

Vertical Dispersion, Contamination Potentials of Heavy Metals and Rare Earth Elements in Soil of Ode Aye bitumen rich Area, Ondo State, Southwest, Nigeria

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Abstract- This paper aims at studying the vertical concentrations of heavy metals and rare earth elements (REE) on the upper (0-5 cm) and lower parts (5-10 cm) of soil from Ode Aye area with a view to determining their contamination /pollution potentials. The XRF analysed data indicated that all the samples showed a higher Zn concentration than the background in both the upper part of the soil,(0-5 cm) as well as in the lower part (5-10 cm), for the large parts of the areas studied. The average concentrations of Cr, (44.53), Co (145.10), Mo (1.35), and Zn (44.35) at 5-10 Cm depth are higher than those at 0-5 Cm depth with Cr (42.60), Co (61.50), Mo (1.09) and Zn (23.20) respectively. The concentrations and the averages of the REEs follow the same vertical increase downwards. Pollution by these metals is examined using the enrichment factor,(EF), contamination factor, (CF), geoaccumulation index, and pollution load index (PLI) respectively. EF data show that Rb, Sr, Zr, Ba, and Pb are less than unity and are therefore naturally derived from no other source than bitumen. The EF of Cr, Co and Nb at locations OD1 and OD3 are slightly above unity, implying that they are minimally enriched while Zn is moderately enriched in the soil. The low to moderate values of EF (0.26-11.08) of the soil shows a minimal impact of anthropogenic origin of the elements. The CF values for Ni, Rb, Zr, and Pb are less than unity and consequently show low contamination. Zn shows considerable contamination while Co is considered to display very high contamination of the soil because the CF values are > 6. The results of PLI indicate that sample locations OA1, OA3, OA5,

OA6 and OA7 are not polluted because they fall within the range of $0.5 \leq \text{PLI} < 1$ class, while sample location OA2 has its PLI values > 1 and therefore indicates deterioration of the soil. Elements Cr and Pb found to fall within the uncontaminated class of $0 < \text{Igeo} \leq 1$ are usually toxic. Co falls within the high value I-geo class of $0 < \text{Igeo} \leq 1$ and it is expected to contaminate the soil. The presence of the positively loaded Zn, Ni and V in the three principal component matrix loadings suggest derivation from natural processes.

IndexTerms—Bitumen contamination, dispersion, potential , elements, Ode-Aye.

I. INTRODUCTION

Ode Aye area lies within the active bitumen seepage belt of Ondo State, Nigeria. It lies between latitudes $6^{\circ} 34'$ and $6^{\circ} 64'$ and longitudes $4^{\circ} 54'$ and $4^{\circ} 74'$ of the tropical rainforest belt of Nigeria. Vast deposit of bitumen is located in one of the palm tree plantations of Ode Aye area. The sticky bitumen is seen to flow during the hot weather and hardens when the temperature cools. Ode Aye is not a pristine area since weathering, heavy metals occurrence, anthropogenic, natural processes and presence of bitumen exist.

Ode Aye area is underlain by the Imo shale group of the Paleocene Akinbo formation (Fig 1)

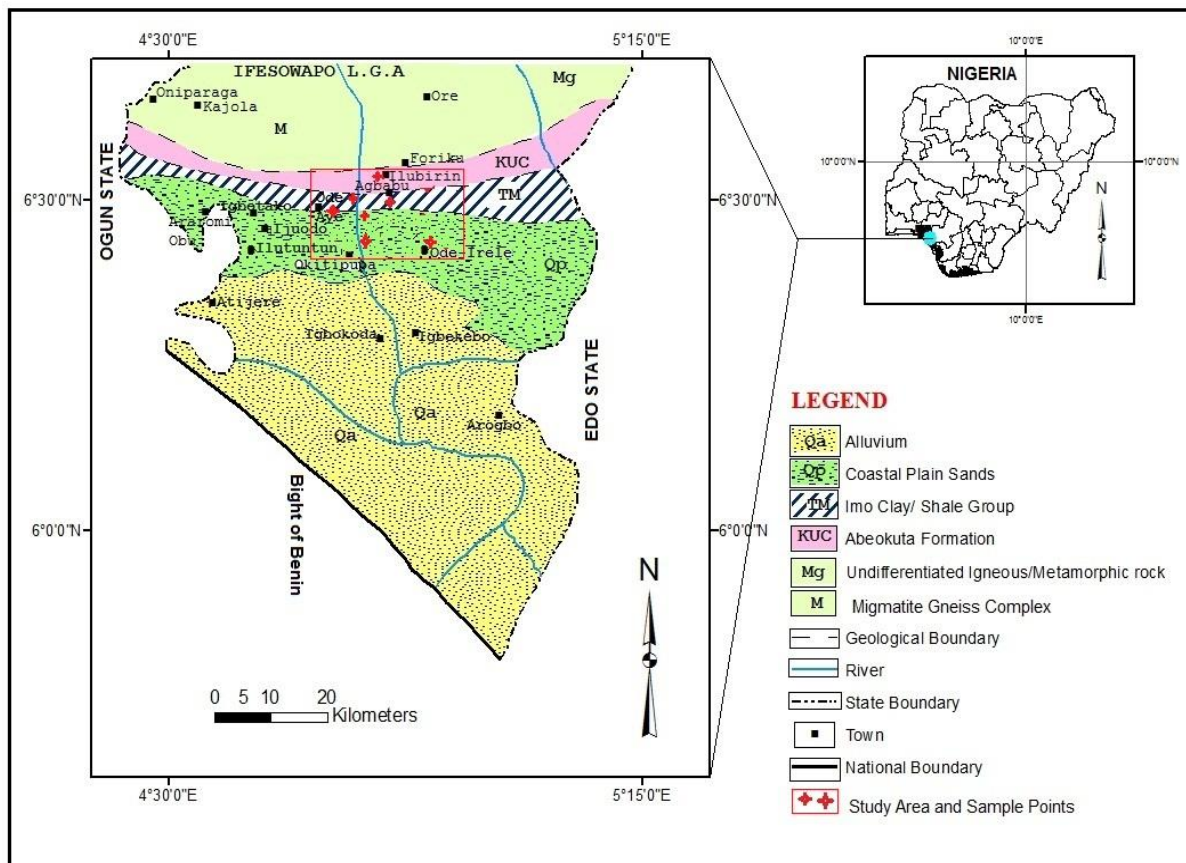


Fig 1. Geological map of Ode Aye.

