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TRACE ELEMENT GEOCHEMISTRY OF A REUSED ILLICIT MINE AREA FOR AN AGRICULTURAL PURPOSE IN NADOWLI DISTRICT OF NW GHANA

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ABSTRACT

Trace elements in soils depending on the pathways, mode of exposure and concentrations can be essential or non-essential to human-life developments. However there are some that are potentially toxic. Mobilization of the trace elements can be influenced by environmental conditions. Whilst others cause depletion others contributes to metal-ion enrichments that generally depends on surface processes and the prevailing human activities in the area. The 18 trace elements analysed from the 154 soil samples collected and studied; 2 chalcophile elements As and Cd listed among the potentially toxic elements (PTEs) were identified to be extremely and moderated polluted. Enrichment factors (EF) of 42.3 and 1.45 were computed for these 2 PTEs. On the contrary the essential elements Cu, Ni and Zn required for human metabolism rather showed depletions of 10.5, 24.0 and 21.0 respectively. Copper, Ni and Zn had computed geoaccumulation indeces (Igeo) of 0.17, 0.14 and 0.14 representing no-pollution. The quantities of these essential trace elements may not be enough for human and animal metabolisms and the non-essential PTEs may be detrimental to human health. Average concentrations of trace elements, essential and non-essential elements alike have not been published for the District. Besides the relationships between trace elements and health had not been thoroughly investigated so there is the need for geoscientists to intensify research on trace elements in the environment and together with professionals in public health so as to identify health issues arising from trace elements in the environment..

Keywords: Trace elements; Health; Essential elements; Potentially toxic elements; Nadowli; Ghana.

INTRODUCTION

Trace elements exposure and ingestion may or may not help in human development because beyond certain dose limit exposure response may be helpful or detrimental to human health. Irrespective of the part per million concentrations of these elements in soils and water depending on their availability; mode and degree of exposure; the trace elements can bio- accumulate and that can impact on health. Over 94, 388 people in Nadowli District (www.ghanadistricts.com) get their food and water from the lands in the District. Thus reflecting on the statement that was accredicted to Paracelsus that "all things are poison and nothing is without poison; only the dose makes a thing not a poison." Meaning that a substance can produce the harmful effect associated with its toxic properties only if it reaches a susceptible biological system within the body in a high enough concentration. But if there are no attempts to control of removing the bioavailability and the possible bioaccumulation can increase the toxicity over time and may be detrimental even at low concentrations. Hence trace elements concentrations in a previously mine area being reuse for agricultural purposes needs scientific investigations. Trace elements released from respective underlying rocks have different minerals in the reduced environments and are transformd into varying trace, minor and major elements in the oxidized environments. Similarly elements introduced to surface environments via pesticides, insecticides and fertilizer uses will also vary. Relationships between trace elements and human health particularly in northern Ghana is generally unknown. Concentration levels of trace elements in surface soils in the environment where drinking water and food are obtained in the communities have not been investigated and hence unknown. This is alarming because the dose makes the poison and will pose potential health risks to man.

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Trace elements are present at low concentrations (mg/kg) in most soils, plants, and living organisms (He et al., 2005; Basta et al., 2005). Some trace elements (such as Cu, Zn, Fe, Mn, Mo, and B) are essential to the normal growth of plants. Others like Cu, Zn, Fe, Mn, Mo, Co and Se are essential to human and animal growth. However, some of these trace elements (e.g., As, Cu, Zn, Pb, Hg and Cd) are of environmental concern because their prevalence have tendency to cause contamination in soil, water, and food chains (Webber, 1981; Henry et al*.,* 2004). He et al*.* (2005) reported that, accumulation of trace elements, especially heavy metals, in soils have the potential to restrict the soil's function, cause toxicity to plants, contaminate the food chain and impact on human health. Trace elements comprise potentially toxic and essential elements (Arhin et al. 2015; Selinus et al. 2005). Their distributions and concentrations in the surface environment are from surface processes such as weathering and erosion coupled with chemical activities and environmental processes (Martinez et al., 2003). Alloway (1995) assertions that the mode of occurrence, speciation, distribution and concentrations of trace elements can increase all trace elements toxicity in any surface environment. As noted by Selinus et al. (2004) trace elements can be toxic or play an essential role in man and animals. So knowing the relative distributions, pathways and concentrations of trace elements accumulations introduced into the surface environments naturally and anthropogenically can guide in controlling the environmental health concerns relating to human health. To adequately understand these relationships, there is need for geoscientists to intensify research on trace elements in the environment and together with professionals in public health so as to identify health issues arising from trace elements in the environment. The general rural life in developing nations depends on local farm products for their livelihood and Ghana is no exception. The paper therefore seeks to assess the trace elements variations in soils of Nadowli District with the intention to identify trace elements whose concentrations may trigger possible health risks to life.

