

Assessment of metal pollution in surface soils and vegetables of Ifo village, Southwestern Nigeria

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Abstract: We have assessed the extent of metal (Pb, Cd, Zn, Ni, Co, Cr, Cu, Mn, and Fe) pollution in the agricultural soils and vegetables from Ifo village in southwestern Nigeria. Ten (10) samples each of soil and vegetables are collected from the study area and are subjected to analysis. The concentrations of Pb, Cd, Zn, Ni, Co, Cr, Cu, Mn and Fe in soils are 16.9-68.4, 0.6-0.8, 54-89, 30.8-50.2, 10.6-22.3, 100-218, 12.3-24, 515-2215 and 33900-45600 ppm respectively while the concentrations in vegetables are 0.76-8.63, 0.05-0.42, 26.2-80.8, 1.1-17.8, 0.1-6.6, 2.4-77.2, 6.01-11.6, 23-360 and 300-18610 ppm respectively. Enrichment factor (EF), geoaccumulation index (I_{geo}) and transfer factor (TF) are determined and the respective levels of contamination are evaluated in the study area. Correlation analysis are also done to determine the relationship between the metals. The results of EF show that metals in the soil samples vary from no enrichment to minor enrichment, with Cd showing the highest EF value with minor enrichment of Pb, Ni, Cr, Cu and Mn; and moderately high enrichment of Cd and Zn. I_{geo} values show that the vegetable samples are uncontaminated with all the metals analyzed. However, in the soil samples, Cd and Cr are uncontaminated to moderately contaminated. The high values of Cd and Cr could probably be as a result of anthropogenic activities such as agricultural activities, treated and untreated wastewaters and irrigation return water in the study area. The TF value for Zn, Cu and Cd are moderately high compared to other metals. The high TF could also reflect intense agricultural activities in the area. The trend of TF for metals in the area is of the order: Zn>Cu>Cd>Cr>Ni>Fe>Mn>Pb ≥Co. The results of the correlation matrix analysis show that metals in the study area have different degrees of correlation.

Keywords: geoaccumulation index, pollution, enrichment, heavy metals, transfer factor

Introduction

Pollution associated with trace metals pose a serious problem to the environment, health, diet/food, livestock, vegetables, soils among others (Abimbola *et al.*, 2007). However, the term “trace metals” is used to denote elements that are essential for life processes in vegetables and living organisms at low concentration but deleterious at higher concentrations and thus become harmful to the ecosystem (man, vegetables and livestock) and the overall environment (Chibuike and Obiora, 2014). For example copper (Cu) and zinc (Zn) are essential micro-nutrients needed in living organisms but will become toxic if the maximum range of necessary concentration is exceeded thereby acting as a pollutant.

Soil pollution with metals such as cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu) is of major concern because metals are not biodegradable and they have long biological half-lives before being eliminated from living tissues (Suruchi and Khanna, 2011). Trace metals are believed to be naturally present in soils but contamination could still emanate from different sources including industry (e.g. power plants, iron and steel and chemical industries among others), agriculture (e.g. polluted irrigation waters, phosphate-based fertilizers, raw sewage and pesticides), waste incineration, combustion of fossil fuels and road traffic, mining (Onder *et al.*, 2007; Chopra *et al.*, 2009; Wuana and Okieimen, 2011; Das and Chakrapani, 2011).

The concentration of trace metals in soils is influenced by several

factors such as age, drainage, vegetation, among others (Kabata-Pendias, 2004; Wuana and Okieimen, 2011). The mobility and availability of trace elements is complex and governed by factors such as the geochemical, climatic and biological origin while the risk of a certain trace element to the environment or human health is dependent on mobility and bioavailability (Kabata-Pendias, 2004).

The environmental pollution with metals in the Ifo area has not been previously studied as none was found in the literature. However, such an investigation is required if the environmental impacts in the area are to be understood quantitatively and qualitatively. Therefore this study is aimed at determining the concentration of metals in the soil and vegetables grown on the soil and to assess the extent and degree of metals and the origin of these metals using the enrichment factor and geoaccumulation index of the metals. The metals considered in this study include Pb, Zn, Cd, Ni, Co, Cr, Cu, Mn and Fe.

