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Assessment of potentially toxic metals in soil and sediments of the Keana Brinefield in the Middle Benue Trough, Northcentral Nigeria

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Abstract: This research was conducted in the Keana area of the middle Benue trough endowed with abundant mineral deposits (brine/salt, lead-zinc sulfide ores, barite and limestone) and has a long history of mining activity. Small scale mining activity in the area is currently increasing in intensity causing immeasurable damage to the environment and to the surrounding communities. Potentially toxic metal releases and remobilization from the mining sites into the surrounding arable soils and stream sediments poses serious human health risks since the surrounding communities live and grow their food from such environment. This research assesses the accumulation and the extent of contamination of Potentially Toxic Metals (PTM) in the vicinity of the mining environment using standard pollution indices such as geo-accumulation index (I_{geo}), Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI). A total of 40 samples were analyzed for As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Sc, Sr and Zn, using ICP-OES geochemical technique. Analysis of geochemical data shows that the soil and stream sediments in the area are extremely polluted by Zn, Cr and Ni, having I_{geo} values of 4.9, 3.8 and 2.9 respectively. Igeo levels of Pb, Cr and Ba indicate moderate to no pollution. Zn and As with EF of 128.60 and 87.66 respectively, are severely enriched in the environment, while Pb, Ni and Cr with EF between 6 and 8, are moderately enriched. The calculated CF and PLI values for Cu, Sr and Sc in the soil and sediments remain very low, indicating these media are not contaminated by these elements. A pollution load index of < 1 as seen in most locations for those elements, indicate no pollution. The continued exposure of the populations living in this area particularly those in the mining locations who depend on the soil (for subsistence farming) and water from ponds, wells and boreholes (for drinking, cooking and other domestic uses), would result in various health risks and concerns, if not checked or abated. Lead, for example is known to be toxic even at very low exposure, with chronic lethal effects. This study recommends an immediate plan for analysis of the quality of drinking water and some staple crops grown in the area to determine the levels of these noxious metals and uptake by plants, to be followed by a comprehensive mitigation or remediation plan.

Keywords: Potentially Toxic Metals, Contamination, Human Health, Soils, Sediments, Benue Trough

1. Introduction

The Keana brinefield is endowed with widespread occurrences of lead-zinc, baryte, limestone, as well as the brines, in a geology dominated by continental and marine sediments represented by sandstone, shale, mudstone and limestone, and is associated with mineralized hydrothermal veins that are a consequence of the tectonic rifting that led to the emplacement of the Benue Trough. The area is characterized by a proliferation of artisanal mining activities as a result of the mineral deposits. This area is located between Longitudes 8° 45′ 00″E and 8° 15′ 25″E and Latitudes 8° 05′ 00″ N and 8° 15′ 00″ N in the southern quadrant of the Lafia topo degree sheet 231SE.

This area is an important location, known for the production of NaCl salt, used for diverse domestic and industrial purposes since the early 15th century. Also, mining

activities for the production and processing of baryte ($BaSO_4$) and lead-zinc (Pb-Zn sulphides) have also become highly ubiquitous. The mining of these mineral deposits has become the main economic and revenue earning activities of the people of the area, besides subsistence farming. Salt and brine are used for human consumption, while mine wastes, tailings, abandoned mine ponds, etc, practically releases potentially toxic trace elements into agricultural and non-agricultural soils, sediments, drinking and irrigation water, and may be absorbed by humans, plants and subsequently into the food chain, thereby affecting the environment, human and animal health.

In recent times, a lot of attention, including a global consensus, has been drawn, to the impact of human activities such as mining, on the environment, not minding the socio-economic benefits of the people and country where such mineral deposits are exploited. Some studies [14], [5] , [7] have demonstrated the negative impacts of heavy metals such as Pb, As, Cd and so on, on the environment and human health resulting from exposure through food, water and inhalation of these toxic metals. These and other studies [18], [6] have also revealed that the geographical distribution and occurrence of certain diseases could be correlated to the presence of trace elements in the geologic environment.

The justification for selecting the Keana area for this study is owing to the many years of domestic consumption of edible salt and other uses, coupled with the occurrence, mining and processing of the listed mineral deposits versus the impact of these on the environment and human health. Furthermore, the research has become necessary in view of the dearth of information (data) on trace element levels in soil, sediments and water, as the people continue to depend on these basic life support media for their survival. This paper therefore seeks to assess the distribution and contamination levels of elements such as Pb, As, Zn, Cd, Cr, Se, I, and likely impact.

1.1. The Study Area

The Benue Trough is geologically divided into the upper, middle and lower depositional sub basins, stretching from the Gombe area in the north to the Abakaliki area in the south, towards the Niger Delta. The Keana Brinefield is located in the middle and is part of a long narrow stretch of sedimentary basin, extending from the Gulf of Guinea upwards to the northeast. Stratigraphically, the area is made up of five rock units which are essentially continental and marine sediments. These include the Asu River group of sediments (sandstone-shale series) which are the oldest, the Awe formation (sandstone-shale-siltstone), the cretaceous Keana formation (sandstones), EzeAku formation (sandstone-shale-mudstone) and Awgu formation as the youngest, is entirely shale. The major structural feature in the area is the Keana anticlinorium with the Brinefield and environs located along the western limb of the anticline.

