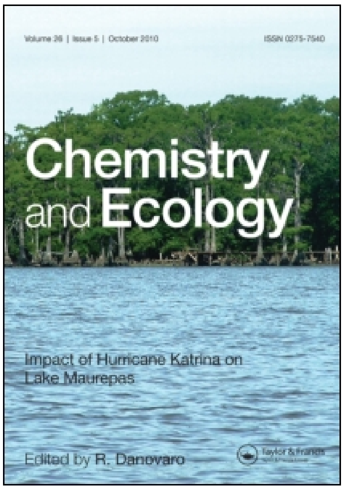


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# Assessment of element accumulation from bitumen deposit by vegetation using Energy Dispersive X-ray Fluorescence (EDXRF) spectroscopy technique

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RESEARCH ARTICLE

# Assessment of element accumulation from bitumen deposit by vegetation using Energy Dispersive X-ray Fluorescence (EDXRF) spectroscopy technique

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Vegetation samples from the bitumen deposit area of Southwestern Nigeria were analysed for element contents to assess their level of accumulation from a bitumen deposit area and to provide a framework for the establishment of relationships between the chemistry of the mineral deposit and the vegetation. The element concentrations of the samples were determined using the EDXRF spectrometry technique. Thirteen elements – K, Ca, Cr, Ti, V, Mn, Ni, Cu, Zn, Ga, Rb, Sr and Fe were detected. The results of the calculated concentration ratio (CR) showed that the vegetation samples have high uptake ability (CR > 0.9) from the soil for most of the elements determined. Strong and significant positive correlations exist between some elements, indicating a common source, chemical similarity and/or common natural background levels in the samples. Positive correlations were shown by the results of the cross-plot analysis of the vegetation/soil and vegetation/bitumen, suggesting inter-element correlations between components of the ecosystem and that ecosystem vegetation accumulated the elements via the soil as a result of contamination with the bitumen and also establishing relationships between the aforementioned components of the ecosystem and the bitumen deposit in the area.

**Keywords:** bitumen; EDXRF; element; soil; vegetation

## 1. Introduction

One of the foremost environmental problems that the scientific society faces today is the pollution of soil, air, water, food and biological material by toxic elements. Metals are a major category of globally distributed pollutants. They are mostly extracted from the earth and used in industry for various purposes; they have the tendency to accumulate in selected tissues of the human body and some are toxic even at relatively trace levels of exposures.

Analysis of different plant samples has revealed some cases of trace metal contamination. For instance, the concentrations of heavy metals in vegetables grown in Southwestern Nigeria were reported by Fasasi and Obiajunwa [1]. Similarly, results have been obtained for some Nigerian medicinal plants [2]. A study of heavy metal distributions in some coastal seaweeds of Alexandria (Egypt) showed the presence of toxic metals such as Cd, Hg, Ni and Pb at high concentrations [3] while the results of an investigation in Tokat (Turkey) by Tuzen [4] on mushroom and plant samples

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showed high ratios of Ca, Zn and Cu concentrations in plants compared to the corresponding soils, indicating that the metals have accumulated in these samples. The presence of toxic metals such as Cd, Cu, Pb, Cr and Hg in selected vegetable and food crops was further reported by Islam [5]. It was further reported that some aquatic plant species have the potential to remove heavy metals from polluted water [6–8]; likewise some terrestrial plant species can be used in bioremediation of heavy metals in polluted soils [9]. It has been reported that all plants have the capacity to accumulate elements which are essential for their growth and development from soil and water, while certain plants also have the ability to accumulate elements which have no biological function [10,11] and that the concentrations of Pb, Cu and Zn accumulated by plants grown in the vicinity of smelting may reach 10–1000 times the normal levels [12]. It was also stated by Abdul et al. [10] that excessive accumulation of elements can be toxic to most plants. The elements are absorbed and accumulated by plants when present in certain forms. For instance Ca, Mg and K from their salts such as $SO_4^{2-}$, $Cl^-$, etc; Fe from $Fe^{2+}$ and $Fe^{3+}$ salts; Mn from $Mn^{2+}$ salts; Cu and Zn from their salts, etc. [9].

Nigeria is among the nations of the world that are endowed with large deposits of bitumen [13,14]. Nigerian bitumen deposits occur in the Southwestern part of the country and the recoverable bitumen is estimated to be about 35–50 billion barrels in a 5–8 km belt stretching over 120 km (Figure 1) [13,15]. The physico-chemical properties and elemental composition of Nigerian bituminous sand and its fractions (bitumen, sand and water) have been determined [15–20]. In this study, we report the elemental characterisation of the vegetation in the Nigerian bitumen deposit area to assess the level of element accumulation from the bitumen deposit by the vegetation via the soil and to provide a framework for the establishment of relationships between the chemistry of the mineral deposit and the vegetation component of the ecosystem. It is imperative to carry out a detailed study of the elemental composition of the vegetation component of the ecosystem of the natural deposit area in Nigeria because the foremost profession of the inhabitants is crop farming. Consequently, the potential for uptake of environmental pollutants into the crops and associated transfer to the food chain is likely to be associated with the exploitation of bitumen in the region. The assessment of this pathway for exposure is crucial to provide a basis for assessing the potential impacts on human health of the exploitation of vast Nigerian bitumen deposits.



