

HYDROGEOCHEMICAL EFFECTS OF OIL SHALE ON SOIL AND WATER QUALITY IN MBANO AREA, SOUTHEAST, NIGERIA.

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GSM: 08030715958

Received: 30-07-19

Accepted: 12-08-19

ABSTRACT

Environmental pollution from solid waste landfillings or exposure is of major concern to both the environmentalists and individual citizens. The necessity for studying contaminant generation and control is becoming more urgent in view of the risks associated with such sites. Oil shale and its tailing at Umuezeala Nsu and Umualumaku, were chosen as a case study. Soil samples, water samples and oil shale and its tailings were collected from the site and analyzed for their compositions. The analytical results revealed that the soil and groundwater were contaminated to various degrees by several chemicals or pollutants from the oil shale exposure and its tailings. The major environmental problems associated with the area were acidification of soil and groundwater, high content of heavy metals and sulphate in soil and groundwater and organic contamination of soil and in particular, carcinogenous benzo[a] pyrene and other polycyclic aromatic hydrocarbons (PAHs). Geochemical method was applied to reveal the sources of the contaminants. Soil and groundwater contamination show that the nearer the sampling area to the oil shale or its tailing, the heavier the soil and groundwater contamination. The different water sample compositions have same chemical characteristics. The soil and water samples were analyzed for 14 PAHs. The result shows that PAHs were retained mostly in the soil, which consisted of mainly naphthalene, fluorene, phenanthrene and anthracene. Analysis for PAHs source revealed that they were also from the oil shale and its tailing.

Keywords: oil shale waste, soil contamination, groundwater contamination, PAHs

INTRODUCTION

The study area lies within latitudes 5°34' and 5°40' N, and longitudes 7°13' and 7°26' E with an area of around 5,100 sq km (Fig. 1) and is within the Anambra basin.

Oil shale is a naturally occurring mixture of sand, clay or other minerals, water and bitumen; it is heavy and extremely viscous,

and requires treatment before it can be used by refineries to produce usable fuels such as gasoline and diesel. Oil shale which is also referred to as tar sand (Bituminous sand) has a similar composition as the light crude. It is believed to have been formed from biodegradation and water washing of light crude due to lack of cap rock (Akinyemi *et*

al., 2013). Bitumen is about 20% of the actual oil shales found in Nigeria while 76% is for mineral matter that includes clay and sand and 4% water (Akinyemi *et al.*, 2013).

The recovery process includes extraction and separation systems to remove the bitumen from the sand and water. The oil shale history started with the development of oil sand separation in the 1920s by Dr. Karl Clark. In 1936, Max Ball developed a way to produce diesel oil from oil shale (Nate, 2008). Nate (2008) also reported that the actual commercial production started in 1963 when the Sun Oil Company – later Suncor in 1979 was formed. Construction of the Great Canadian Oil sands plant in Alberta was the first commercial oil sand production plant which began in 1964, and production began in 1967. The first barrel of commercial production by open pit mining was produced in 1967 (Syncrude, 2003). The Syncrude consortium was formed in 1964, with an initial objective of researching the economic and technical feasibility of mining oil from the Athabasca oil sands (Syncrude 2006). Geological studies (Adedimila, 1987) and physicochemical properties (Ukwuoma, 1999) confirmed that Nigerian bitumen is an important source of energy and an alternative source of hydrocarbon and raw material for the petrochemical industries. Oil shales, tar sands or, more technically, bituminous sands, are a type of unconventional petroleum deposit. Oil shales are either loose sands or partially consolidated sandstone containing a naturally occurring mixture of sand, clay, and water, saturated with a dense and extremely viscous form of petroleum technically referred to as bitumen (or

colloquially tar due to its similar appearance, odour, and colour). Oil produced from oil shales is often referred to as unconventional oil or crude bitumen, to distinguish it from liquid hydrocarbons produced from traditional oil wells. Solid bituminous sand (Oil shale) is formed in a number of ways. These include thermal attraction, microbial degradation, water washing or gas de-asphalting of the fluidly hydrocarbon. In Southwestern Nigeria, within the Dahomey basin, oil shale deposits has been found and localities studied include Idiobiolayo (Akinmosin and Shoyemi, 2010), Agbabu (Amigun *et al.*, 2012), Imeri (Akinmosin *et al.*, 2011), Idiopopo (Odunaike *et al.*, 2010), Onikitibi (Akinmosin *et al.*, 2012), and Imobi (Ikhane *et al.*, 2011).

