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TOXIC ELEMENTS IN SOIL AND SEDIMENT OF THE AWE BRINEFIELD, NORTHCENTRAL NIGERIA: SOURCES, POTENTIAL ENVIRONMENTAL AND HEALTH IMPACT.

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Abstract

Soil and sediment in the Awe brinefield were studied in the light of their trace element content with the view to determining their toxicity levels. Forty samples (33 soil, 7 stream sediment) were collected and analysed from disturbed and undisturbed areas. Geochemical data were subjected to analysis using standard pollution assessment indices such as enrichment factor (EF), geo-accumulation index (Igeo), amongst others. Results showed that soil of the Awe brinefield has been polluted by elements such as Pb, Cd, As, Zn, Sr amongst others. EF indicated enrichment of As (154.10) and Zn (125.80), a similar trend was also revealed by Igeo for these elements. However, variability exists in the levels of contamination and geoaccumulation of individual trace element investigated. PLI values in most of the areas sampled indicated heavy metal pollution with PLI greater than one. The PI_{Avg} results showed the soil around Mahanga area to be of low quality with values ranging between 0.1-20.4. On the whole, Zn, As and Co portray potential risk elements, as revealed by ecological risk assessment. High concentrations of As, Pb, Zn and Sr in the soil and sediment could be due to activities of artisanal miners and partly agricultural chemicals used. Also, the contributions from the basaltic rocks around the Jangerigeri is also inferred to be another source. The high concentration or enrichment of these elements which are considered potentially toxic implies pollution.

Keywords: Awe brinefield; Trace elements; Pollution; Pollution indices; Nigeria.

Introduction

Research regarding the environmental impact of trace elements in soil and sediment continue to derive attention worldwide particularly in the last decade. This is because soil as a natural resource is utilised by both human and plants and remain a place for interaction of environmental elements (Chen *et al.*, 2003; Zhao and Tang, 2011), thus the possibility of contamination cannot be overruled. Contamination that would subsequently leads to pollution is either derive from natural sources through rocks and minerals (geogenic) or through emission, be it direct or indirect from human activities (anthropogenic) such as mining, agricultural practice, smelting (Adriano,

1986; Al *et al.*, 1997; Jordan, 2009; Navarroa *et al.*, 2008; Sallau *et al.*, 2014, 2015). Works of Lar and Tejan (2008) and Sallau *et al.*, (2014, 2015) all point to the fact that, distribution of trace elements (such as Pb, As, Cr, Se) by both natural and anthropogenic processes can result in their deficiency or toxicity in the environment and can be detrimental to plants and animals. Lead (Pb) for example is known to be toxic even at low exposure levels and has acute and chronic effects on humans (neurological, renal gastrointestinal and reproductive effects), especially children and pregnant in the tropics are the most vulnerable. Deficiency in water or soil of iodine, selenium, and zinc, in the same vein, are attributable to iodine deficiency disorders -IDDs (such as goitre), human immune-deficiency syndrome and slow or stunted growth rate respectively. In the Awe brinefield, salt mining, as well as artisanal mining of limestone, lead-zinc and other minerals, support the economy of the inhabitant aside the agricultural practice, thus resulting in the release of trace elements. These metal ions, which are not degraded, persist and are retained in the ecosystem indefinitely and may be absorbed by humans, plants and subsequently into the food chain, thereby affecting the environment. Recent studies in Nigeria have revealed that the geographical distribution and occurrence of certain diseases could be correlated to the presence of trace elements in the geologic environment (Lar and Tejan, 2008; Sallau et al., 2014). This paper is aimed at assessing the environmental risk of potentially toxic trace elements that may be contained in the soil and sediment of the Awe brinefield with a view of updating the current knowledge which will help to raise awareness among the populations at risk and to alert state authorities where necessary.

Synopsis of geology and mineralisations of the study area

The area of study (Figure 1) fall within the Middle Benue Trough of Nigeria represented by six sedimentary formations namely the Asu River Formation (oldest), Awe Formation, Keana Fomation, Ezeaku Formation, the Awgu Formation and Lafia Formation being the youngest (Sabo, 1985; Nwajide, 1990; Obaje, 1994; Sallau, 2002; Tijani and Loehnert, 2004).

1) The Asu River Formation consists of essentially olive-green to grey dark and pinkish micaceous siltstones, shales, mudstones and subordinate clays. This Formation has been reported to contain numerous fossil ammonites (Offodile and Reyment, 1976) and all the fossils records confirm the Middle Albian age for the formation. The environment of deposition of the Asu River during the Albian is associated with the first influx of the sea following the rifting of the Benue Trough. Limestone deposit is reported to have been mined from this formation particularly around Jangerigeri.
2) The Awe Formation (Offodile and Reyment, 1976) also refer to as "passage beds" (Falconer, 1911; Nwajide, 1990; Obaje, 1994)

consist of flaggy, whitish, medium to coarse grained sometimes calcareous sandstones, interbedded with carbonaceous shales or clays from which brines issue out. Towards the base, the sandstones become finer – grained and successively more micaceous and sometimes finely current – bedded (Petters, 1982; Obaje, 1994). The Formation by its stratigraphic position appears to have been deposited towards the end of the Albian marine episode to the early Cenomanian, in a transitional environment between the predominantly marine and fluviatile conditions. The brines deposit in this basin mostly emanate from the Awe Formation (Akiri brines springs, Awe brines and the Keana brines).

3) The Keana Formation can be traced down southwards into the Makurdi Formation (thought to be its lateral equivalent). The Bima Sandstones, Keana and Makurdi Formations are, therefore, possibly part of the same lithologic unit which appears to get progressively younger in age from the northeast to the southeast. The sandstones are typically massive, heavily current-bedded, fine to very coarse, sometimes conglomeratic, at times indurated, gritty and arkosic. This Formation flanks both sides of the Keana anticline and its massive outcrops occurs at various localities including Keana, Noko, Chiata, Chikinye, Daudo, Jangerigeri and Azara areas. The Keana Formation is more or less barren in terms of their fossil content as opposed to the Awe Formation riddled with worm tracks and burrows in the basal parts. The Keana Formation is thought to be the southern extension of the Bima Delta which apparently moved down with the retreating Albian Sea. The formation is thought to be totally Cenomanian in age and is deposited under continental conditions (Sabo, 1985; Petters, 1982; Obaje, 1994). The formation is notable for its lead-zinc and associated mineralization.