The Imo shale lateral equivalent of Akinbo outcrops are seen around a spring at Ode Aye. The Akinbo shale is underlain by the continental Cretaceous sediments of the Abeokuta Formation.[1]. The Akinbo shale is thick dark grey to black shale with some sandstone lenses.

Heavy metals have been reported in literature in soils of different areas to be toxic and potentially hazardous. Mostly known elements that contaminate the soil include; Pb, U, Cr, Zn, Fe, and Cd as well as Cu.[2, 3]. Some of the toxic chemicals that accumulate in the soil can cause many human diseases, such as hepatitis, lung diseases, tuberculosis and cancer[4]. Bitumen substances usually transform into insoluble chemicals and humic materials in the soils. By so doing, the substances degrade the soil by changing and increasing the organic carbon contents.[5]. If the soil can be degraded by any of these natural and anthropogenic processes, it then implies that no area can be regarded as pristine more so where bitumen is involved. The Tibetan Plateau (TP) reported to be one of the cleanest places in the world [6] has endemic diseases due to abnormality of trace elements in the soil [7]. The understanding of the geochemical characteristics of any area can be done by studying the rare earth elements of the soil. [8,9,]. [10] studied the organic, chemical and elemental characterization of components of Nigeria bituminous sands and found high concentrations of Zn, Ni, V and Fe.

There are many sources through which the soil is enriched and or contaminated with trace and rare earth elements (REE) and some of such sources are from oil refineries or any form of hydrocarbon workings and anthropogenic activities related to agriculture. Trace elements can also occur naturally in rock forming minerals and ore minerals, thus, they can migrate into the environment from natural processes such as weathering and erosion of minerals. Since no particular area can be regarded as unpolluted, and this study is within the bitumen belt of Ondo State, it is important therefore to ascertain how much the soil has been contaminated or polluted with the bitumen. This work therefore aims at determining the degree of vertical contamination and its lateral effects on the palm tree plantation housing the deposit of bitumen as well as the general impact on the soil. The determination of the contamination and/or pollution potentials with the heavy metals would be done using some analytical indices.

II. FIELD STUDY

A reconnaissance survey of Ode-Aye was carried out in April, 2014 around the palm plantation farm (Fig. 2) which stretches over seven (7 km²) with some kola nut trees at intermittent places.



Fig 2: The Palm Plantation farm in Ode Aye area. (Arrow towards the slope)

In places, the bitumen melts and flows on the surface of the ground when the temperature is high, and becomes gummy solid to the touch when the temperature cools. The terrain is undulating with the bitumen flowing towards the direction of the slope. Many stunted palm trees and grasses are well exposed in the direction of flow of bitumen in contrast to those of the same age in the upland (arrow in Fig. 2). The scenario along the direction of flow of bitumen is an indication of the negative effects in growth of the palm trees and grasses

III. MATERIAL AND METHODS

Sample collection.

Fifteen (15) soil samples were collected by using hand auger from the surface to the depth of 10 cm. The first eight (8) was taken from 0-5cm while the second set of the samples of seven (7) was taken from 5-10cm depth vertically. The intervals of sample collection were based on a simple random and judgemental sampling techniques. Sampling points were geo-located with geographical position system (GPS) to ensure consistency. Samples were collected into polythene bags and labelled accordingly.

Sample Preparation

The collected samples were dried at room temperature to a constant weight and sieved using a 80 μ m mesh in the Department of Geology laboratory, of the Ekiti State University, Ado Ekiti. Further preparations were made in the laboratory of Stellenbosch University, South Africa. Fusion disks were prepared for x-ray fluorescence (XRF) analysis by

an automatic calisses M4 Gas fusion instrument and ultrapure calisses flux, using a ratio of 1:10 sample flux. The samples were coarsely crushed and a chip of sample was mounted along with up to 12 other samples in a 2.4cm round resin disk. The mount was mapped, and then polished for analysis.

Geochemical Analysis

The samples that have been polished for analysis were now set up instrumentally. A Resonetics 193nm Excimer laser connected to an Agilent 7500ce . ICP-MS is used in the analysis of trace elements in bulk rock samples as well as on single mineral grains. Ablation is performed in He gas at a flow rate of 0.35L/min, then mixed with argon (0.9L/min) and Nitrogen (0,004L/min) just before introduction into the ICP plasma. For traces in fusions, 2 spots of 173 μ m is ablated on each sample using a frequency of 10Hz and 100mJ energy. The total concentrations of the trace and rare earth elements were determined

IV. RESULTS AND DISCUSSION

Table 1 presents the concentrations of heavy metal distribution in the Ode Aye bitumen rich soil along with different averages and background values (BGV). The data reveal that the average values of the metals at depth 0-5 cm for V (46.12), Cr (41.51), Cu (10.32) , and Pb (10.10) do not surpass the background values. Zn (45.16) and Mo (1.16) exceeded the background values of Zn (23.20) and Mo (1.09) ppm respectively