Environmental pollution from solid waste landfills (SWLs) or exposure is of major concern to both the environmental scientists and to individual citizens. Because of the inappropriate disposal of solid wastes, or the failure of lining system, SWLs inevitably generate chemicals or pollutants that reach their surroundings, such as soils, groundwater resources, and even the ambient air, and which can cause adverse impacts on the environment and to public health (Ding, 1998; Schreck, 1998; Kofi, 1996; Wildung and Zachara, 1981). The necessity for studying contaminant generation and control is becoming more urgent in view of the risks associated with such areas.

Human activities often pollute fragile systems by modifying their quality to such an extent that their subsequent use becomes more restricted (Beatriz *et al.*, 1998).

Prevention, control and resolution of environmental problems derived from groundwater pollution need detailed hydrochemical research in order to understand and evaluate the different processes and mechanisms leading to the degradation of the water quality so that preventive or corrective measures can be adopted (Beatriz *et al.*, 1998).

The main objectives of this study were to describe the environmental issues associated with oil shale exposure and the resulting geochemical implications, and to determine the source of contaminants, the knowledge of which is needed for remediation of the polluted area.

MATERIALS AND METHODS

A total of 8 samples were collected from oil shale and its tailings in two locations of Umuezeala Nsu (MBA) and Umualumaku (MBB). The number of samples from the localities was based on the accessibility of the sample area and the extent to which the oil shale is developed at the outcrop (Figs 2 and 3) while Figure 4 shows water from mining pit.

The sample locations are shown in Figure 1, and their descriptions in Table 1. The four water samples comprising two soil samples and two oil shale samples, were taken in order to determine the characteristics and hydrogeochemical behaviour of contaminants. Variables for the four water samples are shown in Table 2.

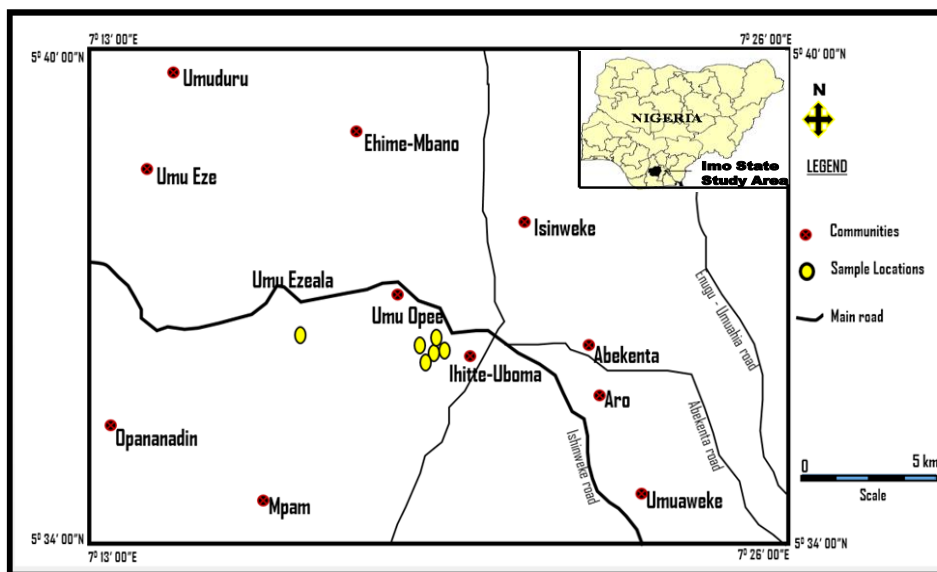


Fig. 1: Physiographic map of Imo State (inset: map of Nigeria showing the location of Imo State).

