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GEOCHEMICAL MAPPING OF METAL CONTAMINATION AND DISTRIBUTION IN TOPSOIL, WESTERN OBAN MASSIF SOUTHEASTERN NIGERIA

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ABSTRACT: *This study is to examine heavy metal contamination of topsoil around the western flank of the Oban Massif and environs, southeastern Nigeria. Soil samples were collected in seven locations in farming and quarrying land use locations across the study area. Heavy metals (Al, Fe, Zn, Cu, Mn, V, Pb, As, Cr, Co, Ni, and Mo) were analyzed in soil samples using ICP-Ms. Computation of enrichment factor (EF) and Pollution index (PI) was performed on concentration values of potentially toxic heavy metals (Zn, Cu, Pb, As, Cr, Ni and Co), to determine the extent of pollution caused by human activities in topsoil of farming and quarrying areas. The concentration values of heavy metals in soils were also compared with world average background values of heavy metals. Results showed that the potentially toxic heavy metals enrichment factors and pollution index values were below values considered to be harmful to human health. The soil samples with respect to PI can be classified as deficient to minimal enrichment factor. With exception of Pb, Cr and Co which had PI values slightly above 1 and mean values exceeded 1, other potentially toxic heavy metals do not pose any health threat. The heavy metals: Pb Cr and Co are a health threat. Excess Pb and Co are carcinogenic to human system, while excess chromium causes diabetes and bronchitis. Sources of Pb, Cr and Co should be further investigated to institute appropriate remediation measures and also the bioavailability of these heavy metals be conducted in the human population inhabiting the study area.*

KEYWORDS: Enrichment Factor; Pollution index; potentially toxic; carcinogenic; bioavailability; remediation

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INTRODUCTION

The most common contaminants of heavy metals are Cd, Cr, Pb, Zn, and As. Heavy metals contamination to and other environmental media has been accentuated in modern society due to industrialization, rapidly expanding world population and intensified agriculture (He, et al., 2015).

Ambient background levels of major, minor and trace elements in natural soils are relatively little studied, particularly with respect to soil and arable land. The factors that govern element mobility in soils need to be defined to appreciate element migration across soils, in order to investigate the behavior of elemental anthropogenic inputs. Potentially toxic metals such as Zn, Mn, V, Cu, Pb, Ni, Mo, Co, Cr etc. constitute one of the most insidious and dangerous pollutants known to humans. When these elements are present in the environment they are not easily converted to harmless components. They are often accumulated in the tissues of organisms, which cannot excrete them. This leads to an amplification of their concentrations along the food chain and exposure of humans at the apex to the peril of metal poisoning (Akpan, et al., 2002).

In developed climes, geochemical maps of soils are prepared to delineate land for cultivation, grazing, building and road construction. This is because, geochemical elements are the deciding factor for cultivation of crops, types of grasses suitable for grazing and elements concentration in soils for building and construction.

The incidence of Pb, As, Ni poisoning in soils is due to cultivation in soils that little or no knowledge of the geochemical constituents is at the disposal of the land user. The elements concerned with micronutrients such as Mn, Fe, Zn, Cu, Mo, Na, K etc. are essential for the growth of plants and animals. Potentially toxic elements such as Pb, As, Cr, Co, Ni (Tye, 1995), were also considered in this study. Trace elements concentration in soils vary with depth, soil type and size fraction. Trace elements concentrations are in the top gravel of 30 inches of soil profile and their abundance decrease with depth (Levinson, 1974). Essential nutrients metals and other metals in food crops are translocate through soil into the food web. Natural contents of potentially toxic elements in soils are generally low, unless, soil develop from rocks with high content of one or more elements from ore bearing rocks or enhanced by human activities (Siegel, 2002).

Similar works on heavy metal geochemical mapping in the study area are non-existent. The nearest work to the area is the work conducted by Ekwere, et al., (2014), on heavy metal distribution on urban soils in the Calabar area. However, heavy metal analysis in soil in other parts of the world were undertaken by Sahah, et al., (2013), in heavy metal concentrations in urban soils in Fullajah City, Iraq. Chen, et al., (2005), assessed heavy metals concentrations in surface soils in Urban Parks in Beijing China. In Nigeria, similar works were conducted by Onyeobi and Imeokparia, (2014), in Abakaliki District. Also, Chiroma, et al., (2014), worked on heavy metals assessment in soils and vegetables in Yola and Kano.

This study was conducted around the western flank of the Oban Massif and environs. Currently, there is no geochemical soil map showing the distribution of micronutrients and potentially toxic metals in the study area. Cultivation and livestock grazing activities are carried out in the area without a soil guide map. The ultimate aim of this study is to evaluate the geochemistry of top soils of the western flank of Oban Massif and environs. The specific objective is to produce the geochemical maps showing the spatial distribution of potentially toxic metals and micronutrients in the study area, which serve as guide for cultivation and grazing purposes.

Study area description

The study area is situated between latitude 05^0 10’ 45”N to 05^0 41’ 5.7’’N and longitude 08^0 13’ 46”E to 08^0 3’ 34’’E. The southern part is bounded by Calabar River and the northern part by Adim in Biase. The eastern and western parts are bounded by Great Kwa River and Itu Road/Calabar Municipality respectively (Fig 1). From field measurements using GPS, the highest elevation of about 142m above sea level is at Gnarc Quary site at Mbarakom and the lowest elevation of 27m is at is at Calabar River Bridge at Odukpani.

