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TXRF Characterization of EDTA Extractable Metals from Soils of Bituminous Sands Occurrence Area, Agbabu, South Western Nigeria

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Abstract: Ethylenediamine Tetra-acetic Acid (EDTA) extractable metals were determined in soils of bituminous sands occurrence area of Agbabu in southwestern Nigeria using Total reflection x-ray Fluorescence (TXRF) technique. Soil samples were collected at two different depths (0-50 and 50-100 cm) along a transverse line cutting across the main road in the study area. Fourteen metals; K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ce, Eu, Au, Pb and Co were detected in all. However, Co, Pb and Ni were not detected in samples from 0-50 cm depths and Pb and Rb in some samples from 50-100 cm depths. The concentration, mean, range, standard deviation and correlation coefficients were calculated for the detected metals. Moderate correlations were found to exist between K, Ti, Ni, Zn, Rb and Sr; very high correlations between Ca, Cu Pb and Au in 0-50 cm depth samples. In the 50-100 cm depth samples, moderate correlations were observed between Ca, Cu and Zn; between Fe, Ti, Co and Ni. Pb was found to be highly correlated to Ca, Ti, Ni and Sr. This study provides a pre-exploration baseline data in the region and the need for the extension of such a baseline analysis to other environmental sensitive media-water resources, crops and local air quality in the region is emphasized.

Key words: Bituminous sands, biogeochemical, EDTA, soluble complexes, tailings, TXRF

INTRODUCTION

Reserves of heavy oil have been reported to occur in the same ecologically sensitive mangrove environments of Niger Delta of Nigeria, where crude oil and natural exploration and extraction have been going on for some time. Bituminous sands, also known as oil or tar sands occur in these areas but mostly along the upper fringe of this region[1,2]. The bituminous sands deposit in the Southwestern Nigeria is one of the notable natural deposits, estimated to be the second largest in the world with a belt of about 120×6 km extending approximately in the south-easterly direction from Ijebu-Ode (6°50'N and 4°54' E) ridge/western feather edge of tertiary Niger Delta to as far as east of Okitipupa (6°30'N and 4°50' E) in Ondo State (Fig. 1). It has an estimated reserve of about 40 billion barrels of bituminous sands in place[3-5].

Bituminous sand is composed of bitumen, water and mineral matter. Since this natural resource is of vast deposit in Nigeria, colossal quantities of tailings (bituminous sands mineral matter and water with dissolved substances) will be generated in the course of its exploitation. The need therefore arises for the trace metals characterization of the host agricultural soils in their current undisturbed state to serve as a baseline data from which future changes could be based.

Trace metals form an important component of tailings that are generated during the exploration, mining and extraction phases. Heavy metals in particular pose health risk to man as well as impact on the flora and fauna through the dynamics of the metals in the ecological system in the region and eventual uptake by tissues through the food chain[6,7]. Some of them could also have impact on materials corrosion and damage[8].

Ethylenediamine Tetra-acetic Acid (EDTA) is a chelating agent capable of forming soluble complexes with large number of cations in strong covalent bonding. The tendency of forming complex salts increases with higher oxidation state of metals. EDTA is an effective agent for the extraction of available trace metals from the soils. The complexes formed have the general equation:

$$Metal_{cation} + EDTA \Rightarrow (Metal_{cation}\text{-}EDTA)Complex$$

Typical examples of these include Co $(EDTA)^{2-}$, (Fe (EDTA) $H_20)^{-}$, $(Fe\ (EDTA))_2\ 0^{4-}$and (Mn EDTA $(H_20)^{-}$) etc.[9,10].

This study will contribute to the understanding of the physical and chemical properties of soils in the region with deposits of bituminous sands in Nigeria in terms of the elemental content, distribution and their likely biogeochemical pathways. It will also add to existing