Physico-chemical parameters were determined for water samples by following standard and official methods of analysis (USEPA, 1982). Variables determined,

their units and the analytical technique used for their measurement were: pH (pH units, YSIM90), temperature ($^{\circ}\text{C}$, YSI-M90), electrical conductivity ($\mu\text{S}/\text{cm}$, YSI-M90),

bicarbonate (mg/L, acid-base titration), chloride (mg/L, silver nitrate titration), sulfate (mg/L, weight balance), nitrate (mg/L, spectrophotometer), ammonia (mg/L, spectrophotometer), ferrous/ ferric (mg/L, spectrophotometer), carbon dioxide (mg/L, titration), total alkalinity (mg/L, titration), total organic carbon (TOC, mg/L, Phoenix 8000 TOC analyzer), potassium (mg/L, atomic absorption spectroscopy, AAS), sodium (mg/L, AAS), calcite (mg/L, AAS), magnesium (mg/L, AAS),

manganese (mg/L, AAS), copper (mg/L, AAS), lead (μ g/L, AAS) and cadmium (μ g/L, AAS).

Soil and oil shale tailing samples were analyzed for polycyclic aromatic hydrocarbons (PAHs) according to USEPA Method 625 (USEPA, 1979). The samples were freeze dried, then serially extracted with methylene chloride; the extracts were dried, concentrated and analyzed by GC/MS (HP5890GC/5972MS).



Fig. 2: Field photograph of oil shale outcrops at Umuezeala Nsu. Magnifications X 50

The GC-MS analyses of the fractions were performed on a Hewlett-Packard 6890N gas chromatograph interfaced to a Hewlett-Packard 5972MS Mass spectrometer. The gas chromatograph was equipped with a

DB-5 MS fused silica capillary column (30 m x 0.25 mm) and helium was used as carrier gas with a flow rate of 1ml/min.



Fig. 3: Field photograph of oil shale outcrops at Umualumaku localities. Magnifications X 50

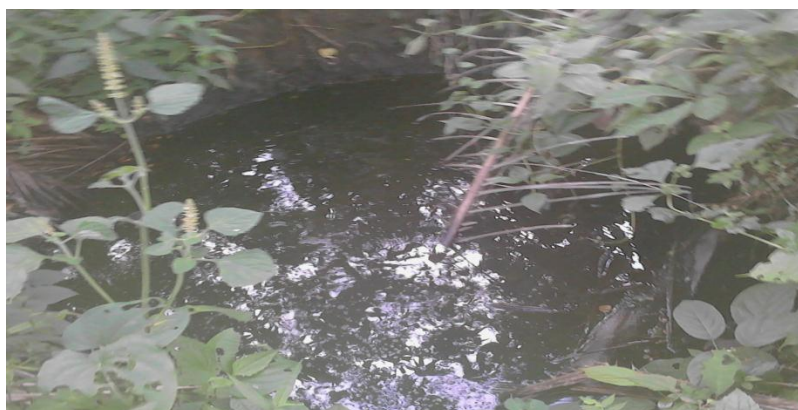


Fig. 4: Field photograph of stagnant water in the mining pit at Umualumaku localities.
 Magnifications X 50.

The Mass spectrometer was operated with electron impact energy of 70 eV and ion source temperature of 230 °C. The GC oven temperature was isothermal for 1min at 80 °C and then programmed from 80 to 280 °C at 3 oC/min and isothermal for 20 min at 280 °C. Individual saturated, aromatic and NSO- compounds were monitored by selected ion monitoring (SIM) at a cycle time of 1s. The GC-MS data were acquired and processed with a Hewlett-Packard Chemstation data system.

Table 1: Description of samples collected from Mbano oil shale area.

Sample No.	Locality	Sample type	Description of samples
MBA1	Umuezeala Nsu	Groundwater	Village well, water table 6 m deep
MBA2	"	Surface water	Percolated water from mining pit
MBB1	Umualumaku	Groundwater	Village well, water table 5 m deep
MBB2	"	Surface water	A run off water from the area
MBA3	Umuezeala Nsu	Oil shale	Black powder or granular with clay
MBB3	Umualumaku	Oil shale	Black powder or granular with clay
MBA4	Umuezeala Nsu	Soil	Brownish fine sandy soil, unsaturated zone
MBB4	Umualumaku	Soil	Brownish fine sandy soil, saturated zone

RESULTS

Analysis of the water samples show that the main environmental problems near the landfill are: (a) acidity of water, the pH of surface water reaching as low as 2.95, groundwater 4.42, and leachate 3.05; (b) the high content of sulphate in the waters; and (c) the high concentration of heavy metals, such as iron, manganese and lead (Table 2).