4) The Ezeaku Formation is described as a sequence of hard, dark, grey to black, flaggy calcareous shales, siltstones and sandstones, seen in the streams south of the Okigwe – Afikpo road. The rock is seen to be highly fossiliferous with abundant fauna consisting essentially of ostracods and foraminiferas (Offodile, 1976a). Sallau (2002) also confirmed some undifferentiated bivalves (pelecypods) and gastropods on the outcrops of the Ezeaku Formation southeast of Keana and 2km north of Keana. The environment of deposition of the Ezeaku Formation is related to the trangressive movement of the sea during the Late Cenomanian, appears to have been deposited in a shallow, marine coastal environment during a period of

low input of terrigeneous material due to low run-off (Offidole, 1976b). This formation host the barite mineralization predominantly found as veins traversing the sandstones series in the northwest/southeast direction.

5) The Awgu Formation to consist essentially of black shales and limestones with local seams of coal (coking type), around Obi – Agwatashi up to Jangwa area (northwest of the study area). Sabo (1985) and Sallau (2002) described the Awgu Formation to be deposits consisting of shales, clay-shales and shelly limestone. The Awgu Formation was deposited during the widespread Coniacian transgression, and the sea was generally shallow. A very low gradient paleoslope existed as a result of quiet folding episode in The Santonian and only low energy sediments were deposited. Also, extensive shallow marine shelves developed along the Benue Valley linking up with the Saharan sea and half passed laterally into swampy environments in which the coals were formed (Offodile, 1976b).
6) The Lafia Formation is the youngest lithological unit in the Middle Benue stratigraphy. In the light of its lithologic description, opinions varied. Lithologically, the formation consists essentially of continental ferruginised sandstones, red, loose sands, with some flaggy mudstones and clays within the vicinity of Lafia town up to areas around Doma to the West, Assakio to the East, Shabu to the North and Agyaragu to the South. Identifiable fossils have not yet been obtained from the formation. Exposures of this formation can also be seen to overlie the Awgu shales around the area west of Obi towards Giza area (Sallau, 2002). It is believed to have been deposited under continental conditions created by the diversion of the Trans – Saharan sea way. This is probably a syndepositional feature arising from the strong oxidizing tendency that seems to have existed in the continental conditions that prevailed.

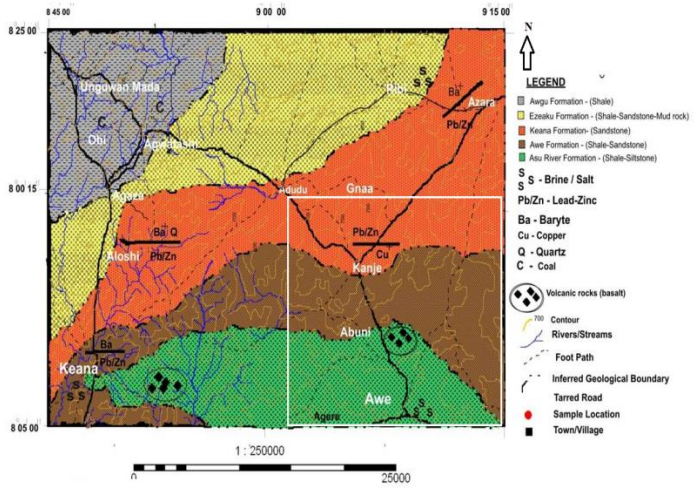

Figure 1: Geological map of Awe brinefield (white rectangle) within the broader Keana-Awe-Obi Coal and brinefields (modifield from Sallau *et al.,* 2014**).**

Methodology

Sampling and analytical methods

Two major media namely soil and sediment were sampled with a total of 40 samples collected (33 soil, 7 stream

sediments). Samples were collected from mining areas, cultivated and uncultivated farmlands. The soil and stream sediment samples were collected in clean, zipped and sterilized sample bags, well labelled according to the location, date of collection for easy referencing. Adequate precautionary measures were taken during the collection, packing, transportation and storage. The soil samples were collected in the N-E and S-W directions while the stream sediment samples were randomly collected. In the geochemical laboratory, the soil and stream sediment samples were pulverized and made to pass through a 0.067mm mesh size, after which a 100 mg of the now powdered soil sample was weighed into a Teflon crucible and then dissolved in aqua regia after 6 hours of heating the solution to dryness on a hot plate (250ºC). The crucible containing the sample is then allowed to cool. Two (2) ml of 2 M HCl is added and then topped with de-ionized water to about ¾ full. It is re-heated on the hot plate and again allowed to cool. The content is diluted to 100 ml and filtered using size 42, 125 mm diameter, ashless filter paper into a flat bottom flask ready to be run on the analytical equipment. The instrument was calibrated prior to the introduction of the sample by measuring in-house standards and blank solutions, the results turn-out have an accuracy range of ± 2–5 % depending on the number of standards and concentrations used. All the samples were analysed using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at the Geology Department of the University of Jos. This technique was chosen because of its numerous advantages in multi-media tolerance, multi-element and low detection limits, its precision and accuracy, among others. A total of 26 elements were analysed but elements of discussion include I, Mo, Zn, As, Pb, Co, Cr, Cu, Ba, Ni, Sr, and Sc.

Data presentation and analysis

To assess the environmental risk or vulnerability of the local populace and ecosystem within the study area, pollution indices were employed. Single pollution indices which are indicators used to calculate only one metal contamination; such as the index of enrichment factor (EF), geo-accumulation index (Igeo), and contamination factor (Cf), as well as the use of potential ecological risk factor (Er) were employed. Also, integrated indices which are indicators used to calculate more than one metal contamination, although based on the single indices were also used in this study. This include sum of pollution index (degree of contamination (Cd) and ecological risk index (RI)), pollution load index (PLI) as well as average pollution index PI_{Avg}. Pollution index in this study became necessary as it has proven to be a powerful tool for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and the public (Caeiro *et al.*, 2005; Gong Qingjie *et al.*, 2008).

