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The Impact of Tar Sand Deposit on the Water Quality in Siluko

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Abstract

The presence of tar sand deposit in a location poses threat to the environment, aquatic lives and humans. Toxic elements and metals are usually associated with tar sand deposit. Nigeria has a huge reserve of tar sand deposit and some of these deposit are yet to be investigated for the environmental impact they might have caused to the environment. Tar sand deposit occur in Siluko, Edo State, Nigeria. This research was aimed at determining the physiochemical and chemical properties of water samples collected from Siluko. This is to investigate the impact that the tar sand deposit may have caused in the environment. The water samples were collected from a borehole, river and stream in Siluko. The results from the physiochemical properties of Siluko water such as the pH, electric conductivity, total dissolved solids, total suspended solids, colour and turbidity met WHO maximum permitted standard. The chemical properties such as chlorine, hydrogen trioxo carbonate iv, chemical oxygen demand, sodium, potassium, nitrate, sulphate, phosphate, iron, manganese, copper, zinc, lead and cadmium, also met WHO maximum permitted standard while the calcium, magnesium and iron concentration in the river water and phosphate concentration in the stream water were higher than the recommended limit by WHO, indicating that the water is not completely fit for consumption by the individuals from that community. The presence of tar sand deposit in the place had effect on the water quality due to leaching that may have occurred in the environment where the tar sand is located.

Keywords: *Tar Sand; Water Quality; Environment; Nigeria; Physiochemical Properties.*

1. Introduction

Tar sand (also referred to as oil sands) are a combination of clay, sand, water and bitumen, a heavy black viscous oil [1-8]. Tar sands can be mined and processed to extract the oil-rich bitumen, which is then refined into oil [9-13]. The bitumen in tar sands cannot be pumped from the ground in its natural state; instead tar sand deposits are mined, usually using strip mining or open pit techniques, or the oil is extracted by underground heating with additional upgrading [14-16]. Nigeria has a considerable large deposit of natural bituminous tar sand. Bitumen and extra-heavy oils are unconventional oils that generally require additional processing to extract, transport, and refine into petroleum products than lighter or conventional oils. It occurs, in varying quantities, in nearly every part of the world and throughout the whole range of geological strata. It is noteworthy that there are close similarities between crude oil and bitumen. Besides, their exploration has triggered adverse environmental impacts in Nigeria through incessant environmental, socio-economic and physical disasters that have been recorded over the years due to limited scrutiny and risk assessment [17].

The Nigeria tar sand deposit can be found within the confine of the eastern margin of Dahomey basin which lies within the three major states which include: Ogun, Ondo, Edo and some part of Lagos state in the South-West and South-South of Nigeria [18-22]. Tar sand is composed mainly of heavy oil and clays that are rich in mineral and water. This heavy oil content of tar sand is commonly called bitumen. In raw state tar sand is a sticky viscous black substances. The total reserve of heavy oil in Nigeria was estimated to exceed 36 billion barrels.

Bitumen was discovered in Nigeria in the early 18th century. The interest of the colonial masters in Nigeria was to explore this important mineral. However, the discovery of oil in 1956 in commercial quantity brought to a close the exploration of bitumen in Nigeria. The bitumen found in Nigeria occur in large commercial quantities with both chemical and physical characteristics similar to those of Athabasca in Canada. Billman [23], Adegoke *et al.* [24] did many research work on the geology of the bitumen ore deposit Nigeria and categorised the oil sand as Araromi Shale formation, Abeokuta formation, Nkporo shale, lower cretaceous, upper cretaceous, lower senonian, Afowo formation, albian sand and Ise formation etc with prediction that there are minor dissimilarities between the Nigeria bitumen and Athabasca oil sands [1].