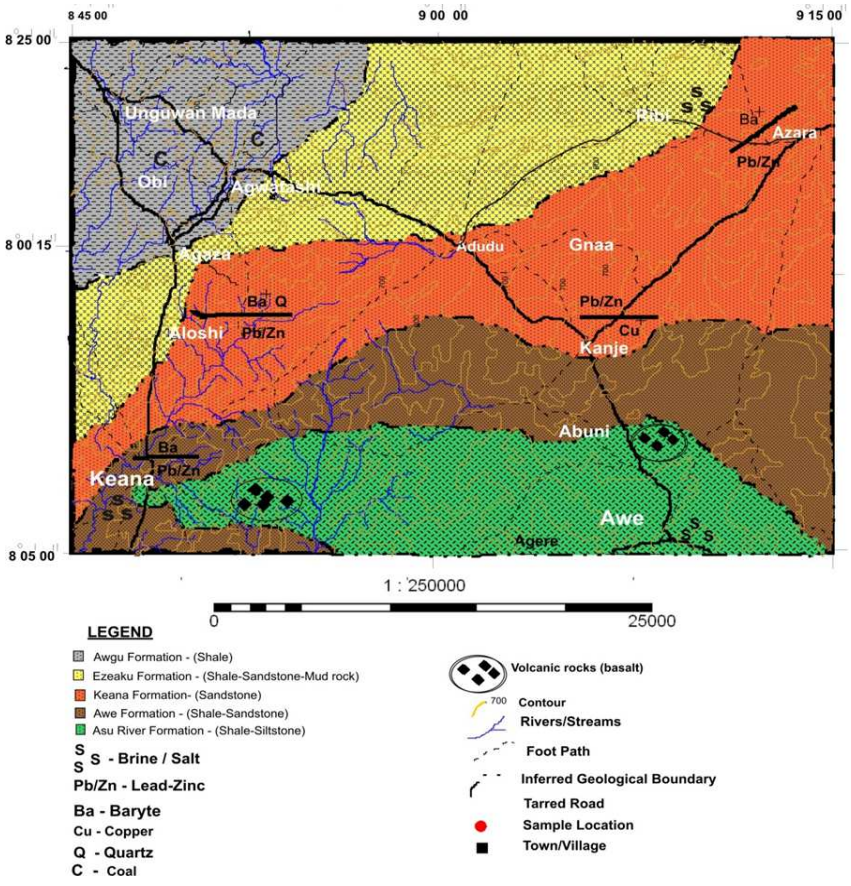

Fig 1. *Geological Map of the Keana Brinefield*

The study area is endowed with enormous occurrences of mineral deposits such as brine/salt, lead zinc, baryte and limestone. The mineral deposits are found around the axial part of the Keana anticline. Salt is mined in many locations around Keana; while baryte is mined in Aloshi, Bature, Chiata and Keana (Fig. 1). The brines are hosted by the Awe formation which is transitional between the Asu River and the Keana formations, with the brines oozing out along the east and western limbs of the Keana anticline in valleys and depressions undercutting the Awe formation. The baryte and lead-zinc minerals are found in veins and lodes, and occur with quartz and the carbonates of Mg, Fe and Ca (siderite and ankerite) with most pronounced ridges found in the area marking the mineral veins.

The mineralization (baryte, lead-zinc) is believed to be associated with mineralized hydrothermal veins that are a consequence of the tectonic rifting that led to the emplacement of the Benue Trough, connected with the stress that developed following the continental separation of Africa and the South American plates [12], [13] [1].

2. Materials and Methods

2.1. Sampling and Sample Preparations

Two major media namely soil and sediments were sampled with a total of 40 samples collected (33 soil, 7 stream sediments. Samples were collected from mining areas, cultivated and uncultivated farmlands. Sample locations are shown in Fig. 2.

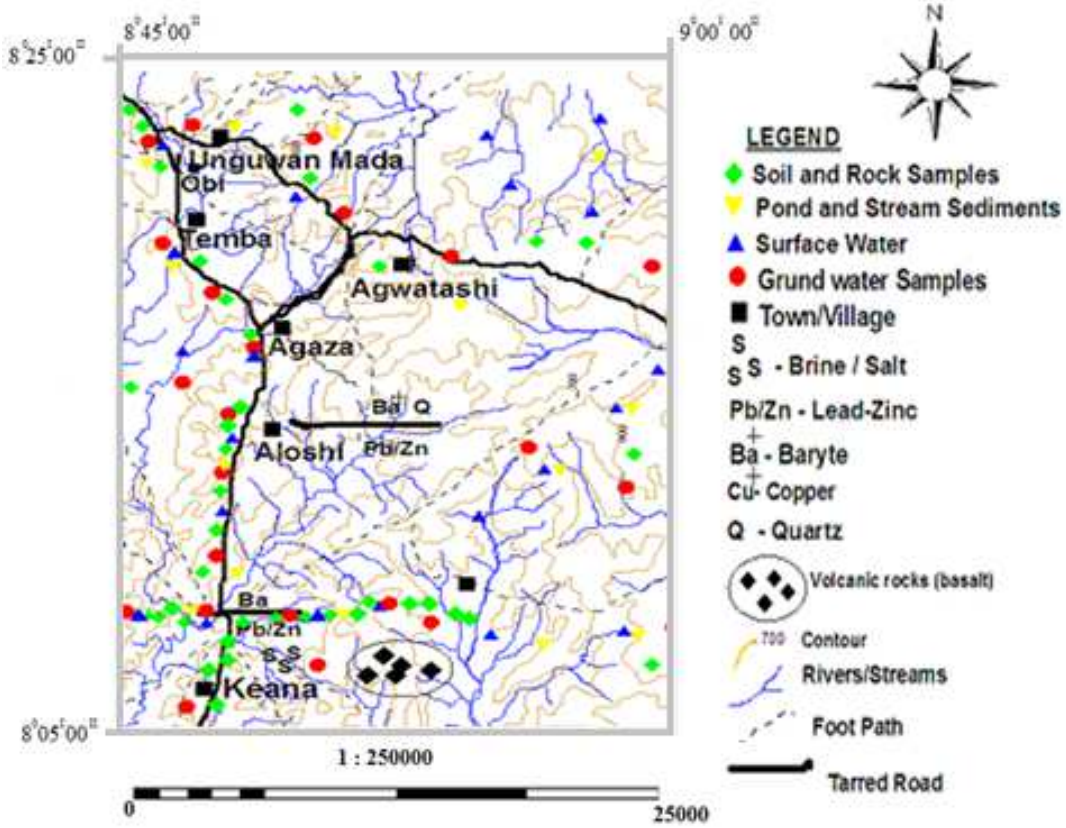

Fig 2. *Map of the Keana Brinefield Showing Sample Locations*

The soil and stream sediment samples were collected in special clean, zipped and sterilized sample bags, well labeled according to the location, date of collection for easy referencing as well as 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 but the stream sediment samples were randomly distributed and so was the sampling pattern. 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 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 analyzed 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 analyzed and include Ca, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, I, Sb, Se, Sr, Ti, V, Ba, K, Na, La, Zn, P, S and SC, with only half of these discussed.

2.2. Data Analysis

The assessment of the levels of enrichment or contamination of the trace elements in soil and sediments was carried out using standard pollution measurement indices such as the index of geo-accumulation (I_{geo}), enrichment factor (EF), contamination factor (Cf) and the pollution load index (PLI), as well as the use of Surfer^R software, to determine the spatial distribution of the elements.