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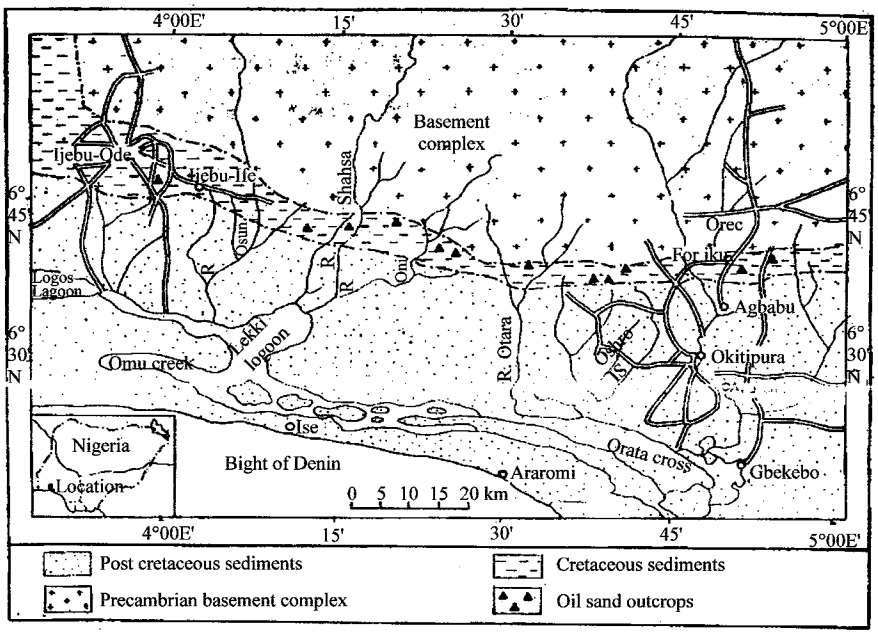

Fig. 1: Geological map of southwestern Nigeria showing bituminous sand outcrop belt[1]

database on Nigerian bitumen deposits which would be of value to a wide range of stakeholders interested in safe mining of the bituminous deposits and the potential impacts on the agricultural system and human health in the region.

MATERIALS AND METHODS

Study area: The study area (Fig. 2) is located within latitude 6°35'to 6°40'N and longitude 4°48' to 4°54'E, slightly mid-way between Okitipupa and Ore towns in Ondo State. The area covered by field sampling is located about 4.5 km north of Agbabu village along the road linking Agbabu with Foriku. The location is within a few kilometers of the coastline of the Bight of Benin and is known for fishing and farming. The crops grown include food crops and cash crops-cocoa, cola, oil palm and rubber trees. Most farmers in the region are peasant farmers who still practice subsistence agriculture. There, however, appears to be a steady increase in the use of insecticides and fungicides for the treatment of cocoa farms, which may have a steady impact on the trace element profile of the soils in the region.

Sample collection, preparation and analysis: The soil samples were collected along a transverse line (1 km by length) cutting across the road that leads to Agbabu village in the study area. Samples were collected at 100 m from both sides of the road. At each sample point, two soil samples at depths of 0-50 and 50-100 cm were collected from twenty-five points along the transverse line (giving a total of 100 samples) using a Dutch Hand Soil Auger[11] after the decomposing materials have been removed. The Global Positioning System (GPS) was used to locate the exact geographical coordinates of these points (Fig. 2). The detailed methodology for use of the soil Auger is described elsewhere[11].

The composites and representative soil samples were dried by air at room temperature in the laboratory but adequately screened from particulate deposition. Samples were then crushed to 2 mm mesh size using Agate mortar, after homogenizing by coning and quartering[11,12].

The metals in the soils were extracted from 10 g of each sample using 50 mL of mixture of 0.05 M EDTA and 35% m/m NH_3 (pH 7). An equal volume of the mixture of EDTA and NH_3 was prepared from the same containers for the purpose of blanks correction determinations[13].

A 5 µL aliquot of each of the extracted samples was pipetted unto a sample carrier and dried using infrared lamp. The sample on the carrier was then irradiated with an x-ray beam from a secondary Mo-target x-ray tube operated at a tube voltage of 40 keV and current of 20 mA. Gallium was used as internal standard with an irradiation and spectra acquisition time of 1000 sec.

Fluorescence x-rays from each sample were analyzed using an x-ray spectrometer, GENIE2K inspector data acquisition software. The quantitative analysis of the spectra obtained was carried out using the QXAS software analysis package[11].