LOCATION, AND GEOLOGY, CLIMATE AND REGOLITH OF THE STUDY AREA

LOCATION AND GEOLOGY

The portion of the Lawra Birimian Belt studied (Fig. 1) is in northern Ghana (Kesse, 1985), 700 km northwest of Accra, the national capital. The rocks here comprise metavolcanic rocks intruded by mafic granitoids and dolerites intruded by gabbro (Kesse, 1985; Leube et al. 1990). In close contact with the metavolcanic rocks are metasedimentary units that consist of phyllite, sericite-schist and meta-greywacke that are locally intruded by felsic granitoids and mafic dykes (Griffis et al. 2002; Baratoux et al. 2011).

The mafic granitoids comprise hornblende-rich varieties and are classified as 'Dixcove' or 'belt' type granitoids whilst the felsic granitoids contain mica–rich varieties and are known as 'basin' type (Leube et al. 1992). The belt granitoids are small discordant to semi-discordant, late or post-tectonic soda-rich hornblende-biotite granites or granodiorites that grade into quartz diorite and hornblende diorite (Hirde et al., 1996). On the contrary the basin granitoids are large concordant and syntectonic batholithic granitoids commonly banded and exhibit black and white foliations. They are potash-rich and contain both biotite and muscovite, with the biotite dominating (Leube et al., 1990)

CLIMATE AND REGOLITH OF STUDY AREA

Climate

The climate of the area is Guinea savannah with annual rainfall range of 600-1200 mm (Webber, 1996a). Short single rainy season with long period of dryness characterizes the area (Dickson and Benneh, 1995). Monthly totals of rainfall increase slowly from March and peaks in August after which there is a sharp decrease of

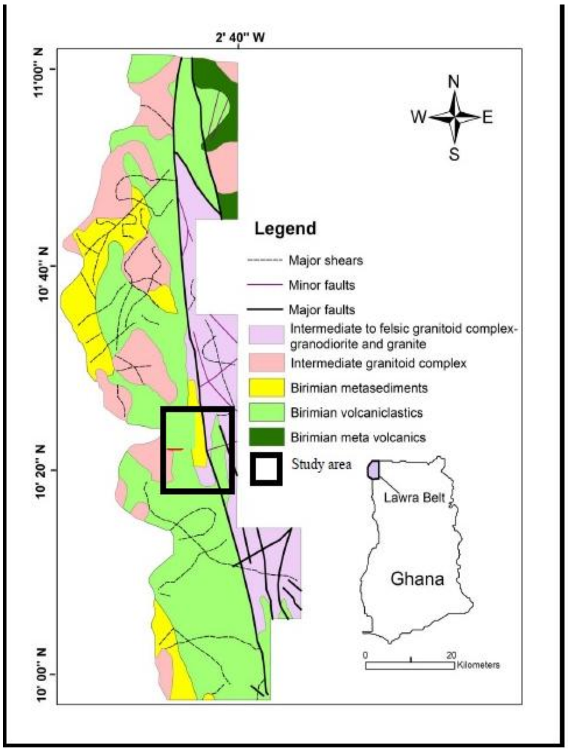

Fig. 1 Location and geology of the study area

rains after October (Kranjac-Bersaljevic et al. 1998). The average monthly rainfall estimate is 986 mm per month. Monthly temperatures are consistently high and averages at 28.6°C. Average monthly temperature range from 26.4°C and occur during the peak seasons of the rains in August and can increase to a maximum of 32.1°C in April (Dickson and Benneh, 1995).