Enrichment factor (EF)

An element enrichment factor (*EF*) was initially developed to speculate on the origin of elements in the atmosphere, precipitation, or seawater (Duce *et al.*, 1975; Zoller *et al.*, 1974), but it was progressively extended to the study of

soils, lake sediments, peat, tailings, and other environmental materials (Reimann and de Caritat, 2005). Application of EF in pollution study is to evaluate among others the level of soil contamination and the possible natural or anthropogenic input and impact on soils and sediments. This helps to identify anomalous metal contamination and geochemical normalization of the heavy metal to an immobile element such as Al, Fe, Sc and Si. EF is usually used to compare with and also to verify/certify the geo-accumulation status of geologic materials such as soil. In this assessment, aluminum (Al) was used as the immobile element to differentiate between natural and anthropogenic components and is associated with crustal rocks. Metal to aluminium ratios is widely adopted, presumably because the concentration of Al in weathering products and their parent material are generally comparable. Al is also the normalizing element assumed not to be consequentially enriched owing to local contamination, Sutherland (2000). Baseline values were adopted from Kabata-Pendias and Sadurski (2004). The formula to calculate EF is given below;

$$EF= [(M/A1)s/(M/A1)b]$$

Where EF is the enrichment factor, M_s and M_b are the concentrations of the investigated elements in the sample and crustal materials (background) while Al_s and Al_b are the concentrations of Al in the sample and crustal abundance respectively. According to Zhang and Liu, (2002), EF values lower than and around 1.0 indicates the element in the sediment originated predominantly from the crustal/background material and /or weathering process. EF values greater than 1.0 displays anthropogenic origin of the element. According to Chen *et al,* (2001);

EF = < 3 indicates minor or minimal enrichment (anthropogenic impact),
EF = 3-5 indicates moderate enrichment,
EF = 5-10 indicates moderately severe enrichment,
EF = 10-25 indicates severe enrichment,
EF = 25-50 indicates very severe enrichment,
EF > 50 indicates extreme severe enrichment.

Geo-Accumulation Index (Igeo)

The geo-accumulation index has found application in the determination and defining metal contamination in sediments and was introduced by Müller (1969). Subsequently, workers in the field of environmental pollution assessment applied this pollution index. This index allows evaluation of contamination levels by comparing present concentrations with background levels. The Igeo is expressed as;

$$Igeo=\log2[(Cn/1.5Bn)]$$

Where C is the measured concentration of the given heavy metal examined in the soil or sediment, B is the geochemical background value of the element, 1.5 is incorporated in the relationship to account for possible variation in background data (the background matrix correction factor) owing to lithogenic effects, according to Loska *et al*., (1997).

The geo-accumulation index (Igeo) was distinguished into seven classes by Müller

(Buccolieri *et al.,* 2006; Sallau 2014) based on the increasing numerical value of the index and ranges from unpolluted to extremely polluted. The standard Igeo classification is presented in Table 1.

Table 1: Classification of index of Geo-accumulation (Igeo)

Igeo Value	Grade	Classification
≤0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly polluted to extremely polluted
>6	6	Extremely polluted

Contamination factor (CF), Degree of contamination (C_d) and Pollution load index (PLI)

Pollution Load Index (PLI) and Contamination Factor (CF) have been used in this study, to measure the contamination levels of heavy metals in soils and sediments. PLI is obtained by calculating the n-root from the total contamination factors (CF) of the different trace elements, while CF itself is the quotient obtained by dividing the concentration of the elements. The pollution load index and contamination factor are expressed as by the following equations (Tomlinson *et al.,* (1980),

$CF = C_{metal} / C_{background\ value}$

$PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \ldots \times CFn}$

Where;

CF = contamination factor

n = number of metals

C_{metal} = metal concentration in polluted sediments

$C_{background}$ =background value of the metal

According to the equation, PLI value of > 1 is polluted whereas PLI value of < 1 indicates no pollution.

Contamination factor and level of contamination advanced initially by Hakanson (1980) and modified by several other workers, universally used, is shown in the table 2. Also, the degree of contamination (Cd) is obtained by summing all the CFs within a given basin.

$\mathbf{C_d}=CF_1 + CF_2 + CF_3 \ldots\ldots CFn.$

Terminologies used in their description is contained in table 3 (Caeiro *et al.,* 2005; Pekey *et al.,* 2004).

Where **Cd** is the degree of contamination, **n** is the count of the heavy metal species investigated.

Table 2: Classification of Contamination factor and level of contamination

Contamination Factor	Level of Contamination
Cf < 1	Low contamination
1 ≤ Cf < 3	Moderate contamination
3 ≥ Cf < 6	Considerable contamination
Cf > 6	Very high contamination

Table 3: Classification of Degree of Contamination

Degree of Contamination	Level of Contamination
Cd < n	Low degree of contamination
n ≤ Cd < 2n	Moderate degree of contamination
2n ≥ Cd < 4n	Considerable degree of contamination
Cd > 4n	Very high degree of contamination

In this study, for the purpose of calculating the PLI which is a function of all the CFs measured for the elements, the established worldwide average concentration of elements in soils, adopted after Kabata-Pendias and Krakowiak, (1998) and Kabata-Pendias and Pendias, (2001) were used for the analysis. Mean values for the elements used here include iodine = 2.4; Mo = 1.8; Zn = 62; As = 4.7; Pb = 25; Co = 6.9; Cr = 42; Ba = 362; Ni = 18; Sr = 147 and Sc = 9.5.

Potential ecological risk assessment

The potential ecological hazard index takes into consideration not only the effects of a single trace element in a particular environment but also the compound influence of many trace elements. This index as suggested by Hakanson (1980) uses quantitative methods to parse the degree of potential ecological hazard degree and is widely used in pollution assessments of trace elements in soils and sediments. The potential ecological risk index (RI) is obtained as a product of concentration factor (CF) and toxic response coefficients (Tr), (RI= CF*Tr,).

