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Trace element and physico-chemical characteristics of the sand and water fractions of Nigerian bituminous sands

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Bituminous sands from south-western Nigeria were separated into water and sand fractions, and these were analysed for their physico-chemical properties and trace-metal contents to evaluate their potential environmental hazards. The samples were obtained from five different locations (Ilubirin, Agbabu, Mile 2, Olowo-Irele, and Loda) in Ondo State, south-western Nigeria. The water content was extracted using Dean and Stark apparatus, while the sands were collected as left-over from the thimble. The trace metal content was determined using total X-ray fluorescence (TXRF) spectrometry. The physico-chemical parameters (conductivity, pH, total alkalinity, total acidity, salinity, colour, organic matter, Cl^- , SO_4^{2-} , and NO_3^-) were determined using standard analytical methods. Copper, Cr, Zn, and As, which are known to be toxic metals, were highly enriched (enrichment factor, $\text{EF} > 10$) in the sand fraction samples, while comparison of some of the physico-chemical parameter values of the water and sand fractions with recommended standards showed that the values of some of the parameters were relatively high. These values indicate their potential environmental hazards. This calls for proper management of the tailings that will be produced during the exploitation of the bituminous sands. Analysis of certified IAEA standard reference material (IAEA-soil-7) was carried out to ensure accuracy and precision of the TXRF technique.

Keywords: Bituminous sand; Pollution; Tailings; TXRF

1. Introduction

Industrialization and technological advances in the development of a nation also bring with them problems and unavoidable costs in terms of environmental pollution; more so if environmental protection is not taken into account at the initial stages of developmental planning. The situation with many nations today is a good example of the dilemma of industrial progress and environmental degradation. Environmental degradation which used to be peculiar to industrialized nations is now a major problem in developing countries too. Pollution of water, and of air and land are very closely interrelated if not properly managed. That is, pollutants from one medium are transferable to the other media. Mine waste and other forms of waste (solids

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and liquids), arising from exploitation of mineral resources, are major sources of pollution to our environment. The indiscriminate discharge of these wastes into the environment could eventually lead to environmental degradation and alter the ecology of the area. Therefore, efficient and effective management of mine tailings and other solid/liquid waste is an essential component of the environmentally friendly development of any mining industry.

Large quantities of tailings are usually produced during separation of bitumen from bituminous sands, especially if aqueous extraction method is used in extracting the bitumen [1, 2]. Bituminous sand is composed of heavy oil or bitumen, sand, and water, and it is known to be about 10–100-fold more toxic than crude oil [3, 4]. A physico-chemical analysis of water associated with petroleum is important in exploration [5], especially for corrosion of oil-well tubular-structure management [6], the production of certain valuable elements such as Na, K, V, and Ni [7], and to evaluate the potential environmental hazards.

There is growing interest in the exploitation of Nigeria's vast deposits of bituminous sands [3, 8], and it is therefore hoped that in the process of exploitation, a large quantity of tailings will be produced during separation of bitumen from the bituminous sands. The tailings, if not properly managed, may cause serious environmental degradation. The first step in taking care of the likely environmental consequences of the exploitation of these deposits is to have clear knowledge of the physico-chemical and elemental properties of the various fractions of the bituminous sands that would be separated during the mining and refining of them.

Several studies have been performed on the Nigerian bituminous sands, including geological [9, 10], physico-chemical, and elemental characterization of the bituminous sands and bitumen (heavy oil) extracted from the bituminous sands [11–13], but there are no data available on the physico-chemical and elemental properties of the sand and water fractions of the bituminous sands, which is crucial from an environmental pollution consideration.

We report here on the nature and concentrations of the physico-chemical and elemental parameters (which are indicators of pollution) of the sand and water fractions of the bituminous sands. These parameters include pH, conductivity, acidity, carbonate/alkalinity, chlorinity, salinity, SO_4^{2-} , nitrate, sulphate, colour, organic matter, and trace-element contents.

2. Experimental

2.1 Sample collection

Surface samples of bituminous sands were collected from five different locations, Ilubirin, Agbabu, Mile 2, Loda, and Olowo-Irele sites, where bituminous sand outcrop occurs. The study area falls between longitudes $4^\circ 48'$ and $4^\circ 54'$ E and between latitudes $6^\circ 35'$ and $6^\circ 39'$ N. The area falls within the 1:50 000 standard topographic sheets 282 (Okitipupa south-east). Each sample location was plotted using a global positioning system (figure 1).