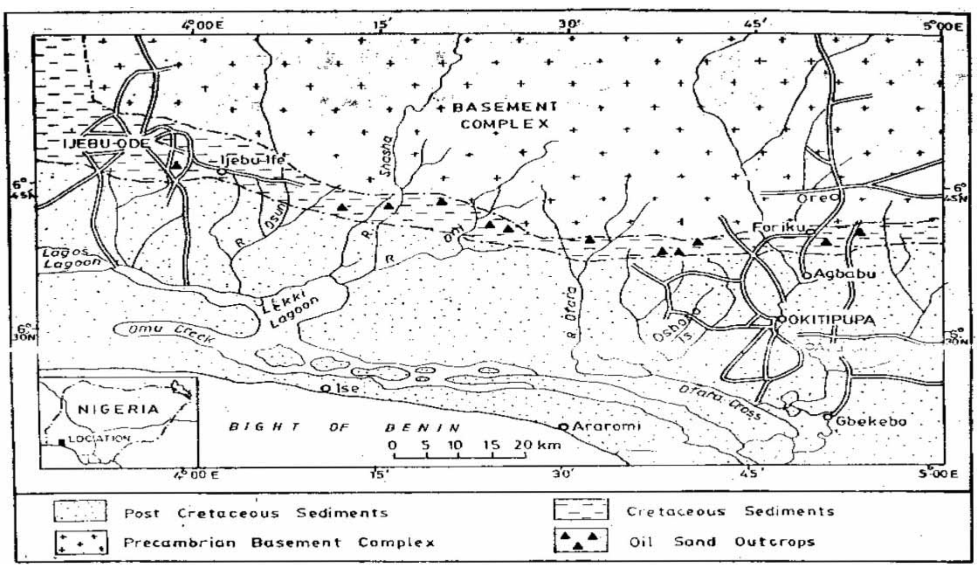


Figure 1. Geological map of Southwestern Nigeria showing bitumen deposits. Source: Adegoke et al. [13].

## 2. Material and methods

### 2.1. *Study area*

The study area (Figure 2) falls between Latitudes 006° 35′ and 006° 39′ North and Longitudes 004° 48′ and 004° 54′ East. The area lies within the 1:50,000 standard topographic sheet 282 (Okitipupa South-East) map of Nigeria. Three major roads run through this study area: these are Olowo-Agbabu, Lamudifa-Oluagbo and Olowo-Irele roads. The settlements along the Olowo-Agbabu road are Foriku, Boridele, Mulekagbon, Camp II, Orisunbare Camp, Ilubirin, Bisi camp and Agbabu village. Along the Lamudifa-Oluagbo road, there are Palm Oil Estate and Camp I, while those of the Olowo-Irele road include Loda II, Akinmegha Camp, Loda I, Gbelejuloda, Ayadi and Legbogbo.

### 2.2. *Quality assurance and quality control*

The IAEA reference materials (Hay – 1207 powder and Soil – 7) were prepared and analysed for elements following the same protocols as the vegetation and soil samples, respectively, and the results compared with the certified values [21]. All analytical instruments used were calibrated by established protocols and duplicate analyses were made.

### 2.3. *Sample collection and treatment*

Soil samples were collected randomly within the study area. At each sampling point, two soil samples at depths 0–15 cm and 15–30 cm were collected using a Dutch Hand Auger after the litter had been removed. Vegetation samples were collected from the same spots where soil samples were collected by plucking the mature leaves from the parent plants because mature leaves are expected to have maximum accumulation of the elements. This made it plausible to determine the elemental concentration ratio and relationships between the vegetation and the soil and bitumen deposit. The plant species were identified by their botanical and common names and each sample was put in polythene bag and labeled. Each vegetation sample was washed extensively in doubly distilled water in order to remove superficial dust. It was then oven dried at 60 °C for 48 h. The dried samples were ground separately with a laboratory ball mill. The powdered vegetation samples were put in polythene sachets (7 mm × 10 mm), labeled and sealed to avoid any loss of material, while the soil samples were crushed to 2 mm mesh size using an agate mortar. The crushed