2.3. Calculation of Geo-Accumulation Index (Igeo)

The geo-accumulation index is generally used to determine the anthropogenic contamination in sediments as introduced by [10], [11] and corroborated by prominent works like [3]; [8]; [9] and [19]. This index allows us to evaluate the contamination levels by comparing present concentrations with background levels. The I_{geo} is expressed using the following Muller equation:

$$I_{\text{geo}} = \log_2 \frac{Cn}{1.5Bn}$$

Where C_n is the measured concentration of the given heavy metal examined in the soil or sediment, B_n 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 [8].

The geo-accumulation index, consist of seven grades (0 to 6) based on the increasing numerical value of the index and ranges from unpolluted to extremely polluted. The standard Igeo values are presented below (Table 1).

Table 1. *Classification of Index of Geo-accumulation (Igeo).*

I_{geo} 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

2.4. Calculation of Enrichment Factor (EF)

Enrichment Factor is used to evaluate the level of soil contamination and seeks to know the possible natural or anthropogenic input and impact in soils and sediments. In this assessment, aluminum (Al) was used as the immobile element to differentiate between natural and anthropogenic components and is associated with crustal rocks. Al is also the normalizing element assumed not to be consequentially enriched owing to local contamination, [15]. Baseline values were adopted from [24].

EF of a heavy metal in sediments can be calculated using the following equation;

$$\text{EF} = \frac{\left[\frac{\text{M}}{\text{A1}}\right] \text{Sample}}{\left[\frac{\text{M}}{\text{A1}}\right] \text{Background (crust)}}$$

Where EF is the enrichment factor, M_{sample} and $M_{background}$ are the concentrations of the investigated elements in the sample and crustal materials (background) while Al_{sample} and $Al_{background}$ are the concentrations of Al in the sample and crustal abundance respectively.

According to [16], EF values lower than and around 1.0 indicates that 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 [19];

EF = < 3 indicates minor or minimal enrichment,
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 extremely severe enrichment.

As the EF values increases, the contribution of the anthropogenic origins also increases [15].

2.5. Calculation of Contamination Factor (CF) and Pollution Load Index (PLI)

Pollution Load Index (PLI) is obtained as a product of the measured contamination factors of the different trace elements, while CF itself is the quotient obtained by dividing the concentration of the elements. Generally, the PLI is calculated by obtaining the n-root from the n-Cfs measured.

The pollution load index and contamination factor are expressed, as developed by [17] by the following equation:

$CF = C_{metal} / C_{background\ value}$
$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \ldots \times CFn}$
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 [10] and modified by [11] and several other workers and universally used, is shown below (Table 2);

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

3. Results and Discussion

The concentrations of trace elements in soil and stream sediments collected and analyzed from the study area are presented in Tables 3 and 4 respectively. Tables 5, 6 and 7 represent the Igeo, EF and CF/ PLI of soil while Tables 8, 9 and 8 show the calculated Igeo, EF and CF/PLI of stream sediments in the area. A summary of the interpretation of the pollution indices (Igeo, EF, CF/PLI) of the two sample media are presented in Tables 5, 6 and 7.

From the results, zinc (Zn), barium (Ba), chromium (Cr), nickel (Ni) and iodine (I) appear to be more concentrated in both stream sediments (>1800ppm) and in the soil samples (>1000ppm) than the other trace elements. The mean concentrations of Zn, Ba, Cr and Ni in the stream sediments (in ppm) of 7427, 2253, 2174 and 1176 respectively, are higher than concentrations in soil.

Unlike Zn which display very high concentrations in virtually all locations, iodine generally occur below detection limit in 70 percent of soil samples and has maintained this trend in sediments, in most of the locations. The very high values of iodine recorded in some 30% of the samples, occur in locations around cultivated lands, connecting that, perhaps fertilizers containing iodine have been used, and or other anthropogenic sources.

The mean concentrations of strontium-Sr (150.87 ppm), cobalt-Co (129.88 ppm) lead-Pb (105.38 ppm) and copper-Cu (50.18 ppm) in stream sediments are higher than their levels in the soil, having (in ppm) 85.34, 22.41. 50.24, 27.27, for Sr, Co, Pb and Cu respectively. Arsenic (As) has maintained a narrow range of concentrations (33.95 ppm - 43.54 ppm) in both soil and sediments samples while molybdenum (Mo) remain the least concentrated in both sample media.

The mean values of Zn, Ba, Cr and Ni are higher than reported global trace elements concentrations but consistent with those of mineralized areas. This study area has widespread sulphides (lead-zinc and baryte) mineralization thus making the concentrations of elements like Zn and Ba very high and uncommon. However, the occurrence of molybdenum, for example, which ranges between 1.61 ppm to 3.11ppm in both soil and sediments, resemble its abundance in crustal or parent rocks, as does Sr.

Generally, the natural content of most elements in soils stems from parent rocks while high concentrations are related to mineralization. Abundance of these elements in sediments, especially in a sedimentary terrain such as the Keana area, is a function of clay fraction, soil organic matter (SOM) as well as other physico-chemical condition such as Eh and pH, and thus argillaceous sediments contain more (like Pb) than sands, sandstones and limestone. In mining areas, elements such as Pb may be dispersed due to the erosion and chemical weathering of tailings. The severity of these processes depends on chemical characteristics, and the minerals present in the tailings [2].