2.2 Extraction of sand and water fractions from the bituminous sands

2.2.1 Sand fraction. Each sample of bituminous sands weighing about 50.0 g was subjected to extraction in a Soxhlet extractor using double-distilled toluene. The extracting solvent with the bitumen extract was allowed to reflux until the solvent returning to the flask was colourless; this was taken to be the end of the extraction, and the process was stopped. The sand fraction was placed together with the thimble in the oven at about 70°C for 3 h in order to evaporate residual water and solvent [14].

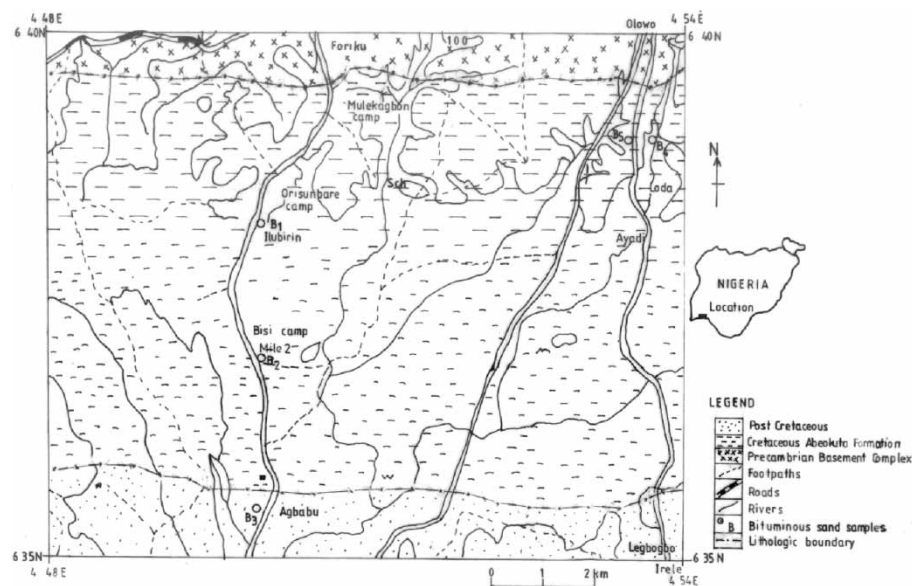


Figure 1. Study area.

2.2.2 Water fraction. The water content determination was carried out using the Dean and Stark apparatus, which is based on the principle of reflux. The water content of the bituminous sands was easily evaporated by a mixture of double-distilled toluene and xylene (in a ratio of 1:4) as a carrier solvent. About 50 g of bituminous sands sample was placed into an Erlenmeyer flask, and about 250 ml of carrier solvent was added. Heat was then applied from a heating mantle to the mixture; this was adjusted so that the condensate was discharged from the condenser at the rate of two to five drops per second. The distillation continued until the volume of water in the trap remained constant for about 3 minutes. The heater was then turned off, and the trap and contents were allowed to cool to room temperature. This process was repeated so as to collect a large volume of water [14].

2.3 Determination of physico-chemical properties

2.3.1 pH determination. The pH of the samples was measured using a standardized digital pH meter HI8519 (Hanna instrument) at 25 °C. Two standard alternative procedures (sand/water and sand/0.01 M CaCl₂) involving a ratio of 1:2 of sand to solvent were used to determine the pH of the sand samples [15, 16]. The pH of the water sample was measured at 25 °C using the standardized digital pH meter. The accuracy of the pH value was ensured by calibrating the glass electrode pH meter used with standard pH 4.0 (Potassium biphthalate) and pH 10.0 (carbonate) buffers. The pH of the buffers was equally confirmed with a hand-held glass electrode pH meter model CD 70 (WPA instrument). A duplicate analysis was also carried out [17].

2.3.2 Conductivity determination. The conductivity of the sand samples was measured using a pH/conductivity meter model 20 at 25 °C after calibration with 0.001 M KCl. This was carried out after pre-treatment with saturated CaSO₄ solution [16, 17], while that of the water samples was measured using the same instrument [17].