Regolith

Regolith-landform of the area is characterized by deep weathering profile with preserved-pre-existing and erosional surfaces. In association with these regolith-landforms are widespread lateritization that has a surface veneer of pisoliths and depositional cover of exotic origin. Regolith materials at lowland terrains are sheet wash deposits moved downslope during the flash floods. These regolith units originate from redistributed sediments that differ from the weathered materials from the underlying rocks. The regolith units cover at the upland areas contain degraded weathered rocks and materials that decreases in fragment size down-slope/

The topography is generally low, undulating with isolated hills at some places (Arhin and Nude, 2009). Some of the hills are capped by hardpans withthe slopes marked by scree, consisting of small fragments of visibly mineralised and altered rock that decrease in fragment size down-slope.

METHODOLOGY

Methods used in the study involved field and laboratory works. The fieldwork involved collection of 23 soil samples from a circular hole of 30 cm nominal diameter dimension. The holes were dug up to 20 cm depth from the land-surface. The collected samples were from known gold mineralized area where an illicit mining operation had occurred before and some agricultural and residential areas. The samples were collected at 200 m intervals and the sample locations were controlled by the nature of the

Table 1: Summary statistics of trace elements samples analysed by XRF (ppm)

Elements	MIN	MAX	Mean	Median	STDEV	Bn	EF	Igeo
V	96.11	865.00	292.35	160.45	218.36	120.00	172.35	0.49
Cr	104.12	1177.00	281.82	188.66	225.78	102.00	179.82	0.55
Co	11.79	210.00	57.29	29.25	56.62	25.00	32.29	0.46
Ni	2.60	171.60	60.05	50.40	41.44	84.00	-23.95	0.14
Cu	17.86	176.20	49.55	39.24	39.20	60.00	-10.45	0.17
Zn	15.30	126.20	48.93	42.19	26.78	70.00	-21.07	0.14
Ag	1.10	3.60	2.23	2.00	1.27	0.08	29.78	5.98
As	4.70	143.70	44.56	30.90	39.30	1.80	42.76	4.97
Se	0.30	0.65	0.49	0.50	0.11	0.05	0.44	1.95
Rb	14.90	105.01	51.19	48.95	31.26	90.00	-38.81	0.11
Sr	12.60	77.47	37.09	37.01	14.85	370.00	-332.91	0.02
Y	4.90	26.08	16.37	18.43	6.46	33.00	-16.63	0.10
Zr	79.10	691.06	307.40	315.90	123.32	165.00	142.40	0.37
Nb	1.80	18.39	9.67	9.40	3.43	20.00	-10.33	0.10
Mo	0.90	5.30	2.95	2.90	1.34	1.20	1.75	0.49
Sn	0.40	19.50	4.63	2.80	5.42	2.30	2.33	0.40
Sb	0.85	5.70	1.87	1.68	1.32	0.20	1.67	1.88
Ba	60.71	1102.00	418.60	431.62	238.21	425.00	-6.40	0.20
La	5.10	118.53	27.75	22.49	25.29	39.00	-11.25	0.14
Ce	18.30	334.80	77.33	50.04	78.80	66.50	10.83	0.23
W	1.36	3.12	2.38	2.53	0.85	1.25	1.13	0.38
Pb	4.00	42.50	12.68	10.53	9.13	14.00	-1.32	0.18
Th	2.20	10.76	5.31	5.14	2.16	9.60	-4.29	0.11
U	1.43	3.76	2.21	2.10	0.64	2.70	-0.49	0.16
Cd	1.00	2.20	1.60	1.60	0.85	0.15	1.45	2.14

topographical settings. Sample weight of 1000 g was collected from each hole with no considerations to the regolith types. The samples were sun dried whilst the 23 samples were sieved to <2 mm sieve size fractions. Sampling information such as soil type, lithology of sampling environment and possible weathering and geomorphic histories were recorded. The sieved and logged samples were then sent to Ghana Geological Survey Department laboratory for XRF analysis.

