

Inherent Errors in Using Continental Crustal Averages and Legislated Accepted Values in the Determination of Enrichment Factors (EFs): A Case Study in Northern Ghana in Developing Environmental Policies

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Abstract

Health problems related to geological and environmental processes often have been assessed using enrichment factors derived from global and legislated accepted values. The petrological studies and the analysis of soils in this study reveals elements storage and concentrations in the environment exposed to life depends on several factors which are not incorporated using the example the continental crustal averages and the accepted legislated values. The results from the study suggest the establishment of local background values particularly from more large-scale surveys where quality and statistically significant environmental data had been collected for local background value estimation for enrichment factors. The continental crustal averages and legislated values either overestimate or underestimate the enrichment or depletion factors hence making policies developed from them unreal. General name granite can be given to a suite of rocks but their mineralogical and modal compositions will vary. Same continental crustal average can be used for them whilst disregarding the local environmental activities. The study concludes from the results in the petrological studies of rocks in Bongo and environmental soil studies at Nadowli that EFs calculated from the local background values can be used appropriately to propagate the true environmental policy to clean up the environment against the related health issues connected with the geogenic and anthropogenic processes than continental crustal averages as well as the legislated accepted values that may have no relationship with the study environment.

Keywords: Inherent error; Environmental policy; Legislated value; Background value; Environmental health

Introduction

Most popular mechanisms of recognizing and reckoning human interference with global element cycles from the underlying rocks are through the calculation of the enrichment factor (EF). This method has been used for many years in order to evaluate the environmental risk areas. However, the EF calculation is only rooted in the background value of an element in an uncontaminated rock or soils without considerations to several other possible factors that influence the metal transport from the lithosphere to the biosphere. The calculated Enrichment factor (EF) refers simply to the difference between the elemental concentrations of the analysed element in the sample and its crustal average, i.e.:

$$EF = \text{Conc of element } x \text{ (analysed in a sample)} - \text{average caon of element } x \text{ (analysed in the crust)}$$

The result from this computation can either be positive depicting an enrichment or negative signifying depletion. Similarly the EF can be calculated for a given element by dividing the measured concentration of that element in the sampling medium investigated by the concentration of the same element in the Earth's crust, i.e.:

$$EF = \text{Conc of element } x \text{ in sample} / \text{Conc of element } x \text{ in crust}$$

Where EF is the enrichment factor in the investigated sample and x is the element type. The net value determines whether it is deficient or enrichment.

The continental crustal averages used in EF calculations are considered to have been obtained from uncontaminated rocks and soils, which ignore many factors that can influence element concentrations and distributions. Typical examples are environmental activities, nature of regolith, as well as the biogeochemistry and microbial community influence on metal transports. The normalization of the

concentration of element x analysed in sample to an average total crustal value can lead to over exaggeration of the EF hence influencing environmental policies either positively or negatively. The consequence of its use in developing environmental policies is exacerbated because of the geochemical variations in the earth's environment.

It just becomes binding when an environmental policy is promulgated from unrealistic background value for some trace elements. This has been demonstrated by McLennan [1] on the realization that estimates of average composition of various crustal rocks show considerable disagreement for a number of trace elements (e.g. Ti, Nb, Ta, Cs, Cr, Ni, V, Co). Further demonstration suggesting the superiority of local background values of elements over the global continental values in the crust and some safe-guideline values is presented in this paper. This paper therefore presents a case study from the northern regions of Ghana where we compare local background values from investigated soil samples with their global crustal averages and their safe guideline values. The purpose of this investigation is to highlight the likely intrinsic flaws of using EF based only on global crustal values in estimating enrichments and depletion values. The other objectives include the comparison of locally computed

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Received June 02, 2017; **Accepted** June 08, 2017; **Published** June 09, 2017

Citation: Arhin E, Mouri H, Kazapoe R (2017) Inherent Errors in Using Continental Crustal Averages and Legislated Accepted Values in the Determination of Enrichment Factors (EFs): A Case Study in Northern Ghana in Developing Environmental Policies. J Geogr Nat Disast 7: 204. doi: [10.4172/2167-0587.1000204](https://doi.org/10.4172/2167-0587.1000204)

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background values with safe-guide and continental crustal values with the hope of identifying most suitable values practically appropriate for environmental health studies.