Table 1. Concentration of trace elements (ppm) for soil samples at 0-5 and 5-10 cm depths in Ode Aye area.

| Sample | V | Cr | Co | Ni | Cu | Zn | Mo | Pb |
|--------------------|--------------|--------------|---------------|--------------|--------------|--------------|-------------|--------------|
| 0-5 cm | | | | | | | | |
| OA 1 | 47.83 | 41.98 | 58.06 | 13.30 | 6.16 | 35.76 | 1.24 | 10.49 |
| OA 2 | 59.11 | 50.65 | 64.89 | 16.00 | 11.30 | 54.48 | 1.11 | 13.96 |
| OA 3 | 39.75 | 39.38 | 72.82 | 12.94 | 17.17 | 69.84 | 0.84 | 8.15 |
| OA 4 | 41.39 | 38.70 | 44.36 | 10.87 | 8.00 | 50.55 | 1.17 | 8.69 |
| OA 5 | 52.90 | 44.03 | 51.30 | 12.66 | 10.94 | 42.49 | 1.49 | 11.4 |
| OA 6 | 41.07 | 38.10 | 51.63 | 12.14 | 7.90 | 29.10 | 1.18 | 9.78 |
| OA7 | 40.78 | 37.95 | 516.91 | 16.84 | 10.78 | 33.92 | 1.1 | 8.23 |
| Average | 46.12 | 41.51 | 122.85 | 13.54 | 10.32 | 45.16 | 1.16 | 10.1 |
| CA average(mg/kg) | - | 61.00 | - | 26.90 | 22.60 | 74.20 | - | 22.00 |
| Av UEC (mg/kg) | - | 35 | 11.6 | 18.6 | 14.3 | 52 | - | 17 |
| BGV | 53.27 | 42.69 | 61.50 | 19.54 | 14.42 | 23.20 | 1.09 | 15.21 |
| 5-10 cm | | | | | | | | |
| OA 1 | 53.03 | 46.66 | 58.93 | 16.42 | 10.62 | 35.93 | 1.57 | 11.32 |
| OA 2 | 63.64 | 53.46 | 101.33 | 20.78 | 16.83 | 50.80 | 1.55 | 15.12 |
| OA 3 | 40.98 | 38.01 | 61.24 | 13.95 | 15.24 | 63.99 | 0.96 | 8.92 |
| OA 4 | 46.37 | 40.32 | 126.43 | 13.63 | 12.71 | 52.34 | 1.23 | 10.50 |
| OA 5 | 48.25 | 41.34 | 437.50 | 14.05 | 8.58 | 32.15 | 1.45 | 9.79 |
| OA 6 | 49.64 | 47.37 | 85.30 | 16.76 | 10.30 | 30.91 | 1.35 | 13.98 |
| Mean | 50.32 | 44.53 | 145.12 | 15.93 | 12.38 | 44.35 | 1.35 | 11.61 |
| BGV | 53.27 | 42.69 | 61.50 | 19.54 | 14.42 | 23.20 | 1.09 | |

Av UEC. Average upper earth crust after [11]

Chinese average (CA).General environment monitor station of China [12]

The concentrations of the lower part from 5-10 cm depth indicate different characteristics. Apart from V (50.32), Cu (12.38) and Pb (11.61), the average values of other metals exceeded the background values. The background contents of Co and Zn are almost twice their analysed contents. It is notable that all the samples indicated a higher Zn concentration than the BG, both in the upper part of the soil, depth 0-5 cm as well as in the lower part of depth 5-10 cm, for the large part of the areas studied.

Generally the average concentrations of the heavy metals from the soil surface (0-5cm) to 5-10 cm downwards reveal an

increase with depth except Zn that showed minimal metal decrease. However, bitumen analysis for trace metal components showed high concentration of Zn, Ni, V and Fe [10]. The average concentration of most of the heavy metals are lower than the standard average values in the upper earth crust [11] and in the [12] except Cr and Co that are higher in the upper earth crust. (Table 2).

The concentrations of Cu, Cr, Pb, Ni, and Vi in this work are higher than those analysed by [13] for the Agbabu bitumen rich soil, an adjacent town to Ode Aye.

Table 2 presents the average values of the elements for 0-5 cm and 5-10 cm depths.

Table 2. Average concentrations from different areas.

| | V | Cr | Co | Ni | Cu | Zn | Mo | Pb |
|----------------------|-------|-------|--------|-------|-------|-------|------|-------|
| Average UOA | 53.27 | 42.69 | 61.50 | 19.54 | 14.42 | 23.20 | 1.09 | 15.2 |
| Average LOD | 50.32 | 44.53 | 145.12 | 15.93 | 12.38 | 44.35 | 1.35 | 11.61 |
| AUC | - | 35 | 11.6 | 18.6 | 14.3 | 52 | --- | 17 |
| Chinese Average (CA) | -- | 61 | -- | 26 | 22.6 | 74.2 | - | 26 |
| MAL | -- | 100 | 50 | 100 | 100 | 100 | -- | 100 |
| GB | -- | 50 | -- | 50 | 100 | 300 | -- | 100 |

UOA Average for 0-5cm depth Ode Aye soil .

LOD Average for 5-10cm depth Ode Aye soil

AUC Average upper earth crust [11]

CA General environment monitor station of [12].

The average concentrations of V, Cr, Co, Ni, Cu, Zn, Mo, and Pb at both depths are less than the Chinese averages[13]. However, the average concentrations of V, Cr, Co, Ni, Ni and Cu for both depths are higher than that of the upper earth crust [11.] The average concentrations of Cr,(44.53), Co (145.10), Mo (1.35), and Zn (44.35) at 5-10 Cm depth are higher than

those at 0-5 Cm depth with Cr (42.60), Co (61.50), Mo (1.09) and Zn (23.20) respectively. It is noted that Co at 5-10 Cm is twice that for 0-5 Cm depth

Rare earth element (REE) concentrations in the soils

The concentrations and the averages of the REEs for 0-5 and 5-10 Cm are presented in Table 3. They indicate that the elements increase with depth.