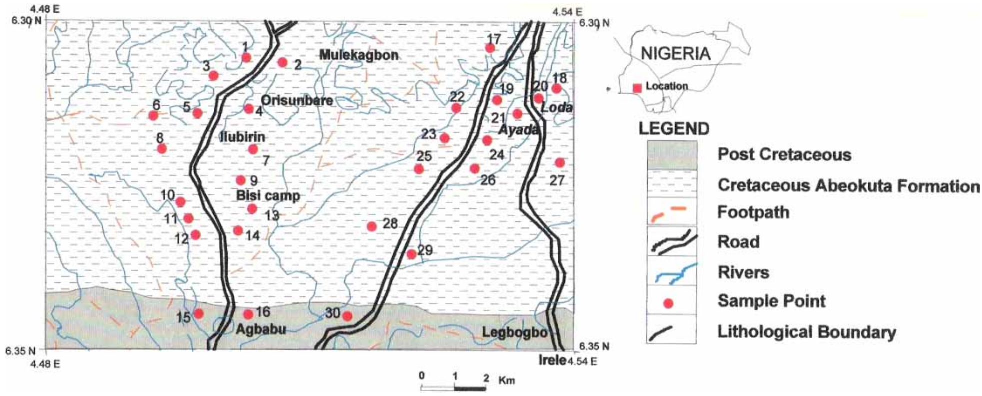


Figure 2. Map of the study area showing sample locations.

samples were mixed thoroughly and sub-sampled by coning and quartering to provide composite and representative samples for analysis [22]. The soil and vegetation samples were taken to the laboratory for processing and analysis of their element contents. In the laboratory, the samples were prepared and pressed into thick pellets of 13 mm diameter in spec-caps without binder for energy dispersive x-ray fluorescence (EDXRF).

### 2.4. *Energy dispersive x-ray fluorescence (EDXRF)*

The elemental analysis of the soil and vegetation samples was performed by an EDXRF spectrometer. The spectrometer composed of a Siemens FKO-04 tube with Mo anode, a kristalloflex 710H X-ray generator, a Canberra series 7300 Si(Li) detector (of resolution 165 eV at 5.9 KeV), with Canberra Model 1510 integrated signal processor and a Canberra S100 MCA card interfaced to a 486 IBM/PC. This equipment operates under Quantitative X-ray Analysis System (QXAS) software [23], which includes facilities for data acquisition, spectrum analysis and interpretation, and quantitative analysis. Each sample pellet was irradiated for 20 min at fixed tube conditions of 30 kV and 10 mA. All data are the results of an average of three measurements on each sample.



### 2.5. *Treatment of data*

*Pearson correlation matrix*

The elemental concentrations of the analysed samples were also subjected to statistical analysis to determine the Pearson correlation matrix of the elements. This was calculated using Statistical Package for Social Scientist (SPSS), and correlation was considered significant at the 0.05 level (2-tailed).

*Cross plot*

Cross plot analysis was carried out to determine the relationships between vegetation/soil and vegetation/Nigerian bitumen using elemental concentrations as variables. The statistical analysis was conducted using Microsoft Excel to determine the R square ($R^2$), which is a measure of the degree of the relationship between the vegetation/soil and vegetation/bitumen deposit.

*Concentration ratio (CR)*

The concentration ratio (CR) was calculated for each element to determine the uptake ability for the element by the plant or alternatively, if the soil is not the only source of the element to the plant. The CR has been used to systemise the relationship between the soil and the plants. By definition, the CR is given by:

$$CR = (C_x)_{veg.}/(C_x)_{soil},$$

where $(C_x)_{veg.}$ and $(C_x)_{soil}$ are the concentrations of element $\boldsymbol{x}$ in vegetation and soil samples, respectively. It is agreed in principle that if the value of CR is greater than 0.9, it implies that the vegetation sample has high uptake ability for the element or indicates that the soil is not the only source of contribution of the element [1]. In this study, the elements in soils collected from 0–15 cm depth were used to calculate the CR for shallow rooted plants, while the elements in soils collected from 15–30 cm depth were used to calculate the CR for deep-rooted plants.

## 3. Results and discussion

### 3.1. *Quality assurance and quality control*

Tables 1 and 2 show the accuracy of the EDXRF analytical technique used by analysing the IAEA reference materials (HAY – 1207 powder and Soil - 7). The material was prepared under the same conditions as the vegetation and soil samples. The results are in good agreement with the certified values [23].

### 3.2. *Elemental characterisation of the vegetation samples*

The codes alongside the particulars of the vegetation samples are presented in Table 3. They are arranged according to their type of root systems, viz. samples $V_1$– $V_{12}$ are shallow-rooted plants while $V_{13}$ – $V_{18}$ are deep-rooted plants. The concentrations of the elements determined in the vegetation samples are shown in Table 4. As expected, Fe (Mean 401 $\mu g/g$), K (Mean 313 $\mu g/g$) and Ca (Mean 239 $\mu g/g$), being major elements, have the highest concentrations in that order, while Ga and V are not detectable for most of the samples. The coefficients of variation (CV) of the elements determined in the samples are relatively high due to the fact that the vegetation samples are of different families and root systems, whose abilities to accumulate minerals are different.