2.3.3 Nitrate [NO₃⁻] determination. The sand samples were pre-treated with CaSO₄ for NO₃⁻ determination. The nitrate determination of the sand and water samples was carried out using the AOAC [17, 18] method of analysis.

2.3.4 Chloride ion [Cl⁻] determination. The sand samples were pre-treated with CaSO₄ before Cl⁻ determination. The Mohr (titrimetry) method was used to determine the Cl⁻ in both the sand and water samples in this study [17, 18].

2.3.5 Salinity determination. The salinity of the samples was determined using the equilibrium relationship between chlorinity and salinity as follows [19]:

$$S(\%) = 1.80655 \text{ Cl}^-(\%)$$

2.3.6 Sulphate [SO₄²⁻] determination. The turbidimetric method of analysis was used for SO₄²⁻ determination [18].

2.3.7 Acidity determination. Acidity was determined using a titrimetric method of analysis [17].

2.3.8 Alkalinity/carbonate determination. Carbonate of sand samples was determined by the gravimetric method for loss of CO₂ [15], while that of water samples was determined by titration with standard HCl acid to the end-point pH between 4.2 and 5.4 using Methyl Orange indicator [18].

2.3.9 Organic-matter determination. Black *et al.*'s [16] method of organic-matter analysis was used to determine the organic-matter content of the sand samples.

2.3.10 Sand-colour determination. The colour of the sand samples was measured by comparison with the modified version of the colour chart of the Munsell Book of Colour. This was done after moistening the sand samples with water [20].

2.4 Digestion of sand and water samples

2.4.1 Sand fraction. A powdered sand sample weighing 0.20 g was put into a Teflon bomb, and 2.5 ml HCl was added to the sample followed by the addition of 5 ml of HF acid. The mixture was then heated at 70 °C in an oven for 3 hours. This was allowed by cooling to room temperature, and 2.5 ml of saturated boric acid was added. The mixture was then left overnight. The digested sample was transferred into a 25 ml volumetric flask and made up to the mark (dilution factor of 125) with double-distilled water. A blank sample (as control) was also treated in the same way [21].

2.4.2 Water fraction. Twenty-five millilitres of the sample was transferred into a 100 ml conical flask, and 2.5 ml of concentrated HNO₃ was added. This was heated on a hot plate to boiling point and evaporated to about 10 ml. The digested sample was then transferred into a 50 ml standard flask volumetric flask and made up to the mark with double-distilled water. Blank-sample determination was also carried out as a control [17].

2.5 Elemental analysis

The elemental analysis of the sand and water fractions was carried out using total reflection X-ray fluorescence (TXRF) spectrometer in the Environmental Research Laboratory, Department of Physics, Obafemi Awolowo University, Ile-Ife, Nigeria. The TXRF Spectrometer consists of a Compact 3K5 X-ray generator with an X-ray tube (Model IS 221520), with a Mo anode, manufactured by Ital Structures, and a Canberra (SL 80175) Si (Li) detector (resolution 175 eV at 5.9 KeV) coupled to a Canberra Inspector-2000 Digital Signal Processor. Canberra Genie-2000 software was used for data acquisition.

A 5 μ l aliquot of each of the digested sample was pipetted into a quartz sample carrier and dried using an infrared lamp. The sample and Ga internal standard were then irradiated with an X-ray beam from a secondary Mo-target X-ray tube operating at a tube voltage of 40.0 KeV and current of 20.0 mA. An irradiation and spectra acquisition time of 1000 s was used. Fluorescence X-rays from each sample were analysed using an X-ray spectrometer with a Genie 2K inspector data-acquisition software. The quantitative analysis of the spectra obtained was carried out using the QXAS software analysis package [21].

For quality assurance, the IAEA reference material (IAEA-soil-7) was prepared and analysed following the same protocols as that for the sand samples. Solvents for extraction and water used were double-distilled, and all reagents used were of BDH Analar grade.

3. Results and discussion

3.1 Quality assurance

The results of the analysis of the IAEA Standard Reference Soil (Soil 7) are presented in table 1 alongside the certified values for the reference soil. The results are in agreement with the certified values, which imply reliability of the elemental concentration results for the various samples analysed.