Exaggerations in using continental averages in environmental studies

The premise of the authors' argument is that the modal composition of an uncontaminated rock can show percent modal compositional variations but despite these variations in modal compositions in general rock-type example granites, scientists in environmental studies still assign same continental crustal average value anywhere on the globe to them. For instance a rock having primary minerals Quartz, K-feldspar and Plagioclase feldspars is technically known as granite by virtue of the mineralogical composition. However, granite might have different textures and modal proportions of such minerals. Hence, elements mobility in this type of rocks for example may be influenced by a number of factors occurring at the scale of the rock, this includes for example the textures and other deformational features such as faults, joints, shear zones etc., at the scale of the rock. The impacts of such factors will not be seen at regional scale. However, in some areas such factors can contribute to the creation of easy pathways for metal transport and excellent receptacles for anomalous concentrations for a particular element/metal. In the case of certain elements and metals, their movements will be rather restricted by the textural and deformational features. Soils developed from the underlying rocks probably from the same melt may have different compositions depending on the pressure-temperature (P-T) conditions and may have elements mobility be influenced for example by nature of environmental activities, regolith types and structure, microbial communities in addition to the surface and chemical processes. It is apparent that most of these factors raised by the current authors and by Riemann and Caritat [2] were not accounted for in the estimation of the global crustal averages. Exacerbating the use of continental crustal averages of elements in environmental health work and the possible serious implications it has on some environmental policies are cherished in the following facts:

1. The variability of earth crust composition at any given point compared to the global averages,
2. The processes involved in the mechanisms of natural fractionation of elements during their transfer from the crust to the atmosphere,
3. The impact of climate on physical and chemical processes during the elements transport in the oxidised environment,
4. The complicated characteristics of the regolith atop the bedrocks
5. The differential solubility of elements/minerals in weak chemical digestions generally used in environmental studies and,
6. The impact of biogeochemical processes in the surface environment (e.g. influence of microbial community on metal migration etc.).

Highlighting the need to use local background values over the global accepted values is demonstrated by several researchers [3,4] where different continental crustal average values for some uncontaminated rocks which supposedly should be constant everywhere had been obtained. Taylor [5] also confirms differences in previously estimated continental crustal values of trace elements purported to have

been measured in uncontaminated rocks. This makes the use of the crustal averages contentious more particularly for environmental geochemistry studies where environmental policies are developed. In developing countries where we depend on locally produced food, drink mostly untreated water from groundwater and surface water sources from the local environment; using global crustal averages in designing environmental policies can lead to disastrous outcomes.

Location and geological background of study area

Two locations in northern Ghana all situated on the Birimian Greenstone Belts were chosen for this investigation. The areas were Bongo, which is situated on the Bole-Navrongo-Nangodi Birimian Belt and Nadowli on the Wa-Lawra Birimian Belt (Figure 1). Bongo is at the northeast whilst Nadowli is at the north-western portion of Ghana. The distance by road from the national capital Accra to Nadowli is 732.1 km whereas that to Bongo is 773.7 km.

The two areas have similar geological settings both of them underlain by metavolcanic and metasedimentary suite of rocks intruded at places by Belt granitoids in the volcanic rocks and Basin granitoids in the sedimentary basins. The metavolcanic rocks consist of metamorphosed lavas and pyroclastic rocks containing basalts, andesite, rhyolites and dolerites [6-8]. Some of the volcanic rocks exhibit partial assimilation and show melanocratic relicts (xenoliths) in close association with the Belt granitoids. In contrast the metasedimentary units comprise phyllite, sericite-schist and metagreywacke.

The Belt granitoids that intrude the metavolcanic rocks is made up of hornblende-rich-granitoids in addition to small discordant to semi-discordant, late or post-tectonic soda-rich hornblende-biotite granites or granodiorites that grade into quartz diorite and hornblende diorite [9]. Contrastingly, the basin granitoids are large concordant and syntectonic batholithic granitoids commonly banded and foliated.

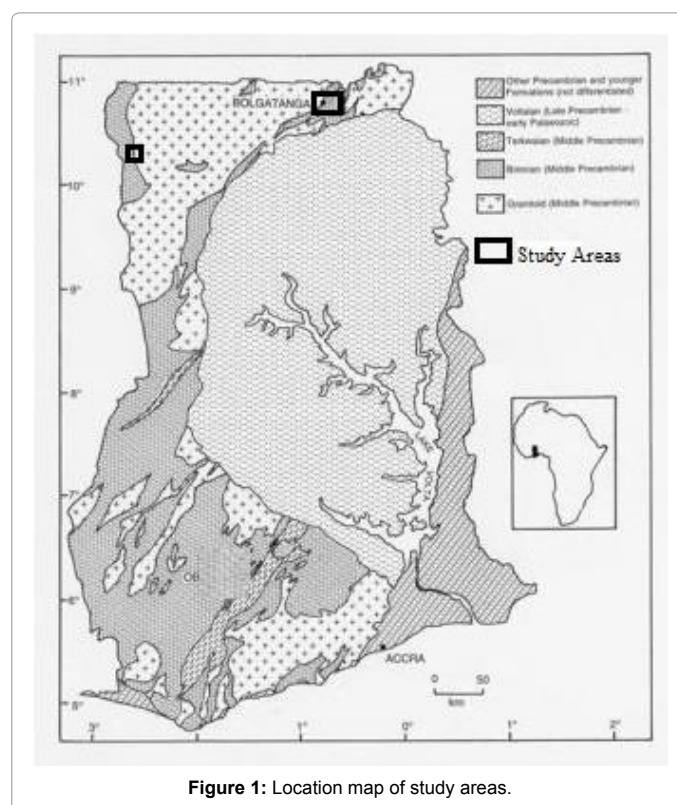


Figure 1: Location map of study areas.