The results of the Pearson correlation matrix for the elements in the vegetation samples are presented in Table 5. In order to determine which of the correlations are *significant* in the statistical sense, the critical multiple correlation coefficient $r$ was obtained from the table of significant values. The value of $r$ with $n = 18$ is 0.445 or more at 95% confidence interval level. Strong and significant positive correlations exist between K and Rb ($r = 0.515$), Ti and V ($r = 0.624$), V and Ni ($r = 0.664$), V and Zn ($r = 0.614$), Ni and Cu ($r = 0.471$), Ni and Zn ($r = 0.505$), Ti and Fe ($r = 0.615$), Ti and Zn ($r = 0.567$) and Zn and Fe ($r = 0.716$), while strong and significant negative correlation exists between K and Mn ($r = -0.446$). The above associations



Table 1. IAEA reference material HAY – 1207 (powder) analysis results.

| Element | Measured value | Certified value |
|---|---|---|
| K | 2.25% w | 2.10% w |
| Ca | 2.23% w | 2.16% w |
| Mn | 51.2 $\mu g/g$ | 47.0 $\mu g/g$ |
| Fe | 191 $\mu g/g$ | 186 $\mu g/g$ |
| Zn | 24.0 $\mu g/g$ | 24.0 $\mu g/g$ |

Table 2. IAEA reference material Soil – 7 analysis results ($\mu g/g$).

| Element | Certified value | 95% Confidence Interval | This study |
|---|---|---|---|
| Ti | 3000 | 2600–3700 | 2700 |
| V | 66 | 59–73 | 57 |
| Cr | 60 | 49–74 | 53 |
| Mn | 631 | 604–650 | 620 |
| Fe | 25700 | 25200–26300 | 26000 |
| Ni | 26 | 21–37 | 22 |
| Cu | 11 | 9–13 | 10 |
| Zn | 104 | 101–113 | 108 |
| As | 13.4 | 12.5–14.2 | 15 |
| Rb | 51 | 47–56 | 56 |

Table 3. Codes and particulars of vegetation samples analysed.

| Sample code | English name | Local name | Botanical name | Family name | Type of root system |
|---|---|---|---|---|---|
| V1 | Maize | Agbado/Oka | *Zea mays* | Gramineae | Shallow rooted |
| V2 | Water leaf | Gbure | *Talinum triangulare* | Potulacaceae | Shallow rooted |
| V3 | N.A | Tete | *Amaranthus hybridus* | Amaranthacea | Shallow rooted |
| V4 | Okra | Ila | *Abelmuscus esculentum* | Tiliaceae | Shallow rooted |
| V5 | N.A | Ooyo/Ewedu | *Corchorus tridens* | Tiliaceae | Shallow rooted |
| V6 | Tomatoes | Kuujekuje | *Lycopersicum cernunm* | Solanacea | Shallow rooted |
| V7 | Beans | Ewa/Eree | *Vigna unguculata* | Papilionaceae | Shallow rooted |
| V8 | N.A | Sokoyokoto | *Celosia argentia* | Tiliaceae | Shallow rooted |
| V9 | Melon | Egusi | *Eucus meloz* | Carcarbitoceae | Shallow rooted |
| V10 | Pepper | Ata | *Capscicum annum* | Piperaceae | Shallow rooted |
| V11 | N.A | Efirin | *Occimum gratissinium* | Labiateae | Shallow rooted |
| V12 | Cocoyam | Isu-koko | *Xanthosoma mafaffa* | Sterculiaceae | Shallow rooted |
| V13 | Bitter leaf | Ewuro-oko | *Vernonia tenoreana* | Compositae | Deep rooted |
| V14 | Cassava | Ege/Gbaguda | *Manihot esculenta* | Euphobiaceae | Deep rooted |
| V15 | Palm tree | Ope | *Elaeis guinensis* | Palmae | Deep rooted |
| V16 | Kola | Obigbanja | *Cola nitida* | Sterculiaceae | Deep rooted |
| V17 | Cocoa | Koko | *Theobrama cacao* | Sterculiaceae | Deep rooted |
| V18 | Mango | Mangoro | *Mangifera indica* | Anacardiaceae | Deep rooted |

Note: N.A = Not available. Source: Gbile [35].



can be explained in terms of a common source, chemical similarity and/or common natural background levels in the samples. Potassium and Rb show significant positive correlation because they have a strikingly similar nature of occurrence with exhibition of +1 oxidation state. The other elements that show significant positive correlations are first-row transition group metals with similar transition metal properties, while the negatively correlated metals such as K and Mn do not have common source in these samples, neither are they chemically similar nor have the same natural background levels in the samples.