The presence of tar sand in a location poses threat to the environment as a result of some toxic heavy metals that are associated with their deposit [5,25-26]. Exposure to these chemicals could impact the health of individuals. It could also cause the pollution of the water bodies within the environment. Anochie *et al.* [27] investigated three samples of bitumen from Agbabu in Ondo State, Nigeria for their heavy metal concentration. They found out that iron was the highest metal in all the samples and the concentration of iron was above the recommended limit. Lead was found in one of the samples studied. Their studies also show that Abgabu bitumen contains cadmium, manganese, nickel, chromium. Hence the presence of these metals possess threat to humans and the environment. Asubiojo *et al.* [28] investigated the impact of the deposit of bitumen on the quality of groundwater in an area in Nigeria. They found out that the groundwater have higher concentrations of chromium, manganese, copper and zinc. They attributed the presence of these elements in the water were due to leaching that may have taken place in the bitumen deposit.

The experience of tars sand exploitation has created pollution and contamination in the host communities, affecting land, crop, water and welfare of host communities. Local communities that house these raw materials have raised concern over health and quality of life the pollution has on their environment, aquatic life, and crops. The introduction of toxic chemicals into the water body during the process of tar sand exploration causes massive migration of various fish species from aquatic environment. Tar sand deposit is also found in Siluko, Edo State and there are water bodies around the deposit where the mineral is located. This research therefore investigated the impact of the bitumen deposit on the water quality in Siluko.

2. Methodology

2.1. Materials and apparatus

The materials and apparatus used in this research include: HACH spectrophotometer, reflux condenser, pipette**,** conical flask, hydrazine sulphate, hexamethylene tetramine, burette, glass beads, $K_2Cr_2O_7$, NaCl, $AgSO_4$, H_2SO_4, $FeSO_4$, Fe $(NH_4)_2$ $(SO_4)_2.6H_2O$, gelatine, barium chloride, SO_4^{-2}, anhydrous K_2SO_4, refrigerator, $AgNO_3$, Brucine, KNO_3, chloroform, pH meter, ammonium citrate, H_3BO_3, sodium hydroxide, bis-cylohexanone, oxalydihyrazone, $CUSO_4.5H_2O$, hydroxylamine hydrochloride, orthophenanthroline, ammonium acetate, ferrion ammonium sulphate, H_3PO_4, desiccator, plastic funnel, filter paper, oven, KIO_4, $KMNO_4$, EDTA, triethanolamine, ethanol, ammonium chloride, zinc, HCl. TDS meter, flame photometer, hydroxylamine hydrochloride, triethanolamine, Patton and Reeder's reagent, KOH, triethanolamine, phenol, sodium potassium, tartrate , sodium hypochlorite, $CdSO_4$, hexamine, diphenylcarbazide, dimethylglyoxime, orthophrnanthroline, monohydrate, phenolphthalein and ethanol.

2.2. Sample collection

Water samples were collected from a borehole drilled in Siluko and a river and stream in Siluko, Ondo State, Nigeria. The samples were stored in separate plastic containers, properly labelled and transported to the laboratory for analysis.

2.3. Determination of turbidity of the water samples

The turbidity of the water samples was determined by dissolving 1 g of hydrazine sulphate in 100 mL of water. Also 10 g of hexamethylene tetramine, 1 g of hydrazine sulphate, 10 g of hexamethylene tetramine were also dissolved in 100 ml of water in different flask. 5ml of each solution prepared above was mixed in a 100 mL flask and allowed to stand for 24 hours at room temperature. Then each of the solution was diluted to 100 ml mark. This mixed solution is called 400 FTU. From the 400 FTU, 0-50 FTU were prepared as working standards in 50 ml flask. Each of the samples were placed in a spectrophotometer and the absorbance was read at a wavelength of 450 nm. Water was used as the blank sample during the measurement. Equation 1 was used to calculate the turbidity of the samples.