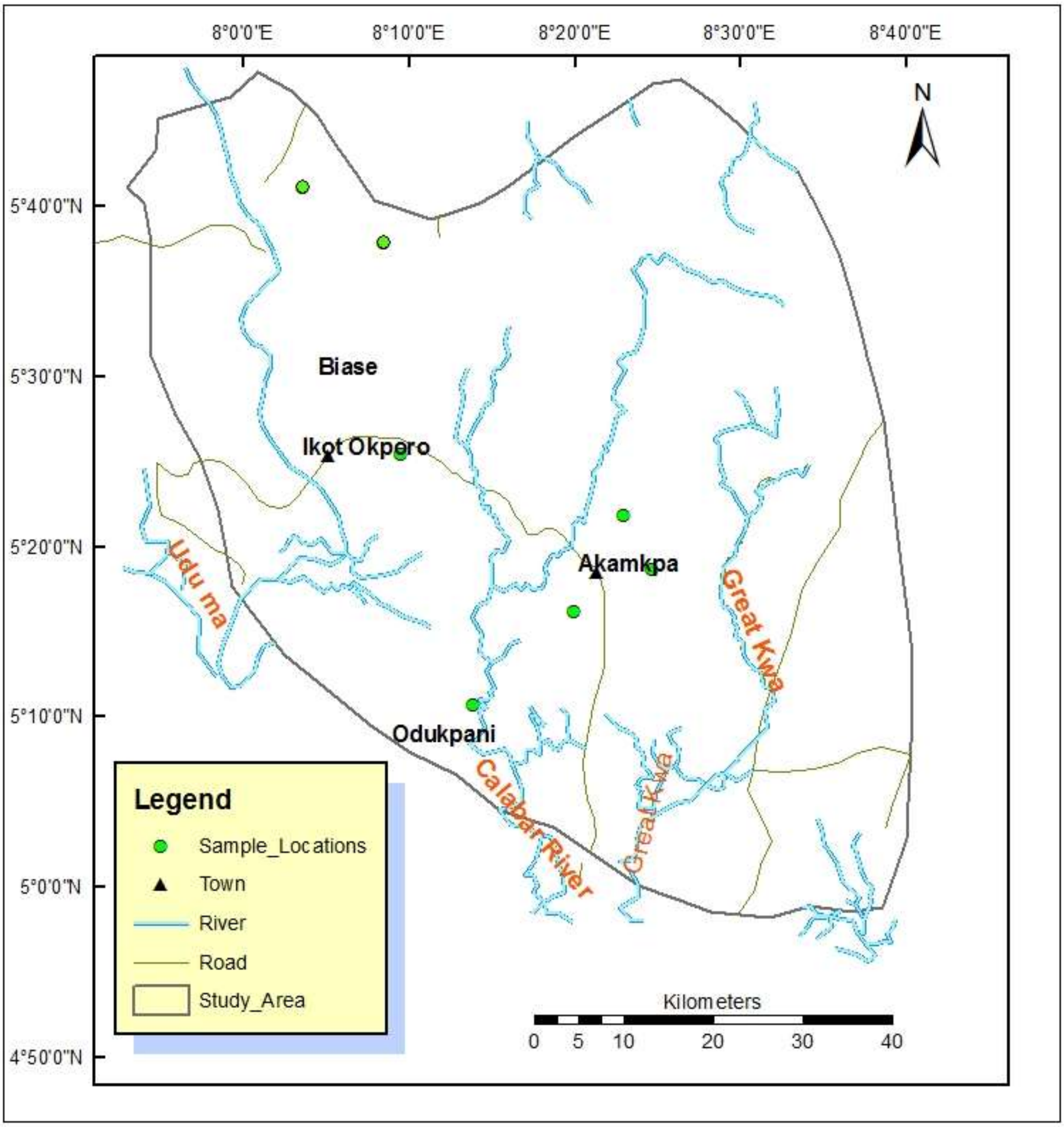

Fig. 1 Sample location map showing study area

The study area is characterized by a hot and humid climatic condition. The mean annual temperature is about 30.1^0 C at Calabar. The area is characterized by wet and dry seasons of equatorial climate with rainfall amount of more than 1000mm reaching about 3000mm around

Calabar (Edet, et al., 1996). The rainy season starts from April and end November, while the dry season starts from December and end by March. The Massif Oban Massif is within a wet climate with an annual rainfall of about 2000mm (Edet and Okereke 1997).

The vegetation in the study area is variable. In Odukpani and Akamkpa and Biase areas, the vegetation is dense with tall trees that form canopies. This can be described as tropical forest. The major rivers which drain the area are Cross River, Great Kwa River, Okom Ita River, Akpa and Yafe Rivers (Fig. 1) which are perennial streams flowing southwards and empties into the Gulf of Guinea (Edet and Okereke, 1998). The drainage pattern ranges from trellis to rectangular in the study area.

Geology

Rocks within Odukpani area in the Calabar Flank are mainly loose, friable deposits of shales, clays, gravels and loose deposits of tertiary age sands (Fig.2). These sedimentary deposits consist of mainly: conglomerates, sandstones, shale, siltstone, moisture and loose sands which are Cretaceous to Tertiary in age (Edet, et al., 1996). The Oban Massif is underlain by the Precambrian basement complex which consist of magmatic and sheared gneissic rocks, paraschist, phyllites, metaconglomerates, quartzites, amphibolites and metadolerite, foliated pegmatites, aplites and pyroxenite. The synkinematic to late kinemtic older granite intrusive series comprising rocks of varying composition from metadiocrites, granodiorites, adamelite to granulitic rocks which are weakly foliated to unfoliated pegmatite, aplite and quartz veins were all described by Edet, et al., (1994), and Ekwueme, (1993). The unmetamorphosed dolerite to microdiocritic intrusion were identified by Rahman, (1981), Ekwueme, (1993), Edet, et al., (1994). The authors identified charnockites which are metamorphic rocks in Oban Massif and attributed this to granulite facies metamorphism.