Description and Geology of the study area

The study area is located in Ifo area of Ogun State in Nigeria

(Fig. 1) within longitudes $6^{\circ}48'57''$ and $6^{\circ}48'60''$ E and latitudes $3^{\circ}14'17''$ and $3^{\circ}14'20''$ N. The area is accessible through an untarred road which branched from the Lagos -Abeokuta express road. The study area falls within the Ilaro Formation and Ewekoro Formation. Ilaro Formation is made up of both marine and continental, massive yellowish consolidated sandstone. They are fine to medium grained and poorly sorted with some clay fractions. Ferruginous sandstone and ironstone bands indicative of the hiatus in the depositional environment occur as capping to the formation. The formation is poor in fossils but pollens and spores present indicate Eocene age (Adegoke, 1969). Ewekoro Formation consists of limestone of Paleocene – Eocene age, and overlies the Araromi member of the Abeokuta Group.

Materials and Methods

Sample Collection and Analysis

Ten soil and plant samples labelled as SS1-SS10 and PS1-PS10 respectively were collected from agricultural lands for analyses. The plant samples are vegetables (spinach). Both the soil and vegetable samples were collected from the same location in a grid pattern within the study area (Fig. 2). The vegetable samples

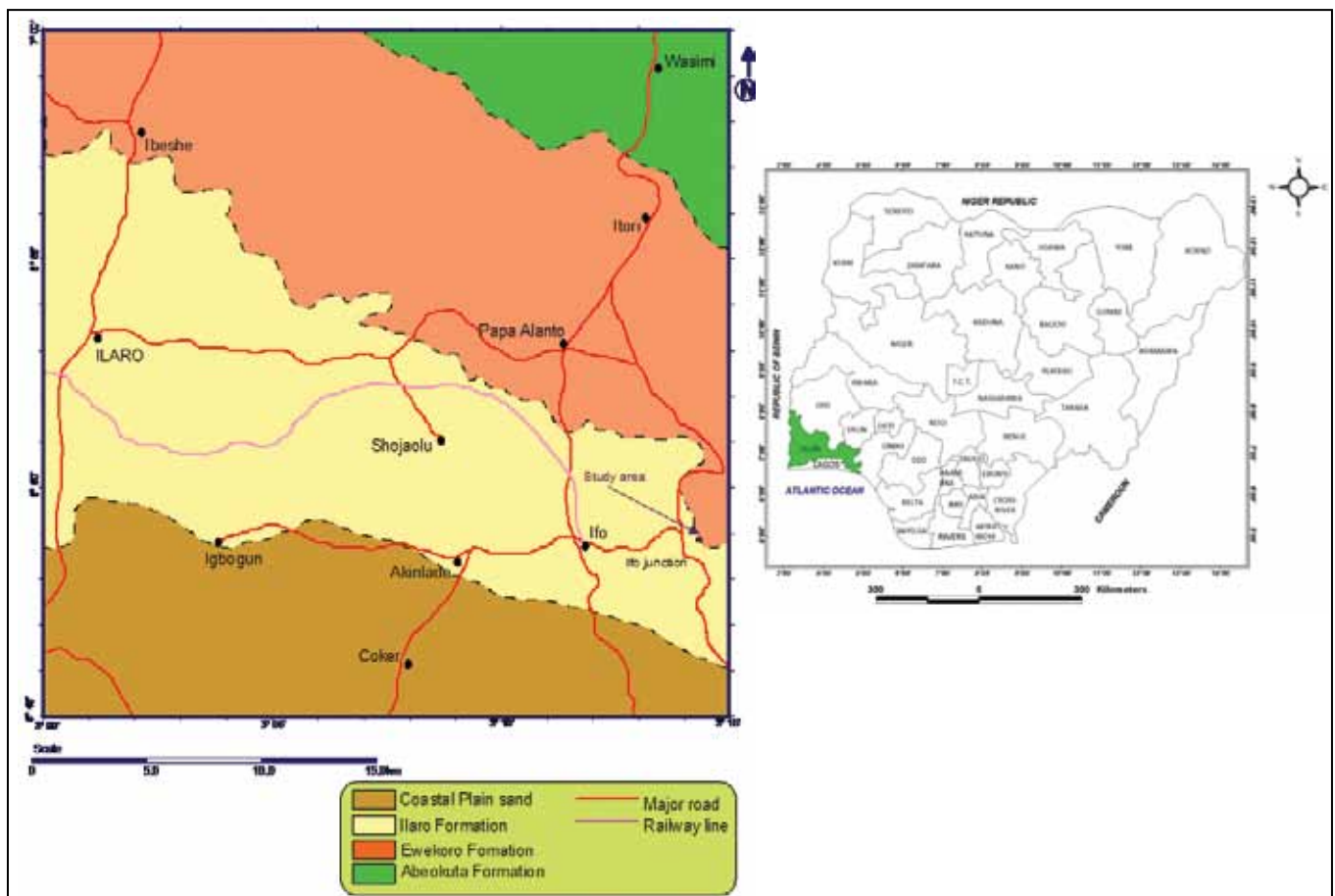