3.2 Results of physico-chemical characterization and elemental composition

3.2.1 Sand fraction. The values of the physico-chemical parameters of the sand fraction of the bituminous sand samples are shown in table 2. The values obtained have the following ranges: conductivity (2.45–8.27 ms cm⁻¹), pH using distilled water (2.75–3.90),

Table 1. IAEA-Soil-7 analysis results.

Element	Certified value (ppm)	95% confidence interval (ppm)	This study (ppm)
K	12 100	11 300–12 700	8 500*
Ca	163 000	157 000–174 000	135 700*
Ti	3 000	2 600–3 700	2 700
V	66	59–73	57
Cr	60	49–74	53
Mn	631	604–650	600
Fe	25 700	25 200–26 300	26 000
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

*Values outside the certified values for soil 7 analysis.

Table 2. Physico-chemical parameters of the sand fraction of bituminous sands of south-western Nigeria.

Sand sample	Conductivity (mS cm ⁻¹)	pH at 25 °C		NO ₃ ⁻ (ppm)	SO ₄ ²⁻ (ppm)	CO ₃ ²⁻ (%)	Cl ⁻ (ppm)	Salinity (‰)	Organic matter (g kg ⁻¹)	Munsel moist colour
		Ratio 1:2 of sample/solvent								
		Water	0.01 M CaCl ₂							
Ihubirin	8.27 ± 0.9	2.75 ± 0.6	2.74 ± 0.5	16.0 ± 1.0	82.0 ± 8.7	0.41 ± 0.2	n.d.	n.d.	52.1 ± 3.4	Black (5YR 2/1)
Olowo-Irele	2.54 ± 0.6	3.50 ± 0.7	3.20 ± 0.7	24.8 ± 2.2	58.0 ± 4.9	1.34 ± 0.8	23.3 ± 1.2	0.04 ± 0.01	25.8 ± 1.4	Grey (5YR 6/1)
Loda	2.45 ± 0.5	3.90 ± 0.7	3.92 ± 0.8	17.4 ± 1.9	30.0 ± 1.4	0.43 ± 0.1	30.6 ± 1.1	0.06 ± 0.01	65.9 ± 2.6	Grey (5YR 5/1)
Mean	4.42	3.38	3.29	19.4	56.7	0.73	18.0	0.03	47.9	
Range	2.45–8.27	2.75–3.90	2.74–3.92	16.00–24.8	30.0–82.0	0.41–1.34	0.00–30.6	0.00–0.06	25.8–62.9	

*n.d.: not detected.

Table 3. Elemental concentration and the enrichment factor (EF) of the sand fraction of Nigerian bituminous sands (ppm).

Sand sample	Elements											
	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Ilubirin	103 ± 0.10	31.1 ± 0.01	497 ± 0.21	28.3 ± 0.02	76.7 ± 0.02	198 ± 0.05	131 ± 0.05	43.3 ± 0.1	189 ± 0.03	263 ± 0.1	51.6 ± 0.02	3.04 ± 0.01
Olowo-Irele	98.1 ± 0.02	78.3 ± 0.1	314 ± 0.1	19.1 ± 0.02	64.5 ± 0.03	212 ± 0.1	129 ± 0.04	19.2 ± 0.01	31.3 ± 0.04	165 ± 0.1	63.7 ± 0.03	6.01 ± 0.01
Loda	63.2 ± 0.04	37.8 ± 0.03	235 ± 0.12	23.2 ± 0.01	83.0 ± 0.03	156 ± 0.1	118 ± 0.1	22.7 ± 0.02	97.2 ± 0.1	294 ± 0.13	40.1 ± 0.02	7.01 ± 0.01
Mean	88.1	49.1	349	23.5	74.7	189	126	28.4	106	241	51.8	5.35
Range	63.2–103	31.1–78.3	235–497	19.1–28.3	64.50–83.00	156–212	118–131	19.2–43.3	31.3–189	165–294	40.1–63.7	3.04–7.01
EF*	0.72	0.21	1.00	2.36	12.0	3.19	0.05	5.70	34.0	51.5	554	6.14

*EF values larger than 10 are shown in bold.

pH using 0.01 M CaCl₂ (2.74–3.92), NO₃⁻ (6.00–24.8 ppm), SO₄²⁻ (30.0–82.0 ppm), CO₃²⁻ (0.41–1.34 %), Cl⁻ (0.00–30.6 ppm), salinity (0.00–0.06%), organic matter (25.8–62.9 g/kg); and the colours range from grey to black with reference to Munsell moist colour. The pH value of the sand sample using water is slightly higher than in 0.01 M CaCl₂ because the pH of a soil measured in 0.01 M CaCl₂ is independent of dilution over a range of soil-to-solution ratios [16]. The pH results also indicate that the sands are strongly acidic (pH 2.74–3.90), which is usually associated with south-western Nigeria soils [22].