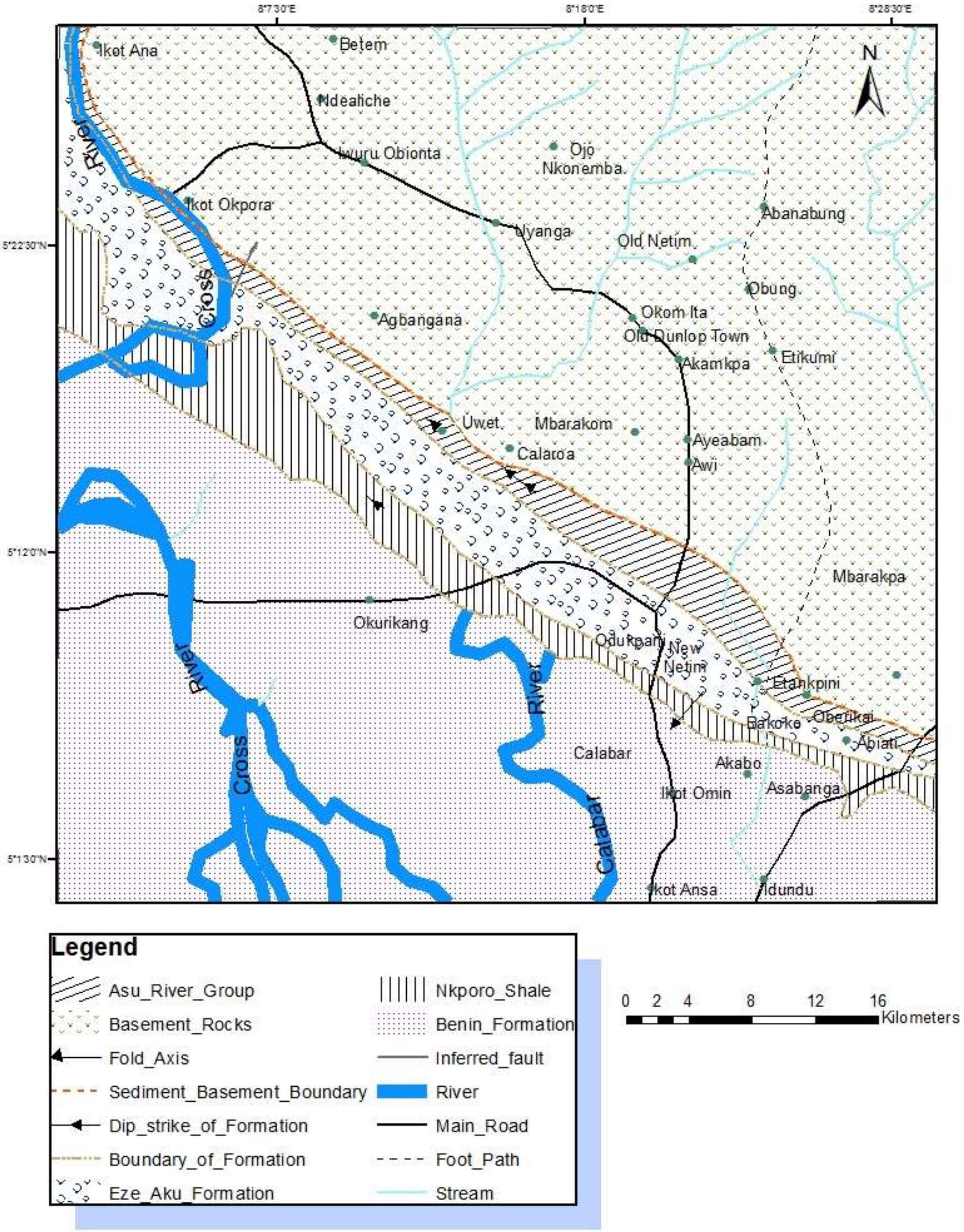

Fig.2 Geological map of the study area

MATERIALS AND METHODS

Sample Collection and preparation

Soil samples were collected across the study area (Fig.1). Samples were collected using a hand driven auger from a depth of about 0-15cm and packaged in cleaned polyethylene bags. The samples were taken to the laboratory and sundried for about five days. The dried samples were later disaggregated in the laboratory using an agate mortar and pestle and further sieved using -80 mesh nylon sieve.

Sample Analysis

A weight of 0.5g of the sieved samples were put in properly labelled envelopes. The samples were moistened with few drops of deionized water and 10ml of concentrated $4HNO_3$ added into each beaker. The beakers were then covered with glass discs and placed on a sand bath cover, in a hot plate into a fume cupboard. The mixture was refluxed at moderate temperature ($<100^0$C) for one hour and then evaporated at temperature ranging between 180^0-190^0C into dryness forming a white cake. The white cake residue was leached with 5ml of 6M HCl into already calibrated labeled test tubes and made up with deionized water. The test tubes were then allowed to stand for a clear aliquot to separate out. The test tubes were then sealed with plastic stoppers. The digested samples were then analyzed for major and trace elements using ICP-Ms at the ACME analytical Laboratories LTD at the University of Ibadan Nigeria.

Assessment of soil contamination

Pollution index (PI) of heavy metals in soils

Heavy metal contamination in the surface environment is associated with more than one metal. In most cases pollution index of soils is used to identify multi element contamination resulting in increased overall metal toxicity (Jung, 2001). Generally, PI can be computed by averaging the ratios of metal concentration in sampled soils to the assumed permissible level of metals. In this study, the tolerable limits for soils suggested by WHO were adopted for assumed permissible levels and PI was calculated by the equation PI= (As/20+Cu/100+pb/100+Zn/300)/4

Enrichment Factor (EF)

This factor reflects the status and degree of soil environmental contamination (Salah, et al., 2013). The EF calculation compared each value with a given background level, either from the level site, using older soils formed under similar conditions, but without anthropogenic input or from a regional or global average composition (Choi, et al., 2012). The equation for EF calculation proposed by Sinex and Helz, (1981) is given by EF= $(C_x/C_{Fe})/\ (C_x/C_{Fe})$. Where (C_x/C_{Fe}) sample is the metal to Fe ratio in the sample of interest, (C_x/C_{Fe}) reference soil is the natural background value of metal to Fe ratio. In this study, world average values were used for background values. Fe is selected as reference element because Fe has a relatively high concentration in tropical soils. The redox sensitive Fe-hydroxide and oxides constitute significant sinks for heavy metals and is one of the widely use reference elements Sinex and Helz, (1981).

RESULTS AND DISCUSSION

Concentrations of major and heavy metals in soil

Table 1 Statistical summary of major and heavy metals mg/g

Parameter	N	Mean	STD	Maximum	Minimum	Median	Background (mg/g
Ca	7	1914.29	3554	9900	200	400	NA
Mg	7	3085.7	24465	7300	300	2300	NA
P	7	572.85	214.53	850	310	570	NA
K	7	22371.14	8616.59	337.10	10309	23900	NA
Na	7	3177.14	4733.23	13480	300	109	NA
Al	7	93700	34898.85	144100	35300	99700	NA
Fe	7	36357	16550.11	54800	12400	31800	50000
Zn	7	60.57	29.88	96	12	56	300
Cu	7	17.98	11.62	44.1	11.8	14.4	100
Mn	7	155.71	128.58	419	48	130	2000
V	7	106.71	70.46	228	20	84	130
Pb	7	48.7	30.55	116.9	30.1	39.2	100
As	7	3.28	2.81	8	1	2	20
Cr	7	75.57	71.19	227	17	53	100
Co	7	7.91	3.65	13.3	2.2	9	50
Ni	7	16.4	12.48	43.2	4.1	12.6	50
Mo	7	1.37	0.91	3.1	0.4	1.4	NA

NA=Not Available

Statistical summary of the results of major and heavy metals are presented in Table 1. Major and heavy metals concentrations are in ppm dry weight. The mean, standard deviation, maximum, minimum and median values are of 95% confidence limit. The major elements (Ca, Mg, P, Al, Na and K), were analyzed in soil samples. The heavy metal geochemical constituents concerned with micronutrients (Mn, Fe, Zn, Cu, Mo, V, Na, Ca, Mg, P and K) essential for the growth of plants and animals and potentially toxic elements (Pb, As, Cr, Co, Ni and V), were also analyzed in soil samples.