The field prepared samples of < 2 mm sizes were milled to powder at the laboratory. 7 g portion of the milled powder was placed into a small plastic beaker. The beaker and its content were weighed using a beam balance. 8 to 10 drops of Moviol 88 solution binding agent was added to the 7 g weighed portion of the powder to bind the mixture (powder and binding agent) together in small lumps. Pressed pellets were formed from the powdered mixture. The pellets were placed in XRF analyzer which takes 20 samples at a time. The XRF analyzer was connected to a computer with Spectro X-lab software that records major and trace elements in the samples. The trace elements and major oxides in the samples are then measured.

RESULTS AND DISCUSSION

RESULTS

The summary statistics of the trace elements in the samples, average continental crustal values (Bn), the derived enrichment factors (EF) and geo-accumulation index (Igeo) of the measured trace elements were presented in Table 1.The average continental crustal values were used as background values and were applied in the normalization of trace elements concentrations in samples. The difference between trace element concentration and average crustal value (Bn) of a particular element in a sample gave the status of enrichment or depletion or considered as the enrichment factor (EF) of an element. Thus given the trace element concentration in sample 1 is xi and average continental crustal value is (Bn) i, then:

$$(EF)i = xi - (Bn)i$$

The geo-accumulations (**Igeo**) indices were also calculated following Muller (1969) method to estimate the pollution indices (Igeo). The geo-accumulation index is calculated as:

$$Igeo = log2(Cn + 1.5Bn) \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \textit{Muller}\ (1969)$$

where Cn is the concentration of the element measured in a sample and Bn is the average crustal value while 1.5 is a constant which is introduced to minimize the effect of the variation of background values. This was compared with Muller (1979) pollution index classes (Table 2). The last column of Table 1 labelled Igeo shows the index of geo-accumulations in soil samples.