These intrusive granitoids are light coloured enriched in both micas (muscovite and biotite) with biotite dominating in addition to k-feldspar.

Materials and Methods

Two sets of samples (rocks and soils) media-types were collected for trace elements geochemistry analysis. The rocks were collected at Bongo and soils at Nadowli, all in northern Ghana.

Rock samples

Nine (9) rock samples with sample prefix UBS were collected at Bongo area for petrological and geochemical investigation. Six (6) out of the nine (9) rock samples (numbers UBS001, UBS002, UBS003, UBS006, UBS007, and UBS008) were igneous rocks of plutonic origin with granitic composition. The other three (3) rock samples were from silica-rich rock (sample number UBS 004 from strongly deformed weakly metamorphosed mylonitic quartzite The mylonitic quartzite (this need to be mentioned above when you introduced the silica rich rocks (i.e., the silica-rich rock) was included in this study as a control sample because it contained predominantly quartz mineral as against the rocks with granitic compositions containing quartz, K-feldspar and Plagioclase feldspars. The two other samples UBS 009 and UBS 010 are mica schist. ICP-MS analytical technique was used to measure the trace elements in the rock samples at ALS-Chemex laboratory in Kumasi whilst the petrological studies of the sample rock specimens were carried out at the Earth Science Department of the University of Ghana, Accra.

Soil samples

38 soil samples were collected from dugout pits (Figure 2) at the Nadowli area, a different area from where the rocks were taken. 1 kg weight field samples were taken from the upper layer of the regolith and were sun dried, then homogenized, split into library and laboratory samples (Figure 3).

The laboratory samples were then sieved into different size fractions but it was only the <2 mm particle size fraction that was further processed for ICP-MS analyses. The further sample preparations for trace elements analysis involved the collection of 100 g sub samples from the <2 mm sieved samples into powdered samples. These samples were vaporized using laser cells, and then introduced into ICP-MS instrument for the analyses of the potentially toxic elements (PTEs) and essential elements (EEs).



Figure 2: Pit profile sampling at 10 cm interval at Nadowli.

Results and Discussions

Results

Rock petrology and geochemistry: The petrological studies of the rocks (UBS 001 and UBS 002 identified as granites) revealed different mineralogical compositions and modal proportions between samples UBS 001 and UBS 002. Photomicrograph showing the mineralogical compositions of the plutonic igneous rocks with granitic compositions (UBS 001 and UBS 002) is presented in Figures 4 and 5 and that of the mylonitic quartzite (UBS 004) are presented in Figure 6.

The modal proportions, the mineralogical compositions and general characteristics of these rocks are presented in Tables 1-3. Table 4 compares the measured trace elements concentrations in samples relative to different baseline values to evaluate the enrichment and depletion factors.

Figure 7 which is constructed from the data presented in Table 4



Figure 3: Field sample preparations.

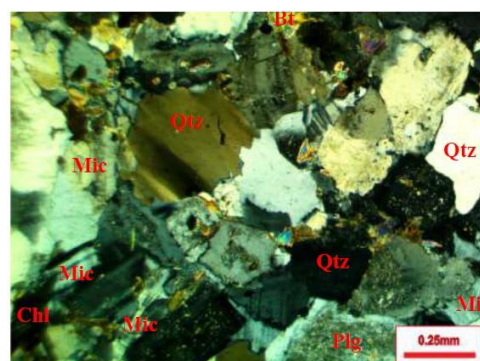


Figure 4: Photomicrograph of sample UBS 001.

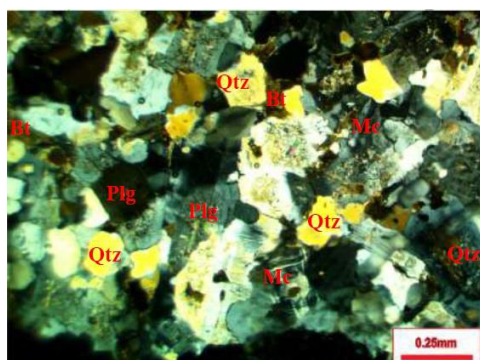


Figure 5: Photomicrograph of sample UBS 002.