Table 3. Concentration of rare earth elements (REE) in soil.

| 0-5cm Depth | | | | | | | | | | | | | | | |
|-------------|-------|-------|------|-------|------|------|------|------|------|------|-------|------|-------|------|------|
| OA1 | La | Ce | Pr | Nd | Sm | Eu | Tb | Tm | Yb | Lu | Hf | Ta | Pb | Th | U |
| OA1 | 17.87 | 35.75 | 3.83 | 12.13 | 2.16 | 0.37 | 0.34 | 0.27 | 2.01 | 0.28 | 13.97 | 1.28 | 10.49 | 7.33 | 2.34 |
| OA2 | 27.48 | 57.48 | 6.40 | 23.02 | 4.20 | 0.72 | 0.55 | 0.32 | 2.11 | 0.35 | 13.35 | 1.31 | 13.96 | 8.56 | 2.84 |
| OA3 | 14.55 | 30.02 | 3.25 | 10.91 | 1.86 | 0.41 | 0.29 | 0.24 | 1.70 | 0.25 | 11.82 | 1.27 | 8.15 | 5.31 | 1.73 |
| OA4 | 15.11 | 30.83 | 3.12 | 10.27 | 2.01 | 0.37 | 0.27 | 0.23 | 1.54 | 0.23 | 11.82 | 1.05 | 8.69 | 4.95 | 1.85 |
| OA5 | 21.54 | 41.44 | 4.51 | 14.56 | 2.41 | 0.45 | 0.39 | 0.31 | 1.97 | 0.34 | 13.26 | 1.30 | 11.46 | 8.50 | 2.38 |
| OA6 | 17.70 | 35.70 | 3.53 | 12.71 | 2.36 | 0.47 | 0.41 | 0.29 | 2.21 | 0.36 | 13.45 | 1.04 | 9.78 | 6.55 | 2.33 |
| OA7 | 14.20 | 30.22 | 2.96 | 9.62 | 1.66 | 0.28 | 0.27 | 0.19 | 1.71 | 0.24 | 11.78 | 1.68 | 8.23 | 6.90 | 1.86 |
| Average | 18.35 | 37.35 | 3.94 | 13.32 | 2.38 | 0.44 | 0.36 | 0.26 | 1.89 | 0.29 | 12.78 | 1.28 | 10.12 | 6.87 | 2.19 |

| 5-10 cm Depth | | | | | | | | | | | | | | | |
|---------------|-------|--------|-------|-------|------|------|------|------|------|------|-------|------|-------|-------|------|
| OA1 | La | Ce | Pr | Nd | Sm | Eu | Tb | Tm | Yb | Lu | Hf | Ta | Pb | Th | U |
| OA1 | 20.34 | 41.71 | 4.08 | 13.21 | 2.39 | 0.42 | 0.39 | 0.30 | 2.05 | 0.31 | 15.63 | 1.24 | 11.32 | 8.47 | 2.51 |
| OA2 | 35.51 | 68.53 | 7.98 | 29.18 | 5.19 | 0.95 | 0.65 | 0.41 | 3.01 | 0.45 | 14.43 | 1.61 | 15.12 | 10.85 | 3.02 |
| OA3 | 15.00 | 30.33 | 3.09 | 10.54 | 2.05 | 0.34 | 0.42 | 0.30 | 2.29 | 0.32 | 13.42 | 1.12 | 8.92 | 5.16 | 1.96 |
| OA4 | 17.80 | 35.94 | 3.76 | 12.06 | 2.50 | 0.40 | 0.34 | 0.24 | 1.68 | 0.25 | 11.79 | 1.39 | 10.50 | 6.66 | 2.14 |
| OA5 | 17.62 | 34.75 | 3.57 | 11.71 | 2.22 | 0.37 | 0.37 | 0.25 | 1.96 | 0.29 | 14.25 | 1.29 | 9.79 | 8.15 | 2.21 |
| OA6 | 22.40 | 46.08 | 4.69 | 16.91 | 2.97 | 0.56 | 0.46 | 0.31 | 2.23 | 0.31 | 15.22 | 1.17 | 13.98 | 8.47 | 2.97 |
| Average | 21.45 | 42.89 | 4.55 | 15.60 | 2.89 | 0.51 | 0.44 | 0.30 | 2.20 | 0.32 | 14.12 | 1.3 | 11.61 | 7.96 | 2.47 |
| CS | 74.11 | 163.13 | 15.53 | 52.21 | 8.07 | 0.68 | 0.64 | 0.28 | 2.05 | 0.31 | 26.23 | 1.02 | 15.21 | 41.69 | 4.25 |
| WA | 40 | 50 | - | 35 | 4 | 0.76 | 0.7 | - | 3 | 0.4 | - | - | - | - | - |

The averages for all the elements at 5-10 Cm depth are higher than those from 0-5 Cm depth. The averages of Tm (0.30), Yb (2.20), Lu (0.32) and Ta (1.3) are slightly higher than the Chinese average, [13]. The increase with depth can be attributed to the solubility of the bitumen and migration of the elements downwards particularly at elevated temperatures. It can also be as a result of vertical upward

movement or seepage of the bitumen to the surface of the ground.