This is assess using the following four steps (Hakanson, 1980):

1. The contamination factor of a single trace element, or Cr, $Cr=C_{surface}/C_{ref}$

Where $C_{surface}$ is the measured concentration of trace elements in the soil (or sediment); and C_{ref} is the reference value.

2. The toxic response factor of trace elements, Tr is used to reflect the response of trace elements in water, sedimentary and biological phases. The toxic response coefficients are Be=Ba=Zn=1<V=Cr=2<Cu=Ni=Co=Pb=5 <As=10<Cd=30<Hg=40 (Xu *et al.,* 2008; Xu *et al.,* 2008a).

3. The potential ecological risk index, Er can then be calculated for each trace element: Er= Tr x Cr

Terminologies used in describing the risk factor are contained in table 4.

4. The potential ecological risk index of various trace elements or RI can be divided in to five levels (table 5) such that the potential ecological harm is;

$RI=\sum_{i=1}^{n} Er^{i}$

Results and Discussion

Trace elements concentrations in the two media investigated (soil and sediment) are presented in Table 6 and figure 2.

Table 4: Classification of Ecological Risk factor

Risk Factor	Ecological Risk
Er<40	Low potential ecological risk
80≤Er<160	Considerable potential ecological risk
160≤Er<320	High potential ecological risk
Er≥320	Very high ecological risk.

Table 5: Classification of Ecological Risk index

Risk Index	Ecological Risk
***RI*<150**	Low ecological risk
150□*RI*<300	Moderate ecological risk
300□*RI*<600	Considerable ecological risk
***RI*>600**	Very high ecological risk

Tables 7, 8 and 9 represent the EF, Igeo, and CF/Cd/ PLI of soil. A summary of the interpretation of the pollution indices (EF, Igeo, CF/PLI) of the two sample media is presented in Tables 10, 11, 12, 13 and 14.

Among the selected trace elements in the Awe brinefield, I, Zn, As, Pb, Co, Cr, and Ni show concentrations above background levels. The mean concentrations of I (562.71 ppm), Zn (1013.87 ppm), Ba (246.90 ppm) and Sr (112.50 ppm) are higher than the mean concentrations in another trace element. The maximum concentration of Zn, Pb, Co, Cr, Cu, Ba, Ni, Sr, and Sc was recorded in the southwestern Awe towards Jangerigeri area. Arsenic (As) on the other hand is more concentrated around northeastern part of Awe towards Azara. Iodine (I) has maximum concentration around Mahanga axis. Within the list of selected trace elements in the Awe brinefield, Zn and Sc manifested almost comparable mean and median concentrations and exhibited the highest and lowest mean-median values respectively when compared. Other trace elements showed that median values were less than their mean concentrations except in the case of As. There is a wide variation of trace element contents in the study area as shown in the large standard deviations (SD) values found in all elements (Table 6), also, all the trace elements are positively skewed toward low values, largely greater than zero, an indication that their median concentrations were lower than their mean concentrations.

Enrichment Factor (EF) of trace elements in the Awe Brinefield

The Awe brinefield is highly enriched in arsenic (As) and zinc (Zn) having an average EF of 154.1 and 125.8 respectively (Figure 3). Arsenic showed an extreme enrichment for most sample locations and Zn only severe in a few (15%) locations. Strontium (Sr) and molybdenum (Mo) with EF of 60 and 20 respectively while Pb, Cu, Co, Cr, Ni, displayed EF values of 14.80, 10.00, 9.20, and 6.60 respectively (Table 10).

Table 6: Trace elements concentrations (ppm) in the Awe brinefield

Sample #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr	Sc
103	0.00	0.00	2480.00	0.00	152.60	72.83	114.20	48.89	2343.00	124.70	267.90	0.00
104	0.00	0.00	303.50	0.00	51.07	37.42	190.30	42.10	489.20	64.88	106.30	2.83
105	0.00	10.26	504.90	132.80	36.44	6.81	7.30	6.70	93.50	17.66	117.40	0.18
106	0.00	0.00	465.30	18.64	17.93	10.20	68.96	8.29	79.40	7.32	23.70	2.62
108	0.00	0.00	1739.00	88.27	56.67	5.39	61.06	31.12	181.80	19.81	251.50	0.00
110	0.00	0.00	390.00	29.35	16.67	1.79	72.93	6.73	57.20	6.47	20.04	1.17
114	0.00	0.00	1536.00	47.66	70.63	9.90	60.81	28.30	214.10	13.37	199.00	0.30
117	0.00	0.33	583.30	65.21	24.59	4.12	32.65	6.31	66.61	5.87	20.55	0.68
118	0.00	5.35	1427.00	101.10	56.22	3.85	64.47	33.67	103.30	15.19	221.90	0.57
119	0.00	0.00	1123.00	83.92	23.83	3.29	83.40	7.28	27.38	4.15	67.72	1.59
120	0.00	0.00	1123.00	83.92	23.83	3.29	83.40	7.28	27.38	4.15	67.72	1.59
121	0.00	0.00	1056.00	71.39	71.30	2.75	169.20	30.97	85.76	15.81	198.30	0.00

Table 8 Continuation

Sample	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr	Sc
124	0.00	6.03	866.50	76.58	25.18	4.30	29.83	6.88	58.76	6.03	64.70	1.72
125	0.00	0.00	972.30	89.17	77.07	8.14	73.85	37.60	157.50	13.95	258.40	1.05
126	0.00	0.00	804.50	59.64	31.58	6.64	50.07	9.09	82.57	8.38	24.83	2.63
129	0.00	8.36	1348.00	77.77	22.71	2.82	19.78	9.45	81.13	4.99	80.49	1.64
131	3282.00	0.00	1310.00	30.82	57.30	29.76	66.94	23.16	335.90	22.82	102.70	4.77
132	962.20	0.00	255.20	0.00	12.76	21.60	90.73	19.00	135.00	26.60	29.95	7.52
134	7010.00	0.00	1679.00	34.24	36.58	15.71	74.31	34.51	201.40	31.21	99.51	7.59
Mean	562.71	1.52	1013.87	54.52	44.19	12.87	74.03	20.61	246.90	21.22	112.50	2.31
Median	0.00	0.00	1014.15	62.43	34.01	6.73	67.95	16.95	98.40	13.66	90.00	1.59
STDV	1693.71	3.197	587.69	38.831	32.588	17.037	44.039	14.098	505.65	28.035	87.619	2.568
Skewness	3.43197	1.937	0.67167	0.0084	2.0681	2.6889	1.2808	0.5113	4.141	3.0809	0.6682	1.347