For heavy metal geochemical constituents concerned with micronutrients, results showed that the mean and standard deviation of Mn 155.71±128.58 and ranged from 419-48ppm with a median value of 130ppm. The highest value of 419ppm was recorded at location 3 (Nsan village) which is used for cultivation, and in the basement area. Concentrations of Fe ranged from 1.24-5.48ppm with a mean and standard deviation of 3.63±1.65, and possess a median value of 3.18ppm. The relatively high Mn and low Fe values could be as a result of the presence of high marcasite and low pyrite (Onyeobi and Imeokpara, 2014) in the area.

Zinc and copper recorded mean and standard deviation values of 60.57±29.89 and 17.98±11.62 respectively. Zinc ranged from 96-12ppm with a median of 56ppm, and Cu ranged from 44.1-11.8ppm with a median of 14.4ppm. Zinc mobility in soils is moderately high limited by the tendency to absorb by Fe-Mn oxide and insoluble organic matter (Onyeobi and Imeokpara, 2014). Copper can be added to soil by deterioration of vehicles on the roads (Tong-Bin Chen et al., (2005).

Molybdenum (Mo) and Vanadium (V) had mean and standard deviations of 1.37±0.91 and 106.71±70.46. Mo values ranged from 228-20ppm. The highest value of Molybdenum was recorded at location 6 (barite mine site) at Ibogo in Biase, which is a basement terrain. Molybdenum recorded a median value of 1.4ppm and V had a median value of 84ppm. Molybdenum appears as isomorphic substitution to Fe in oxides, while Vanadium occurs as isomorphic substitution for Fe in pyroxenes and amphiboles and for Al in micas, substitution for Fe in oxides (Chesworth, 2008).

Major elements concerned with micronutrients essential for plants growth (Na, K, Mg, Ca, and P (Chesworth, 2008) are presented in 1. Sodium, potassium and magnesium achieved mean and standard deviation values of 0.3177±0.4733, 2.237±0.8617 and 0.9514±0.8000 respectively. Sodium obtained concentration range of 1.348-0.03ppm, potassium ranged from 3.37-0.03. Also, Magnesium had a range of 5.0-0.03ppm. Potassium and sodium are caused by dissolution of feldspars in soil. Potassium has low geochemical mobility and is a biophilous element (Siegel, 1974).Magnesium is derived from Magnesium carbonate.

Calcium ranged from 0.99-0.02 with a mean and standard deviation of 0.1914±0.3554 and a median value of 0.04. Phosphorous had a mean and standard deviation of 0.0572±0.0214 and a median of 0.057 and ranged from 0.085-0.031. Aluminum recorded a mean and standard deviation of 9.37±3.4899, with a range from 14.41-3.53ppm and a median value of 9.97ppm. Calcium is a biophilous element, the low value can be explained by low dissolution of feldsparthic minerals in the soil. Phosphate is a natural constituent of soil, in most cases caused by the application of fertilizers.

Potentially toxic heavy metals (Pb, As, Cr, Co and Ni) recorded the following concentrations: The mean and standard deviation of Pb was 48.7±30.50 and ranged from 30.1-116.9ppm with a median of 39.2ppm. Pb is toxic under high concentration. The concentration of potentially toxic elements in uncontaminated soils is related to parent material, soil forming processes, degree of mineral alteration and soil clay content (Zubillga and Lavado, 2008). The mean concentration of Pb (48.7ppm) is lesser than the value of 100µg/g recommended in soils by WHO (Table 2).Arsenic ranged from 1-8ppm, with a mean and standard deviation of 3.2857±2.8115 with a median of 2ppm. Many metals are essential as important constituents of pigments. The mean and standard deviation of Cr is 75.57±71.19, with a range from 17-225ppm and a median of 9ppm. Nickel recorded a mean and standard deviation of 16.4±12.47 and ranged from 4.1-43.2 and a median of 12.6ppm.

The mean concentrations of Fe, Zn, Mn, Cu, Pb, Cr, Co, Ni and As are below the permissible limits for uncontaminated soils recommended by WHO (Table 1). Generally speaking, sources of heavy metals in the soil mainly include natural occurrence derived from parent materials and human activities (Cui, et al., 2004).

Manganese, V, Cr and Zn recorded higher mean concentrations than other heavy metals. Lead (Pb), Ni, Cu, Al and Co had moderate mean values while Fe, As and Mo recorded the lowest mean concentrations in this study (Table 1). Lead (Pb) causes mental lapse, Cr and As affects kidney, liver and nervous system respectively (Donahue and Auburn, 2000).

In general, Zn has higher mobility while Cu and Pb has lower mobility and solubility (Jung, 2001). That explains why Zn has higher mean concentration than Pb and Cu in this study. The high mean concentration of Mn, V, Cr and Zn may be associated with their high solubility and mobility in soil. Moderate and low concentration of Pb, Cu, Cr, Al, Fe, As and Mo in this study are in agreement with the views of Jung, (2001), that these metals are relatively less mobile and soluble in soils.

The average abundance of heavy metals contents in soils is Mn>V>Cr>Zn>Pb>Cu>Ni>Al>Co>Fe?As>Mo. These findings are almost in concord with the views of Kabata-Pendeas and Murkharjee, (2007), that the mean abundance order of elements in unpolluted Cambisols loamy soils with more than 20% clay fractions is Zn>Pb>Ni>Cu. The relatively low concentrations of Al, Co, Fe, As and Mo in the soil may suggest very low mobility for these elements during weathering and soil formation.