Fig. 1. Location and geological map of the study area (Nigerian Geological Survey Agency, 2004)

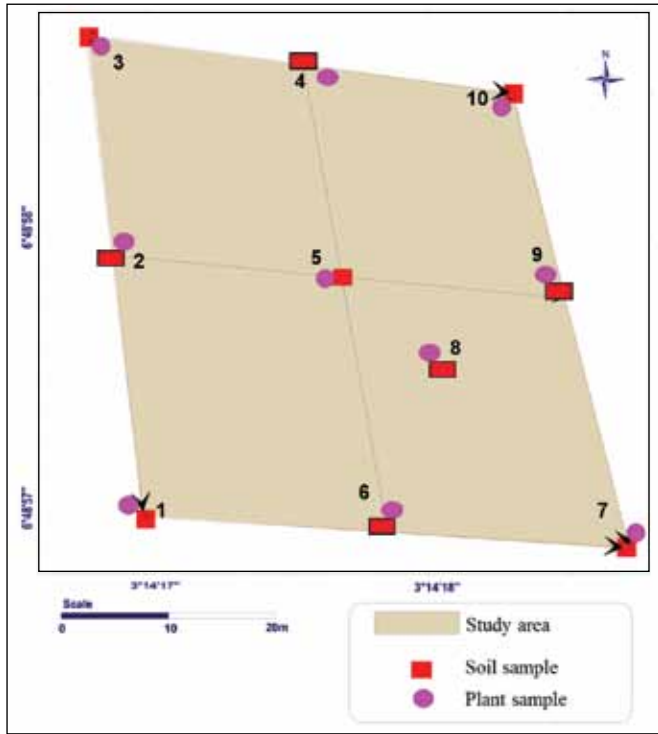


Fig. 2. Map of the study area showing geochemical sampling points

were first thoroughly washed with tap water and finally with deionized water. The collected soil samples were dried at 60°C in an oven. The dried soil samples were homogenised using Agate mortar and pestle; kept in polyethene bags in a desiccator until analysis.

Trace elements analyses were done on soil and vegetable samples in the study area by using Flame Atomic Absorption Spectrometry (F-AAS) technique. All chemical analyses of the soil and vegetables were carried out by a certified commercial ACME Laboratory in Canada.

Data Analysis

Magnitude of Contaminants in Soil Profile

In order to evaluate the magnitude of metal contamination in the samples, three geochemical parameters were used namely geoaccumulation index (I_{geo}), enrichment factor (EF) and transfer factor (TF).

Geoaccumulation (I_{geo}) Index

The degrees of metal contamination in the samples were determined using the I_{geo} classifications. I_{geo} index was calculated using the crustal average values for the metals (Turekian and Wedepohl, 1961). The geoaccumulation index used in quantifying

the metal accumulation in soil or sediments is given in equation 1 (Muller, 1981).