Table 3. *Trace Elements Concentrations (in ppm) in Soil of the Keana Area*

Sample Location #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr
2	555.90	0.00	1410.00	0.00	73.01	111.40	89.18	71.09	60.23	53.73	32.09
5	0.00	0.00	144.00	0.00	23.34	6.54	111.20	16.49	218.70	13.72	18.31
6	1200.00	0.00	0.00	0.00	129.60	104.00	9879	80.97	138.30	7322.00	255.90
8	0.00	0.00	851.80	49.99	26.31	4.51	40.74	14.26	146.00	7.38	18.27
9	0.00	0.00	1854.00	0.00	61.68	9.53	167.00	40.19	124.90	21.90	201.80
11	2412.00	0.00	1255.00	16.54	46.73	11.29	84.34	20.22	956.30	18.62	28.96
12	0.00	0.00	990.40	0.00	14.70	31.26	74.54	25.62	227.20	53.84	109.20
14	0.00	0.00	1998.00	71.20	66.92	10.39	233.90	35.16	36.87	155.60	237.60
15	0.00	6.54	1617.00	57.01	28.00	2.92	15.42	9.09	99.31	7.97	75.38
17	879.50	0.00	644.20	14.29	33.02	10.44	42.74	19.07	313.10	13.33	22.95
19	0.00	0.00	2590.00	75.99	63.10	8.01	126.80	20.47	44.72	15.76	229.20
20	144.80	2.21	1088.00	79.00	27.10	4.18	26.57	5.53	41.96	7.01	21.69
21	0.00	0.00	479.80	14.28	17.47	1.34	33.29	6.91	500.50	6.06	17.82
22	0.00	0.00	2732.00	213.10	121.40	6.41	50.03	37.16	64.68	14.37	213.60
23	5752.00	9.66	1592.00	123.80	36.50	3.88	23.11	10.95	2270	6.66	24.06
24	2531.00	0.00	763.80	4.70	37.49	11.04	55.54	18.65	61.83	21.95	28.77
26	0.00	1.48	1271.00	101.20	25.04	4.15	24.80	7.65	58.30	4.99	73.45
28	0.00	1.50	755.10	15.44	20.83	7.10	28.83	10.78	71.70	7.47	23.71
30	2256.00	7.85	1471.00	66.60	20.59	2.89	21.86	5.64	104.70	13.78	21.47
33	0.00	110	2281.00	101.20	64.95	4.34	45.32	31.41	76.57	12.43	270.20
34	0.00	0.00	699.20	54.29	23.49	3.16	24.84	9.20	42.19	7.56	20.07
35	2849.00	7.08	1093.00	94.19	18.57	3.75	25.48	5.03	81.39	5.04	21.60
36	0.00	0.00	623.90	30.14	23.82	2.10	28.31	6.19	101.40	6.87	20.34
38	0.00	0.00	0.00	78.42	60.50	12.10	853.50	26.25	78.51	633.20	195.90
41	6562.00	5.40	1203.00	54.27	24.61	4.84	18.84	6.97	136.10	7.45	23.30
43	0.00	0.00	436.60	13.99	27.97	10.25	58.74	13.75	60.45	11.60	23.80
44	0.00	0.00	782.60	85.49	25.25	5.42	49.08	8.55	212.20	10.94	21.78

Sample Location #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr
45	5747.00	0.00	2934.00	0.00	3.46	16.41	127.60	72.05	59.57	107.80	39.07
47	2150.00	0.00	670.10	5.91	25.14	6.06	50.31	11.08	60.10	10.34	20.02
50	2350.00	0.00	1066.00	15.94	28.98	5.93	94.68	15.17	435.10	15.96	24.12
51	0.00	0.00	0.00	0.00	224.70	164.70	282.40	85.17	1369	47.11	22.73
52	0.00	0.00	3958.00	0.00	147.70	136.10	196.10	125	155.70	112.90	422.10
53	2112.00	0.00	971.10	0.00	86.09	12.99	238.00	42.13	252.10	28.84	36.97
MC	1136.40	1.61	1218.96	43.54	50.24	22.41	400.67	27.70	262.44	266.19	85.34

MC = Mean Concentration

Table 4. *Trace Elements Concentrations (in ppm) in Stream Sediment of Keana Area*

Sample Location #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr
3	1018.00	0.00	46110	0.00	192.40	220.40	14150	86.18	509.80	12170	78.13
18	0.00	10.07	1789.00	53.29	65.57	3.95	32.40	25.59	92.86	9.57	216.70
24	1509.00	0.00	152.90	0.00	68.36	16.82	291.20	41.76	7621.00	17.17	147.40
27	0.00	0.00	1850.00	48.55	83.63	9.09	52.46	39.65	248.40	24.18	252.50
42	2394.00	0.00	676.40	0.00	90.11	195.90	90.33	44.02	1942.00	83.60	41.23
49	0.00	0.00	671.30	0.00	232.10	463.00	398.00	153.50	5250.00	111.80	270.90
94	7697.00	11.73	745.80	135.80	5.48	0.00	207.60	23.54	113.30	21.92	49.21
MC	1802.57	3.11	7427.91	33.95	105.38	129.88	2174.57	59.18	2253.91	1776.89	150.87

MC = Mean Concentration

Table 5. *Index of Geo-accumulation of Trace Elements in Soils of the Keana Brinefield*

Sample Location #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr	Sc
2	3.24	0.00	0.47	0.00	0.19	0.19	0.53	0.48	0.12	0.15	0.02	0.03
5	100.33	0.00	0.00	0.00	1.04	3.02	47.33	2.35	0.08	81.63	0.35	0.00
6	0.00	0.00	2.76	2.13	0.21	0.13	0.20	0.41	0.08	0.08	0.02	0.02
8	0.00	0.00	6.00	0.00	0.50	0.28	0.80	1.17	0.07	0.24	0.28	0.00
9	201.67	0.00	4.06	0.71	0.38	0.33	0.40	0.59	0.53	0.21	0.04	0.03
11	0.00	0.00	3.21	0.00	0.12	0.91	0.36	0.75	0.13	0.60	0.15	0.14
12	0.00	0.00	6.47	3.04	0.54	0.30	1.12	1.02	0.02	1.73	0.32	0.00
14	0.00	0.73	5.23	2.43	0.22	0.08	0.07	0.26	0.06	0.09	0.10	0.01
15	73.54	0.00	2.08	0.61	0.27	0.30	0.20	0.55	0.17	0.15	0.03	0.04
17	0.00	0.00	8.38	3.24	0.51	0.23	0.61	0.60	0.02	0.18	0.31	0.00
19	12.11	0.25	3.52	3.37	0.22	0.12	0.13	0.16	0.02	0.08	0.03	0.01
20	0.00	0.00	1.55	0.61	0.14	0.04	0.16	0.20	0.28	0.07	0.02	0.01
21	0.00	0.00	8.84	9.10	0.97	0.19	0.24	1.08	0.04	0.16	0.29	0.00
22	480.93	1.08	5.15	5.29	0.29	0.11	0.11	0.32	1.26	0.07	0.03	0.02
23	211.62	0.00	2.47	0.20	0.30	0.32	0.27	0.54	0.03	0.24	0.04	0.07
24	0.00	0.16	4.11	4.32	0.20	0.12	0.12	0.22	0.03	0.06	0.10	0.01
26	0.00	0.17	2.44	0.66	0.17	0.21	0.14	0.31	0.04	0.08	0.03	0.04
28	188.63	0.88	4.76	2.84	0.17	0.08	0.10	0.16	0.06	0.15	0.03	0.01
30	0.00	1.27	7.38	4.32	0.52	0.13	0.22	0.91	0.04	0.14	0.37	0.00
33	0.00	0.00	2.26	2.32	0.19	0.09	0.12	0.27	0.02	0.08	0.03	0.01
34	238.21	0.79	3.54	4.02	0.15	0.11	0.12	0.15	0.05	0.06	0.03	0.01
35	0.00	0.00	2.02	1.29	0.19	0.06	0.14	0.18	0.06	0.08	0.03	0.01
36	0.00	0.00	0.00	3.35	0.49	0.35	4.09	0.76	0.04	7.06	0.27	0.00
38	548.66	0.60	3.89	2.32	0.20	0.14	0.09	0.20	0.08	0.08	0.03	0.02
41	0.00	0.00	1.41	0.60	0.22	0.30	0.28	0.40	0.03	0.13	0.03	0.04
43	0.00	0.00	2.53	3.65	0.20	0.16	0.24	0.25	0.12	0.12	0.03	0.02
44	480.51	0.00	9.50	0.00	0.03	0.48	0.61	2.10	0.03	1.20	0.05	0.26
45	179.76	0.00	2.17	0.25	0.20	0.18	0.24	0.32	0.03	0.12	0.03	0.04
47	196.49	0.00	3.45	0.68	0.23	0.17	0.45	0.44	0.24	0.18	0.03	0.04
50	0.00	0.00	0.00	0.00	1.80	4.79	1.35	2.48	0.76	0.53	0.03	0.12
51	0.00	0.00	12.81	0.00	1.19	3.96	0.94	3.65	0.09	1.26	0.58	0.00
52	176.59	0.00	3.14	0.00	0.69	0.38	1.14	1.23	0.14	0.32	0.05	0.07
53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 6. *Contamination Factor (Cf) and Pollution Load Index (PLI) of Trace Elements in Soil of the Keana Brinefield*