Table 7: Enrichment Factor of Trace Elements in Soil of the Awe brinefield

Sample #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr
102	0.00	0.00	6.20	0.00	0.93	1.23	1.96	1.32	0.40	0.76	1.88
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
104	0.00	0.00	16.41	0.00	6.85	18.18	15.19	10.08	4.53	12.08	19.80
105	0.00	304.21	434.63	1508.01	77.79	52.68	9.28	25.56	13.78	52.36	348.10
106	0.00	0.00	27.17	14.36	2.60	5.35	5.94	2.14	0.79	1.47	4.77
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110	0.00	0.00	50.99	50.62	5.40	2.11	14.08	3.90	1.28	2.91	9.02
114	0.00	0.00	776.75	317.93	88.58	44.99	45.39	63.38	18.54	23.29	346.63
117	0.00	2.56	131.44	193.83	13.74	8.34	10.86	6.29	2.57	4.55	15.95
118	0.00	49.45	382.93	357.88	37.41	9.27	25.54	40.01	4.75	14.04	205.10
119	0.00	0.00	107.95	106.42	5.68	2.84	11.83	3.10	0.45	1.37	22.42
120	0.00	0.00	107.95	106.42	5.68	2.84	11.83	3.10	0.45	1.37	22.42
121	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
124	0.00	18.52	77.19	89.99	5.56	3.44	3.92	2.71	0.90	1.85	19.85
125	0.00	0.00	142.43	172.31	28.00	10.72	15.97	24.39	3.95	7.04	130.38
126	0.00	0.00	46.94	45.91	4.57	3.48	4.31	2.35	0.83	1.69	4.99
129	0.00	26.96	126.25	96.08	5.27	2.37	2.73	3.92	1.30	1.61	25.97
131	2722.39	0.00	42.06	13.05	4.56	8.59	3.17	3.29	1.85	2.52	11.36
132	506.61	0.00	5.20	0.00	0.64	3.96	2.73	1.71	0.47	1.87	2.10
134	3658.26	0.00	33.92	9.12	1.83	2.85	2.22	3.09	0.70	2.17	6.92

Stat**istical Parameters**

Parameters	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr
Minimum	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maximum	3658.3	304.2	776.7	1508.0	88.6	52.7	45.4	63.4	18.5	52.4	348.1
Mean	344.4	20.1	125.8	154.1	14.8	9.2	9.3	10.0	2.9	6.6	59.9
Standard Deviation	991.5	68.1	193.8	335.7	25.3	14.3	10.8	16.4	4.8	12.3	110.4
Median	0.0	0.0	49.0	48.3	5.3	3.5	5.1	3.1	0.9	1.9	13.7

This thus indicates severe to moderate enrichment. Ba with EF of 2.90 is minimally enriched in the soils of the Awe brinefield. Like the Keana brinefield, EF levels for Zn and As as reported by Sallau *et al.*, (2014) were similar as in Awe brinefield probably due to the same type and intensity of geological and geochemicalsimilarities,like mineralization and weathering activities.

Arsenic EF, was, however higher in Awe soil than in soil of Keana brinefield which itself, in turn, had higher EF trends for Pb, Co, Cr, Cu, Ni and Ba. The Awe soil is extremely enriched in arsenic and zinc, with minimal to moderate enrichment in the other trace metals. Table 10 and figure 3 show the summary of the EF values of soil from the Awe brinefield.

Index of Geo-accumulation (Igeo) of trace elements in the Awe Brinefield

Zinc (Zn) and Arsenic (As) are strongly polluted to moderately polluted with Igeo class values of 4 and 3 respectively according to Muller Igeo classification scheme (table 11 and figure 4). Other trace elements investigated showed Igeo class value of 1, indicating unpolluted to moderately polluted. Ultimately, it can be said that only three chemical elements (I, Zn and As) play the role of pollutants when considering in terms of geo-accumulation. Contamination factor in Awe (table 12) more or less follow a similar trend as reported in the Keana brinefield by Sallu *et al.*, (2014) where iodine displayed >6 CF.

Table 8: Index Of Geo-accumulation Of Trace Elements In Soil Of Awe Brinelfield

Sample #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr	Sc
102	0.0	0.0	1.0	0.0	0.2	0.2	0.3	0.2	0.1	0.1	0.0	0.2
103	0.0	0.0	8.0	0.0	1.2	2.1	0.5	0.7	1.3	1.4	0.4	0.0
104	0.0	0.0	1.0	0.0	0.4	1.1	0.9	0.6	0.3	0.7	0.1	0.1
105	0.0	1.1	1.6	5.7	0.3	0.2	0.0	0.1	0.1	0.2	0.2	0.0
106	0.0	0.0	1.5	0.8	0.1	0.3	0.3	0.1	0.0	0.1	0.0	0.1
108	0.0	0.0	5.6	3.8	0.5	0.2	0.3	0.4	0.1	0.2	0.3	0.0
110	0.0	0.0	1.3	1.3	0.1	0.1	0.3	0.1	0.0	0.1	0.0	0.0
114	0.0	0.0	5.0	2.0	0.6	0.3	0.3	0.4	0.1	0.1	0.3	0.0
117	0.0	0.0	1.9	2.8	0.2	0.1	0.2	0.1	0.0	0.1	0.0	0.0
118	0.0	0.6	4.6	4.3	0.5	0.1	0.3	0.5	0.1	0.2	0.3	0.0
119	0.0	0.0	3.6	3.6	0.2	0.1	0.4	0.1	0.0	0.0	0.1	0.0
120	0.0	0.0	3.6	3.6	0.2	0.1	0.4	0.1	0.0	0.0	0.1	0.0
121	0.0	0.0	3.4	3.0	0.6	0.1	0.8	0.4	0.0	0.2	0.3	0.0
124	0.0	0.7	2.8	3.3	0.2	0.1	0.1	0.1	0.0	0.1	0.1	0.0
125	0.0	0.0	3.1	3.8	0.6	0.2	0.4	0.5	0.1	0.2	0.4	0.0
126	0.0	0.0	2.6	2.5	0.3	0.2	0.2	0.1	0.0	0.1	0.0	0.1
129	0.0	0.9	4.4	3.3	0.2	0.1	0.1	0.1	0.0	0.1	0.1	0.0
131	274.4	0.0	4.2	1.3	0.5	0.9	0.3	0.3	0.2	0.3	0.1	0.1
132	80.5	0.0	0.8	0.0	0.1	0.6	0.4	0.3	0.1	0.3	0.0	0.2
134	586.1	0.0	5.4	1.5	0.3	0.5	0.4	0.5	0.1	0.3	0.1	0.2