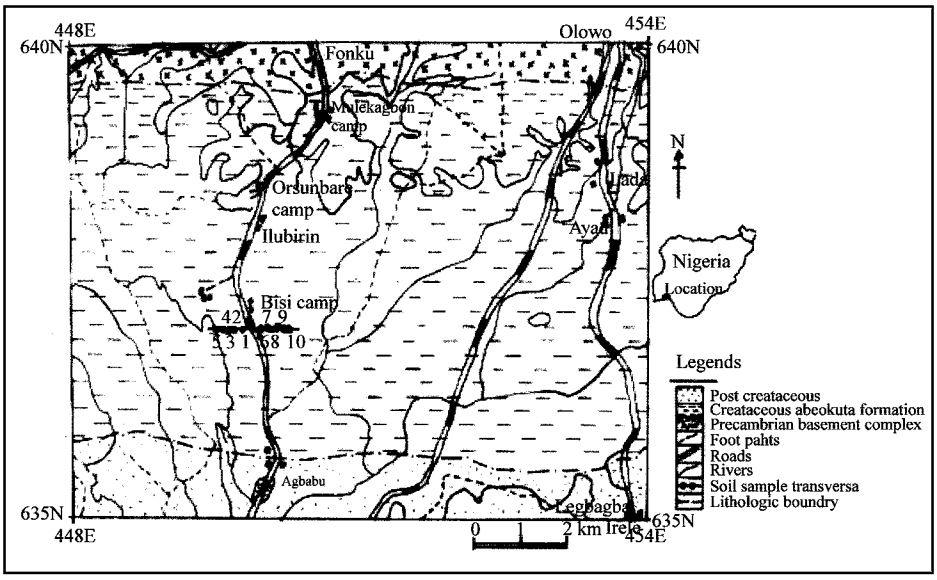

Fig. 2: Geological map of the study area showing sampling locations

The calibration of the TXRF spectrometer for the analysis used the IAEA-Soil-7 as reference standard. The standard was prepared and analyzed using the same protocols as the samples.

Statistical analysis: The elemental concentrations of the analyzed samples was subjected to statistical analysis to determine the Enrichment Factors (EF) of the elements, level of correlation between the elements using the correlation coefficients as well as clusters. The EF is the quotient of the ratio of the concentration of element x to the concentration of reference element f in the sample to the same ratio in the reference soil. This is expressed as:

$$EF = \frac{\left(\frac{C_x}{C_f}\right)_{sample}}{\left(\frac{C_x}{C_f}\right)_{ref.soil}}$$

where, C_x and C_f are the concentrations of element x and reference element f in soil and reference samples. The correlation coefficients were calculated using the SPSS statistical package and correlation coefficients of 0.5 were considered significant. The cluster analysis was carried out using the furthest neighbour (complete linkage) grouping of the hierarchical cluster analysis in the SPSS package.

RESULTS AND DISCUSSION

Reference standard analysis: The values obtained for all the elements (except K and Ca) are comparable with the reference values for the standard (Table 1). This implies that in exception of K and Ca, the analytical results of the other elements are with some high level of confidence.

Elemental analysis: Results of the elemental analysis from TXRF spectrometer indicate the identification of 14 metallic elements in the soil samples analyzed. These include K, Ca, Ti, Mn, Fe, Co, Ni and Cu. Others are Zn, Rb, Sr, Ce, Au and Pb. Out of these, nine are transition metals, while five are non-transition metals. These results indicate the effective role played by EDTA in the selective extraction of metals from the samples.

Table 1: IAEA soil 7 analysis result

Element	Recommended value (ppm)	95% confidence interval (ppm)	Obtained values (ppm)
K	12100.0	11300-12700	8500*
Ca	163000.0	157000-174000	135700*
Ti	3000.0	2600-3700	2700
V	66.0	59-73	57
Cr	60.0	49-74	53
Mn	631.0	604-650	700
Fe	25700.0	25200-26300	26800
Ni	26.0	21-37	22
Cu	11.0	9-13	10
Zn	104.0	101-113	108
As	13.4	12.5-14.2	15
Rb	51.0	47-56	66

Table 2: Average elemental compositions (μg g^{-1})