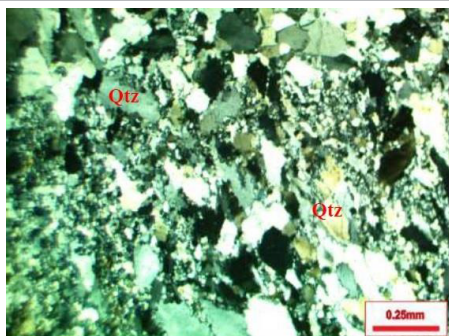


Figure 6: Photomicrograph of sample UBS 004.

Mode	Volume%	Characteristics
Quartz	40	Anhedral, Exhibit undulose extinction
Microcline	36	Subhedral, plagioclitic at places, may be altered
Plagioclase	20	Subhedral, zoned, altered
Biotite	4	Short, blade-like, altered.
Chlorite	<1	Secondary, altered product of biotite and amphibole
Opaque mineral	<1	Occurs as smears on the chlorite

Table 1: Modal composition of UBS.

Mode	Volume%	Characteristics
Quartz	50	Anhedral, also occurs as blebs on microcline, undulose
Microcline	32	Subhedral, plagioclitic, altered
Plagioclase	14	Subhedral, tabular or lathlike altered
Biotite	4	Altered shredded with preserved pseudomorphs

Table 2: Modal composition of UBS 002.

Mode	Volume%	Characteristics
Quartz	44	Anhedral, undulose, cracked
Microcline	30	Relatively coarse, may be plagioclitic
Plagioclase	18	Zone altered.
Biotite	5	Blade-like, shredded at places, altered
Muscovite	2	Shredded
Sphene	1	Euhedral, secondary.

Table 3: Modal composition of UBS 004.

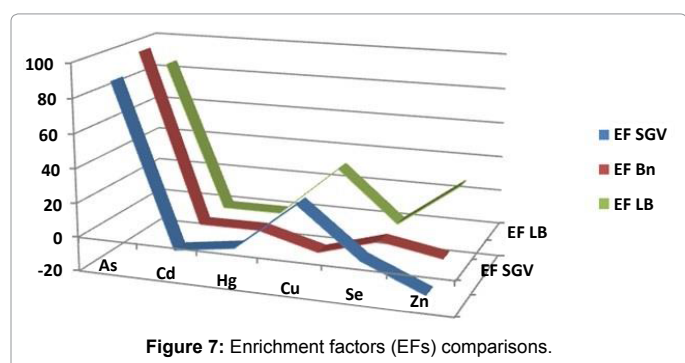


Figure 7: Enrichment factors (EFs) comparisons.

Trace element	Measured	Safe Guide Values (SGV)	EF SGV	Crustal averages (Bn)	EF Bn	Local Background-clac (LB)	EF LB
As	101	12	89	1.5	99.5	15	86
Cd	0.05	5	-4.95	0.15	-0.1	0.02	0.03
Hg	0.17	0.04	0.13	0.09	0.08	0.01	0.16
Cu	50.17	22	28.7	60	-9.3	20	30.7
Se	1.2	0.25	0.95	0.05	1.15	0.4	0.8
Zn	65	79	-14	70	-5	38	27

Table 4: Measured trace elements in samples and calculated enrichment factors from different baselines values.

shows the enrichment and depletion factors between safe-guide values (SGV), continental crustal averages (Bn) and the local background values (LB) derived statistically from trace elements results in the study.

Soil Geochemistry: The geochemistry results obtained in analyzing the soil samples for their trace elements contents and concentrations and comparison with some known baseline values and locally computed background values are presented in Figures 8-10. Demonstration of local background value estimation is shown in Figure 8. Figure 9 is the box-plot of some selected potentially toxic and essential elements.

The box-plot compares the means of the continental crustal averages, safe-guide or legislated values as well as the locally derived background values. The practicality of the use of the correct baseline value in developing environmental policies for environmental clean-ups is demonstrated in Figures 9 and 10. These data represent the relationship between the commonly used baseline values in environmental health issues studies (i.e. the continental crustal average (Bn), the safe guide or legislated accepted values) and the estimated local background values.

Discussions

According to Taylor the continental crustal average is an estimate of equal amount of basalt and granite average compositions of elements in an uncontaminated crust. These averages are used in many environmental health studies to evaluate areas where trace elements concentrations in the natural environments can impact on public health. Though the method had been used for this purpose for long time but it is possible that environmental policies developed from its outcome may not always address its conclusions. The reason is, it will be impossible to obtain equal amount of elements averages in basalt and granite for the calculation of the crustal values everywhere. These averages were computed statistically and might not factor some geologic and environmental processes that impacts on elements migration to environments for human exposures. The name basalt or granite is a general name for some rocks containing specific major minerals. The modal mineralogical compositions for granite or basalt vary on the continent, so is the global geochemistry of the continental crust.