Sample Location #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr	Sc	PLI
2	1.35	0.00	0.01	0.00	0.01	0.03	0.01	0.03	0.00	0.01	0.00	0.00	1
5	41.81	0.00	0.00	0.00	0.04	0.44	1.13	0.17	0.00	4.53	0.00	0.00	0
6	0.00	0.00	0.04	0.45	0.01	0.02	0.00	0.03	0.00	0.00	0.00	0.00	1
8	0.00	0.00	0.10	0.00	0.02	0.04	0.02	0.08	0.00	0.01	0.00	0.00	0
9	84.03	0.00	0.07	0.15	0.02	0.05	0.01	0.04	0.00	0.01	0.00	0.00	1
11	0.00	0.00	0.05	0.00	0.00	0.13	0.01	0.05	0.00	0.03	0.00	0.02	1
12	0.00	0.00	0.10	0.65	0.02	0.04	0.03	0.07	0.00	0.10	0.00	0.00	1
14	0.00	0.40	0.08	0.52	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	1
15	30.64	0.00	0.03	0.13	0.01	0.04	0.00	0.04	0.00	0.01	0.00	0.00	1
17	0.00	0.00	0.14	0.69	0.02	0.03	0.01	0.04	0.00	0.01	0.00	0.00	1
19	5.04	0.14	0.06	0.72	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	1
20	0.00	0.00	0.03	0.13	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	1 4
21	0.00	0.00	0.14	1.94	0.04	0.03	0.01	0.08	0.00	0.01	0.00	0.00	0
22	200.39	0.60	0.08	1.12	0.01	0.02	0.00	0.02	0.00	0.00	0.00	0.00	1
23	88.17	0.00	0.04	0.04	0.01	0.05	0.01	0.04	0.00	0.01	0.00	0.01	1
24	0.00	0.09	0.07	0.92	0.01	0.02	0.00	0.02	0.00	0.00	0.00	0.00	1
26	0.00	0.09	0.04	0.14	0.01	0.03	0.00	0.02	0.00	0.00	0.00	0.00	1 4
28	78.59	0.49	0.08	0.60	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0
30	0.00	0.71	0.12	0.92	0.02	0.02	0.01	0.07	0.00	0.01	0.00	0.00	1
33	0.00	0.00	0.04	0.49	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	1
34	99.25	0.44	0.06	0.86	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0
35	0.00	0.00	0.03	0.27	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	1
36	0.00	0.00	0.00	0.71	0.02	0.05	0.10	0.05	0.00	0.39	0.00	0.00	0
38	228.61	0.33	0.06	0.49	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	1
41	0.00	0.00	0.02	0.13	0.01	0.04	0.01	0.03	0.00	0.01	0.00	0.00	1
43	0.00	0.00	0.04	0.78	0.01	0.02	0.01	0.02	0.00	0.01	0.00	0.00	0
44	200.21	0.00	0.15	0.00	0.00	0.07	0.01	0.15	0.00	0.07	0.00	0.03	0
45	74.90	0.00	0.03	0.05	0.01	0.03	0.01	0.02	0.00	0.01	0.00	0.00	1
47	81.87	0.00	0.06	0.14	0.01	0.02	0.01	0.03	0.00	0.01	0.00	0.00	1
50	0.00	0.00	0.00	0.00	0.07	0.69	0.03	0.18	0.00	0.03	0.00	0.01	1
51	0.00	0.00	0.21	0.00	0.05	0.57	0.02	0.26	0.00	0.07	0.00	0.00	1
52	73.58	0.00	0.05	0.00	0.03	0.05	0.03	0.09	0.00	0.02	0.00	0.01	1
53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1