Cross-plot analysis is applicable in virtually all disciplines. It is used primarily in the Earth sciences to describe a specialised chart that compares multiple measurements made at a single time and location along two or more axes. The axes of the plot are commonly linear, but may be logarithmic. It has been used in comparison of soil microbial biomass, soil nutrient status and nematode tropic groups [24], as well as in vegetation analysis for young plants of brachytic maize *Zea mays L.* varieties [25] and spatial and temporal analysis of vegetation change in the agricultural landscape [26]. Cross-plot analysis is used in this study to establish inter-elemental relationships among the vegetation and soil components of the study area, assess the level of accumulation of trace elements from the bitumen deposit by the vegetation of the area of study, and also to provide a framework for the establishment of relationships between the chemistry of the mineral deposit and vegetation system in the area. R square ($R^2$) which is a measure of the degree of relationship between the vegetation/soil and vegetation/bitumen deposit was determined using the elements determined as variables. The results of the cross plot analysis of the vegetation, soil samples and literature values of the elements in bitumen are presented in Figure 3 (a,b). Moderate positive correlations exist between soil and vegetation ($R^2 = 0.4297$), while correlation between vegetation and bitumen ($R^2 = 0.1043$) is weak. The positive correlations imply inter-element correlations between the vegetation, soil and the bitumen deposits in the area. For instance, elements such as V, Ni, Zn, Cu, Cr and Fe that are associated with hydrocarbon formation might have leached from the bitumen deposit into the soil and/or meteoric water, then moved upwards by the percolation process and in turn adsorbed and accumulated by the vegetation. The positive correlations shown by the results of the cross plot analysis of the vegetation, soil and bitumen using analysed elements as the variables imply inter-element correlations between the vegetation, soil and the bitumen deposit in the area, and that contamination of any one aspect of the ecosystems

Table 4. Elemental composition of the vegetation samples (± SD $\mu g/g$).

| Sample code | K | Ca | Cr | Ti | V | Mn | Ni | Cu | Zn | Ga | Rb | Sr | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V1 | 237 | 245 | ND | ND | ND | 38.9 | 24.5 | 26.3 | 25.7 | 3.51 | 16.9 | 10.1 | 110 |
| V2 | 680 | 406 | ND | ND | ND | 82.1 | 15.1 | 21.5 | 46.4 | ND | 28.7 | 10.3 | 416 |
| V3 | 557 | 131 | 15.7 | ND | ND | 74.4 | 14.6 | 28.6 | 32.1 | ND | 55.2 | 78.9 | 135 |
| V4 | 267 | 120 | ND | ND | ND | 85.2 | 18.2 | 26.0 | 53.0 | ND | 13.4 | 63.0 | 101 |
| V5 | 340 | 111 | ND | 278 | ND | 74.3 | 17.1 | 23.9 | 42.5 | ND | 30.8 | 24.4 | 366 |
| V6 | 318 | 160 | ND | 58.8 | ND | 21.8 | 9.78 | 22.1 | 36.5 | ND | 24.3 | 26.1 | 246 |
| V7 | 379 | 165 | ND | 52.3 | ND | 177 | 9.49 | 29.7 | 54.3 | ND | 28.7 | 37.4 | 1053 |
| V8 | 159 | 159 | 16.4 | 91.6 | ND | 33.8 | 11.7 | 28.9 | 62.1 | ND | 46.9 | 27.7 | 274 |
| V9 | 474 | 193 | ND | 339 | ND | 98.0 | 43.3 | 35.5 | 137 | ND | 31.5 | 38.9 | 1709 |
| V10 | 444 | 104 | 13.1 | ND | ND | 33.4 | 39.4 | 56.9 | 59.6 | ND | 27.4 | 23.2 | 308 |
| V11 | 352 | 169 | 12.3 | 60.4 | 16.78 | 35.2 | 27.8 | 26.8 | 52.8 | ND | 25.3 | 30.7 | 457 |
| V12 | 299 | 524 | ND | ND | ND | 99.5 | 25.4 | 27.3 | 31.5 | ND | 28.7 | 22.2 | 792 |
| V13 | 392 | 779 | 17.8 | ND | ND | 134 | 16.7 | 35.3 | 81.3 | ND | 38.3 | 22.4 | 144 |
| V14 | 212 | 904 | 22.4 | ND | ND | 120 | 30.1 | 32.6 | 86.8 | ND | 22.1 | 63.4 | 683 |
| V15 | 125 | 436 | 14.0 | ND | ND | 224 | 26.4 | 27.3 | 26.5 | ND | 10.9 | 13.4 | 81.9 |
| V16 | 128 | 125 | 15.5 | ND | ND | 114 | 23.6 | 28.4 | 23.3 | ND | 20.9 | 31.8 | 127 |
| V17 | 147 | 113 | 13.3 | 35.4 | ND | 535 | 21.2 | 25.3 | 41.3 | ND | 20.2 | 30.8 | 82.7 |
| V18 | 127 | 188 | ND | ND | ND | 621 | ND | 33.6 | 28.5 | ND | 14.7 | 31.9 | 138 |
| Mean | 313 (158) | 280 (239) | 7.81 (8.31) | 48.1 (48.5) | 0.93 | 145 (167) | 20.8 (10.7) | 29.8 (7.88) | 51.2 (28.1) | 0.20 | 25.3 (11.3) | 32.6 (18.6) | 401 (426) |
| Range | 125–680 | 104–904 | 0.00–22.4 | 0.00–339 | ND–16.78 | 21.8–621 | 0.00–43.3 | 21.5–56.9 | 23.3–137 | ND–3.51 | 10.9–56.2 | 10.1–78.9 | 81.9–1709 |
| CV | 50 | 85 | 106 | 137 | 426 | 115 | 51 | 27 | 55 | 415 | 42 | 57 | 106 |

Note: CV = Coefficient of variation (%), ND = Not detected, SD = Standard deviation.