As seen in this study and confirming the assertion that the modal proportions and mineralogical compositions of granite vary across the globe was demonstrated in Figures 4, 5, Tables 1 and 2. From the literature the major minerals of a granitic rock are: quartz, K-feldspar and plagioclase feldspar. These major minerals are present in the two samples that are studied here (Tables 1, 2, Figures 4 and 5) but with varying volume percentages. These samples also show different amounts of *muscovite*, *biotite*, *hornblende* and *amphibole* (Tables 1 and 2). Granite sample UBS 001 has less quartz, more orthoclase and plagioclase feldspars than granite sample UBS 002. In addition sample UBS 001, has other minerals such as chlorite and opaque minerals present as accessories, which are not seen in sample UBS 002. Using average composition of elements in the continental crust

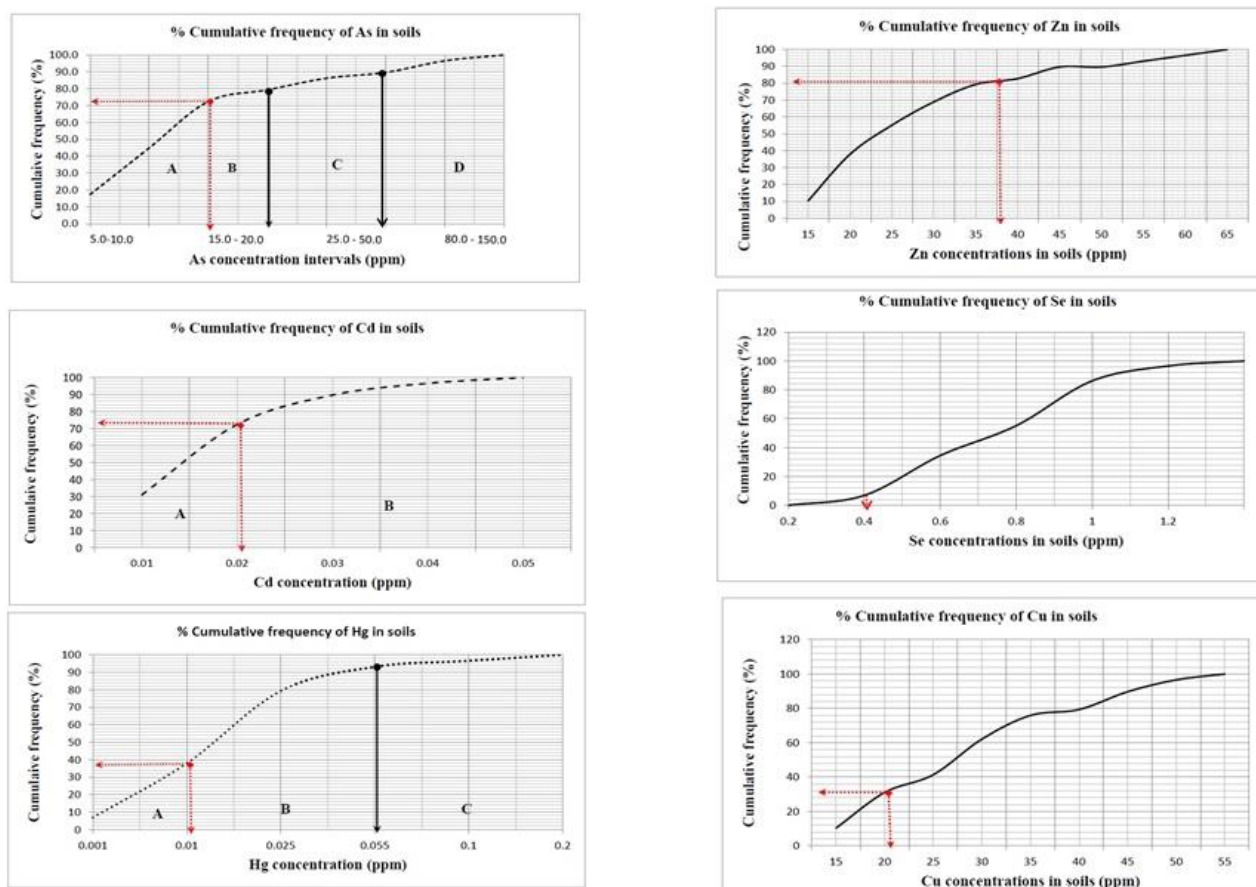


Figure 8: Local background values estimations.

