2006). "Assessing Mn, Fe, Cu, Zn and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan". Chemosphere, 1-8

[5] **Onder, S., Dursun, S., Gezgin, S. and Demirbas, A.** (2007). "Determination of heavy metal pollution in grass and soil of City Centre Green areas (Konya, Turkey)". Polish J. Environmental Studies, Vol. 16, No. 1, 145-154

[6] **Abulude, F. O. and Adesoje, H.** (2006). "Characterization of heavy metal pollution around cassava processing factory using Atomic Absorption Spectrophotometer", Research J. Appl. Sci 1 (1-4)., 16-18.

[7] **Güne, A., Alpaslan, M. and Inal, A.** (2004). "Plant growth and fertilizer". Ankara University of Agriculture publication. No: 1539, Ankara, Turkey.

[8] **Chen, T. B., Wong, J. W. C., Zhou, H. Y. and Wong, M. H**. (1997). "Assessment of trace metal distribution and contamination in surface soils in Hong Kong". Environmental Pollution, Vol. 96, No. 1, 61-68

[9] **Ndiokwere, C. l.** (1984). "A study of heavy metal pollution from motor vehicle emissions and its effect on roadside soil, vegetation and crops in Nigeria". Environmental pollution B 7, 35-42

[10] **Celik, a., Kartal, A. A., Akdogan, A. and Kaska, Y**. (2005). "Determining the heavy metal pollution in Denizli (Turkey) by using *Robinio pseudo-acacia L.*". Environmental International 31, 105-112

[11] **Meneses, M., Llobet, J. M., Granero, S., Schuhmacher, M. and Domingo, J. l.** (1999). "Monitoriing metals in the vicinity of municipal waste incinerator; Temporal variation in soils and vegetation". Science of the Total Environment 226, 217-227

[12] **Domingo, J. L., Schuhmacher, M. Granero, S. Llobet, J. M. and de Kok H. A. M**. (2001). "PCDD/F levels in the vicinity of an old municipal solid waste incinerator: Temporal variation in soils". Environmental Monitoring Assessment 69, 175-193

[13] Schuhmacher, M., Bocio, A., Agramunt, M. C., Domingo, J. L. and de Kok, H. A. M. (2002). " PDCC/F and metal concentration in soil and herbage samples collected in the vicinity of a cement plant", Chemosphere, 48, 209-217.

[14] **Nadal, M., Schuhmacher, M. and Domingo, J. L**. (2004). "Metal pollution of soils and vegetation in an area with petrochemical industry". Science of Total environment 321, 59-69

[15] **Isikli, B., Demir, T. A., Ürer, S. M., Berber, A., Akar, T. and Kalyoncu, C.** (2003). "Effects of Chromium exposure from a cement factory". Environmental research 91, 113-118

[16] **Bilen, S.** (2010). "Effect of cement dust pollution on microbial properties and enzyme activities in cultivated and no-till soils". African Journal of Microbiology Research, vol. 4 (22), 2418-2425

[17] **Bayhan, Y. k. and Özbay, O.** (1992) " In: Isikli et al, 2006, "Cadmium exposure from the cement dust emissions: a field study in a rural residence". Chemosphere, 63, 1546-1552.

[18] Demir, T. A., Isikli, B., Urer, S. M., Berber, A., Akar, T., Canbek, M. and Kalyoncu, C. (2005). "Nickel exposure and its effects". Biometal 18, 7-13

[19] **Al-Khashman, O. A. and Shawabkeh, R. A.** (2006). "Metal distribution in soils around the cement factory in Southern Jordan". Environmental Pollution 140, 387-394

[20] **Zerrouqi, Z., Shaa, M., Oujidi, M., Elkharmouz, M., Bengamra, s. and Zerrouqi, A**. (2008). "Assessment of cement's dust impact on the soil using principal component analysis and GIS". Int. J. of Environmental Science Technology, 591, 125-134

[21] **Asubiojo, O. I., Aina, P. O., Oluwole, A. F., Arshed, W., Akanle, O. A. and Spyrou, N. M.** (1991). "Effect of cement production on the elemental composition of soils in the neighbourhood of two cement factories". Water, Air and Soil 57-58, 819-828