The levels of manganese in soil was relatively low. Soil generally contains 200-300mg/kg of manganese with average value of 600mg/kg (Olukanni and Adeoye 2012). The mean value of Mn (155.71mg/kg) and the highest value of 419mg/kg obtained in this study is lower than the average posited by these authors. The concentration of manganese in this study is lower than those conducted in other parts of Nigeria and other parts of the world. Manganese values of 2532mg/kg recorded in USA, 1740mg/kg in China, 608.11mg/kg in Yami, 132mg/kg in Kaduna, and 1122mg/kg in Poland (Olukanni and Adeoye 2012: Yahaya, et al., 2009). Manganese and Nickel has to do with related sources such as corrosion of metallic parts, concrete materials, re entrained dust from roads and tear and wear of tyres and engine parts.

Soil contamination

Pollution index (PI)

The mean values of pollution index of potentially toxic metals (Zn, Cu, Pb, As, Cr, Ni and Co) in this study ranged from 0.138-0.600. The mean values were less than 1 in all the locations (Table 2). All the PI values were below 2, this can be classified as low contamination (Mohammed, et al., (2014).

Table 2 PI of Zn, Cu, Pb, As, Cr, Cr, Ni and Co in the study area

Location	PI
1	0.232
2	0.216
3	0.249
4	0.303
5	0.453
6	0.600
7	0.138

Enrichment Factor (EF)

Table 3 EF of potentially toxic elements in the study area

Location	Zn	Cu	Pb	As	Cr	Ni	Co	Mn
1	0.354	0.393	0.860	0.200	0.757	0.234	0.950	0.088
2	0.472	0.383	1.303	0.040	0.500	0.276	0.550	0.129
3	0.809	0.533	1.120	0.040	0.570	0.252	1.212	0.419
4	0.872	0.480	1.177	0.100	0.870	0.350	1.150	0.152
5	0.727	0.496	1.040	0.300	1.371	0.864	1.662	0.202

6	0.509	1.470	3.340	0.400	3.243	0.238	0.275	0.052
7	0.109	0.430	0.900	0.050	0.243	0.082	1.125	0.047
Mean	0.550	0.600	1.391	0.164	1.076	0.321	0.989	0.156

The enrichment factor for Zn ranged from 0.109-0.872 with a mean value of 0.550. Cu enrichment factor ranged from 0.393-1.47 with a mean of 0.600. The EF value of Pb ranged from 0.860-1.303 with a mean value of 1.391ppm. The range of EF for As was from 0.04 to 0.40 with a mean of 0.164. The EF of Cr ranged from 0.243-1.371, with a mean value of 1.076. Also, the EF of Ni ranged from 0.082 to 0.864ppm with a mean of 0.321ppm. Cobalt had an EF range from 0.550-1.662 with a mean of 0.989. The mean EF value of manganese was 0.156 and EF values ranged from 0.047-0.419ppm.

The enrichment factor (EF) was used to assess the extent of pollution and the potential human activities effect on top soils in agricultural and mining soils in the western flank of the Oban Massif. Fundamentally, as increase in EF values is a function of contribution from anthropogenic sources. When EF is higher than 1, this is evidence that the abundance of the heavy metals in soil may not originate from local soil background, but other natural and anthropogenic sources such as vehicle emissions or industrial discharge (Salah, et al., 2013: Sutherland, 2000). Soil contamination classification as elucidated in Sutherland, (2000) is applied in this study. In this study, no enrichment of heavy metals was higher than 1. This result, shows that agricultural and quarry site soils are not highly enriched with heavy metals under investigation.

Spatial distribution of heavy metals

Estimated maps of Zn, Cu, Pb, As, Cr, Co Ni, are presented in Fig. 3, 4, 5, 6, 7, 8 and 9. Zn displayed spatial distribution as shown in fig. 3. The highest concentration of Zn is found in the NW part of the study, while the lowest is in the SE part (Fig. 3). Copper exhibited the highest spatial distribution in the eastern part of the study and the lowest was located in the western part of the study (Fig.4). Manganese spatial distribution showed highest distribution in the NE and the lowest in the SE and western part of the study area (Fig.5). The spatial distribution of Pb was highest in SE and least distribution in the SW of the study (Fig.6). Arsenic (As) distribution was highest in the SE, while the lowest was at the NW and extreme SE part of the study area (Fig. 7). The highest spatial distribution of Chromium (Cr) was at the SE part of the study, while the lowest was at the NW part of the study (Fig. 8). Cobalt (Co) distribution was highest at the south central area, and the lowest distribution was at the SE part of the study (Fig.9). Figure 10 showed that the spatial distribution of Ni was highest at the south central part of the study while the lowest distribution was at the SE and NW parts of the study area.

There was no significant correlation in the distribution of the heavy metals in the study area. This shows that there was no anthropogenic factor controlling their distribution rather than geogenic sources.