Turbidity (FTU) = Instr. Reading × Slope Recip (1)

2.4. Determination of chemical oxygen demand (COD)

The chemical oxygen demand of each sample was determined by dissolving 24.5 g of 0.00833 M of $K_2Cr_2O_7$ in water. 10 g of the salt was also dissolved in a concentrated solution of H_2SO_4. To prepare the indicator, 1.485 g of orthophenanthroline monohydrate was dissolved in 100 ml of 0.025 M ferrous sulphate. Then 0.025M Fe $(NH_4)_2$ $(SO_4)_2.6H_2O$ was dissolved in 9.8 g of the salt in water, 5 ml of concentrated H_2SO_4 was added to the solution and diluted to 1 litre mark in the flask. 25 ml of water sample was poured into a conical flask and 10 ml of the 0.00833 K_2CrO_7 solutions was added to the flask. 1 g of $HgSO_4$ and 10 ml of Ag_2SO_4–H_2SO_2 solution was also added to the flask. A reflux greaseless condenser was fitted to the flask and the flask was heated gently to boil for 10 minutes. The flask was allowed to cool and two drops of terrain indicator was added to the flask. The solution was titrated with 0.025M Fe $(NH_2)_2$ $(SO_4)_2.6H_2O$ until the colour changed from blue green to red brown. A blank sample was also used titrated as well. Water was used as the blank sample. The difference in value between the two titres gives the titre of the sample.

2.5. Determination of some elements and compounds

The sulphate, chloride, nitrate, copper, iron, manganese, nickel, cadmium, carbonate, bicarbonate and hydroxyl ions, alkalinity, ammonium nitrogen (NH_4N) and zinc content contained in the water samples were also determined using the stoichiometry method. This approach enables the determination of the amount of elements contained in the water samples.

2.6. Determination of total dissolve solid (TDS) and total suspended solids (TSS) and conductivity

A Whatman filter paper No.1 (15 cm) and a 250 mL conical flask was oven dried for 3 hours. There were cooled in a desiccator and the weight of the filter paper and flask were determined. 100 mL of the water sample was poured through the filter paper into the conical flask. The filter paper and conical flask were dried to remove the water content and weighed using a weighing balance. The TSS and TDS were calculated using equation 2 and 3. The conductivity of the samples was determined using a TDS meter.

TSS (mg/L) = $(X_2 - X_1) \times 1000 \times 10$ (2)

TDS (mg/L) = $(Y - X) \times 1000 \times 10$ (3)

where: weight of filter paper = X_1; weight of filter paper + residual = X_2; weight of empty conical flask = X; weight of flask + Residual = Y

2.7. Determination of exchangeable Na, Ca and K and Mg

2.54 g of NaCl was dissolved in water. 10 mL of the sodium chloride solution was mixed with 100 mL of ammonium acetate. From the resulting solution, 0-10 ppm working standards was collected. Ammonium acetate extract was used for the determination of the sodium ions. The flame photometer was adjusted according to its instruction manual. Aspirate the standards to obtain reliable curves before aspirating the samples. Note the blank (zero ppm) is the Ammonium Acetate. Perform same procedure to determine the potassium ions by dissolving 1.91 g of KCl in water. Then calculate the exchanageable sodium and potassium ions using equation 4. The exchangeable calcium and magnesium ions were determined using EDTA.

$$\frac{\text{Instr. Reading} \times \text{Slope Recip.} \times 100\text{ml} \times \text{Dilution Factor} \times 10\text{\^{}}{-3}}{\text{Weight of sample} \times \text{Eq. Wt}} \quad (4)$$

3. Results and discussion

3.1. Physio-chemical analysis of Siluko water

Table 1 shows the physio-chemical analysis of Siluko water samples. Water sample were taken from a stream, river and borehole drilled in Siluko. The various properties of each of the water samples were determined; pH, electric conductivity, TDS, TSS, colour and turbidity. The results show that the stream water had a pH of 7.51, while the pH of the water samples from the river and borehole were 7.27 and 7.36 respectively. This indicates that the water samples (stream, river and borehole) all fall within the range specified by WHO.