The levels of 11 trace elements, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, and Pb, were determined, as shown in table 3. Also listed in the table are the enrichment factors for the elements which were calculated using Ti as reference element and the elemental concentrations of reference soil from Brady [23]. Copper, Cr, Zn, and As which are known to be toxic metals are highly enriched (EF > 10) in the sand fraction samples. The high EF values obtained for these toxic metals should be a cause of concern due to their possible adverse effects on human and animal health. This calls for proper management of the wastes that will be produced during mining and processing of the oil sands.

Table 4 compares the ranges and mean of values of some of the parameters determined with their standard values. The comparison indicates that Cr, As, and Pb concentrations fall within the range of maximum concentrations (except for Pb concentration in the Ilubirin sample and As concentration in the Loda sample), while the concentration of Cu in the Ilubirin sample is considered to be excessive. Also, the Zn concentration of the Ilubirin and Loda samples are in excessive levels. The results of the physico-chemical parameters and elemental compositions

Table 4. Comparison of trace elements in the sand fraction samples with their maximum permissible limits (ppm).

Parameter	Maximum concentration [24]	Excessive levels in soil [25]	Sand fraction in this study (range and mean)
K	n.a.	n.a.	63.21–103.23 (88.19)
Ca	n.a.	n.a.	31.11–78.31 (49.07)
Ti	n.a.	n.a.	235.10–497.14 (348.82)
V	n.a.	n.a.	19.13–28.33 (23.56)
Cr	5.00–50.00	100.00	64.50–83.00 (74.74)
Mn	n.a.	1500.00	156.00–212.34 (188.78)
Fe	n.a.	n.a.	118.14–131.41 (126.24)
Ni	n.a.	100.00	19.20–43.31 (28.41)
Cu	n.a.	100.00	31.28–189.01 (105.84)
Zn	n.a.	250.00	165.11–294.01 (240.71)
As	5.00–500.00	n.a.	40.06–63.72 (51.80)
Pb	5.00–500.00	200.00	3.04–7.01 (5.35)

*n.a.: not available.

Table 5. Physico-chemical properties of the water samples.

Water sample	Conductivity (mS cm ⁻¹)	pH	Total alkalinity (ppm)	Total acidity (ppm)	Cl ⁻ (ppm)	Salinity (‰)	NO ₃ ⁻ (ppm)
Ilubirin	0.53 ± 0.02	3.30 ± 0.10	n.d.	348 ± 8.7	391 ± 6.2	0.71 ± 0.03	4.85 ± 0.28
Mile 2	1.98 ± 0.07	8.10 ± 0.88	1072 ± 8.8	n.d.	732 ± 7.8	1.32 ± 0.83	10.90 ± 1.08
Agbabu	0.72 ± 0.03	7.60 ± 0.76	480 ± 5.3	56.0 ± 1.2	349 ± 9.1	0.63 ± 0.02	5.15 ± 0.98
Loda	0.09 ± 0.02	3.90 ± 0.10	n.d.	160 ± 7.6	150 ± 7.4	0.27 ± 0.12	1.75 ± 0.06
Mean	0.83	5.73	388	141	406	0.73	5.66
Range	0.09–1.98	3.30–8.10	0.00–2072	0.00–348	150–732	0.27–1.32	1.75–10.9

Table 6. Elemental composition of the water fraction of bituminous sands of south-western Nigeria (ppm).