DISCUSSIONS

Surface processes including weathering,

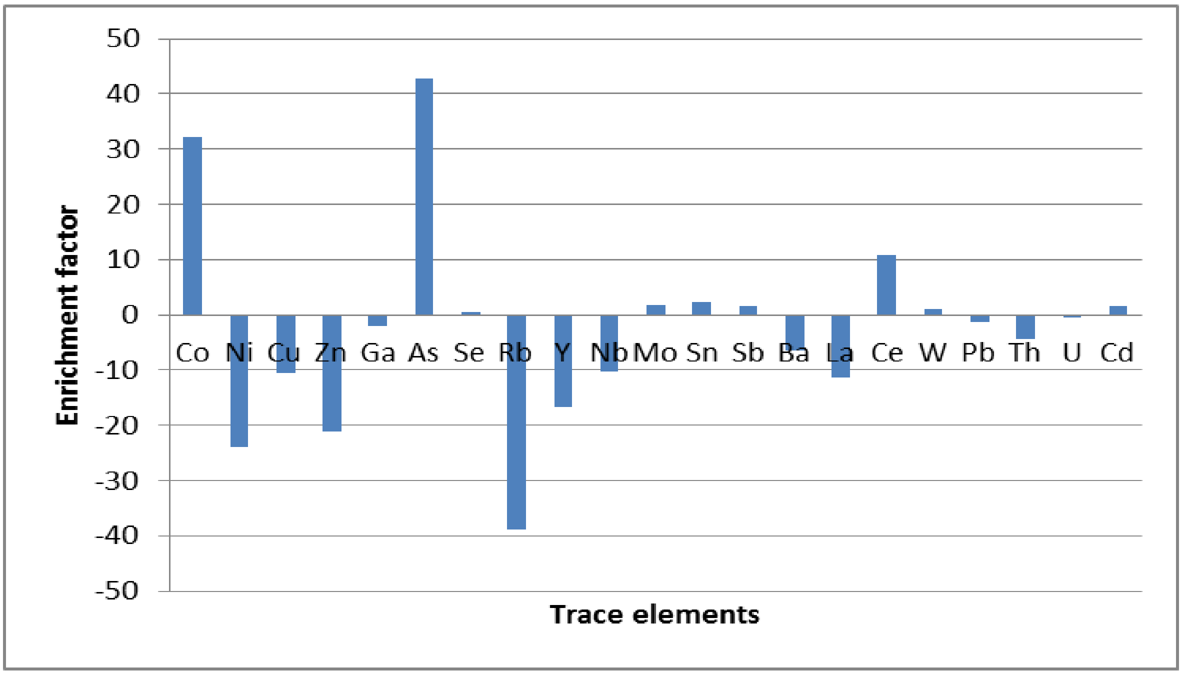

Fig. 2 Enrichment-Depletion of trace elements in samples

erosion and deposition helped the enrichment and depletion of trace elements in an aerated soil under a pH condition of 5.0 and 5.5 (Marques et al., 2003). Elements such as V, Cr, Zr, Ga and Y normally accumulate under such conditions whereas Zn, Cu, Ni, Pb and Co are mostly depleted (Marques *et al.,* 2003. The underlying rocks of the studied area are volcanoclastic and metasedimentary units intruded at places with granites which bear no relationship to Cr hence its enrichment in the soils may had come from an anthropogenic actions. The authors agree with Marques et al., (2003) that the high Co contents recorded (Fig. 3) perhaps were formed due to its strong complex affinity with organic matter in the oxidized zone.

Table 2 Igeo classification classes (after Muller, 1979)

Igeo value	Igeo class	Pollution Intensity
< 0	0	Pollution intensity
0 – 1	1	Unpolluted
1 – 2	2	Unpolluted to moderately polluted
2 – 3	3	Moderately polluted
3 – 4	4	Moderately to strongly polluted
4 – 5	5	Strongly polluted
5 – 6	6	Strongly to extremely polluted
		Extremely polluted

The trace elements can be harmful or harmless (Arhin et al. 2015). However those listed to be potentially toxic by the United States Environmental Protection Agency (USEPA) are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu) nickel (Ni), lead (Pb) and zinc (Zn). Soil samples at the study area showed enrichments of 42.80 in As, 1.45 in Cd, 180.00 in Cr and depletion of 10.45 in Cu, 23.95 in Ni, 1.32 in Pb and 21.00 in Zn. All these trace elements classed under PTEs are essential for the metabolism of living organisms. Example Cr, Cu, Ni and Zn are required by organisms at low level and become toxic at some higher levels of exposure. The trace element geochemistry study of the Nadowli District measured high Cr content in samples (Table 1) where enrichment factor (EF) was about 180.00. Chromium does not occur naturally in elemental form but only in compounds. The high Cr identified is likely to come from disposal of chromium containing waste as there are no electroplating processing plants in the District. The environmental concerns here is Cr exists in the environment in two stable oxidation states, Cr^{6+} and Cr^{3+}, which have different toxicity and transport characteristics. Cr^{6+} is commonly found at contaminated sites (Cynthia, 1997) and exists typically as oxyanion chromate (CrO42−) and dichromate (Cr2O72-), which precipitates readily in the presence of metal cations such as Ba2+, Pb2+, and Ag+. From Table 1 Nadowli District soils are rich in silver (Ag) meaning more Cr will be precipitated. Adsorption of Cr on soil surfaces especially Fe and Al oxides has also been reported. Report by Arhin and Nude, (2009) portrays extensive coverage of Fe-oxide rich regolith in the area which probably is leading to elevated Cr contents. Cr^{6+} has high solubility in soils and waters and tends to be mobile in the environment making its exposure easy because of its prevalence and possible biological uptake. Pagotto et al. (2001) had reported chronic exposure to Cr^{6+} can induce renal failure, anaemia, haemolysis and liver failure. The indiscriminate waste disposal practices may enhance the spread of Cr^{6+} and ultimately expose the inhabitants to the health problems of Cr exposure.