Table 1. Physio-chemical analysis of Siluko village water samples

Parameters	Stream	River	Borehole	WHO (Max. permitted)
pH	7.51	7.27	7.36	6.5-8.5
EC (µs/cm)	110.5	42.8	80.6	1000
TDS (mg/L)	54.6	22.1	40.2	500
TSS (NTU)	Nill	5.0	Nill	NS
Colour	Nill	2.0	Nill	NS
Turbidity (mg/L)	Nill	3.0	Nill	5

The electric conductivity of the stream water sample was 110.5 µS/cm, while that of the water sample from the river and borehole were 42.8 µS/cm and 80.6 µS/cm respectively. Therefore, this indicates that the stream water had the highest electric conductivity, followed by the borehole water. The electrical conductivity in water is a measure of the salinity content of the water. It is expressed as micro Siemens per centimetre (µS/cm) and, relates to the concentrations of total dissolved solids (TDS) or salts in a specific water. The TDS of the water sample from the stream was 54.6 mg/L, while that of the samples from the river and borehole were 22.1 mg/L and 40.2 mg/L. Also, the stream water possessed the highest amount of total dissolved solids, followed by the borehole water. The electrical conductivity and TDS of all the water samples were still within the acceptable range specified by WHO.

The total suspended solids (TSS) in the sample collected from the river water was 5.0, but in the case of stream and borehole water, it was nil. There was no record of colour for the stream water and borehole water sample except for the sample collected from the river that recorded a colour of 2.0. Likewise, there was no record of turbidity for stream water and borehole water except for the river water that recorded 3.0 mg/L. This was closely related to the maximum standard specified by WHO which was 5.0 mg/L, which shows that river water turbidity was within the range specified by WHO.

Table 2. Chemical analysis of Siluko village water samples

Parameters (Mg/L)	Stream	River	Borehole	WHO Max. Permitted
Chlorine (Cl^-)	35.45	17.73	53.18	250
HCO_3	24.4	54.9	36.6	NS
COD	20.0	61.2	43.2	NS
Sodium (Na)	0.09	0.18	0.12	100
Potassium (K)	0.108	0.663	0.583	NS
Calcium (Ca)	0.108	2.470	2.119	0.003
Magnesium (Mg)	0.862	0.728	0.131	0.2
Nitrate (NO_3)	3.66	0.88	0.62	45
Sulphate (SO_4)	0.38	0.11	0.21	400
Phosphate (PO_4)	1.28	0.32	0.38	0.4
NH_4N	0.015	0.095	0.240	NS
Iron (Fe)	0.015	0.438	0.038	0.3
Manganese (Mn)	0.022	0.041	0.028	0.05
Copper (Cu)	0.011	0.017	0.013	1.0
Zinc (Zn)	0.033	0.063	0.108	2.0
Lead (Pb)	0.004	0.008	0.003	0.01
Cadmium (Cd)	0.003	0.005	0.005	0.003

Table 2 shows the chemical analysis of Siluko water samples. Water samples collected from the stream, river and borehole drilled in Siluko were analysed to also determine the following parameters; chlorine, hydrogen trioxo carbonate iv (HCO_3), chemical oxygen demand, sodium, potassium, calcium, magnesium, nitrate, sulphate, phosphate, iron, manganese, copper, zinc, lead and cadmium content. The result shows that the borehole water sample had the highest chlorine content of 53.18 mg/L, while that of the water sample from the stream and river were 35.45 mg/L and 17.73 mg/L respectively. WHO reported the safe level to be 250 mg/L and anything more than that is considered unsafe.

The river water sample had the most HCO_3 and its concentration was 54.9 mg/L, followed by borehole water (36.6 mg/L), while the stream water sample had the least concentration of 24.4 mg/L. The chemical oxygen demand (COD) in the stream water was 20.0 mg/L, while that of the river and borehole were 61.2 mg/L and 43.2 mg/L. It can be clearly seen that river water contains the highest level of COD, while the steam water contains the least. The result further shows the sodium content in the water samples. It was observed that the water sample from the stream contained 0.09 mg/L of sodium, river water sample contained 0.18 mg/L and borehole water sample contained 0.12 mg/L of sodium. The concentration of sodium are very low compared to WHO standard which reported a maximum concentration of 100 mg/L. This shows that the level of sodium in the various water samples were very low. Analysis of the water samples also indicated that the stream water contained 0.108 mg/L of potassium, river water sample contained 0.663 mg/L, borehole water sample contained 0.583 mg/L. The level of calcium in the water samples indicated that the stream water contained 0.108 mg/L of calcium, river water contained 2.470 mg/L and borehole contains 2.119 mg/L of calcium. These results were contrary to WHO standard of 0.003 mg/L. This shows that the various water samples contained more than the required concentration of calcium recommended by WHO. In terms of magnesium concentration, the stream water contained 0.862 mg/L of magnesium, river water contained 0.728 mg/L and borehole water sample contained 0.131 mg/L. These results were contrary to WHO standard of 0.2 mg/L since they were higher except that of the borehole water (0.131 mg/L) which was in range with WHO standard.