Table 4 shows a normalized concentration of the REEs at 5-10 Cm depth. The data indicate increased values in most of the locations except location OA5 where they are below unity. The average values also show an increase except EU element which is below 1 (0.58)

Table 4 Normalized data of the REEs

| | La | Ce | Pr | Nd | Sm | Eu | Tb | Tm | Yb | Lu | Hf | Pb | Th | U |
|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| OA1 | 1.14 | 1.17 | 1.10 | 1.09 | 1.11 | 1.14 | 1.15 | 1.11 | 1.02 | 1.11 | 1.12 | 1.08 | 1.16 | 1.07 |
| OA2 | 1.30 | 1.19 | 1.25 | 2.41 | 1.24 | 2.57 | 1.18 | 1.28 | 1.42 | 1.29 | 1.10 | 1.08 | 1.27 | 1.06 |
| OA3 | 1.03 | 1.01 | 0.95 | 0.97 | 1.10 | 0.83 | 1.45 | 1.25 | 1.35 | 1.28 | 1.14 | 1.09 | 0.97 | 1.13 |
| OA4 | 1.18 | 1.17 | 1.21 | 1.17 | 1.24 | 1.08 | 1.26 | 1.04 | 1.09 | 1.09 | 1.01 | 1.21 | 1.35 | 1.16 |
| OA5 | 0.82 | 0.84 | 0.79 | 0.80 | 0.92 | 0.45 | 0.95 | 0.81 | 1.01 | 0.85 | 1.07 | 0.85 | 0.96 | 0.93 |
| OA6 | 1.27 | 1.29 | 1.33 | 1.33 | 1.26 | 1.19 | 1.12 | 1.07 | 1.01 | 0.86 | 1.13 | 1.22 | 1.01 | 1.25 |
| Avg | 1.17 | 1.15 | 1.15 | 1.17 | 1.21 | 0.58 | 1.22 | 1.15 | 1.16 | 1.10 | 1.10 | 1.15 | 1.16 | 1.0 |

Contamination and Pollution Potentials

In order to assess the contamination and pollution potential in the bitumen soil, trace element data are subjected to contamination and pollution calculation methods using the followings; enrichment factor (EF) , contamination factor (CF), geo- accumulation index, (Igeo), degree of contamination (DC) and pollution load index (PLI).

Enrichment factors (EF) .

Enrichment factor assesses the degree of contamination and also gives an idea of understanding of the distribution of the

elements of anthropogenic origin or otherwise.[14] . The magnitude of contamination of any environment is determined using the EF [15] and the formula shown in equation 1.

$$\text{Enrichment factor (EF)} = \frac{C_x / C_{\text{ref}} (\text{sample})}{B_x / C_{\text{ref}} (\text{background})} \quad \text{--Eq 1}$$

where C_x is the concentration of the examined element in the environment. C_{ref} (sample) is the element of low

occurrence, B_x is the concentration of each element in the control samples. B_{ref} = element of low occurrence variability in the control samples. In this work Cs has been chosen as the normalizing element due to its low occurrence variability.

Table. 5 Enrichment factor data.

| Samples | V | Cr | Co | Ni | Cu | Zn | Rb | Sr | Zr | Nb | Mo | Cs(ref) | Ba | Pb |
|---------|------|------|-------|------|------|------|------|------|------|------|------|---------|------|------|
| OD1 | 0.98 | 1.07 | 1.03 | 0.74 | 0.46 | 1.68 | 0.29 | 0.82 | 0.61 | 1.22 | 1.24 | - | 0.39 | 0.75 |
| OD2 | 0.74 | 0.81 | 0.71 | 0.55 | 0.53 | 1.58 | 0.57 | 0.68 | 0.40 | 0.75 | 0.89 | - | 0.86 | 0.62 |
| OD3 | 0.88 | 1.08 | 1.39 | 0.78 | 1.39 | 3.54 | 0.48 | 0.84 | 0.60 | 1.06 | 0.91 | - | 0.73 | 0.63 |
| OD4 | 0.79 | 0.92 | 0.73 | 0.56 | 0.56 | 2.20 | 0.39 | 0.64 | 0.47 | 0.89 | 1.09 | - | 0.63 | 0.58 |
| OD5 | 0.64 | 0.67 | 0.54 | 0.42 | 0.49 | 1.19 | 0.34 | 0.62 | 0.35 | 0.74 | 0.89 | - | 0.39 | 0.49 |
| OD6 | 0.71 | 0.83 | 0.78 | 0.56 | 0.51 | 1.16 | 0.28 | 0.62 | 0.48 | 0.87 | 1.00 | - | 0.39 | 0.60 |
| OD7 | 1.01 | 1.17 | 11.08 | 1.14 | 0.98 | 1.93 | 0.26 | 0.90 | 0.66 | 1.32 | 1.42 | - | 0.33 | 0.71 |
| ODM | 0.82 | 0.94 | 2.32 | 0.68 | 0.73 | 1.90 | 0.37 | 0.73 | 0.51 | 0.98 | 1.03 | - | 0.53 | 0.63 |

The calculated EF is shown in Table 5. [16] postulated that elements which are naturally derived have an EF value close to unity, while elements of anthropogenic origin have values of higher magnitude. If the enrichment factor values is <1, it means a background concentration (natural), if it is between 1-2 it means depletion to minimal enrichment, 2-5 moderate enrichment, 5-20 significant enrichment, 20-40 very high enrichment, >40 indicates extremely high enrichment [17] . Based on the above values, the EF of Rb, Sr, Zr, Ba, and Pb are less than unity and are therefore naturally derived from no other source than bitumen. The EF of Cr, Co and Nb at locations OD1 and OD3 are slightly above unity, implying that they are minimally enriched while Zn is moderately enriched. The low to moderate values of EF (0.26-11.08) of the soil shows a minimal impact of anthropogenic origin of the elements perhaps the interference with palm plantation processing.