Sampling depth (cm)		Elements												
		K	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr	Ce	Pb
0-50	Mean	55.15	490.79	11.90	156.22	133.07	2.06	1.19	8.22	9.62	1.96	4.31	10.96	1.58
		±0.13	±0.20	±1.35	±0.05	±0.10	±0.04	±0.04	±0.02	±0.03	±0.06	±0.05	±0.06	±0.08
	Range	32.64	314.10	4.38	73.52	53.56	0.00	0.00	5.53	2.53	1.41	2.85	7.19	0.00
		-89.61	-32.20	-41.74	-272.93	-241.12	-6.00	-3.83	-12.74	-18.91	-3.53	-6.61	-16.06	-7.00
50 100	Mean	30.33	255.70	6.64	117.24	78.00	5.76	1.39	8.30	5.91	1.73	2.38	10.60	3.72
		±0.13	±0.20	±1.35	±0.05	±0.10	±0.04	±0.04	±0.02	±0.03	±0.04	±0.05	±0.04	±0.08
	Range	19.76	66.96	2.47	38.33	49.61	1.33	0.70	5.15	2.59	0.00	0.86	7.58	0.00
		-48.10	-735.88	-17.83	-331.53	-145.89	-14.54	-4.63	-11.63	-10.14	-2.31	-3.83	-15.33	-18.08

Table 3: Average elemental enrichment factor as a function of distance

	Elements							
	Ni		Cu		Zn		Pb	
Site	Top soil	Sub soil	Top soil	Sub soil	Top soil	Sub soil	Top soil	Sub soil
1	7	49	91	548	84	153	0	2080
2	8	7	36	35	41	32	0	73
3	7	7	82	68	34	55	0	0
4	0	7	68	97	50	38	50	0
5	4	59	42	169	26	75	37	382
6	8	52	98	572	104	187	2180	482
7	5	4	34	35	39	28	68	0
8	7	7	83	72	62	54	48	2490
9	8	11	66	104	37	48	0	0
10	4	32	44	172	28	73	35	262

Analysis provide results for 14 elements (K, Ca, Ti, Mn, Fe, Co, Ce, Ni, Cu, Zn, Rb, Sr, Au and Pb), which is dominated by 9 transition metals (Ti, Mn, Fe, Co, Ni, Cu, Zn, Ce and Au) followed by K, Ca, Rb, Sr and Pb, which are non-transition metals (Table 2). The mean elemental concentrations in the 50-100 cm class decreased considerably compared to the 0-50 cm class for K, Ca, Ti, Mn, Fe, Zn, Rb and Sr with the values of 30.33, 255.70, 6.64, 117.24 78.01, 5.91, 1.74 and 2.38 μg g^{-1}, respectively. The Co, Ni, Au and Pb values are however higher with the values of 5.76, 1.39, 3.17 and 3.72 μg g^{-1}. The mean values for Cu and Ce were observed to be close in the two classes (8.22 and 10.96, respectively for 0-50 cm class and 8.30 and 10.60, respectively for 50-100 cm class). In this class only one metal-Rb was not detected in some samples.

Enrichment factors: The enrichment factor result presented in Table 3 is that of the twenty samples (five from each side of the transverse line and two per site) and shows that the elements-Ni, Cu, Zn and Pb are highly enriched for the two soil categories for the sites at which the elements were detected. The enrichment factors ranged between 4-8 and 4-59, respectively for Top and Sub soils in respect of Ni; between 34-98 and 35-572 for Top and Sub soils, respectively in respect of Cu; between 26-104 and 32-187 for Top and Sub soils, respectively in respect of Zn and between 35-2180 and 73-2490 for Top and Sub soils, respectively in respect of Pb. The enriched elements, which were also found to be highly correlated, could be said to have common anthropogenic origin or influencing factor. Lead (Pb) was not detected for Top soils at sites 1, 2, 3 and 9 and for Sub soils at sites 3, 4, 7 and 9.

Transition metals association with bitumen: Of the nine transition metals identified, four (Mn, Fe, Ni and Cu) are known to be associated with hydrocarbon formations including those of bitumen[14]. Results in Table 4 show that the range and mean values of elemental concentrations of three transition metals (Fe, Ni and Cu) in the nearby bitumen fields are higher than similar values obtained in the soils of Agbabu. However the values of Mn have range and mean values higher than their concentration in bitumen. The comparability of Ni/V ratio for the Agbabu soils could not be established because V and Cr were not detected in both top and sub soil classes analyzed.