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \dots \dots \dots (1)$$

Where C_n is the concentration of measured metal in the sample, B_n is the geochemical background of the element in the underlying parent material while 1.5 is used as correcting factor for the variation of the background data due to lithological variations. The average value of each element in the earth’s crust proposed by Turekian and Wedepohl (1961) was used as background value in this study

Enrichment Factor (EF)

The enrichment factor (EF) is used to assess the level of contamination and the possible anthropogenic impact on the sediments of the study area. Al, Fe, or Si could be used as the geochemical normalization. However, researchers have successfully used Fe for the geochemical normalization of metal contaminants (Baptista Neto *et al.*, 2000; Mucha *et al.*, 2003; Conrad and Chisholm-Brause, 2004; Christophoridis *et al.*, 2009; Meza-Figueroa *et al.*, 2009; Bhuiyan *et al.*, 2011; Esen *et al.*, 2010). Therefore, Fe was used as a conservative tracer to differentiate natural from anthropogenic components in this study.

The EF is defined in equation 2 (Ergin *et al.*, 1991):

$$\frac{(M/Fe)_{sample}}{(M/Fe)_{background}} \dots \dots \dots (2)$$

Where $(M/Fe)_{sample}$ is the ratio of metal and Fe concentration of the sample, and $(M/Fe)_{background}$ is the ratio of metal and Fe concentration of a background.

Transfer Factor (TF)

The concentration of metal in the extraction of soil and vegetables were calculated on the basis of dry weight. The transfer factor (TF) was calculated using equation 3 (Kachenko and Singh, 2006; Jolly *et al.*, 2013). TF indicates the movement of metals from soil to vegetables. This movement is dependent on the physical and chemical properties of the soil and of vegetable species. These properties could be altered by many environmental and human factors including pH, sorbent nature, root exudates and nutrients (Violante *et al.*, 2010; Jolly *et al.*, 2013).

$$TF = \frac{C_{plant}}{C_{soil}} \dots \dots \dots (3)$$

Where $C_{vegetable}$ and C_{soil} represent the toxic metal concentration in extraction of vegetables and soils on dry weight respectively.

Results and Discussion

Soil Sample

The average concentrations of metals in the soil samples are given in Table 1. It was observed that Fe possess the highest average concentration followed by Mn, Cr, Zn, Ni, Pb, Co, Cu and Cd respectively. The table also shows that the average concentration of Pb, Cd, Cr, Mn and Fe are greater than their average crustal values. The high content of these metals could be as a result of anthropogenic sources including fertilizers and pesticides used in agricultural activities in the study area (Ghrefat *et al.*, 2011). Average concentrations of Zn, Ni, Co and Cu are also lower than that of their average crustal values. Also, in soil samples within the study area, most metals fall within the permissible limit given by WHO (1996). However, Cr have concentrations above the WHO

limit in all the locations. This might as a result of discharge of Cr in wastewater and sludge from nearby industries. Mn in SS1 and SS10 are greater than the acceptable limit. This could be due to sewage water irrigation application on soil (Haliru *et al.*, 2014).

Vegetable Sample

The results show that Fe has the highest average concentration in the vegetable samples; then Mn, Zn, Cr, Cu, Ni, Pb, Co and Cd respectively (Table 1). Average concentrations of all the metals are observed to be lower than that of the average crustal values.

Metal distributions in both soil and vegetable samples of the study area showed no patterns but vary from one location to another (Table 1). The concentrations of Pb in soils at SS2 and

Table 1. Average metal concentrations (ppm) in the sediments of Ifo with their minimum, maximum, and standard deviation