Contamination factors (CF)

The contamination factor (CF) expresses the various levels of contamination of the soil by heavy metals. It is the ratio obtained by dividing the concentration of each metal in the soil by base line or background values [18] .

$$CF = \frac{\text{Conc. of each element in the examined soil}}{\text{Each element in the background}} \text{ --Eq 2 .}$$

When the CF is less than 1 (>1) it means low contamination, when it is $1 \leq CF < 3$, it implies moderate contamination, $3 \leq CF < 6$ considerable contamination, and $CF \geq 6$, means very high contamination. The data of the calculated CF are shown in Table 6. The data show that the CF values for Ni, Rb, Zr, and Pb are less than unity and therefore show low contamination. Zn shows considerable contamination while Co is considered to display very high contamination of the soil because the CF values are > 6.

Table 6: Contaminations factor (CF) of trace elements in the soil.

| Spl. | V | Cr | Co | Ni | Cu | Zn | Rb | Sr | Zr | Nb | Mo | Cs | Ba | Pb |
|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| OD1 | 0.90 | 0.98 | 0.94 | 0.68 | 0.43 | 1.54 | 0.26 | 0.75 | 0.56 | 1.12 | 1.14 | 0.92 | 0.36 | 0.69 |
| OD2 | 1.11 | 1.19 | 1.06 | 0.82 | 0.78 | 2.35 | 0.84 | 1.01 | 0.60 | 1.11 | 1.02 | 1.48 | 1.27 | 0.92 |
| OD3 | 0.75 | 0.92 | 1.18 | 0.66 | 1.19 | 3.01 | 0.41 | 0.72 | 0.51 | 0.90 | 0.77 | 0.85 | 0.62 | 0.54 |
| OD4 | 0.78 | 0.91 | 0.70 | 0.56 | 0.55 | 2.18 | 0.39 | 0.64 | 0.46 | 0.88 | 1.07 | 0.99 | 0.63 | 0.57 |
| OD5 | 0.99 | 1.03 | 0.83 | 0.65 | 0.76 | 1.83 | 0.52 | 0.96 | 0.54 | 1.14 | 1.37 | 1.54 | 0.61 | 0.67 |
| OD6 | 0.77 | 0.89 | 0.84 | 0.62 | 0.55 | 1.25 | 0.31 | 0.96 | 0.52 | 0.94 | 1.08 | 1.08 | 0.42 | 0.75 |
| OD7 | 0.77 | 0.89 | 8.41 | 0.86 | 0.74 | 1.46 | 0.21 | 0.68 | 0.50 | 1.02 | 1.07 | 0.76 | 0.25 | 0.64 |

Degree of Contamination (DC).

The degree contamination is one index that defines the sum of all contamination factors for a given location [18] .

$$DC = \sum_1^n CF, \text{ Samples} \tag{3}$$

Where CF is the contamination factor and n is the count of the element present. When the Dc is less than n it shows low degree of contamination;

$n \leq Dc < 2n$, when $2n \leq Dc < 4n$, degree of contamination is considerable and the degree of contamination is very high when $Dc > 4n$ [19, 20] .

Pollution Load Index (PLI)

The pollution Load Index formula in equation 4 by [21] provides that the PLI is able to give an

estimate of element contamination status and the necessary actions that should be taken.

$$PLI = (Cf1 \times Cf2 \times Cf3 \times \dots \times Cfn)^{1/n} \text{---Eq4}$$

Where n is the number of elements, $C_f =$ contamination factor. $n = 13$

Table 7 shows the calculated degree of contamination and pollution load index for the various sample locations.

Table 7: Pollution load index (PLI) and Degree of contamination (DC) in the soil.

| Sample | OD1 | OD2 | OD3 | OD4 | OD5 | OD6 | OD7 |
|--------|-------|-------|-------|-------|-------|-------|-------|
| PLI | 0.7 | 1.06 | 0.80 | 0.72 | 0.88 | 0.72 | 0.79 |
| DC | 11.27 | 15.56 | 13.03 | 11.33 | 13.44 | 10.98 | 18.25 |

[21] proposed that when the PLI value is less than < 1 , it indicates perfection, and when it is $= 1$ it means that only baseline level of pollution is present, $PLI > 1$ indicates deterioration of location quality. [22] suggested that, PLI values ≥ 1 would indicate immediate intervention to ameliorate pollution, $0.5 \leq PLI < 1$ suggests that more detailed study is needed to monitor the site, while

values < 0.5 indicate that there is no need for rectification measures to be taken. From the results of PLI, samples OA1, OA3, OA5, OA6 and OA7 are not polluted because they fall within the, $0.5 \leq PLI < 1$ bracket, Sample location OA2 has its PLI values > 1 and therefore indicates deterioration of the soil.

Geoaccumulation index (Igeo)

The index of geoaccumulation actually enables the assessment of contamination by comparing the current level of metal concentration and the original

pre-industrial concentration of the soils. The equation 5 used to get the Igeo is proposed by [23].

$$I_{geo} = \log_2 \left[\frac{C_n \text{ samples}}{1.5 B_n} \right] \text{---Eq 5}$$



Equation 5 has been used to generate the geoaccumulation index data in Table 8

$C_n =$ Content of examined elements in the examined environment

$B_n =$ Background Value of each element.