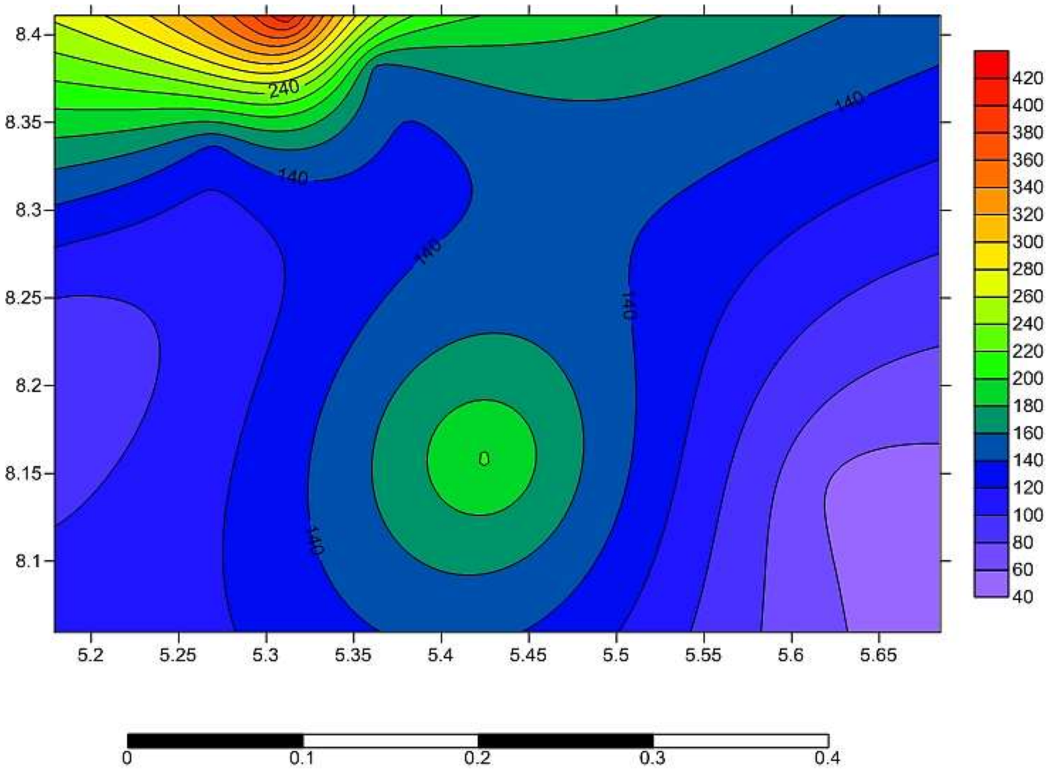

FIG. 3 Saptial distribution of Zinc in the study area

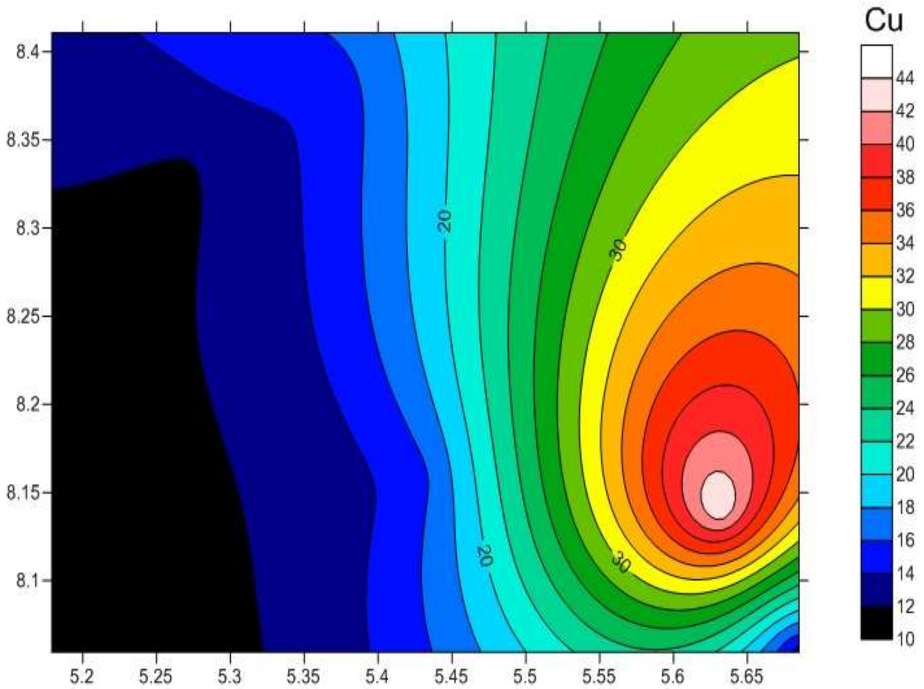

FIG. 4 Spatial distribution of Copper in the study area

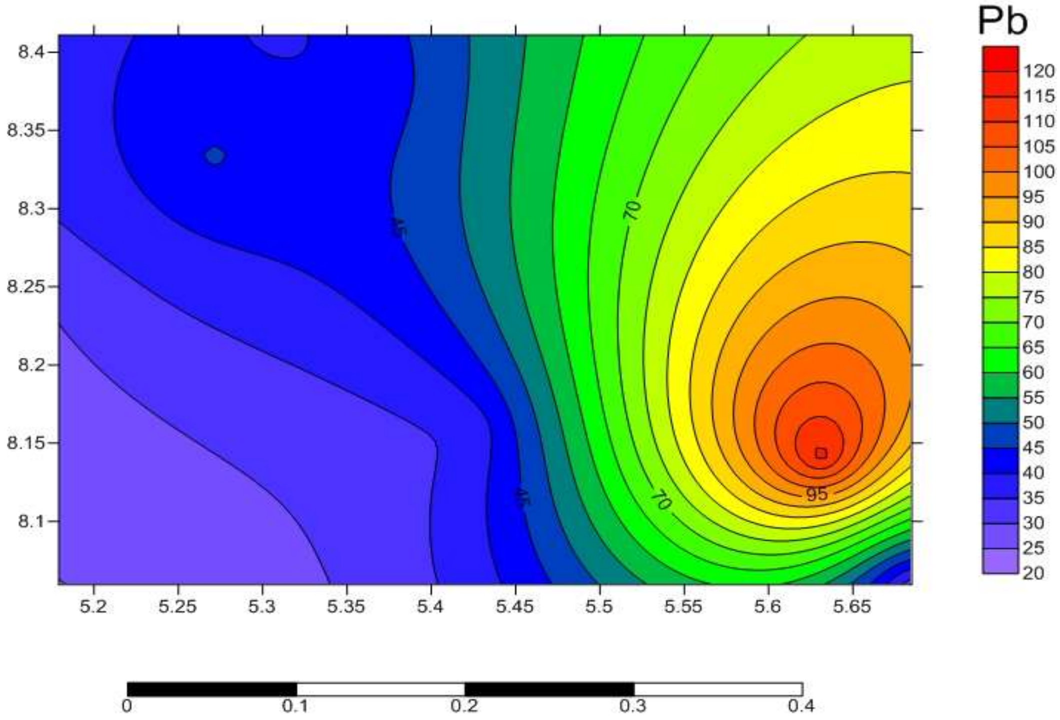

FIG. 5 Spatial distribution of Pb in the study area

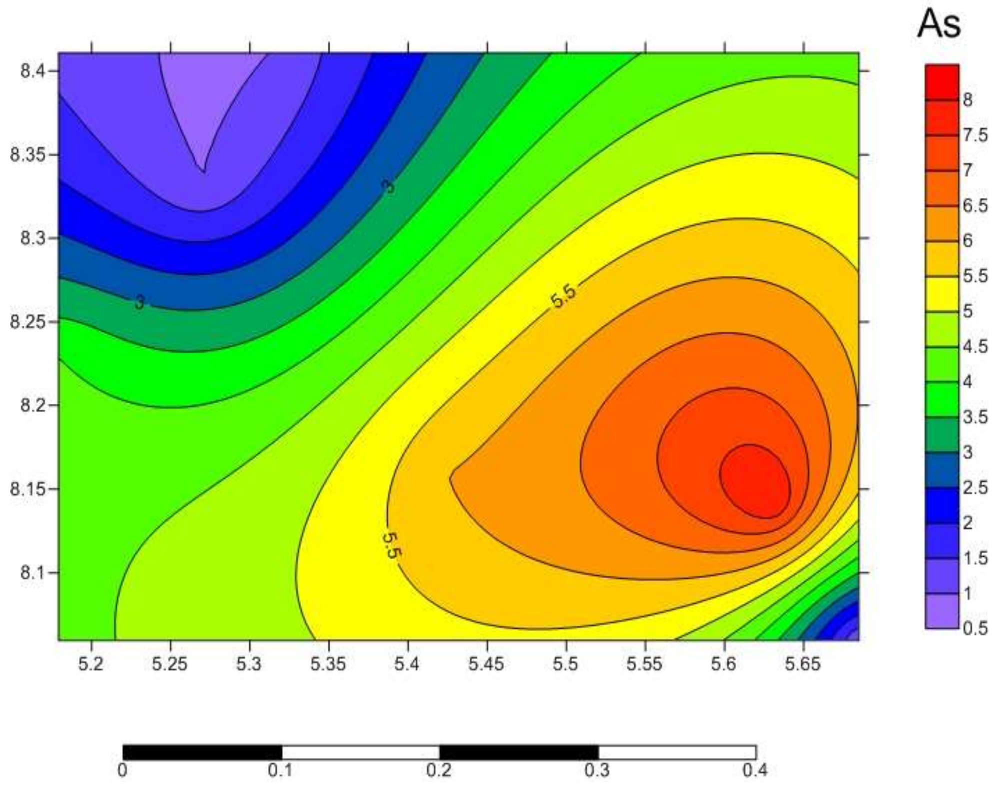

FIG.6 Spatial distribution of Arsenic in the study area

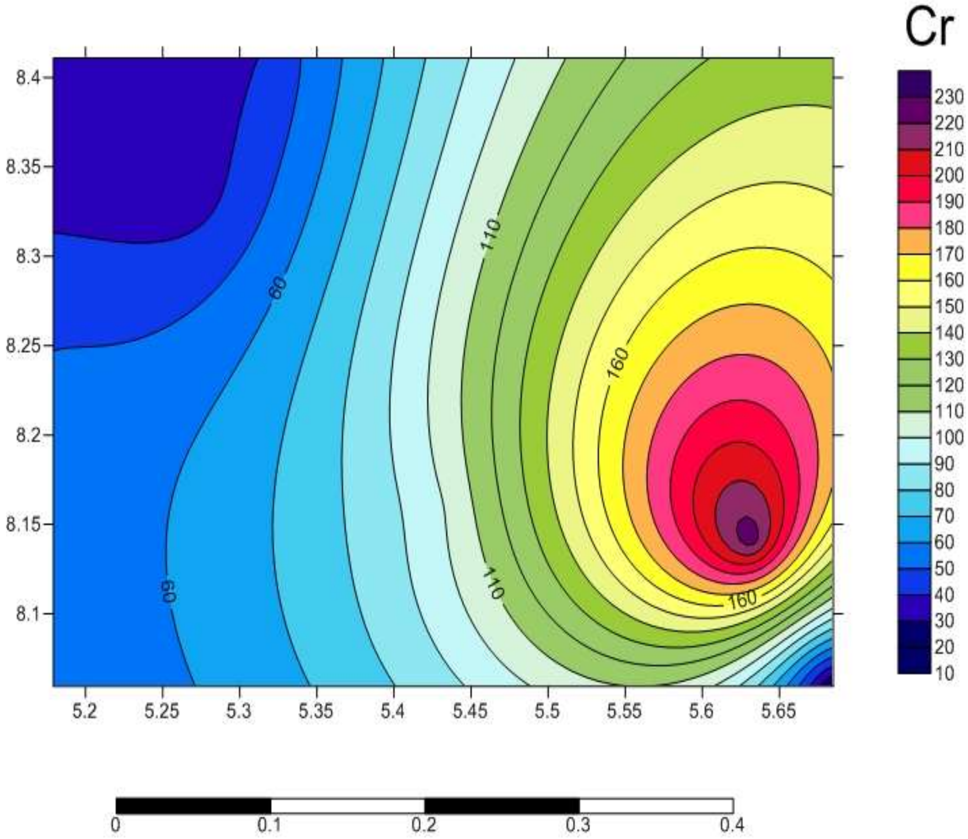

FIG. 7 Spatial distribution of Cromium in the study area

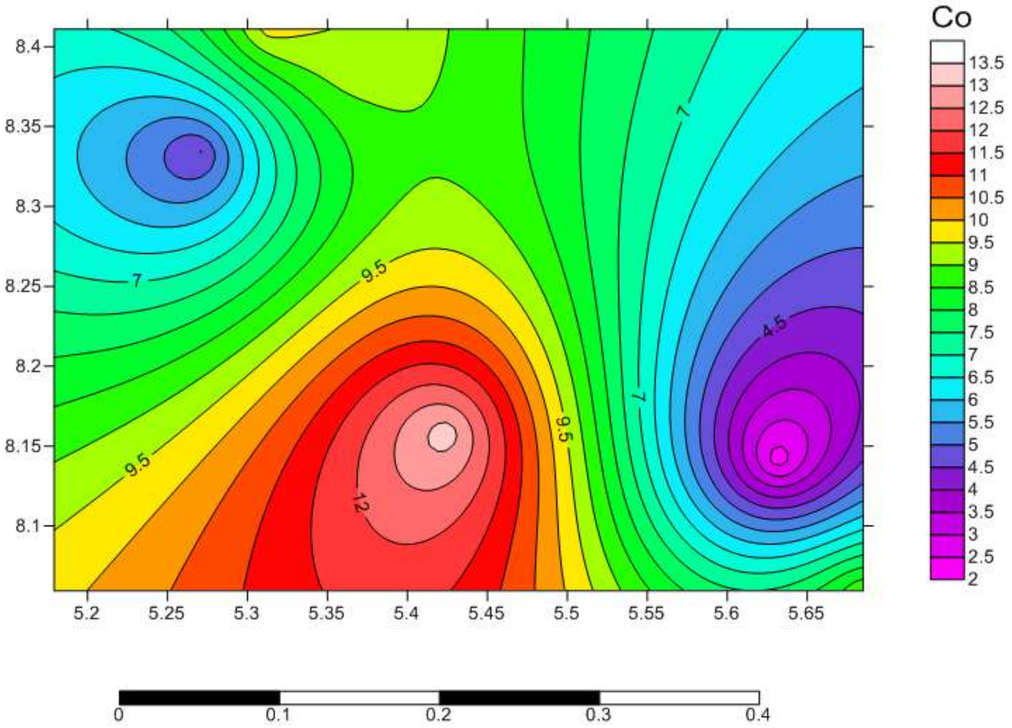

FIG. 8 Spatial distribution of Cobalt in the study area

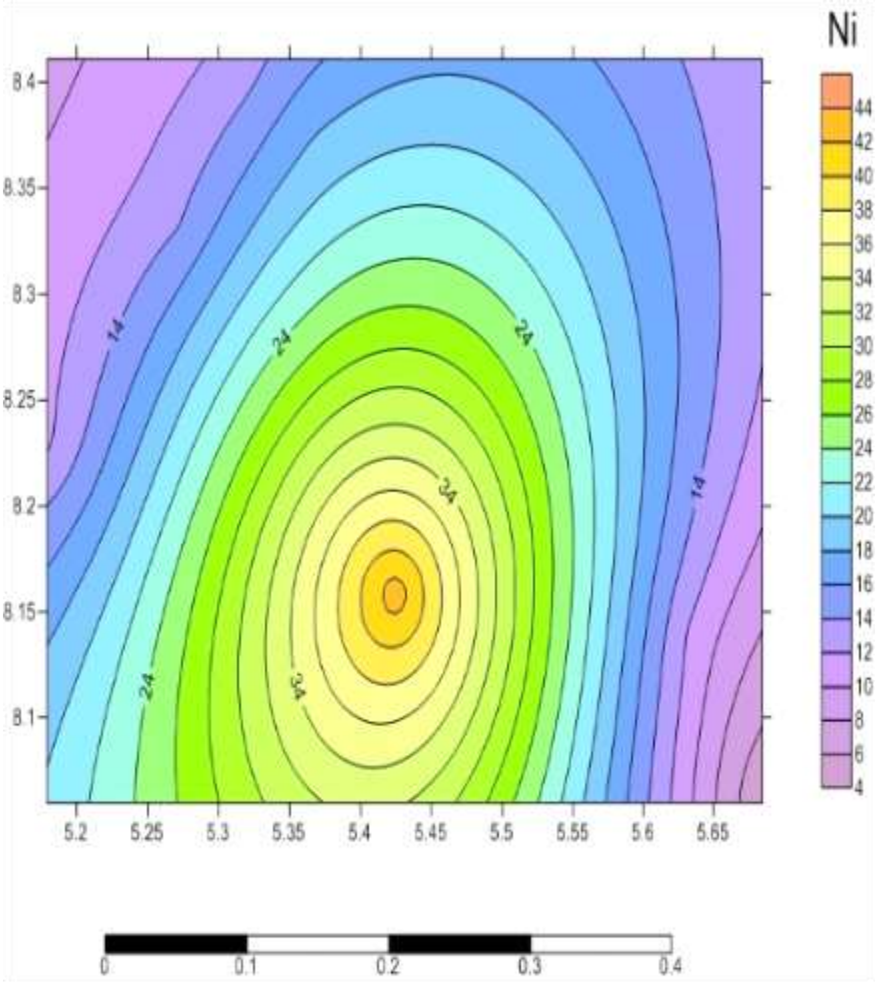

FIG. 9 Spatial distribution of Nickel in the study area

Implication to research and practice

This research will serve as a basis for monitoring soil contamination in the study area. Researchers can improved on this study by deploying more research methodology to validate the findings established in this study. Farmers carrying out cultivation in the area will be guided by this research, with adequate knowledge gained from heavy metals spatial distribution in the area. Grazers can be guided by this study as a safe graze land for cattle rearing and other livestock.

CONCLUSION