Water sample	Elements											
	K	Ca	Ti	Mn	Fe	V	Cr	Ni	Cu	Zn	As	Pb
Ilubirin	116 ± 0.01	39.1 ± 0.03	132 ± 0.1	178 ± 0.1	103 ± 0.1	24.0 ± 0.03	6.02 ± 0.01	13.2 ± 0.01	97.1 ± 0.1	12.2 ± 0.1	24.0 ± 0.1	3.25 ± 0.01
Mile 2	129 ± 0.02	25.6 ± 0.01	534 ± 0.03	183 ± 0.03	168 ± 0.05	21.4 ± 0.02	13.6 ± 0.01	17.7 ± 0.01	36.3 ± 0.01	78.3 ± 0.01	32.3 ± 0.03	5.20 ± 0.01
Agbabu	82.2 ± 0.01	30.1 ± 0.01	143 ± 0.02	99.3 ± 0.02	144 ± 0.03	37.1 ± 0.02	9.13 ± 0.01	9.01 ± 0.02	67.6 ± 0.02	96.3 ± 0.03	49.3 ± 0.05	6.70 ± 0.01
Loda	168 ± 0.03	27.2 ± 0.01	105 ± 0.06	126 ± 0.04	91.4 ± 0.19	18.2 ± 0.01	8.23 ± 0.01	19.9 ± 0.02	49.2 ± 0.03	36.6 ± 0.02	25.1 ± 0.01	7.01 ± 0.01
Mean	124	30.5	229	146	127	25.2	29.8	15.0	62.6	55.9	32.7	5.50
Range	82.2–168	25.6–39.1	105–534	99.3–178	91.4–168	18.2–37.1	6.02–9.13	9.01–19.9	36.3–97.1	12.2–96.3	24.0–49.4	3.25–7.01

of the sand fraction samples, some of which exceed standard limits, show the potentials for environmental degradation of the host areas when exploitation starts, unless the wastes that will be generated are well managed.

3.2.2 Water fraction. The results of the physico-chemical parameters of the water fraction of the bituminous sand samples are presented in table 5. Conductivity varies between 0.09 ms cm^{-1} and 1.98 ms cm^{-1} , with a mean value of 0.83 ms cm^{-1} . The pH varies between 3.30 and 8.10 (mean value = 5.73). The water fractions from Agbabu and Mile 2 had the relatively higher pH values of 8.10 and 7.60, respectively. Salinity varies between 0.27‰ and 1.32‰, with a mean value of 0.73‰; total alkalinity varies between 0.00 and 1072 ppm (mean = 388 ppm). Total acidity varies between 0.00 and 348 ppm (mean = 141 ppm), while Cl^- varies between 150 ppm and 732 ppm, with a mean value of 406 ppm, and NO_3^- varies between 1.75 ppm and 10.9 ppm (mean = 5.66 ppm). The water fractions from Agbabu and Mile 2 have a high salinity (0.63‰ and 1.32‰, respectively) and also high Cl^- values (349 ppm and 732 ppm, respectively). This may be due to the fact that they were collected from a deeper depth, which is very close to the sea with characteristic high salt contents [19].

Table 6 lists the elemental concentrations of the water fraction samples of the bituminous sands at various sites. The data obtained for the concentrations of the elements were the values of elements in each sample, the arithmetic mean and range. Comparison of the results shows that Ti showed a relatively higher range (105–534 ppm) and mean (229 ppm) values, while Pb showed the lowest values, (3.25–7.01 ppm) and (5.54 ppm) respectively. A comparison of the values of the parameters in the water samples in this study together with tolerance limits of these parameters by the Nigeria Federal Environmental Protection Agency (FEPA, 1991) [24] are presented in table 7. Comparison of the physico-chemical and elemental composition of water samples with tolerant limits of FEPA (1991) [24] shows that the concentrations of Cr, Mn, Fe, Ni, Cu, Zn, As, and Pb, but not Ca, exceeded their discharge limits. The pH values of the water samples were low, indicating a high acidity, and did not fall within the range

Table 7. Comparison of physico-chemical and trace elements in the water fraction with tolerant limits of FEPA (1991).