Table 8 Geoaccumulation index of the soil

| Sampl es | V | Cr | Co | Ni | Cu | Zn | Rb | Sr | Zr | Nb | Mo | Cs | Ba | Pb |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| OD1 | -0.74 | -0.59 | -0.67 | -1.15 | -1.84 | 0.04 | -2.47 | -0.31 | -1.43 | -1.25 | -0.40 | -2.06 | -0.62 | -0.34 |
| OD2 | -0.43 | -0.32 | -0.51 | -0.86 | -0.94 | 0.65 | -0.84 | -0.56 | -0.40 | -0.43 | -0.56 | -0.23 | -0.09 | -0.21 |
| OD3 | -1.00 | -0.71 | -0.34 | -1.18 | -0.34 | 1.00 | -1.89 | -1.05 | -1.56 | -0.74 | -0.97 | -1.29 | -0.38 | -0.44 |
| OD4 | -0.94 | -0.74 | -1.05 | -1.43 | -1.43 | 0.54 | -1.94 | -1.23 | -1.69 | -0.79 | -0.49 | -1.64 | -0.49 | -0.42 |
| OD5 | -0.59 | -0.54 | -0.84 | -1.00 | -1.00 | 0.29 | -1.52 | -0.64 | -1.47 | -0.39 | -0.14 | -1.32 | -0.39 | -0.30 |
| OD6 | -0.97 | -0.76 | -0.84 | -0.44 | -0.44 | -0.25 | -2.32 | -0.64 | -1.52 | -0.67 | -0.47 | -1.84 | -0.55 | -0.30 |
| OD7 | -0.97 | -0.76 | 2.49 | -1.22 | -1.00 | -0.04 | -2.94 | -1.15 | -1.59 | -0.56 | -0.49 | -0.30 | -2.53 | -1.47 |

Factor analysis

Pearson's correlation matrix for multi-elements correlation for soil samples was determined and the results are shown in Table 9. Most of the metals are strongly, positively and significantly correlated at P< 0.01 levels (1-tailed). Ni, Ba, Pb, Rb and Mo are significantly high. The

correlation trends show that V correlates with Sc. Cr correlates with Sc and V while Pb is positively correlated with Sc, V, Cr, Rb, Sr and Y. The implication is that these trace elements originated from the same natural sources suggestive of bitumen. Correlation analysis

Table 9. Pearson's correlation matrix of the elements.

| | Sc | V | Cr | Co | Ni | Cu | Zn | Rb | Sr | Y | Zr | Nb | Mo | Cs | Ba | Pb |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----|
| Sc | 1 | | | | | | | | | | | | | | | |
| V | .910* | 1 | | | | | | | | | | | | | | |
| Cr | .960* | .969* | 1 | | | | | | | | | | | | | |
| Co | -.162 | -.308 | -.311 | 1 | | | | | | | | | | | | |
| Ni | .530 | .330 | .398 | .708 | 1 | | | | | | | | | | | |
| Cu | .200 | -.066 | .103 | .048 | .182 | 1 | | | | | | | | | | |
| Zn | .197 | .071 | .245 | -.317 | -.090 | .796* | 1 | | | | | | | | | |
| Rb | .880* | .818* | .889* | -.439 | .184 | .306 | .497 | 1 | | | | | | | | |
| Sr | .769* | .708 | .685 | -.382 | .138 | -.015 | -.158 | .646 | 1 | | | | | | | |
| Y | .817* | .818* | .792* | -.405 | .198 | -.219 | -.213 | .672 | .942* | 1 | | | | | | |
| Zr | .366 | .179 | .178 | .645 | .809* | -.136 | -.562 | -.072 | .363 | .372 | 1 | | | | | |
| Nb | .126 | -.108 | .070 | -.229 | .066 | .591 | .420 | .063 | .166 | .080 | .060 | 1 | | | | |
| Mo | .121 | .415 | .179 | -.041 | -.107 | -.593 | -.638 | -.011 | .353 | .370 | .131 | -.651 | 1 | | | |
| Cs | .769* | .851* | .782* | -.481 | -.014 | -.001 | .057 | .805* | .836* | .805* | -.002 | -.177 | .533 | 1 | | |
| Ba | .885* | .772* | .880* | -.400 | .260 | .346 | .531 | .983* | .614 | .658 | -.009 | .181 | -.162 | .703 | 1 | |
| Pb | .915* | .967* | .949* | -.390 | .277 | -.140 | -.005 | .824* | .815* | .926* | .233 | -.039 | .362 | .856* | .797* | 1 |

*. Correlation is significant at the 0.05 level (1-tailed).

**. Correlation is significant at the 0.01 level (1-tailed).

Principal component analysis.

Principal component analysis (PCA) is introduced to establish possible factors that contribute towards the metal concentration and source derivation. The number of significant principal components (PC) is selected based on varimax orthogonal rotation with Kaiser normalisation with eigenvalue greater than 1 (Table 9) shown in Fig 3.

characterised by Cu (0.892) and Zn (0.886). Cu and Zn are deep-seated elements that are normally associated with sulphide deposits. [24] proposed that sulphide deposits are principal sources of Cu-Zn and gold with low content of Pb. Factor 3

Three components comprising 93.51 % of the total cumulative variance were extracted and retained. The first factor accounted for 41.8% of total data variance and it is mainly characterised by heavy loading of V (0.985), Cr (0.938), and Pb (0.983). Factor 2 accounted for 29.1% of total variance and is

accounts for 22.6% of the total data variance and strongly loaded by Co (0.894) and Ni (0.914). Factor 3 indicates strong geochemical relationship between Co and Ni. These elements are closely related in the veins of sulphide deposits [25].