Following the computation of enrichment factor (EF), pollution index (PI) and comparison of heavy metals with average world standards, there is no heavy metal pollution in the study area. Preparation of geochemical maps of this study also concludes that there is no significant correlation among the heavy metal distribution, this rules out the probability of anthropogenic factor controlling the concentration of heavy metals in the study area. All the values obtained from EF and PI are below the range of heavy metal contamination. It therefore suffice to posit that the soil does not pose any danger for planting crops for human consumption and also for grazing of cattle or ranching, due to acceptable levels of essential micronutrients elements in the area.

With exception of Pb, Cr and Co that exhibited enrichment factors up to 1 or more in some locations, other heavy metals exhibited EF below range of heavy metal pollution. The PI values of potentially toxic heavy metals (Zn, Cu, Pb, AS, Cr, Ni and Co) were all below 2. The soil can therefore be classified as deficient to minimal enrichment factors. The slightly elevate values of Pb, Cr, and Co may be from rocks, automobile exhaust and paints from buildings and dilapidated automobiles.

The average abundance of heavy metals in the soil is in the order: Mn>V>Cr>Zn>Pb>Cu>Ni>Al>Co>Fe>As>Mo. Using pollution index it can be concluded that Pb, Cr and Co are more enriched in the top soils of western Oban Massif, which can be attributed to anthropogenic influence.

All the heavy metals mean values were less than their background values (world average values). Comparison with permissible levels of guidelines set by FAO and WHO (2007) in Europe shows that the mean values are below their regulatory standard values. The mean values of heavy metals did not exceed USEPA guideline for soils. Therefore, the soil in this study is not polluted with respect to the heavy metals analysed in the western Oban Massif with exception of Cr, As and Co which were found to have slightly elevated EF values.

RECOMMENDATIONS

Future research on metals contamination in the study area should adopt modeling and speciation studies of potentially toxic heavy metals and the study of bioavailability of heavy metals on the human population inhabiting the area. Geochemical media such as water and edible plants should also be sampled to assess the media that bio accumulate heavy metals with posing a higher source of danger to environmental contamination.

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