Location	Pb	Cd	Zn	Ni	Co	Cr	Cu	Mn	Fe
Soil Samples									
SS1	19.1	0.8	54	35.2	19.5	100	16.2	2025	33900
SS2	68.4	0.8	71	50.1	22.3	180	15.9	1677	39600
SS3	17.9	0.7	73	36.6	11.6	185	14.9	515	42600
SS4	21.1	0.6	89	47.6	14.6	216	14	621	44600
SS5	21.9	0.6	77	46.2	15.4	200	22	906	42700
SS6	21.2	0.7	78	33.2	22.2	185	24	622	42200
SS7	22.8	0.7	79	50.2	19.4	100	15.8	912	45600
SS8	16.9	0.6	76	36.4	10.6	218	16.1	522	42600
SS9	66.2	0.6	55	47.9	14.8	180	12.3	1654	39900
SS10	17.9	0.8	85	30.8	20.4	100	14.2	2215	34900
Average	29.34	0.69	73.7	41.42	17.08	166.4	16.54	1166.9	40860
Standard Deviation	20.11	0.876	11.40	7.62	4.24	47.8	3.54	658	3861
Acceptable limit*	100	3	300	50	50	100	100	2000	50000
Vegetable Samples									
PS1	0.86	0.18	27.8	1.1	0.1	2.4	9.53	37	260
PS2	2.85	0.27	48.1	4.9	1.62	11.5	10.17	156	2530
PS3	2.79	0.19	43.9	5.4	1.61	22.2	8.16	115	5220
PS4	8.63	0.42	80.8	17.8	6.4	76.9	12.4	360	18610
PS5	1.21	0.05	48.3	2	0.13	2.7	6.01	26	310
PS6	8.6	0.2	79.2	3.1	1.6	77.2	10.05	340	2000
PS7	2.86	0.06	44.3	16.8	6.6	2.6	7.68	32	320
PS8	0.76	0.22	26.2	5.2	0.2	21.3	11.6	115	17600
PS9	2.77	0.19	42.1	17.8	0.21	9.6	9.23	23	4880
PS10	1.22	0.26	40.2	1.2	0.1	65.3	6.04	250	300
Average	3.26	0.204	48.09	7.53	1.86	29.17	9.09	145.40	5203
Standard Deviation	2.95	0.105	18.44	7.03	2.54	31.30	2.14	129.4	7049
Background values	20	0.3	95	68	19	90	45	850	47,000
Acceptable limit*	0.30	0.10	100	67	50	0.3	73	500	425

Note: Background values of metals in average shale (ppm) is after Turekian and Wedepohl (1961).

*World Health Organization (1996)

SS9 are very high compared to others although lower than the acceptable limit given by WHO (1996). This is because the samples are taken from the roadside. However, Pb, Cd and Fe are also the acceptable limit by WHO in the vegetable samples. The variation in the distribution and concentration of metals in the study area may be as a result of difference in clay contents, pH, content of organic matter, cation exchange capacity, among others (Ghrefat *et al.*, 2011).

Enrichment Factor (EF) and Geoaccumulation Index (I_{geo})

Enrichment Factor (EF)

The geochemical background values in the region of study for these metals are not available in the literature for now. Therefore, we used the background concentrations of Pb, Zn, Cd, Ni, Co, Cr, Cu, Mn, and Fe obtained from Turekian and

Wedepohl (1961) (Table 2). These values have been used by several authors to determine the extent and degree of pollution of metal in sediments (Datta and Subramanian, 1998; Sanchez *et al.*, 1998; Loska and Wiechula, 2003; Cevik *et al.*, 2009; Nobil *et al.*, 2010; Ghrefat *et al.*, 2011).

Zhang and Liu (2002) stated that EF values that fall between 0.5 and 1.5 show the metal is mostly from crustal materials or are formed from natural processes, while those having EF values of greater than 1.5 could imply that their origin are probably from anthropogenic processes. However, Table 2 gives EF values for Pb, Zn, Cd, Ni, Co, Cr, Cu, and Mn. The values of EF imply that Zn, Ni, Co and Cu could be from natural processes for soil samples while Pb, Cd, Cr, and Mn have anthropogenic origin. However, in vegetable samples, Pb, Ni and Co could have their sources from natural processes while Cd, Zn, Cr, Cu and Mn have come from anthropogenic sources.

Table 2. Average (and standard deviation) metal concentrations and average crustal value (Turekian and Wedepohl, 1961) and enrichment factor values in the sediments of Ifo.