Table 7. *Enrichment Factor (EF) of Trace Elements in Soil of the Keana Area*

Sample Location #	I	Mo	Zn	As	Pb	Co	Cr	Cu	Ba	Ni	Sr
2	687.64	0.00	67.52	0.00	8.67	47.93	6.30	15.07	0.49	8.86	5.29
5	0.00	0.00	14.06	0.00	5.65	5.74	16.03	7.13	3.66	4.62	6.16
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	162.94	126.15	12.48	7.74	11.50	12.08	4.78	4.86	12.04
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	6671.91	0.00	134.38	23.36	12.41	10.86	13.33	9.59	17.54	6.87	10.68
12	0.00	0.00	22.37	0.00	0.82	6.34	2.48	2.56	0.88	4.19	8.49
14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	0.00	116.20	834.23	387.99	35.82	13.52	11.74	20.77	8.78	14.16	133.95
17	1778.92	0.00	50.44	14.76	6.41	7.34	4.94	6.61	4.20	3.59	6.19
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	844.13	17.16	245.52	235.17	15.17	8.47	8.85	5.53	1.62	5.45	16.86
21	0.00	0.00	193.47	75.96	17.47	4.86	19.82	12.34	34.56	8.42	24.75
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	28967.35	64.86	310.35	318.36	17.65	6.79	6.65	9.45	75.82	4.47	16.16
24	3135.69	0.00	36.63	2.97	4.46	4.76	3.93	3.96	0.51	3.63	4.75
26	0.00	19.70	491.79	516.55	24.03	14.43	14.17	13.11	3.86	6.65	97.89
28	0.00	4.70	68.67	18.52	4.70	5.80	3.87	4.34	1.12	2.34	7.43
30	14333.87	66.54	361.79	216.08	12.56	6.40	7.94	6.15	4.41	11.67	18.19
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	155.72	159.50	12.97	6.32	8.17	9.07	1.61	5.80	15.40
35	20806.81	68.96	309.00	351.26	13.02	9.53	10.63	6.30	3.94	4.91	21.03
36	0.00	0.00	157.23	100.20	14.89	4.75	10.53	6.91	4.38	5.97	17.66
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
41	36176.30	39.66	256.73	152.78	13.02	9.28	5.94	6.59	4.97	5.48	17.13
43	0.00	0.00	33.40	14.12	5.31	7.05	6.63	4.66	0.79	3.06	6.27
44	0.00	0.00	107.84	155.39	8.63	6.72	9.98	5.21	5.01	5.19	10.34
45	1881.60	0.00	37.18	0.00	0.11	1.87	2.39	4.04	0.13	4.71	1.71
47	5083.88	0.00	61.34	7.14	5.71	4.98	6.80	4.49	0.94	3.26	6.31
50	4787.48	0.00	84.07	16.58	5.67	4.20	11.02	5.30	5.88	4.34	6.55
51	0.00	0.00	0.00	0.00	15.41	40.92	11.53	10.43	6.48	4.49	2.17
52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53	2653.13	0.00	47.22	0.00	10.38	5.68	17.08	9.07	2.10	4.83	6.19