Parameter (ppm)	Water fraction in this study	Limit for discharge	Limit for land
		into surface water FEPA [24]	application FEPA [24]
Conductivity (mS cm^{-1})	0.09–1.98 (0.83)	–	–
Total alkalinity	0.00–2073 (388)	–	–
Total acidity	0.00–348 (141)	–	–
pH	3.30–8.10 (5.73)	6.00–9.00	6.00–9.00
Salinity (‰)	0.27–1.32 (0.73)	–	–
Cl^-	150–732 (406)	600.00	600.00
NO_3^-	1.75–10.9 (5.66)	20.00	20.00
K	82.2–168 (124)	–	–
Ca	25.6–39.1 (30.5)	200.00	200.00
Ti	105–534 (229)	–	–
V	18.2–37.1 (25.2)	–	–
Cr	6.02–91.3 (29.8)	<1.00	–
Mn	99.3–178 (146)	5.00	5.00
Fe	91.4–169 (127)	20.00	20.00
Ni	9.01–19.9 (14.6)	<1.00	–
Cu	36.3–97.1 (62.6)	<1.00	–
Zn	12.2–96.3 (55.9)	<1.00	–
As	24.0–49.4 (32.7)	0.100	–
Pb	3.25–7.01 (5.54)	<1.00	–

of discharge limits. The tailings could thus cause environmental degradation and result in ill health of the inhabitants or alter the ecology of that area if it is not well treated before discharge during exploitation of the bituminous sands.

4. Conclusions

The trace-element and physico-chemical data interpretation of the sand and water samples indicate that the exploitation of the bituminous sands could pose considerable environmental hazards, as shown by the values of some indicators of pollution: conductivity, pH, total alkalinity, total acidity, SO_4^{2-} , Cl^- , salinity and NO_3^- , and trace metals (K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, and Pb) of different chemical affinities. Copper, Cr, As, and Zn, which are known to be toxic metals, are highly enriched ($\text{EF} > 10$) in the sand samples. The high enrichment of the toxic metals should be a cause of concern because of their potential adverse effects on human and animal health, flora, and fauna. If, in the course of exploitation and refining of the bituminous sands, the tailings are not well managed before discharge, they can pollute the soil as well as the ground and surface waters, which are the main sources of drinking and irrigation water for the inhabitants of that area. The major occupation of most residents in that area is farming. Thus, the potential for uptake of such parameters of environmental pollution into crops and eventual transfer to the food chain is an important source which is likely to be associated with exploitation of the bituminous sands in the region. The assessment of such a biogeochemical pathway for exposure is an important task that must be undertaken to provide a basis for assessing potential impact on human health, of the exploration of the vast Nigerian bituminous sand deposits.

It has been reported that the exploitation of bituminous sands can cause environmental pollution by as much as 10–100-fold more than in the case of crude oil [26]. Therefore, workers, neighbours and the operating environment must be protected from the adverse effects of its exploitation. Toxic substances may enter the atmosphere, soil, or water from leaks in equipment, spillages during transportation/handling, plant malfunction, and via effluent liquid and solid wastes during mining and refining processing of the bituminous sands. The pollutants produced during these processes may be hazardous to workers, local residents, fauna, and flora but also can alter the ecology of that area. The stakeholders in the exploitation of the bituminous sands must therefore know the hazards associated with these substances.

This study has provided important baseline data as a basis for establishing future impacts of bituminous sand exploitation and refining in the bituminous sand deposits area of Nigeria. Similar baseline studies should be extended to other environmentally sensitive media such as water resources, soil, and local air quality, and even the crops in the area.

References

- [1] M.D. MacKinnon, J.G. Matthew, W.H. Shaw, R.G. Cuddy. *Use of 'A guide to the management of tailings facilities' at Syncrude*. Environmental Issue and Management of Waste in Energy and Mineral Production, Singhal and Mehrotra (Eds), Balkema, Rotterdam (2000).
- [2] People and Health Pollution. Tar sands will increase Canada's pollution. Available online at www.peopleandplanet.net (accessed May, 2005).
- [3] F.M. Adebisi, I.O. Asubiojo, T.R. Ajayi. Multielement analysis of Nigerian bitumen by TXRF spectrometry and physical constants characterization of its hydrocarbon component. *Fuel*, Elsevier, in press (2005).
- [4] V.A. Adewusi. Aspects of tar sands development in Nigeria. *Energy Sources*, **13**, 121–135 (1992).
- [5] A.A. Kartsev, Z.A. Tabasaransk, H.I. Suubota, G.A. Mogilevsku. *Geo-Chemical Methods of Prospecting and Exploration for Petroleum and Natural Gas* (English translation), P.A. Witherspoon and W.D. Romey (Eds), University of California Press, Berkeley, CA (1995).
- [6] W.F. Rogers. Corrosion. In Chemical properties of waters associated with crude oil. *Indian J. Tech.*, **15**, 535–537 (1956).