Metal	Soil samples		Vegetable samples		Average crustal value	
	Mean±SD	EF	Mean±SD	EF		
Pb	29.34±20.11	1.69	3.26±2.95	1.47	20	
Cd	0.69±0.088	2.65	0.204±0.105	6.14	0.3	
Zn	73.70±11.40	0.89	48.09±18.44	4.57	95	
Ni	41.42±7.62	0.70	7.53±7.03	1.00	68	
Co	17.08±4.24	1.03	1.86±2.54	0.88	19	
Cr	166.40±47.80	2.13	29.17±31.30	2.93	90	
Cu	16.54±3.54	0.42	9.09±2.14	1.82	45	
Mn	1167±658	1.58	145.40±129.40	1.55	850	
Fe	40860±3861	-	5203±7049	-	47,000	

The distribution of EF values shows that Zn, Ni, and Cu are not enriched in the soil samples in the study area (Chen *et al.*, 2007; Table 3). The EF value of Cd is the highest and show minor enrichment of Cd, Pb, Co, Cr, and Mn. The variation in EF values for the different metals in the soil samples could result from the difference in the extent of input for each metal in the soil and/or the variation in the rate at which each metal is being removed from the soil. Metals could be released with the water phase when parameters such as redox potential, pH, ionic strength and the concentration of organic complexing agents change (Calmano *et al.*, 1990; Ghrefat *et al.*, 2011).

EF values in the vegetable samples are generally higher than those of EF in the soil samples. Cd also has the highest value of EF and fall under the category of moderately severe enrichment (Chen *et al.*, 2007). Zn is the next to Cd having EF value of 4.57 and it also has moderately severe enrichment.

EF values show that Pb, Ni, Cr, Cu and Mn have minor enrichment while Co has no enrichment in vegetable samples.

Geoaccumulation Index (I_{geo})

The I_{geo} has seven grades with the highest grade being

Table 3. Interpretation of enrichment factor (Chen *et al.*, 2007)

Enrichment Factor	Implication
<1	No enrichment
1-3	Minor enrichment
5-10	Moderately severe enrichment
10-25	Severe enrichment
25-50	Very severe enrichment
>50	Extremely severe enrichment

referred to as class 6); which means a 100-fold enrichment above background values (Table 4). I_{geo} results show that the soil samples are practically uncontaminated with respect to Pb, Zn, Ni, Co, Cu, Mn and Fe (Table 5). The study area is uncontaminated to moderately contaminated with Cd and Cr (Table 5). The high contents of both Cd and Cr in soil samples may be due to anthropogenic activities such as agricultural activities, treated and untreated waste waters and irrigation return water in the study area. Moreover, the irrigation return water and industrial activities in nearby villages and the application of chemical fertilizers and pesticides for agricultural purposes could also serve as sources of pollution in the area (Salameh, 1996). Cd is known to be a relatively rare metal with no particular biological functions but it could be highly toxic to plants and animals. Cd could pose serious hazard to human health as a result of its chronic accumulation in kidneys (Alloway, 1990).

The I_{geo} results reveal that the vegetable samples in the study area are still practically uncontaminated with all the metals with all having I_{geo} of less than 1.

Table 4. Geoaccumulation Index Classes proposed by Muller (1981)

Classes	Ranges	Class	Indications/Soil quality
0	$I_{geo} < 0$	0	Practically Uncontaminated
1	$0 < I_{geo} < 1$	1	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	2	Moderately contaminated
3	$2 < I_{geo} < 3$	3	Moderately to heavy contaminated
4	$3 < I_{geo} < 4$	4	Heavily contaminated
5	$4 < I_{geo} < 5$	5	Heavily to extremely contaminated
6	$I_{geo} > 5$	6	Extremely contaminated

Table 5. Geoaccumulation index of Elements in the soil

Metal	I_{geo} (Soil)	I_{geo} (Vegetable)
Pb	-0.03	-3.20
Cd	0.62	-1.14
Zn	0.95	-1.57
Ni	-1.30	-3.76
Co	-0.74	-3.93
Cr	0.30	-2.21
Cu	-2.02	-2.89
Mn	-0.13	-3.13
Fe	-0.79	-3.76

Transfer Factor (TF)

TF is a parameter used to describe the transfer of metals from soil to vegetable. The TF of elements in the study area is shown in Table 6.