[22] **Semhi, K., Al-Khirbash, S., Abdalla, O., Khan, T., Duplay, J., Chaudhuri, S. and Al-Saidi, S.** (2010). "Dry atmospheric contribution to plant-soil system around a cement factory: spatial variations and sources- a cases study from Oman'. Water, Air, Soil Pollution 205, 343-357

[23] **Domingo, J. L.** (1994). "Metal-induced developmental toxicity in mammals: A review". J. Toxicol. Environ. Health 42, 123-141

[24] **Chang, L. W.** (1996). "Toxicology of metals". CRC Lewis Publishers, Boca Raton, FL, USA

[25] **Dickson, K. B. and Benneh,** G (2004). "A new geography of Ghana (2nd edn)", Longman Group (EF) Limited, Musselburgh, Scotland, 20p

[26] **Yeung Z.L.L., Kwok, R.C.W. and Yu, K.N**. (2003). "Determination of multi-element profiles of street dust using energy dispersive X-ray fluorescence (EDXRF)". Appl. Radiat. Isotopes, 58: 339-346.

[27] **Bergmann, W.** (1992). "Nutritional disorders of plants", Gustav Fisher, New York.

[28] **Madejon, P., Murillo, J. M., Maranon, T., Cabrera, F. and Lopez, R.** (2002). "Bioaccumulation of As, Cd, Cu, Fe and Pb in wild grasses affected by the Aznalcollar mine spill (SW Spain)", Sci Total Environ. 309, 105-120

[29] **Shallari, S., Schwartz, C., Hasko, A. and Morel, J. L.** (1998). "Heavy metals in soils and plants of serpentine and industrial sites of Albania, science of Total Environ., 209, 133-142

[30] **Taylor, S.R. and S.M. McLennan**, (1985). "The Continental Crust: Its Composition and Evolution". Blackwell Scientific Publications, Oxford.

[31] **Çiçek, A and Koparala, A. S**. (2004). "Accumulation of sulphur heavy metalsmin soil and tree leaves sampled from the surroundings of Tunçbilek Thermal Power Plant", Chemosphere, 57, 1031-1036.

[32] **Shanker, A. K., Cervantes, C., Loza-Tavera, H. and Avudainayagam, S**. (2005). "Chromium toxicity in plants", Environ, Intern, 31, 739-753

[33] **Robson, A. D., Dilworth, M. J. and Chatel, D. L.** (1997). "Cobalt and Nitrogen fixation in Lupimus angustifolius L. I. growth Nitrogen concentrations and Cobalt distribution", New Phytol, 83, 53-62

[34] **Kabata-Pendias, A. and Piotrowska, M**. (1984). "Determination of heavy metal pollution in grass and soil of Centre Green Areas (Konya, Turkey)", In: S. Onder, S. Dursun, S. Gezgin, and A. Demirbas, Polish j. of Environ Stud, Vol. 16, No.1, 145-154

[35] **Robson, A. D. and Reuter, D. J.** (1981). "Diagnosis of copper deficiency and toxicity. In: copper in soils and plants, J. F. Loneragen, A. D. Robson and R. D. Graham, Academic Press, London. 287-312pp

[36] **Kpeglo *et al*** (2011). "Radiochemical pollutants concentration in Ghanaian Cement by Instrumental Neutron Activation Analysis and γ-Ray Spectrometry", Res. J. Environ. & Earth Sciences.

[37] Alvarado, J. and Cristiano, A. R. (1993). "Determination of cadmium, cobalt, iron, niclel and lead in Venezuelan cigarettes by elecrothermal atomic absorption spectrometry". J. Anal. Atomic Spectrometry, 8: 253-259

[38] **Bell, R. M.,** (1992). "Higher plant accumulation of organic pollutants from soils", EPA/600/R-92/138. Cincinnati: United States Environmental Protection Agency.

[39] **Fatoki, O. S.** (2003). "Lead, Cadmium and Zinc accumulation along some selected major roads of Eastern Cape', Inter. J. Environ Studies, 60, 199-204

[40] **Schuhmacher, M., Nadal M. and Domingo, J. L.** (2009). " environmental monitoring of PCDD/F and metals in the vicinity of a cement plant after using sewage sludge as a secondary fuel", Chemosphere 74, 1502-1508.