Correlation matrix and cluster analysis in relation to source identification

Elemental correlation matrix: The metals in the 0-50 cm class of soils (Table 5) displayed very high correlations. For example, K had a correlation of 0.73 and 0.75 with Rb and Au, respectively. Ca has a correlation of 0.75, 0.73 and 0.84, respectively with Cu, Sr and Pb while Fe correlation with Ni, Cu, Zn and Au are, respectively 0.72, 0.74, 0.79 and 0.70. The correlation of Cu with Zn, Au and Pb

Table 4: Transition metals associated with hydrocarbons

Transition metal	Kerogen (ppm) Nwachukwu *et al.*[14]	Bitumen (ppm) Nwachukwu *et al.*[14]	Oils (ppm) Nwachukwu *et al.*[14]	Soils (ppm) (Bituminous area of Agbabu under this study)	
				0-50 cm depth	50-100 cm depth
V	233.93-861.09 (570.67)	2.24-68.67 (17.97)	0.009-1.83 (0.471)	-	-
Cr	146.15	0.99-68.43 (9.89)	0.021-0.219 (0.074)	-	-
Mn	4.75-232.00 (42.34)	1.93-59.26 (15.08)	0.004-0.442 (0.079)	73.52-272.93 (156.22)	38.33-331.53 (117.24)
Fe	2826.19-8333.15 (5604.564)	52.05-6052.14 (728.99)	0.006-20.85 (6.478)	53.56-241.12 (133.07)	49.61-145.89 (78.00)
Ni	150.20-278.36 (198.44)	16.83-91.96 (47.02)	0.351-11.282 (3.081)	0.00-3.83 (1.19)	0.70-4.63 (1.39)
Cu	210.88-358.20 (303.66)	38.39-1318.62 (536.43)	0.547-42.3 (7.872)	5.53-12.74 (8.22)	5.15-11.63 (8.30)
V/V+Ni	0.60-0.80 (0.72)	0.071-0.600 (0.273)	0.01-0.41 (0.12)	-	-

Table 5: Elemental correlation matrix for 0-50 cm depth samples

	K	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr	Ce	Au	Pb
K	1.000													
Ca	.123	1.000												
Ti	.635	-.131	1.000											
Mn	.362	.014	.294	1.000										
Fe	.371	.407	.688	.537	1.000									
Co	-.405	.344	-.176	.441	.386	1.000								
Ni	.685	.127	.919	.246	.719	-.044	1.000							
Cu	.439	.750	.429	.268	.743	.278	.557	1.000						
Zn	.598	.621	.569	.280	.794	.098	.687	.903	1.000					
Rb	.729	.537	.640	.204	.622	-.027	.824	.812	.820	1.000				
Sr	.555	.730	.368	.373	.624	.170	.486	.929	.789	.829	1.000			
Ce	.274	.046	.024	-.012	-.080	-.233	.150	-.200	.087	.143	-.119	1.000		
Au	.752	.413	.778	.220	.703	-.100	.904	.774	.858	.970	.750	.173	1.000	
Pb	-.003	.839	-.215	.222	.402	.572	-.001	.756	.596	.406	.681	-.204	.287	1.000

Table 6: Elemental correlation matrix for 50-100 cm depth samples

	K	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr	Ce	Au	Pb
K	1.000													
Ca	.507	1.000												
Ti	-.123	.100	1.000											
Mn	-.506	-.252	.043	1.000										
Fe	-.018	-.186	.688	.434	1.000									
Co	-.713	-.356	.613	.558	.505	1.000								
Ni	-.239	-.091	.951	.044	.589	.709	1.000							
Cu	.590	.462	.062	-.645	-.321	-.589	-.004	1.000						
Zn	.503	.051	.218	-.473	.307	-.268	.157	.296	1.000					
Rb	-.006	.364	.058	.132	-.004	.159	.053	-.251	.232	1.000				
Sr	.373	.746	.610	-.220	.217	.008	.454	.411	-.025	.072	1.000			
Ce	-.514	.212	.175	.621	.138	.399	.133	-.363	-.376	.249	.126	1.000		
Au	-.466	-.346	-.229	.028	-.186	.302	-.128	-.437	.092	.108	-.612	.096	1.000	
Pb	.118	.858	.253	.048	-.002	-.074	.053	.201	-.120	.278	.701	.635	-.242	1.000

are observed to be 0.90, 0.77 and 0.77, respectively while that of Au with Rb and Sr are 0.97 and 0.75, respectively. This high correlation suggests strong affinity among the metals and may indicate possible common sources for the affected elements likely to be associated with hydrocarbon formations. Nearly half of the metals with the high correlations are transition metals, most of the remaining ones are heavy metals (Rb, Au, Sr and Pb) most likely of anthropogenic influence from farming activities, while Ca and K are elements of crustal origin.