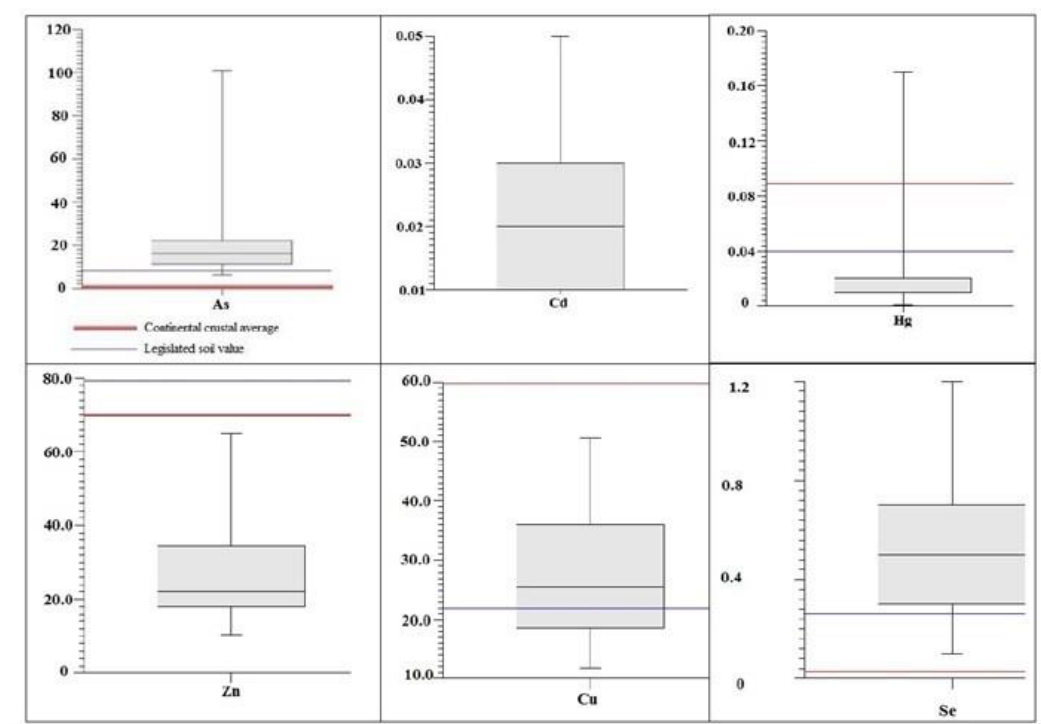


Figure 9: Boxplots of selected elements.

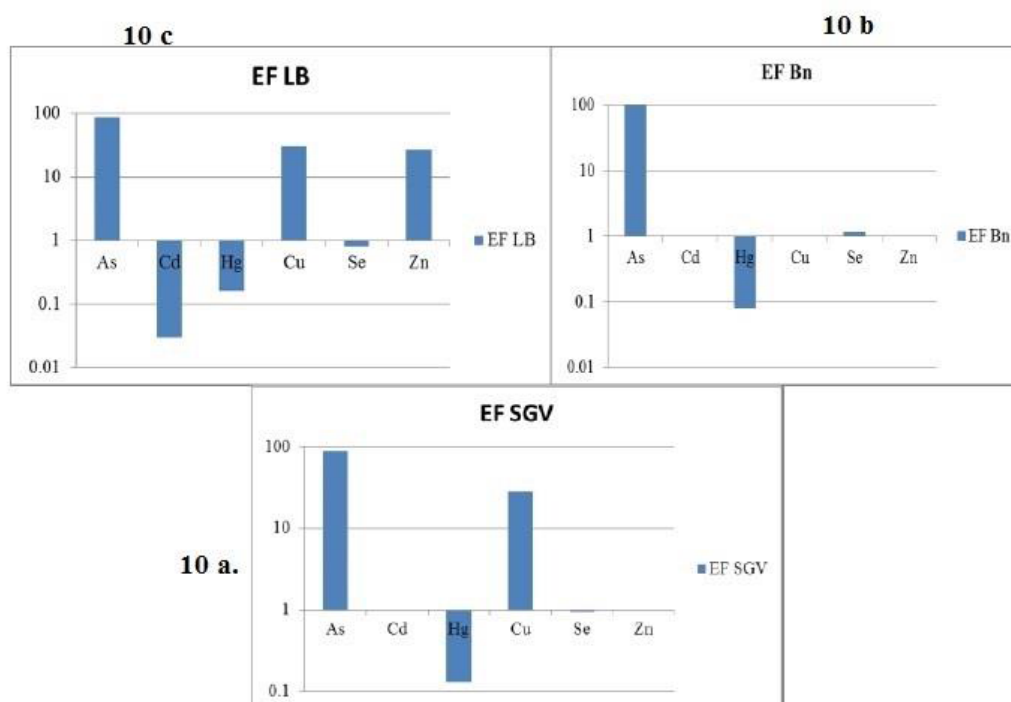


Figure 10: Relationships of calculated EFs.