Table 5. Pearson correlation matrix of the analysed metals in the vegetation samples.

| | K | Ca | Cr | Ti | V | Mn | Ni | Cu | Zn | Ga | Rb | Sr | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K | 1.000 | | | | | | | | | | | | |
| Ca | −.056 | 1.000 | | | | | | | | | | | |
| Cr | −.228 | −.081 | 1.000 | | | | | | | | | | |
| Ti | .180 | .437 | −.318 | 1.000 | | | | | | | | | |
| V | .061 | .258 | .133 | **.624** | 1.000 | | | | | | | | |
| Mn | −**.446** | .186 | −.025 | −.157 | −.164 | 1.000 | | | | | | | |
| Ni | .139 | −.191 | .229 | .279 | **.664** | −.359 | 1.000 | | | | | | |
| Cu | .112 | .122 | .300 | −.043 | −.096 | −.019 | **.471** | 1.000 | | | | | |
| Zn | .309 | .328 | .109 | **.567** | **.614** | −.197 | **.505** | .367 | 1.000 | | | | |
| Ga | −.121 | −.432 | −.234 | −.129 | −.059 | −.158 | .086 | −.109 | −.224 | 1.000 | | | |
| Rb | **.515** | .207 | .277 | .214 | −.036 | −.376 | −.102 | .095 | .250 | −.221 | 1.000 | | |
| Sr | .089 | .391 | .267 | −.029 | −.025 | −.018 | −.028 | .039 | .220 | −.301 | .295 | 1.000 | |
| Fe | .344 | .328 | −.305 | **.615** | .002 | −.179 | .426 | .153 | **.716** | −.169 | .159 | .099 | 1.000 |

Note: $n = 18$, $\alpha$ 0.05, $r \geq 0.445$ at 95% Confidence interval level, positively and negatively correlated metals are presented in bold type.

would easily affect the other. This could be a useful fingerprint for bitumen exploration elsewhere and also for similar mineral deposit settings, such as crude oil and coal deposits. Thus the potential for uptake of such parameters of environmental pollution to crops and eventual transfer to the food chain is an important source, which is likely to be associated with exploitation of bituminous sands in the region. The assessment of such biogeochemical pathway for exposure is an important task that must be undertaken to provide a basis for assessing the potential impact of the exploitation of the vast Nigerian bitumen deposits on human and animal health.

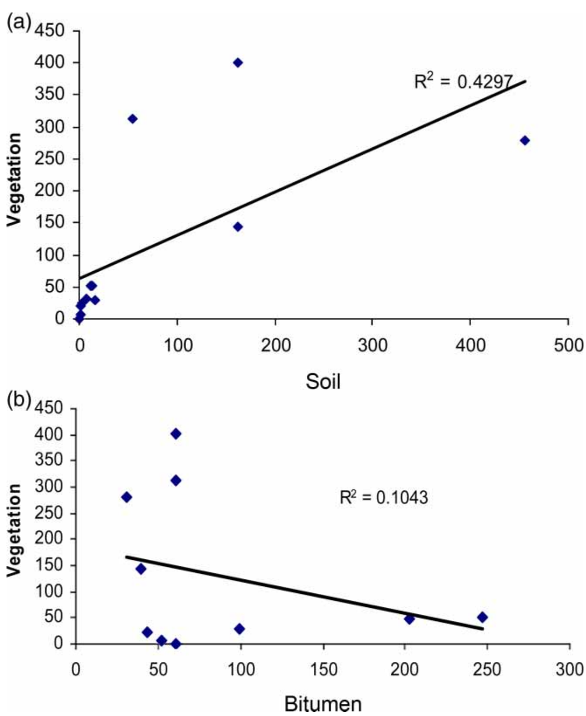


Figure 3. (a) Cross plot of the vegetation versus soil samples. (b) Cross plot of the vegetation versus bitumen samples.

Table 6. Comparing the mean concentrations of hydrocarbon sources associated with transition metals in this study with the same in bitumen.

| Metal | Southwestern Nigeria bitumen Adebiyi et al. [17] | Canadian (Athabasca) bitumen Jacobs and Filby [36] | Vegetation sample | Nigerian Bitumen/Vegetation ($t$-test results) |
|---|---|---|---|---|
| V | 60.5 | 140 | 0.930 | 0.003 |
| Cr | 52.0 | 0.719 | 7.81 | 0.002 |
| Mn | 39.7 | 1.41 | 145 | 0.001 |
| Fe | 60.6 | 127 | 401 | 0.009 |
| Ni | 43.3 | 30.1 | 20.8 | 0.002 |
| Cu | 99.4 | 0.481 | 29.8 | 0.030 |
| Zn | 247 | 0.615 | 51.2 | 0.025 |

Table 6 compares the mean concentrations of hydrocarbon sources- associated transition metals in this study with the same in bitumen. Of the eight transition metals (Ti, V, Cr, Mn, Fe, Ni, Cu and Zn) detected in the samples, seven (V, Cr, Mn, Zn, Fe, Ni and Cu) are known to be associated with hydrocarbon formation [20,27]. As expected, the concentrations of transition metals (except Mn and Fe) are higher in the Nigerian and Athabasca bitumen than in the vegetation samples in this study. The anomaly in the concentrations of Fe is due to the fact that the Southwestern Nigerian soils have high concentration of Fe which can also be accumulated by the vegetation [2,28], while high concentrations of Mn may be due to high mineralogy of the metal from the bed rocks.