In the 50-100 cm depths, only few metals showed very high correlations with one another (Table 6). Ca has a correlation of 0.75 and 0.86 with Sr and Pb, respectively. Ti correlated with Mn (0.95) and Fe with Ti (0.70). These metals, with the exception of Pb, are mainly crustal metals indicating little anthropogenic influence at these soil depths.

Elemental cluster analysis: The elements Rb, Au, Ni, Co, Pb, Sr, Cu, Zn, Ce, Ti and K in one cluster and elements Mn and Fe in the second cluster from the Topsoil were observed to be strongly correlated giving an indication of common source/sources or anthropogenic influence or, at least, a strong affinity for one another. The two clusters generated in the Sub soil class were observed to be identical in elemental memberships to the Topsoil class. The correlations among the clustered elements in the Sub soil were however weak and this may strongly suggest different pathways of contribution to the levels of the affected elements (Fig. 3).

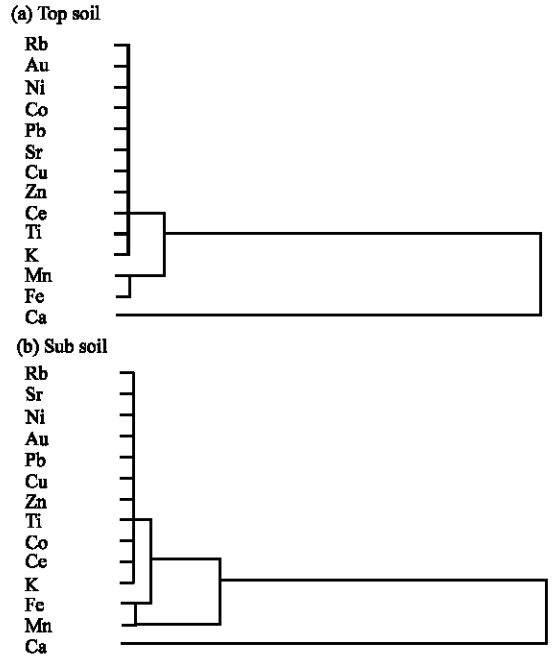

Fig. 3: Cluster analyses result for top and sub soils

Potential human exposure to heavy metals through biogeochemistry: The soils of the area appear to contain substantial metals of different chemical affinity. These include K, Ca, Ti, Mn, Fe, Co, Ni and Cu. Others include Zn, Rb, Sr, Ce, Au and Pb. Some of these, especially Pb, Co and Zn are known to be toxic and posse great danger to human health. The major occupation of most residents of the region is still farming. The assessment of the potential for uptake of such heavy metals into crop and eventual transfer to the food chain is an important source of contamination likely to be associated with the exploitation of bitumen in the region. The assessment of such biogeochemical pathway for exposure is an important task that must be undertaken to provide basis to assess potential impact of health, following the exploration and mining of the region's vast bitumen resources.

CONCLUSIONS

We conclude that EDTA, an effective chelating agent, was successfully used to extract trace metals from the soils of bituminous sands occurrence area of Agbabu, Southwestern Nigeria. Fourteen metals: K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ce, Au, Pb and Co were detected. Many metals are observed to be highly correlated in the 0-50 cm classes of soils while only few observed high correlations among themselves in the 50-100 cm classes. Possibly, it could be concluded that only the metals from the 0-50 cm classes of soils have little influence, probably, from agricultural activities. The research study has provided a pre-exploration baseline data as basis for establishing future impacts of bitumen exploration and mining in the region. Such a baseline analysis needs to be extended to other environmental sensitive media such as water resources, crops and local air quality in the region, while more spatial coverage of the Agbabu soils needs to be attained in future studies.

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