or the background values of elements in granite or basalt may either exaggerate or underestimate the computed enrichment factors, which give information on the degree of contamination of the elements in the environment. From Kim et al. [10] mineralogy of rocks does control mobility and possible bioavailability of elements from the weathering front to the end-stage formed soils that the terrestrial life depends on. Rocks containing more quartz will weather and form sandy soil (e.g. UBS 002) whilst rocks containing more feldspar will form clayey soil after chemical-weathering processes is complete (e.g. UBS 001). Clay minerals are major reducers of porosity and permeability [11] and the lack of incorporating modal mineral composition of the continental crustal average calculations make their use for environmental health studies outcomes precarious and unsuitable. The clay minerals formed from weathering of rocks can fill pores or coat grains consequently impeding elements mobility in the environment. These intrinsic properties particularly of variable mineralogical modal compositions in igneous rocks considered uniform for specific rock types render the continental crustal averages use for environmental health studies dubious.

As seen in Figure 7 and Table 4 the enrichment factors (EFs) using different baseline values showed variable degree of change. Trace elements such as As, Cd, Cu and Se tend to have similar factors using the calculated local backgrounds and safe-guide values for these elements. However mix enrichments factors were obtained using these same baseline values for Zn for example. The depletion of this later was obtained using SGV and showed enrichments for local background and continental crustal average. Clinical examinations in humans had revealed that zinc deficiency as an important malnutrition problem world-wide [12]. Arhin and Zango [13] had also identified the significant role of Zn in human development. Challenging environmental policy development can be deduced for this area considering the enrichment factors computed from the different baseline values used. The SGV and

Bn values are adapted values and it is likely that the environmental issues impacting on the Zn contents were factored into the metal transport in the area. The SGV calculated enrichment factor for Zn is in contrast with the calculated values obtained for LB and Bn factors and could be disregarded to promulgate any environmental policy. The relationship between LB and Bn also varies in enrichment factors. As noted by Riemann the method of using Bn is only useful for inferring large-scale regional patterns and not for assessing detailed geochemical variations [14,15] that will drive environmental policy development. Therefore for effective environmental cleaning work, reference values for soil should be based on baseline concentration levels found in local soils and not based on continental or global crustal averages.

The inappropriateness of using continental crustal averages (Bn) of elements to establish EF at a local-scale is demonstrated in Figure 9 for As, Cd, Hg, Cu, Se and Zn. As shown in Figure 9 apart from As and Cd whose computed EFs were similar for the three baseline values used; the EF calculated from Bn appeared to differ greatly from EFs estimated from SGV and LB especially for Hg, Cu, Se and Zn. The conflict between EF_{Bn} and that obtained for EF_{LB} and EF_{SGV} is critical to develop a holistic environmental policies. The selected elements (As, Cd, Hg, Cu, Se Zn etc.) presented in Figure 9 play critical functions in human and animal development. Some of the elements contribute essentially (Cu, Se, and Zn) to human development whilst others cause adverse health effects (As, Cd, Hg) and even death depending on concentrations ingested and the ability particularly As, Cd and Hg to bioaccumulate. The problem with calculated EF_{Bn} values may suggest an overestimation or underestimation that can lead to improper announcement of unrealistic environmental policies. For instance EF_{Bn} shows a slight rise in Hg and depletion in Cu whereas the other computed EFs portray otherwise. Also in absolute value terms for As enrichment in soils at the study area is $EF_{Bn} > EF_{SGV} = EF_{LB}$.

Another issue recognized in Table 4 is the depletions in Cd and Zn

where EF calculations were based on SGV and Bn values. The local-scale background computation acknowledged enrichments in Cd and Zn though the enrichment in Cd is trace. The low enrichment in Cd should be considered significant because of some elements ability to bio-accumulate at low concentrations due to their bio-availability and bio-accessibility. This thus suggests the wisdom of statistically computing the local backgrounds of elements at local-scales in the determination of EF values. Threat of Cd-related health issues will not be an issue of concern using SGV and Bn in EFs determination in the current investigations because both indicated Cd depletion. Nonetheless, the trace concentrations of Cd in soils when statistically evaluated gave a local background value of Cd as 0.02, which showed an overall enrichment of 003 (Table 4).