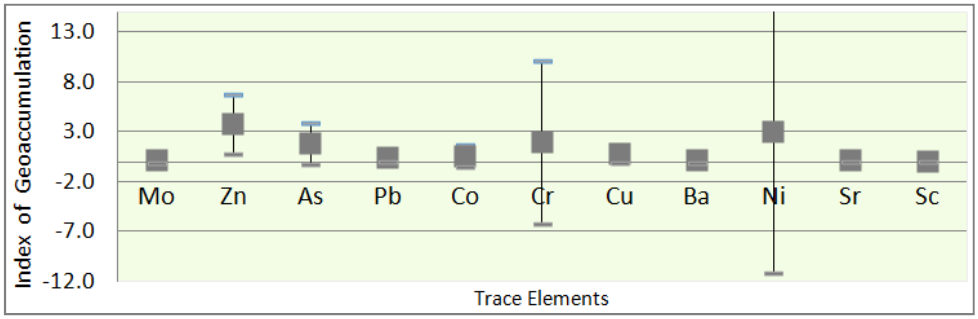

Fig 3. *Igeo of trace elements in soil of the Keana Brinefield*

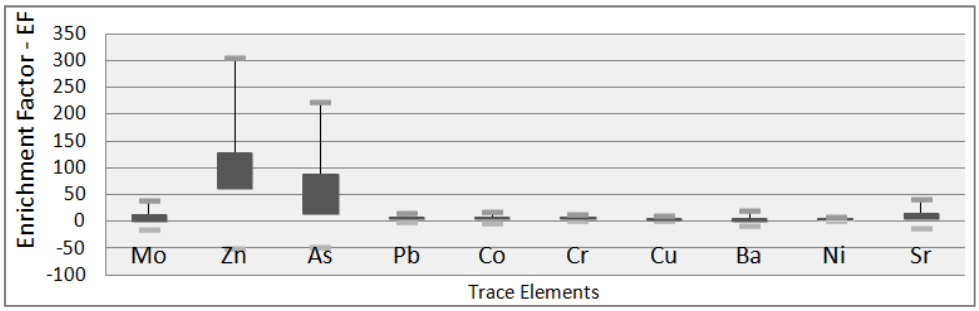

Fig 4. *EF of trace elements in soil of the Keana Brinefield*

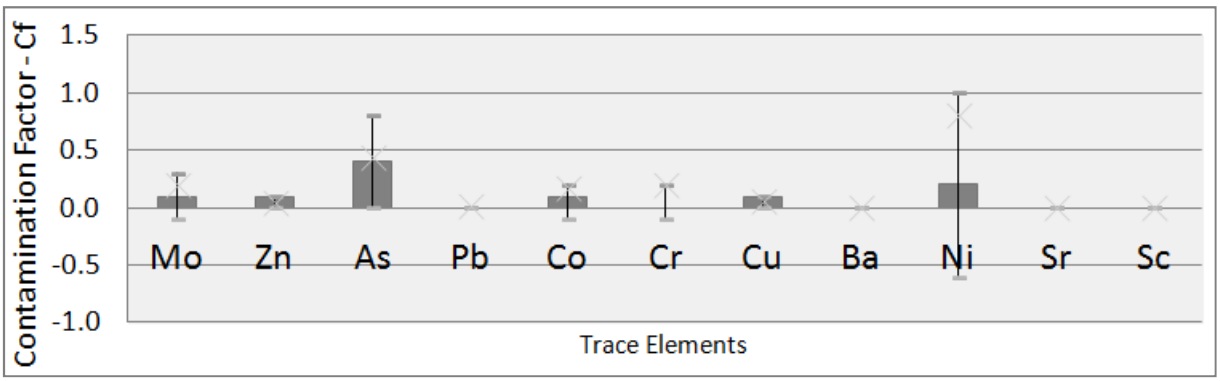

Fig 5. *Cf of trace elements in soil of the Keana Brinefield*

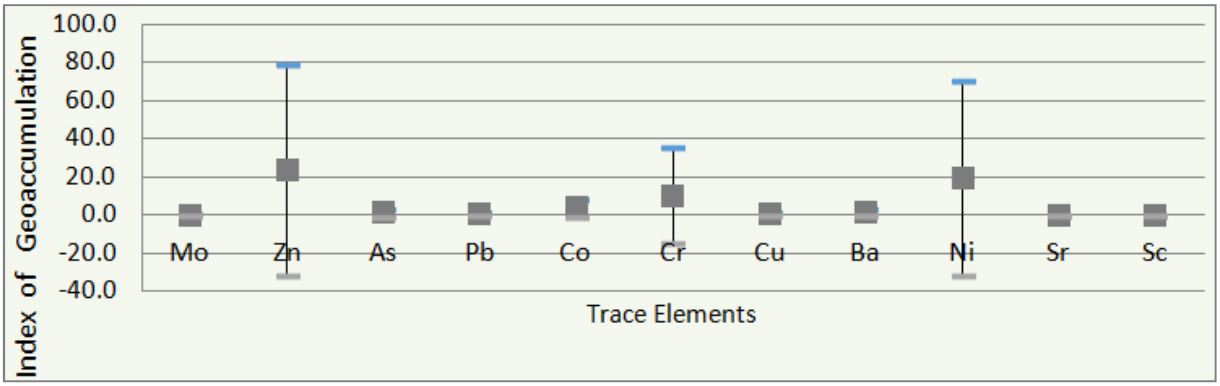

Fig 6. *Igeo of trace elements in stream sediments of the Keana brinefield*

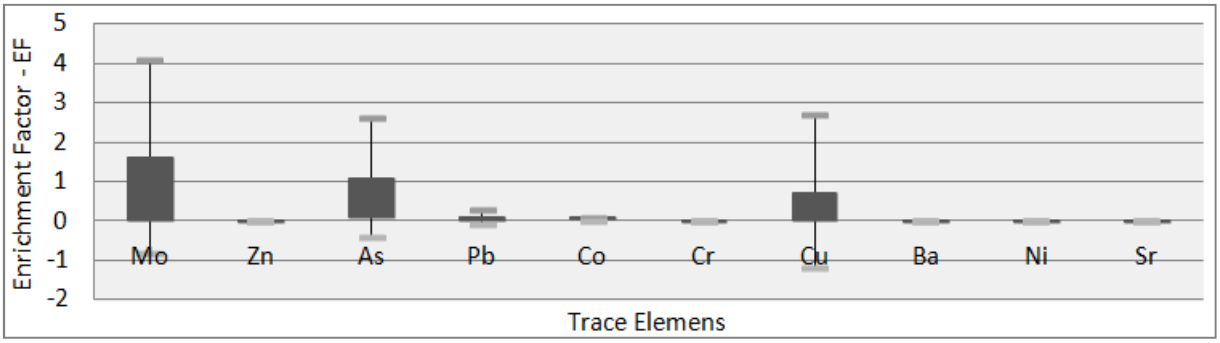

Fig 7. *EF of Trace Elements in stream sediments of the Keana brinefield*

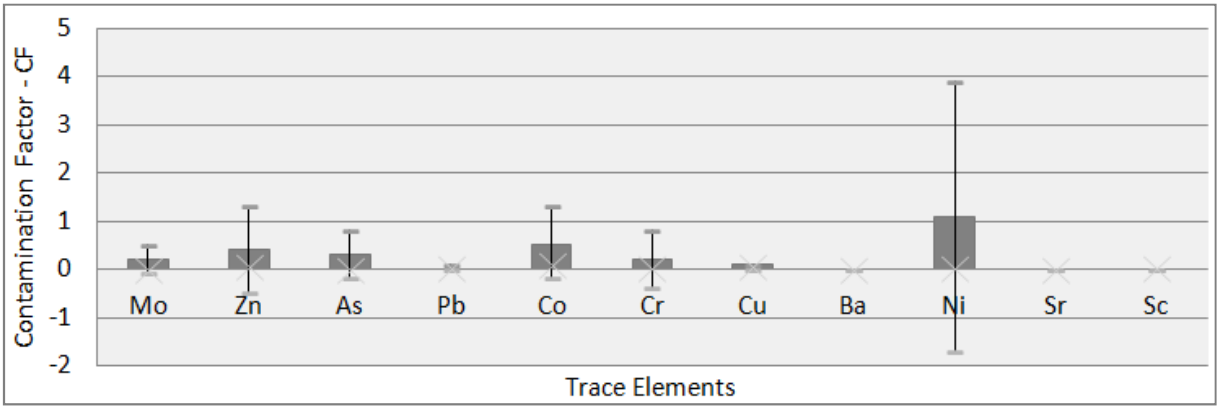

Fig 8. *CF of trace elements in stream sediments of the Keana brinefield*

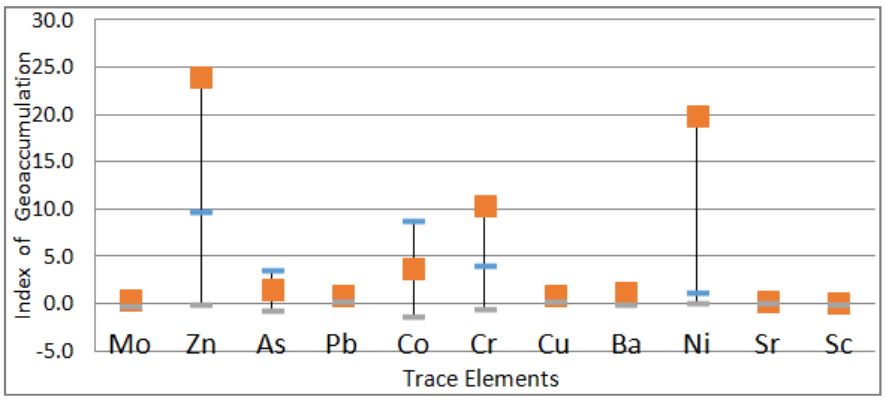

Fig 9. *Index of Geoaccumulation of elements in Stream Sediments of the Keana Brinefield*

Table 8. *Summary of I_{geo} Values of Trace Elements in the Keana Soil*

Elements	I_{geo} Value	Class	Remarks
Mo	0.18	1	Unpolluted to moderately polluted
Zn	3.81	4	Strongly polluted
As	1.86	2	Moderately polluted
Pb	0.39	1	Unpolluted to moderately polluted
Co	0.55	1	Unpolluted to moderately polluted
Cr	1.91	2	Moderately polluted
Cu	0.74	1	Unpolluted to moderately polluted
Ba	0.14	1	Unpolluted to moderately polluted
Ni	2.95	3	Moderately to strongly polluted
Sr	0.12	1	Unpolluted to moderately polluted
Sc	0.03	1	Unpolluted to moderately polluted

Table 9. *Summary of I_{geo} Values of Trace Elements in stream sediments of the Keana Brinefield*