- [7] C.M. Ekweozor. Palaeore construction by means of chemical fossils: Application to Nigerian Sedimentary Basins. *Nigerian Association of Petroleum Exploration*, Bull, **3**, 75–89 (1988).
- [8] Canadian Association of Petroleum Producer (CAPP). Oil sands. In *Industry Facts and Information on Oil and Natural Gas, Canada*, pp. 3–4 (2002).
- [9] O.S. Adegoke. The bituminous sands of Ondo and Ogun States of Nigeria. Geol. Guide to some Nigerian Cretaceous Recent Localities. Geological Nigerian Geoscience Society Publication, **2**, 27–37 (1980).
- [10] S.J.L. Coker. Bitumen saturation and reserve. Estimate of Okitipupa oil sands. *Nig. J. Mining Geol.*, **24**, 1–2 (1988).
- [11] A.F. Oluwole, O.S. Adegoke, L.O. Kehinde, A.B. Borisade, B.D. Ako, T.R. Ajayi, E.I. Enu, J.I. Nwachukwu. Chemical composition of bitumen extracts from Nigerian tar sands. Paper presented at 3rd UNITAR/UNDP International Conference on Heavy Crude and Tar Sands, Long Beach, CA, pp. 24–29 (1985).
- [12] E.I. Enu. Textural characteristics of the Nigerian tar sands. *Sed. Geol.*, **44**, 65–81 (1985).
- [13] E.I. Obiajunwa, J.I. Nwachukwu. Simultaneous PIXE and PIGME analysis of a Nigerian tar sand sample from a deep bore hole. *J. Radioanal. Nucl. Chem.*, **245**, 659–661 (2000).
- [14] J.T. Bulmer, J. Starr. *Syncrude Analytical Methods for Oil Sand and Bitumen Processing*, *Syncrude Canada*, pp. 148–149, Syncrude Canada Limited, Edmonton, Alberta, Canada (1979).
- [15] S. Bailey. The analysis of agricultural materials. In *A Manual of the Analytical Methods Used by Agricultural Development and Advisory Services*, 3rd ed., p. 66, London (1986).
- [16] C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, F.E. Clark. *Methods of Soil Analysis (Chemical and Microbiological Properties) Part 2*, pp. 914–926, American Society of Agronomy, New York (1965).
- [17] American Public Health Association (APHA). American Water Works Association and Water Pollution Control Federation. *Standard Method for the Examination of Water and Waste Water*, 18th ed. E.G. Arnold, S. Lenor, D.E. Andrew (Eds), EPS Group Incorporation Handover, Maryland, USA, pp. 3–5 (1992).
- [18] Association of Official Analytical Chemists. AOAC: Report of Subcommittee A on Recommendation for Official Methods. *J. Assoc. AOAC*, Washington, DC, **63**, 2 (1980).
- [19] P. Henderson. *Inorganic Geochemistry*, 2nd ed., Pergamon Press, Oxford, pp. 255–265 (1984).
- [20] USA Department of Agriculture. Determination of soil color. In *US Department of Agriculture Handbook of Soil Survey Manual*, pp. 1–4 (1954).
- [21] IAEA. *Quantitative X-ray Analysis System (QXAS) User Manual*, International Atomic Energy Agency (IAEA), Vienna (1996).
- [22] Federal Ministry of Agriculture and Natural Resources (FMANR). *Literature Review on Soil Fertility Investigations in Nigeria*, Lagos, Bomba, Ibadan, Nigeria, pp. 61–89 (1990).
- [23] N.C. Brady. *The Nature and Properties of Soils*, pp. 18–23, Macmillan, New York (1984).
- [24] Federal Environmental Protection Agency (FEPA). *Guidelines and Standards for Environmental Pollution Control in Nigeria*, FEPA, Lagos, Nigeria, pp. 33, 103 (1991).
- [25] C.A. Domy. *Biogeochemistry of Trace Metals*, p. 48, Lewis, Boca Raton, FL (1992).
- [26] J.N. Nwankwo. Environmental Aspects of Heavy Crude and Tar Sand Exploration, Production and Transportation with special reference to Nigeria 3rd UNITAR/UNDP International Conference on Heavy Crude and Tar Sands, Long Beach, CA, pp. 65–74 (1985).