[41] **Schuhmacher, M., Granero, S., Bellés, M., Llobet, J. M., and Domingo, J. L.** (1996). "Levels of metals in soil and vegetation in the vicinity of a municipal solid waste incinerator", Toxicol. Environ. Chem. 56, 119-132

[42] **Schuhmacher, M., Domingo, J. L. and Garreta, J.** (2004). "Pollutants emitted by a cement plant: health risk for the population living in the neighbourhood", Environ. Res. 95, 198-206

[43] **Llobet, J. M., Granero, S., Schuhmacher, M and Domingo, D. L.** (1999). "Temporal variation in concentration of metals in soil and vegetation in the vicinity of Municipal Solid W aste incinerator", Toxicol. Environ. Chem. 71, 119-129

[44] **Frink, C. R**. (1996). "A perspective of metals in soil", J. Soil contamination, 32, 329-359

[45] **Lu, X., Wang, L., Lei, K., Huang, J. and Zhai, Y**. (2009). "Contamination assessment of copper, lead, zinc manganese and nickel in street dust of Baoji, NW China", J. Hazardous Materials, 161, 1058-1062

[46] **Muller, G.** (1969). "Index of geoaccumulation in sediments of the Rhine River", 2: 108-118

[47] **Odewande, A. A. and Abimbola, A. F.** (2008). "Contamination indices and heavy metal concentrations in urban soil of Ibadan metropolis, southwestern Nigeria", Environ. Geochem. Health 30, 243-254

[48] **Loska**, **K.; Wiechula, D.; Barska, B.; Cebula, E. and Chojnecka, A**., (2003). "Assessment of arsenic enrichment of cultivated soils in Southern Poland". Pol. J. Environ. Stud., 12 (2), 187– 192

[49] **Manno, E., Varrica, D. and Dongarrá, G.** (2006). "Metal distribution in road dust samples collected in an urban area close to a petrochemical plant at Gela, Sicily", Atmos. Environ, 40, 5929-5941

[50] **Al-Khashman, O. A.** (2004). "Determination of metal accumulation in deposited street dusts in Amman, Jordan", Environmental Geochemistry and Health, 29, (1), 1–10

[51] **Reimann, C. and de Carinat, P**. (2000). Heavy metals contamination in fungicide treated cocoa plantation in Cross River State, Nigeria", In: Aikpokpodion et al (2010). American-Eurasian J. Agric/ & Environ. Sci., * (3): 268-274

[52] **Thomilson, D.C., Wilson, D.J., Harris, C.R. and Jeffrey, D.W.** (1980). "Problem in heavy metals in estuaries and the formation of pollution index". Helgol. Wiss. Meeresunlter. 33(1–4): 566–575.

[53] **Zhang, J. and Liu, C. L**. (2002). "Riverine composition and estuarine geochemistry of particulate metals in China-Weathering features, anthropogenic impact and chemical fluxes", Estar. Coast. Shelf, 54, 1951-1070

[54] **Akoto, O., Ephraim, J. H. and Darko, G.** (2008). "Heavy metal in surface soils in the vicinity of abundant railway servicing workshop in Kumasi, Ghana". Int. J. Environmental research, 2 (4), 359-364

[55] **Hammond, P. B**. (1982). "Metabolism of lead". In: Odewande, A. A. and Abimbola, A. F. (2008). "Contamination indices and heavy metal concentrations in urban soil of Ibadan metropolis, southwestern Nigeria", Environ. Geochem health 30, 243-254

[56] **Thacker, S. B., Hoffman, A., Steinberg, K., Zack, M. and Smith, J.** (1992). "effect of low level burdens of lead on the metal development of children: Limitations of metal analysis in a review of longitudinal data", archives of environmental Health, 477, 336-347

[57] **Schwartz, J.** (1994). "Low-level lead exposure and children's IQ: A metal analysis and search for a threshold", Archives of Environmental Research and Toxicology, 59, 42-55

[58] **Paterson, E., Sanka, M. and Clerk,** L. (1996). "Urban soils as pollutant sinks-A case study from Aberdeen, Scotland", Applied Geochemistry, 11, 129-131