At least no matter how insignificant the enrichment of Cd is an awareness of bio-accumulation will be heightened to monitor concentration levels towards any chronic outcome. Any Cd-related diseases will be monitored and chances of eliminating any chronic outbreak from Cd exposures and ingestions can be controlled. As noted by Arhin and Zango trace concentrations of potentially harmful elements can bio-accumulate and reach chronic levels to impact on human health but observations from the current investigations suggest that the application of the correct baseline value is the key in monitoring the related health issues from out breaking. Similarly from Table 4 and Figure 9 there are relatively high enrichment factors in Hg for $EF_{SGV}=0.13$ and $EF_{LB}=0.16$ compared to $EF_{Bn}=0.08$. Hg can exist in three forms, which are elemental, inorganic and methylmercury. All these forms can produce adverse health effects such as the kidney and the nervous system related issues at sufficiently high concentrations. From Table 4 Hg enrichment factors increases from $Bn > SGV > LB$. However, in comparing EFs from these baseline values; the conclusion of Hg enrichment and depletion in the area may be dubious as the different baseline values returned different EF values. Rounding the EF values off; EF_{SGV} and EF_{Bn} returned approximate factor of 0.1 whereas EF_{LB} was 0.2. The enrichment factors though marginal comparing the various baseline values used but there is 100% change between EF_{SGV} , EF_{Bn} and EF_{LB} . In Developing Countries such as Ghana mercury exposure is expressly risky for the population in northern Ghana where the study was carried out as it can interfere with brain development because of the dependence on locally produced food and generally untreated water. Considering the enrichment factor of about 100% between the continental crustal averages, the legislated safe-guide values and the local background values; the LB pre-empt the necessity to monitor and manage the Hg in the environment. As reported by US Environmental Protection Agency (EPA) the mercury exposure of babies is at 75, 000 each year. This put babies with a greater risk of learning disabilities because of their mothers' exposure to mercury. It's most likely that the US Hg levels are low and did not result in chronic attacks to demand immediate attention or no local-scale Hg investigations were conducted to define the Hg pollution points. The avoidance of many babies being affected indirectly by mothers' exposure to Hg in the environment can be noticed if there are local background values established for the potentially harmful elements. Better still if local background values obtained from environmental samples in the geographical area are used instead of global legislated accepted values derived at regional-scales or continental crustal averages.

Revelation in the current study suggests that EF based on globally accepted values and local background values emphasised the appropriateness of local background values as useful in environmental health assessment for an area (Figure 10a-10c). From this figure (Figure 10a-10c), EF_{SGV} shows enrichments in As and Cu and depletion in Hg

and Se. The depleted factor in Se is just trace amount. The Cu enrichment seen in EF_{SGV} (Figure 10a) was not realized in EF_{Bn} plot (Figure 10b), it however confirmed As enrichment. Contrastingly the Se depletion is realized in EF_{Bn} as trace Se enrichment. Conversely enrichment factors in As, Cu and Zn was recognized in EF_{LB} with depletions in Cd, Hg and Se (Figure 10c). The depiction presented in EF_{LB} (Figure 10c) probably factored the variability of earth crust composition, the processes involved in natural fractionation of elements during their transfer from bedrock to the regolith, the impact of climate on physical and chemical processes during the elements transport in the oxidised environment, and the impact of biogeochemical processes in the geographical area as well as the local environmental activities.

Conclusions

The present work shows that the global baseline values (Bn, SGV, and LB) to have contrasting EFs after computation and thus exaggerate environmental policy outcomes. Typifying these are the EFs obtained in the current study whereas enrichment was 100 times more than Bn value and greater than 80 times than the SGV. A variation in enrichment of 20-folds from the two global accepted values. The LB value showed similar like the SGV. However, there was 20-fold enrichment of Zn from LB, which was not discovered from Bn and SGV for this essential element Zn. Other revelations were the downplaying attitudes of Bn for the essential elements Cu and Zn. Correspondingly Cd, carcinogen enrichment in the soils was only highlighted by LB. The study recognized the differences in EFs using the different baseline values for the trace elements to depend importantly on:

- The underlying geology, chemical and physical processes as well as the human activities.
- The calculated EFs using local background (LB) and legislated soil (SGV) values have similar enrichment/depletion factors in some EEs.
- These suggest that environmental monitoring investigation for clean-up purpose can use LB if available
- However, absent the SGV can be used for environmental health studies as well as develop environmental policies on their applications for.

The study concludes little usage and application of global and legislated values such as the continental crustal average (Bn) and safe-guide values (SGV) in the absence of local background values (LB). But recommends more large-scale surveys supported internationally to collect quality, statistically significant environmental data to estimate and document the local background value that incorporates human interference with natural biogeochemical cycles. It is then that the calculated EFs can be used appropriately to propagate the true environmental policy to clean up the environment to address the related health issues connected with the geogenic and anthropogenic processes.

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Acknowledgements

The fieldwork was partly carried out with the support of UDS-SADA-BDA collaboration to add value to the physical resource base of the savannah ecological area. Analyses of the soil samples by ICP-MS were supported by WAXI-AMIRA 934A project. A word of thanks is due to the members of International Medical Geologist Association (IMGA) Ghana Chapter for contributing in kind during the period of the research. The authors would also like to thank the numerous readers of the manuscript and their useful comments and suggestions.

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