With the exception of three locations, all in the Mahanga axis, north of Awe town, all other locations show zero CF values for iodine. Other elements (Mo, Zn, As, Pb, Co, Cu, Cr, Ba, Ni and Sr) also show CF of zero except for arsenic (CF=1.21) in location 105, northeast of Awe, indicating that the Awe area recorded low contamination when considering CF. The degree of contamination (Cd) in all the samples investigated shows a low degree of contamination with the exception of the Mahanga axis where there is a very high degree of contamination (114.89 and 244.77, table 9), major contributors are Pb and Zn. Pollution load index for the Awe area indicates that though the areas are polluted (with PLI mostly greater than one).

Table 9: Contamination Factor (CF), Degree of Contamination (C_d) and Pollution Load Index (PLI) Of Trace Elements in Soil of Awe Brinelfield**.**

Sample Location #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr	Sc	PLI	Cd
102	0.00	0.00	0.02	0.00	0.01	0.03	0.01	0.02	0.00	0.01	0.00	0.02	12.27	0.10
103	0.00	0.00	0.13	0.00	0.05	0.31	0.01	0.05	0.00	0.08	0.00	0.00	1.00	0.63
104	0.00	0.00	0.02	0.00	0.02	0.16	0.02	0.04	0.00	0.04	0.00	0.01	1.00	0.30
105	0.00	0.64	0.03	1.21	0.01	0.03	0.00	0.01	0.00	0.01	0.00	0.00	56.05	1.93
106	0.00	0.00	0.02	0.17	0.01	0.04	0.01	0.01	0.00	0.00	0.00	0.01	16.44	0.27
108	0.00	0.00	0.09	0.80	0.02	0.02	0.01	0.03	0.00	0.01	0.00	0.00	1.00	0.99
110	0.00	0.00	0.02	0.27	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	2.00	0.32
114	0.00	0.00	0.08	0.43	0.02	0.04	0.01	0.03	0.00	0.01	0.00	0.00	1.00	0.62
117	0.00	0.02	0.03	0.59	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	1.00	0.68
118	0.00	0.33	0.07	0.92	0.02	0.02	0.01	0.03	0.00	0.01	0.00	0.00	1.00	1.41
119	0.00	0.00	0.06	0.76	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	78.69	0.87
120	0.00	0.00	0.06	0.76	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	78.00	0.87
121	0.00	0.00	0.06	0.65	0.02	0.01	0.02	0.03	0.00	0.01	0.00	0.00	1.00	0.80
124	0.00	0.37	0.05	0.70	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	27.00	1.16
125	0.00	0.00	0.05	0.81	0.02	0.03	0.01	0.04	0.00	0.01	0.00	0.00	1.00	0.98
126	0.00	0.00	0.04	0.54	0.01	0.03	0.01	0.01	0.00	0.01	0.00	0.01	20.00	0.65
129	0.00	0.52	0.07	0.71	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	8.00	1.33
131	114.34	0.00	0.07	0.28	0.02	0.13	0.01	0.02	0.00	0.01	0.00	0.01	1.00	114.89
132	33.52	0.00	0.01	0.00	0.00	0.09	0.01	0.02	0.00	0.02	0.00	0.02	1.00	33.69
134	244.21	0.00	0.09	0.31	0.01	0.07	0.01	0.04	0.00	0.02	0.00	0.02	1.00	244.77

Statistical Parameters

Parameters	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr	Sc
Minimum	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maximum	244.2	0.6	0.1	1.2	0.0	0.3	0.0	0.1	0.0	0.1	0.0	0.0
Mean	**19.6**	**0.1**	**0.1**	**0.5**	**0.0**	**0.1**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Standard Deviation	59.0	0.2	0.0	0.4	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Median	0.0	0.0	0.1	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