Table 9. Principal factors and loading for trace elements.

| Loading | Factor 1 | Factor 2 | Factor 3 |
|---------|----------|----------|----------|
| | V 985 | Cu 892 | Cr 060 |
| | Cr 938 | Zn 886 | Co 894 |
| | Mo 522 | Pb 069 | Ni 914 |

| | | | |
|-----------------|--------|---------|--------|
| Eigenvalue | Pb 983 | Mo -715 | V 083 |
| % data variance | 3.344 | 2.329 | 1.807 |
| Cumulative % | 41.806 | 29.118 | 22.586 |
| | 41.806 | 70.924 | 93.510 |

Fig 3 shows strong chemical relationships between V, Cr and Pb in factor 1 and of component

1. Cr and Pb are toxic and can contaminate the soil. Cu and Zn in

Component Plot in Rotated Space

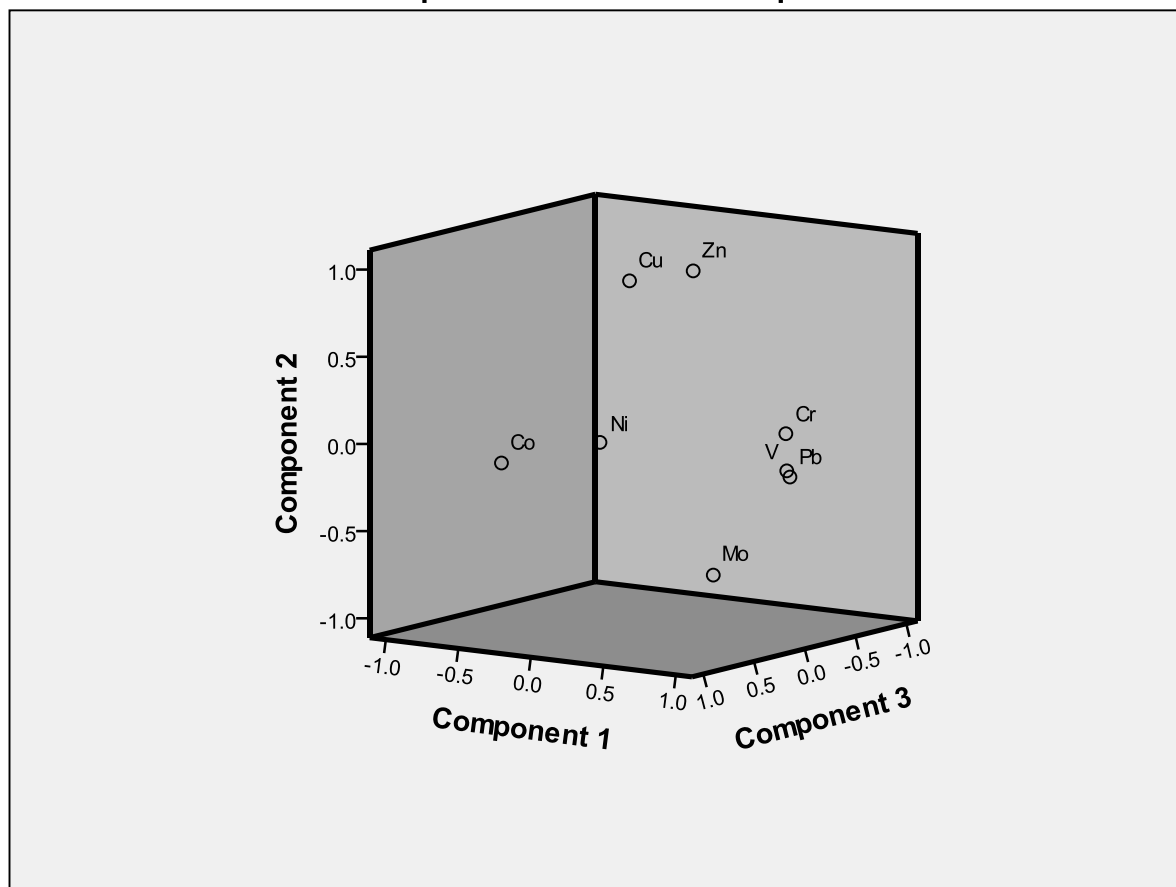


Fig 3. Component plot in rotated space.

component 2 are chemical associates that are strongly and positively loaded. Co and Ni in component 3 are equally strongly related. Zn, Ni and V spread in the principal factors are expected to be contributions from natural processes strongly related to bitumen.

V. CONCLUSION

The Ode Aye soil was studied to ascertain if the bitumen deposits have impacted on it. Heavy metals were analyzed and contamination/pollution factors were used to determine the potentials of contamination of the soil. The result of the contamination factor shows that the Ni, Rb, Zr, and Pb values are less than one suggestive of low contamination of the soils. Zn shows considerable contamination while Co is considered to display very high contamination of the soil because the contamination factor values are greater than 6. The

concentration of all the REEs increased downwards except the Eu

All the average values of elements in the upper (0-5Cm) and lower depths (5-10Cm) are lower than the background or control values except elements Tm (0.30), Yb (2.20), Cu (0.32), and Ta (1.3) respectively.

The results of PLI indicate that locations OA1, OA3, OA5, OA6 and OA7 are not polluted because they fall within the $0.5 \leq PLI < 1$ specifications. Location OA2 has PLI values that are more than unity (> 1) and therefore indicates deterioration of the soil.

Using the classes and applying the enrichment data, it is observed that V, Cr, Zn, Ni and V spread in the principal

factors are expected to be contributions from natural processes strongly related to bitumen.

Ni, Cu, Zn, Rb, Sr, Zr, Nb, Mo, Cs, Ba, and Pb fall within the uncontaminated class of $0 < I_{geo} \leq 1$. However, Co falls within the strongly to moderately contaminated class due to its high values in location 7, and can therefore be said to contaminate the soil. Generally, Zn and Co are the elements that have strongly contaminated the soil especially in areas where the bitumen has been exposed on the surface. This is based on the fact that Zn, Ni and V spread in the principal factors are expected to be contributions from natural processes strongly related to bitumen.

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