Similarly Cu, Ni and Zn with low trace elements concentrations are needed for metabolic activities in living organisms is depleted in the study area. It is likely the food chain produced in the district may be deficient these trace elements and will require some supplements to help the metabolic activities. On the contrary, the non-essential elements including As, and Cd, a known toxic and not required by organisms at any level have elevated contents in the samples (Table 1 and Fig. 3). As has been noted by many authors soil pollutants can be ubiquitous, toxic and persistent (Poggio et al. 2009). They cannot be degraded to non-toxic forms by either biological or chemical means but may redistribute and accumulate locally or be transported over long distances due to surface processes. The trace elements contents computed from soils using Muller (1969) formulae (Table 2) showed extreme pollution of As and moderate to strong pollution of Cd. This therefore raises an environmental concern because food and water in the district are produce from the area. As recognized by He et al. (2004) the contaminated ecosystem will remain a potential threat to life as the livelihood of the people in the district will come from the contaminated lands. The spread and development of small scale illicit mines and an increase in agricultural activities probably contributes to the gradual redistribution and re-concentration of As, Cd and Cr. The sources of the PTEs perhaps are from the earth's crust and are introduced to the environment via mining activities or from pesticides and insecticides use. This mode of trace elements contaminations in the environment has substantially raised the chances

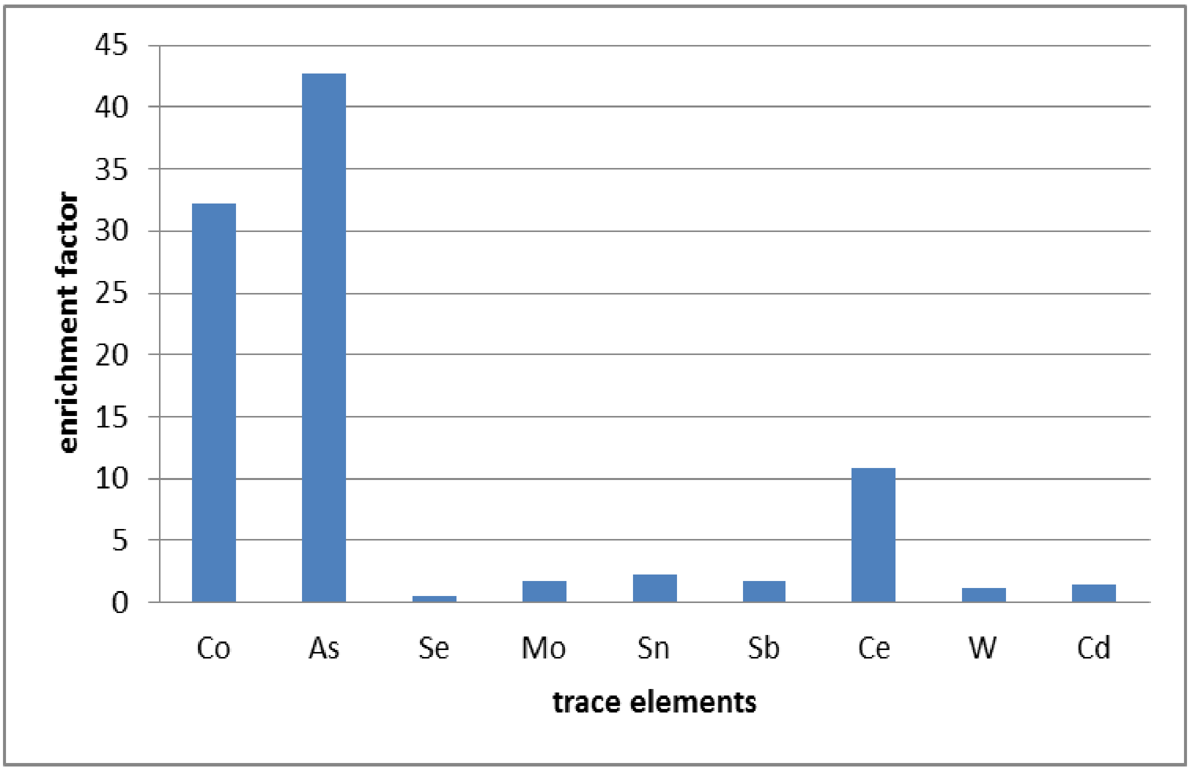

Fig 3 Selected enriched trace elements in samples

of human exposure to PTEs through ingestion, inhalation or dermal contact. The enriched As, Cd and Cr trace elements retained by soils and portions dissociated and mobilised into water by biological and chemical mechanisms have the potential impact on human health. The high As contents of 4.60 to 143.70 mg/kg, Cr contents of 104.00 to 1177.00 mg/kg and Cd contents of 1.00 to 2.20 mg/kg if exceeds the metal sorption capacity of the soil can runoff into rivers or lakes or leach into the ground water, causing accumulation in animals, plants and people. Cadmium enrichment of 1.45 representing moderate to strong polluted areas in the study area can cause nephropathy, pulmonary lesions and lung cancer. These geographic areas need investigations to reduce exposure of Cd contamination.