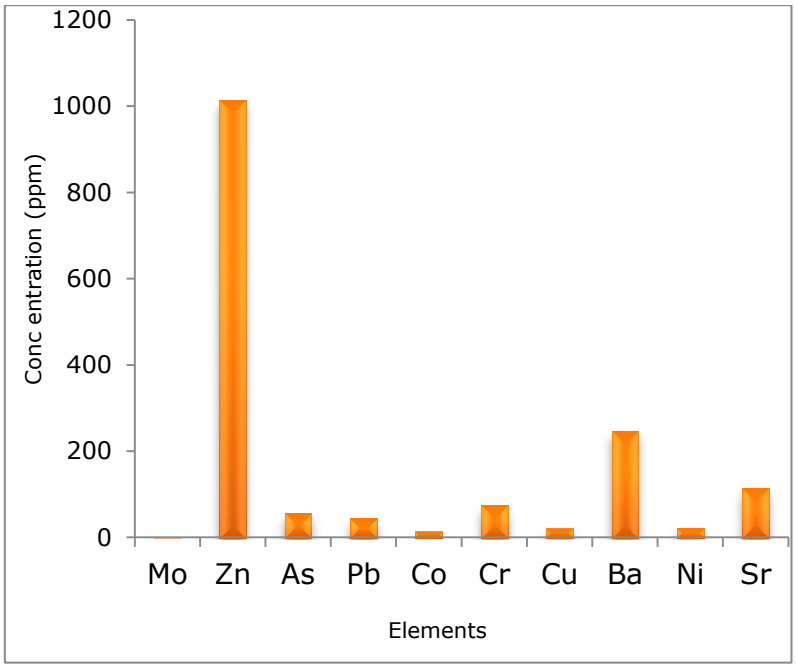

Figure 2: Mean Concentrations of Trace Elements in the Awe Brinefield

Table 10: A Summary of the EF Status of Trace Elements in the Awe brinefield

Element	EF Value	Classification
I	344.40	Extreme severe enrichment
Mo	20.10	Severe enrichment
Zn	125.80	Extreme severe enrichment
As	154.10	Extreme severe enrichment
Pb	14.80	Severe enrichment
Co	9.20	Moderate – severe enrichment
Cr	9.30	Moderate – severe enrichment
Cu	10.00	Moderate – severe enrichment
Ba	2.90	Minor or minimal enrichment
Ni	6.60	Moderate enrichment
Sr	59.90	Extreme severe enrichment

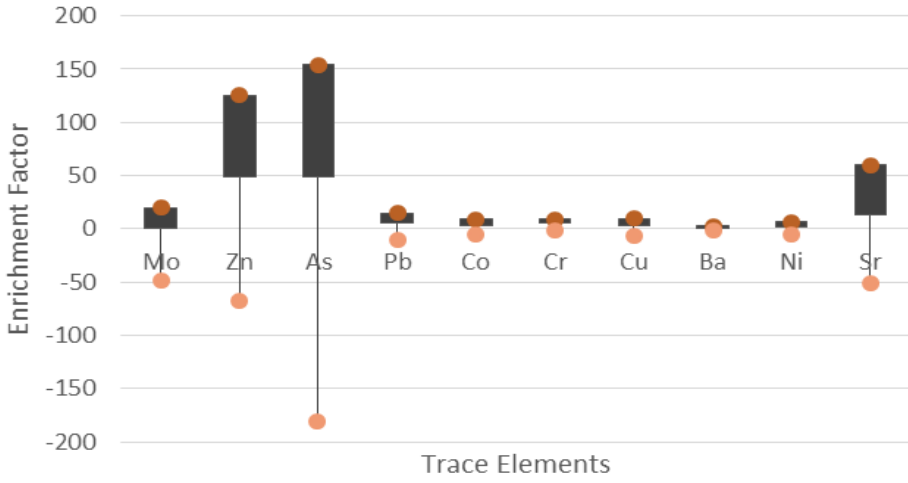

Figure 3: Enrichment Factor plots of Trace Elements in the Awe Brinefield

Table 11: Summary of I_{geo} Values of Trace Elements in the Awe Soil

Elements	**I_{geo} Value**	**Class**	**Remarks**
I	47.0	6	Extremely polluted
Mo	0.17	1	Unpolluted to moderately polluted
Zn	3.28	4	Strongly polluted
As	2.33	3	Moderately to strongly polluted
Pb	0.35	1	Unpolluted to moderately polluted
Co	0.37	1	Unpolluted to moderately polluted
Cr	0.35	1	Unpolluted to moderately polluted
Cu	0.30	1	Unpolluted to moderately polluted
Ba	0.14	1	Unpolluted to moderately polluted
Ni	0.24	1	Unpolluted to moderately polluted
Sr	0.15	1	Unpolluted to moderately polluted
Sc	0.05	1	Unpolluted to moderately polluted

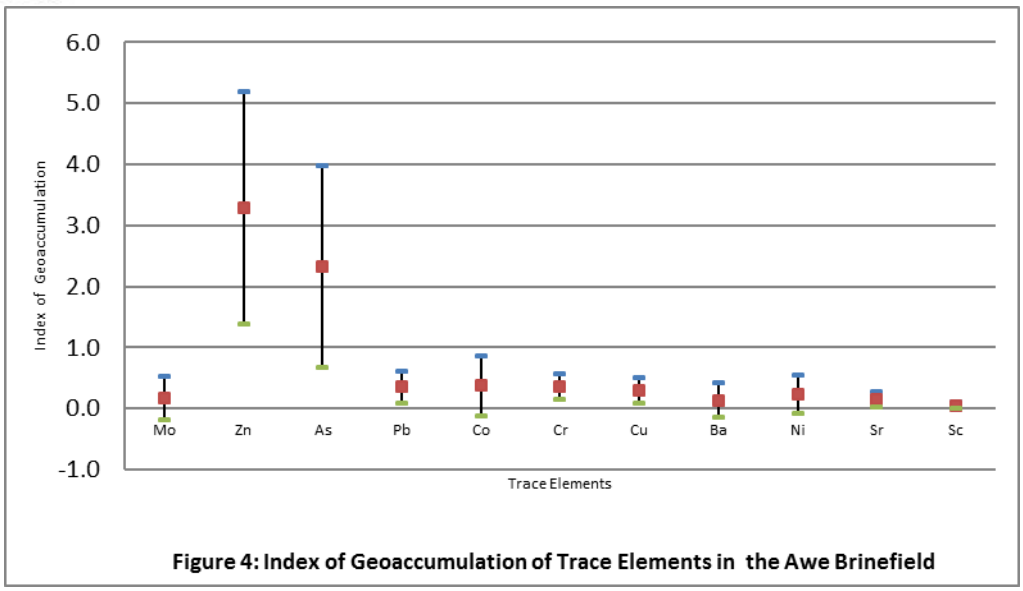

Figure 4: Index of Geoaccumulation of Trace Elements in the Awe Brinefield

Table 12: A Summary of the CF Status of Trace Elements in the Awe brinefield

Element	CF Value	CF Status
I	19.6	Very high contamination
Mo	0.1	Low contamination
Zn	0.1	Low contamination
As	0.1	Low contamination
Pb	0.0	Low contamination
Co	0.1	Low contamination
Cr	0.0	Low contamination
Cu	0.0	Low contamination
Ba	0.0	Low contamination
Ni	0.0	Low contamination
Sr	0.0	Low contamination

Table 13: Contamination factor (CF), Potential ecological factor (Er) and potential ecological index (RI) of potentially toxic trace elements in of Awe brine field.