As presented in Table 6, the results of the $t$-test on the concentrations of the transition metals further confirm this observation. They are higher in bitumen than the vegetation, soil and water because the resin and asphaltene fractions which contain both porphyrin-bound and non-porphyrin-bound metals are concentrated in bitumen [27].

The concentration ratios (CR) of the vegetation samples are shown in Table 7, while the values of the elements in soil samples used for the calculation of the CR are presented in Table 8. All the samples have high uptake ability for K, Ni, Cu, Zn, Rb and Sr but low uptake ability for Mn (except the deep-rooted plants, viz. $V_{15}$, $V_{17}$ and $V_{18}$, followed by Ca and Fe). It is also observed that the shallow-rooted plants, mostly vegetables, viz. $V_2$– $V_{12}$, have high uptake ability for Fe due to high concentration of the element in the soils either as a replacement for Al in clay, or as oxides and hydroxides minerals, e.g. goethite {FeO(OH)}, hematite ($Fe_2O_3$) and lepidocrocite {Fe(OH)}, as reported by Fergusson [29]. Ward [30] has also reported that some elements, most notably Fe, are more concentrated in top-soils of Southwestern Nigeria than the sub-soils due to accumulation of organic matter/humus which adsorbs the elements. This observation is also in agreement with the report of Amusan et al. [31] on the characteristics of soil and crop uptake of metals in municipal waste dump sites in Nigeria. The shallow-rooted plants in this study are therefore potential sources of Fe mineral which is required in blood formation [32]. Conversely, they are also rich sources of toxic metals, viz. Ni and Rb with potential health implications, as excessive levels of Ni may result in dermatitis, respiratory disorder, carcinogenesis, kidney damage, convulsions and asphyxia, while excessive levels of Rb are known to be carcinogenic [33].

A comparison of the trace element levels in vegetation samples in this study with other Nigerian vegetation from non-bitumen deposit areas is shown in Table 9. The values of Mn, Fe, Zn and Cr and are higher in this study than those reported by Fasasi and Obiajunwa [1] and Olajire [34] for vegetables and mosses, respectively. Since these elements are associated with hydrocarbon formation, they might have been leached into the soil from the bitumen deposit and translocated upwards by percolation process to where they were bioaccumulated by the vegetation. On the other hand, the values of Ca, Ti, Ni and Cu are higher in the report of Fasasi and Obiajunwa [1]. The differences could also simply be due to the different types of vegetation in the different studies.

Table 7. Concentration ratio (CR) of vegetation samples analysed.

| Element | V1 | V2 | V3 | V4 | V5 | V6 | V7 | V8 | V9 | V10 | V11 | V12 | V13 | V13 | V14 | V15 | V16 | V17 | V18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K | **4.33** | **12.6** | **10.2** | **4.94** | **6.22** | **5.81** | **6.94** | **2.90** | **8.68** | **8.13** | **6.44** | **5.48** | **7.29** | **5.48** | **3.89** | **2.33** | **2.37** | **2.72** | **2.35** |
| Ca | 0.54 | 0.90 | 0.29 | 0.26 | 0.25 | 0.35 | 0.37 | 0.35 | 0.43 | 0.23 | 0.37 | **1.16** | **1.70** | **1.16** | **2.00** | **0.95** | 0.27 | 0.25 | 0.41 |
| Cr | – | – | **24.9** | – | – | – | – | **26.0** | – | **20.9** | **19.4** | – | **16.8** | – | **35.5** | **13.2** | **14.6** | **12.6** | – |
| Ti | – | – | – | – | **14.76** | **3.81** | **3.39** | **5.94** | **21.98** | – | **3.92** | – | – | – | – | – | – | **2.89** | – |
| V | – | – | – | – | – | – | – | – | – | – | **21.51** | – | – | – | – | – | – | – | – |
| Mn | 0.22 | 0.47 | 0.43 | 0.50 | 0.43 | 0.13 | **1.02** | 0.19 | 0.56 | 0.19 | 0.20 | 0.57 | 0.89 | 0.57 | 0.69 | **1.48** | 0.76 | **3.54** | **4.11** |
| Ni | **14.5** | **8.94** | **8.62** | **10.8** | **10.1** | **5.79** | **5.62** | **6.95** | **25.6** | **23.3** | **16.5** | **15.1** | **8.86** | **15.1** | **17.8** | **14.0** | **12.5** | **11.3** | – |
| Cu | **1.37** | **1.12** | **1.49** | **1.35** | **1.24** | **1.15** | **1.54** | **1.50** | **1.84** | **2.95** | **1.39** | **1.42** | **2.94** | **1.42** | **1.69** | **2.27** | **2.36** | **2.11** | **2.79** |
| Zn | **6.69** | **12.0** | **8.27** | **13.7** | **11.0** | **9.41** | **14.0** | **16.0** | **35.3** | **15.4** | **13.6** | **8.13** | **3.90** | **8.13** | **22.4** | **1.29** | **1.12** | **1.98** | **1.37** |
| Rb | **6.27** | **10.6** | **20.4** | **4.96** | **11.4** | **9.00** | **10.7** | **17.4** | **11.7** | **10.2** | **9.37** | **10.6** | **13.4** | **10.6** | **8.20** | **3.84** | **7.33** | **7.09** | **5.16** |
| Sr | **0.91** | **0.93** | **7.09** | **5.66** | **2.20** | **2.34** | **3.36** | **2.48** | **3.49** | **2.08** | **2.76** | **2.00** | **4.56** | **2.00** | **5.70** | **2.72** | **6.47** | **6.27** | **6.48** |
| Fe | 0.76 | **2.89** | **0.94** | 0.70 | **2.54** | **1.71** | **7.31** | **1.90** | **11.9** | **2.14** | **3.18** | **5.50** | 0.79 | **5.50** | **4.75** | 0.45 | 0.70 | 0.46 | 0.77 |