Table 6. Transfer factor of metals in the study area

Metal	TF
Pb	0.11
Cd	0.30
Zn	0.65
Ni	0.18
Co	0.11
Cr	0.18
Cu	0.55
Mn	0.12
Fe	0.13

The TF value for Zn, Cu and Cd are moderately high compared to other metals. The high TF could be due to agricultural activities in the area. Trend of TF for heavy metal in the area is of the order: $Zn > Cu > Cd > Cr \geq Ni > Fe > Mn > Pb \geq Co$. The mobility of metals from soil to vegetables is dependent on the physical and chemical properties of the soil and of vegetable species, and is altered by many environmental and human factors such as pH, sorbent nature, root exudates and nutrients (Violante *et al.*, 2010; Jolly *et al.*, 2013).

Correlation Analyses

The results of Pearson's correlation coefficients for the metals analyzed in soil and vegetable samples are given in Tables 7 and 8 respectively. The matrices show the linear relationships between each pair of variables. Some metals in the soil samples show significant positive correlation between them; Ni–Pb ($r = 0.58$), Fe–Ni ($r = 0.51$) and Fe–Cr ($r = 0.55$). Most variables show positive linear relationship in the vegetable samples except the pairs Mn–Ni and Cr–Ni which shows negative and no correlations respectively. The positive correlation between some pairs of variables may be an indication of common pollution source or that these metals show similar geochemical behaviour. Negative correlations between metals could mean that these metals have their origin from different sources or different removal techniques (Ghrefat *et al.*, 2011).

Conclusions

Soil and vegetable samples in the study area were assessed for pollution using geochemical approaches such as enrichment

Table 7. Matrix of Pearson's correlation coefficient of metals in soil samples

	Pb	Cd	Zn	Ni	Co	Cr	Cu	Mn	Fe
Pb	1								
Cd	0.055	1							
Zn	-0.467	-0.148	1						
Ni	0.583	-0.343	-0.037	1					
Co	0.230	0.714	-0.004	-0.020	1				
Cr	0.144	-0.711	0.198	0.216	-0.557	1			
Cu	-0.307	-0.054	0.184	-0.214	0.311	0.194	1		
Mn	0.379	0.652	-0.436	-0.108	0.528	-0.662	-0.357	1	
Fe	-0.105	-0.675	0.475	0.509	-0.382	0.547	0.194	-0.876	1

Table 8. Matrix of Pearson's correlation coefficient of metals in vegetable samples

	Pb	Cd	Zn	Ni	Co	Cr	Cu	Mn	Fe
Pb	1								
Cd	0.501	1							
Zn	0.954	0.417	1						
Ni	0.376	0.184	0.292	1					
Co	0.558	0.205	0.520	0.696	1				
Cr	0.731	0.666	0.718	0.000	0.222	1			
Cu	0.503	0.656	0.299	0.332	0.278	0.275	1		
Mn	0.778	0.743	0.763	-0.020	0.290	0.963	0.403	1	
Fe	0.315	0.634	0.193	0.384	0.279	0.331	0.768	0.371	1

factor, geoaccumulation index, transfer factor and correlation analysis. The EF results show that metals in the soil samples vary from no enrichment to minor enrichment with Cd having highest EF value and has minor enrichment. Cd is highly toxic to vegetables and animals and excessive Cd could pose threat to human health by causing chronic accumulation in kidneys. Soil samples in the area are not enriched in Ni and Cu. The vegetable samples are not enriched in Co; having minor enrichment of Pb, Ni, Cr, Cu and Mn and moderately severe enrichment of Cd and Zn. Using the values of I_{geo} , the vegetable samples are practically uncontaminated with all heavy metals.

However, in the soil samples, Cd and Cr are uncontaminated to moderately contaminated. The elevated values identified for Cd and Cr could probably be as a result of anthropogenic activities in the study area such as the effluent of wastewater treatment plants, treated and untreated wastewaters, and irrigation return water. The TF value for Zn, Cu and Cd are moderately high compared to other metals. The high TF could be as a result of agricultural activities in the area. Trend of TF for heavy metal in the area is of the order: $Zn > Cu > Cd > Cr \geq Ni > Fe > Mn > Pb \geq Co$. The results of the correlation matrix analysis show that metals in the study area

exhibit different degrees of correlation. Therefore care should be taken in consumption of vegetables in the study area due to high level of concentration of some metals in the area.

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