Indices	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	RI
CF	0.1	0.5	0.0	0.1	0.0	0.0	0.0	0.0	
Tr	1	10	5	5	2	5	1	5	
Er	0.1	5	0	0.5	0	0	0	0	5.6

Table 14: integrated Pollution indices (PLI, Cd & PIavg) of the Awe brinfield

Sample #	Location	PLI	Cd	PIavg
102	Awe - Jangerigeri Road	12.27	0.1	0
103	Awe - Jangerigeri Road	1	0.63	0.05
104	1 km Awe - NE Road	1	0.3	0.03
105	2 km Awe - NE Road	56.05	1.93	0.16
106	3 km Awe - NE Road	16.44	0.27	0.02
108	5 km Awe - NE Road	1	0.99	0.08
110	6 km Awe - NE Road	2	0.32	0.03
114	9 km Awe - NE Road	1	0.62	0.05
117	3 km Awe to Kakura Road	1	0.68	0.06
118	GSS Kakura Road	1	1.41	0.12
119	5 km Awe to Kakura Road	78.69	0.87	0.07
120	6 km Awe to Kakura Road	78	0.87	0.07
121	Baure Town	1	0.8	0.07
124	1 km Awe - Mahanga Road	27	1.16	0.1
125	2 km Awe - Mahanga Road	1	0.98	0.08
126	3 km Awe - Mahanga Road	20	0.65	0.05
129	5 km Awe - Mahanga Road	8	1.33	0.11
131	7 km Awe - Mahanga Road	1	114.89	9.57
132	8 km Awe - Mahanga Road	1	33.69	2.81
134	10 km Awe - Mahanga Road	1	244.77	20.4

PI_{avg} is derived from 1/n*Cd, where n is the number of count of the heavy metal species used (12).
PI_{avg}>1 imply low quality soil because of contamination (Bhattacharya *et al*., 2006).

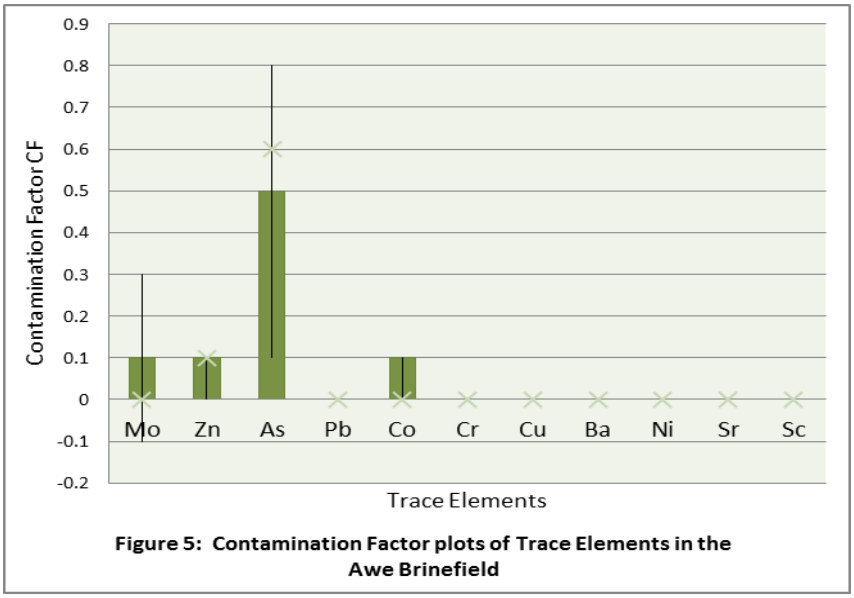

Figure 5: Contamination Factor plots of Trace Elements in the Awe Brinefield

A variability in pollution and contamination in localities exist, with greatest around Mahanga and Jangerigeri areas, and also areas northeast of Awe towards Kekura (Table 14 and Figures 5).

Potential ecological risk assessment

The potential ecological risk assessment takes into consideration not only the effects of a single trace element in a particular environment but also the compound influence of many trace elements. This is a compliment to the pollution load index and degree of contamination already used in this study. Potential ecological factor (Er) and potential ecological index (RI) values are contained in table 13. Tr used in the calculation is the toxic response coefficients of the elements investigated. Zn, As and Co are the only potential contributors in the midst of the trace elements investigated, with the greatest value coming from As (5.0). Both (Er) and (RI) values indicate only slight ecological harm when it comes to matters of trace elements pollution assessment. However, this does not in any way negate the harmful effect of individual trace element (I, As, Pb, Zn and Sr) that have their concentration above acceptable limit as can be seen from tables 6, 7, 8 and 10.

Conclusions

The soil and sediment in the Awe brinefield are polluted and also slight harmful in terms of trace elements pollution assessment. Although, variability exists in the levels of contamination and geoaccumulation of individual trace element (I, As, Pb, Zn and Sr) investigated. Values of pollution load index in most of the areas sampled indicate heavy metal pollution with PLI greater than one (Tomlinson *et al.,* 1980). The average pollution index results (Table 14) shows the soil around Mahanga area to be of low quality with average pollution index value of greater than one. Excess concentrations of As, Pb, Zn and Sr in the soil and sediment could be due to activities of artisanal miners and partly agricultural chemicals (such as fertilizers, pesticides etc) used. Also, the contributions from the basaltic rocks particularly around the Jangerigeri cannot be overruled. However, application of source indicators like principal component analysis will go a long way in revealing the true source(s) of the contaminants. The high concentration or enrichment of these elements which are considered potentially toxic implies pollution. The human and animal populations living in the mining communities are continually exposed and are vulnerable to the effects of these harmful elements, some of which are carcinogenic and even mutagenic. Considering the harmful effects of these contaminants contained in the media (soil and sediment) investigated, there is a dire need to extend the investigation to other media like water and selected biological samples such as human blood, nail, hair and selected food crops, so as to properly ascertain the level of pollution particularly how exposure to these trace metals affect human health in the area. The attention of government and health authorities is hereby called, to prepare or mitigate the imminent health risks in focus.

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