Note: CR values greater than 0.9 are represented in bold type.

Table 8. Mean concentrations of soil and bitumen samples (μg/g).

| Element | 0–15 cm depth | 15–30 cm depth | Bitumen, Adebiyi et al. [18] |
|---|---|---|---|
| K | 54.6 | 53.9 | 60.8 |
| Ca | 453 | 459 | 311 |
| Ti | 15.4 | 12.2 | 203 |
| V | 0.780 | 0.64 | 60.5 |
| Cr | 0.630 | 1.06 | 52.0 |
| Ni | 1.69 | 1.89 | 43.3 |
| Mn | 174 | 151 | 39.7 |
| Fe | 144 | 181 | 60.6 |
| Rb | 2.70 | 2.85 | – |
| Sr | 11.1 | 4.92 | – |
| Cu | 19.3 | 12.0 | 99.4 |
| Zn | 3.88 | 20.9 | 247 |
| As | 0.99 | 1.02 | 52.6 |
| Pb | 2.84 | 1.88 | 10.4 |



Table 9. Comparison of trace element characteristics of the vegetation samples with other Nigerian vegetation (μg/g).

| | This study | Fasasi and Obiajunwa [1] | Olajire [34] |
|---|---|---|---|
| K | 125–680 (313) | 380–2669 (304) | ND |
| Ca | 104–904 (280) | 74.7–1388 (744) | ND |
| Cr | ND–22.4 (7.81) | ND | 8.00–11.0 (14.0) |
| Ti | ND–339 (50.8) | 157–175 (168) | ND |
| V | ND–16.8 | ND | ND |
| Mn | 21.8–621 (145) | 0.937–12.2 (8.01) | 160–1900 (818) |
| Ni | ND–43.3 (20.8) | 160.2–181 (168) | 8.00–16.00 (12.00) |
| Cu | 21.5–56.9 (29.8) | 11.6–102 (41.9) | 3.00–46.0 (24.5) |
| Zn | 23.3–137 (51.2) | 0.00–76.6 (26.4) | 11.0–94.0 (41.5) |
| Ga | ND–3.51 | ND | ND |
| Rb | 11.0–56.2 (25.3) | ND | ND |
| Sr | 10.1–78.9 (32.6) | ND | ND |
| Fe | 81.9–709 (401) | 105–146 (120) | 50.0–560 (236) |

Note: ND = Not detected.

## 4. Conclusion

The results of the calculated elemental concentration ratios (CR) of the vegetation samples show that the vegetation samples have high uptake ability from soil for K, Ni, Cu, Zn, Rb and Sr, and low uptake ability for Mn, while the shallow-rooted plants (mostly vegetables) have high uptake ability for Fe. Some of the elements within the vegetation have strong positive correlation; very few of them have strong negative correlation. These associations can be explained in terms of a common source, such as weathered soils or bedrocks, plant and animal remains, chemical similarity in terms of oxidation state or compound types and/or common natural background levels in the samples. Positive correlations are shown by the results of the cross plot analysis of the vegetation/soil and vegetation/bitumen using analysed elements as the variables. These suggest inter-element correlations between them and also establish relationships between the aforementioned components of the ecosystem and the bitumen deposit in the area. This could be a useful fingerprint for bitumen exploration elsewhere and also for similar mineral deposit settings, such as crude oil and coal deposits. Efforts should be made therefore to ensure proper protection of the ecological resources of the mineral deposit area.

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