Table 1 showed lead (Pb) deficiency. This is good for the inhabitants in the district because high Pb can be very toxic for human health. High concentrations results in reduction in intellectual quotient, hyperactivity, and hearing loss in children and increased blood pressure; liver, kidney and fertility damage in adults. The advantage here is that exposure to Pb-poor soils will not result to any toxicity in human health. Thus, children will not have reduction in intellectual quotient, hyperactivity and hearing loss even when they unknowingly ingest soils. Likewise adults' blood pressures will not increase neither will they have liver and kidney failures and fertility damage. On the contrary zinc deficiency in soils implies food produced in the area may be deficient in this element. The main source of exposure to zinc is from food though there might be oral exposure arising from working in industries where Zn is used as source of raw materials but there is no such industry in the District. Though reports show that high doses of Zn may interfere with calcium metabolism and impair immune responses; the people eating what they grow in the District leave them safe from high dose Zn exposures.

CONCLUSION

Results from soil samples in the studied area comprise PTEs that are essential for human metabolism at low trace elements concentration levels and become toxic at high concentration levels. The data presented supports the findings that trace elements in soils have important inputs in the environment and need to be considered as part of any human health risk assessment. The PTEs (Cu, Ni, and Zn) required at low level concentrations for human metabolism showed depletion in the analysed samples. Rather the non-essential PTEs (As and Cr) for human development showed elements enrichment of 42.80 mg/kg and 1.45 mg/kg respectively. The background value for

As in soils is 1.8 mg/kg but the minimum concentration of As in the analysed soil samples were approximately 5.00 mg/kg with a maximum of 144 mg/kg. The minimum As concentration is far above the safe level of As in soils which mean the inhabitants in the district will be susceptible to As-health problems. The pollution load index (PLI) at the maximum concentration location point for As is 80. This PLI factor of 80 is very high and therefore requires epidemiological studies to assess As-exposure- health issues.

From the findings of the studies, an attention is needed to curtail and abate especially As and Cd distribution, dispersion and transportation to currently uncontaminated sites so as to avoid a major environmental disaster which could arise with continued release of As and Cd into the ecosystem. Addressing environmental health problems emanating from earth-geological processes-health require intensive interdisciplinary research into the various environmental media so as to establish the levels of trace elements in the environment and assess their possible social, economic and human health impacts. It is obvious that scientific information would be needed to aid in designing appropriate sanitary and remedial measures for PTE-impacted areas. Therefore on the basis of the findings of this study, the authors concludes that trace element geochemical investigations of this sort to highlight deficient essential elements locations and elevated PTEs sites in communities where primary health problems are prevalent.

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