The level of nitrate in the water samples indicates that the stream water contained 3.66 mg/L of nitrate, the river water contained 0.88 mg/L and borehole water contained 0.62 mg/L. of nitrate. These results were low compared to WHO standard of 45 mg/L. The level of sulphate in the water samples indicates that stream water contained 0.38 mg/L of sulphate, river water contained 0.11 mg/L and borehole water contained 0.21 mg/L of sulphate. These results were contrary to WHO standard of 400 mg/L which shows that the level of sulphate in the various water samples were extremely low.

Stream water had the highest phosphate content of 1.28 mg/L, followed by borehole water (0.38 mg/L), while river water had the least (0.32 mg/L). These results were also in agreement with WHO standard of 0.4 mg/L except for the stream water (1.28 mg/L) that had a contration of phosphate higher than WHO standard. The concentration of NH_4N in the water samples indicated that stream water contained 0.015 mg/L of NH_4N, river water contained 0.095 mg/L and borehole water contained 0.240 mg/L of NH_4N. The concentration of iron in the water samples indicated that the stream water contained 0.015 mg/L of iron, river water contained 0.438 mg/L and borehole water contained 0.038 mg/L of iron. The concentration of iron in the stream water and borehole water were in agreement with WHO standard of 0.3 mg/L, while that of the river water was higher than WHO standard and it is considered as unsafe.

The concentration of manganese in the water samples indicated that the stream water contained 0.022 mg/L of manganese, river water contained 0.041 mg/L and borehole contained 0.028 mg/L of manganese. The concentration of manganese are in agreement with WHO standard of 0.05 mg/L. The concentration of copper in the water samples indicates that the stream water contained 0.011 mg/L of copper, river water contained 0.017 mg/L and borehole contained 0.013 mg/L of copper. The concentration of copper are in agreement with WHO standard of 1.0 mg/L. The concentration of zinc in the water samples indicated that the stream water contained 0.033 mg/L of zinc, river water contained 0.063 mg/L and borehole contained 0.108 mg/L of zinc. The results are in agreement with WHO standard of 2.0 mg/L.

The level of lead in the water samples indicated that the stream water contains 0.004 mg/L of lead, river water contained 0.008 mg/L and borehole water contained 0.003 mg/L of lead. The concentration of lead are in agreement with WHO standard of 0.01 mg/L of lead concentration. Finally, the concentration of cadmium in the water samples indicated that the stream water contained 0.003 mg/L of cadmium, river water and borehole water both contained 0.005 mg/L of cadmium. The cadmium concentration in the river and borehole water were higher than WHO standard of 0.003 mg/L of cadmium.

4. Conclusion

The results from the physiochemical properties of Siluko water such as the pH, electric conductivity, total dissolved solids, total suspended solids, colour and turbidity met WHO maximum permitted standard.

The chemical properties such as chlorine, hydrogen trioxo carbonate iv, chemical oxygen demand, sodium, potassium, nitrate, sulphate, phosphate, iron, manganese, copper, zinc, lead and cadmium, also met WHO maximum permitted standard while the calcium, magnesium and iron concentration in the river water and phosphate concentration in the stream water were higher than the recommended limit by WHO, indicating that the water is not completely fit for consumption by the individuals from that community.

Many of the elements found in the water were attributed to leaching process that may have occurred around the deposit where the tar sand is located. Hence the presence of tar sand in Siluko had impact on the water quality in the environment.

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