Elements	I_{geo} Value	Class	Remarks
Mo	0.35	1	Unpolluted to moderately polluted
Zn	4.85	4	Strongly polluted
As	1.45	2	Moderately polluted
Pb	0.85	1	Unpolluted to moderately polluted
Co	3.78	1	Unpolluted to moderately polluted
Cr	1.70	2	Moderately polluted
Cu	0.85	1	Unpolluted to moderately polluted
Ba	0.33	1	Unpolluted to moderately polluted
Ni	0.62	3	Moderately to strongly polluted
Sr	0.21	1	Unpolluted to moderately polluted
Sc	0.03	1	Unpolluted to moderately polluted

Table 10. *Summary of the EF Classification of Trace Elements in Soil of the Keana Area.*

Element	EF Value	Classification
I	3872.99	Extremely severe enrichment
Mo	12.05	Moderate – severe enrichment
Zn	128.60	Extremely severe enrichment
As	87.66	Extremely severe enrichment
Pb	8.59	Moderate – severe enrichment
Co	7.65	Moderate – severe enrichment
Cr	7.04	Moderate – severe enrichment
Cu	6.08	Moderate – severe enrichment
Ba	6.01	Moderate – severe enrichment
Ni	4.30	Moderate enrichment
Sr	14.53	Severe enrichment

3.1. Using the Pollution Indices for Assessment

Contamination measurement indicators used for the assessment of soil and sediments in the study area include geo-accumulation index, enrichment factor, contamination factor and pollution load index. Average concentration of background values for world soil and sediments used in the various equations are taken from [21]. Calculated values of the pollution indices are presented in Tables 5 to 9.

Geo-accumulation index (Igeo):

Using the Muller scale for Igeo, zinc (Zn) is the most enriched heavy metal in soil of the study area, having I_{geo} value of 4.9 and 3.81 (Table 8, Figs. 3 and 6) in soil and sediments respectively, and an Igeo class of 4 and 5, indicating that the soil of the Keana area is strongly to extremely polluted, by Zn. Cobalt in the stream sediments has Igeo of 3.8, similar to the Igeo exhibited by Zn and indicates the sediment is strongly polluted by Co, which conversely has a lower Igeo of 0.55 in soil indicating the soil is unpolluted. Arsenic, in both soil and sediment maintains an Igeo of 1.86 and 1.42 respectively, indicating that the soil is moderately polluted by As. This is similar to the Igeo values displayed by Cr, having 1.91 and 1.73 respectively for soil and stream sediments. Another element in the moderate to strong pollution level in the soil is Ni with Igeo value of 2.95, while Mo, Pb, Cu, Ba, Sr and Sc all have Igeo values of less than one (1), in the two sample media indicating the soil and sediments of the Keana area are unpolluted by these elements (Fig.9).

Enrichment Factor (EF):

Trace elements assessment using EF in the Keana area shows that soil of the area is extremely severely enriched by Zn and As, having EF values of 128.60 and 87.66 respectively. However, in stream sediments, the two elements have very low EF values of 0.01 and 1.11 respectively, indicating minor or minimal enrichment. Molybdenum has an EF value 12.05 in soil indicating moderate-severe enrichment but shows minimal level in stream sediments with EF of 1.63. Other elements such as Pb, Co, Cu, Ba, Ni and Sr have EF values between 6 and 8 indicating moderate to severe enrichment in the soil, while Ni is of moderate enrichment with an EF of 4.30. These elements however have EF less than one (1) in stream sediments, indicating minimal

enrichment levels.

Contamination factor (Cf) and pollution load index (PLI):

Both Cf and PLI values of elements in soil and stream sediments of the Keana area are less than one (Figures 5 and 8). This indicates that the there is no contamination by these elements in the two media

In summary, the assessment of the degree of accumulation of heavy metals such as Pb, Zn, As, etc, in soil and stream sediments of the Keana area, calculated using index of geo-accumulation (I_{geo}), enrichment factor (EF), contamination factor (Cf) and pollution load index (PLI), shows that soil and stream sediments in the area are highly polluted by Zn, Cr, Ni and As going by geo-accumulation index. Zn and As are also similarly severely enriched in the two media when EF is measured. In all indices measured, Mo, Co, Cu, Ba, Sr and Sc levels in soil and sediments remain less than one, indicating the media are not contaminated by these elements. A pollution load index of < 1 as seen in most locations (Table 6) indicates no pollution.

The ubiquitous mining activities characterized by indiscriminate dumping of mine wastes, tailings and other foreign materials, coupled with the intense weathering in the area (which predisposes the minerals hosting the trace elements), have contributed to the re-mobilization and re-distribution of the heavy metals into the surrounding soil and sediments. The main source of these trace elements is therefore anthropogenic.

The distribution of these elements by both natural and anthropogenic processes can result in deficiency or toxicity of these trace elements (such as Pb, As, Cr, Se) in the environment and can be detrimental to plants and animals. 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 women who are very vulnerable in nature, particularly in the tropics. Deficiencies in water or soil of iodine, selenium, and zinc, in the same vein, are attributable to iodine deficiency disorders -IDDs (such as goiter), human immune-deficiency syndrome and slow or stunted growth rate respectively [6], [25].

4. Conclusion

The high concentration of trace elements such as Zn, Cr, Ni, As and others in soil and sediments, relate to their properties as transition elements, are easily oxidized to insoluble complex anions which are readily absorbed and co-precipitated in the sediments with Fe^{3+}, Al^{3+} and Si^{4+} [23]. In addition, these elements must have also remobilized from the surrounding basaltic rocks rich in these elements, coupled with remobilization from the widespread sulphides mineralization characterizing the study area.

The use of pollution indices in this research, on the basis of geo-accumulation index and enrichment factor has shown that the soil and sediments in the area are extremely contaminated with Zn, Cr, Ni and As. Pb and Ba are moderately contaminated while the contamination levels of elements such as Mo, Cu, Co, Sr and Sc appear to be insignificant. Contamination factor and pollution load index analysis both indicate no pollution of these elements in the study area.

The continued exposure of the populations living in this study area particularly those in the mining locations who depend on the soil (for subsistence farming) and water from ponds, wells and boreholes (for drinking, cooking and other domestic uses), would result in various health risks and concerns, if not checked or abated. This study would recommend an immediate plan for analysis of the quality of drinking water and some staple crops grown in the area to determine the levels of these noxious metals and uptake by plants, to be followed by a comprehensive mitigation or remediation plan. The mining regulatory body in the country should move to control the proliferation of mining and processing of the minerals as well as the uncontrollable disposal of toxic mine tailings and dumping of other wastes.

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