Sixteen priority polycyclic aromatic hydrocarbons (USEPA, 1982) were measured in the water and soil samples. Naphthalene, phenanthrene, anthracene, retene, benzo[*b*]fluoranthene, benzo[*i+k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene were detected in some water samples, while most of the 14 PAHs were found in soil and oil shale waste (Table 3).

Table 2: Detection limits, maximum, minimum, mean values, and standard deviation of the variables determined in the four water samples.

Variable	Detection limit	Min. - Max.	Mean value	Std Dev.
Temperature (°C)	0.10	23.3-27	25.60	1.20
pH	0.01	2.95-7.1	4.73	1.30
Conductivity (µs/cm)	1.00	132-1986	959.00	828.00
TDS (mg L ⁻¹)	0.10	66.7-1370	493.20	406.00
Chloride (mg L ⁻¹)	0.10	9.1-34.7	16.90	7.50
Sulphate (mg L ⁻¹)	0.10	0.2-975	405.90	337.00
Nitrate (mg L ⁻¹)	0.01	0.24-10	1.61	2.60
Ammonium (mg L ⁻¹)	0.01	0.15-13.6	2.43	3.60
Ferric (mg L ⁻¹)	0.10	0.6-13	3.60	4.30
TOC (mg L ⁻¹)	0.01	0.2-1.6	0.92	0.40
Potassium (mg L ⁻¹)	0.01	1.75-48.95	14.67	13.00
Sodium (mg L ⁻¹)	0.01	4.28-21.4	14.29	5.30
Calcium (mg L ⁻¹)	0.01	6.0-365.29	102.61	97.50
Magnesium (mg L ⁻¹)	0.01	0.3-77.22	23.34	22.50
Bicarbonate (mg L ⁻¹)	0.10	<nd-78.8	27.70	22.50
Manganese (mg L ⁻¹)	0.01	0.29-13.86	6.11	4.90
Lead (µg L ⁻¹)	0.10	3.8-440	72.30	126.00
Cadmium (µg L ⁻¹)	0.10	0.2-2	1.10	0.70

nd – not determined.

DISCUSSION

Distribution of variables

The distribution of the variables was determined in order to investigate the hydrogeochemical characteristics of the water in relation to contamination sources possibly derived from the oil shale. Though geological formations close to aquifer could affect the groundwater composition, human activities, such as mining and landfilling,

are possible important modifiers of the water chemistry. The occurrence of a variety of contamination sources, their locations and the mechanisms of migration of contaminants must be considered (Beatriz *et al.*, 1998). The peak values of pH, nitrate, sulfate and TOC contents are found in the oil shale, especially in areas with dense concentration of human activities.

Table 3: PAHs in soil and water samples

Compounds	MBA1	MBA2	MBB1	MBB2	MBA3	MBB3	MBA4	MBB4
Naphthalene	0.04	nd	nd	nd	0.04	0.04	12.62	3.46
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	7.05	1.15
Fluorene	nd	nd	nd	nd	nd	nd	7.05	1.73
Phenanthrene	0.08	0.04	nd	nd	nd	nd	nd	nd
Anthracene	0.08	nd	nd	nd	nd	nd	36.73	23.95
Methyl phenanthrene	nd	nd	nd	nd	nd	nd	5.94	2.02
Dimethyl phenanthrene	nd	nd	nd	nd	nd	nd	1.11	0.29
Trimethyl phenanthrene	nd	nd	nd	nd	nd	nd	0.37	nd
Retene	nd	nd	0.04	nd	nd	nd	nd	nd
Chrysene	nd	nd	nd	nd	nd	nd	4.08	2.89
Benzo[b]fluoranthene	nd	nd	nd	0.04	nd	nd	nd	nd
Benzo[i + k]fluoranthene	nd	nd	nd	0.04	nd	nd	7.42	2.89
Benzo[e]pyrene	nd	nd	nd	0.04	nd	nd	nd	nd
Benzo[a]pyrene	nd	nd	nd	0.04	nd	nd	12.24	1.73
Perylene	nd	nd	nd	nd	nd	nd	12.99	2.02
Dibenzo[a, k]anthracene	nd	nd	nd	nd	nd	nd	0.37	nd

PAHs in water: µg/L, in soil: µg/kg

n.d. – non-detectable

The distribution of some variables and facies suggests the following hydrogeochemical considerations: (a) the highest nitrate, sulfate and TOC are located very near to the oil shale tailing indicating this as the possible contamination source; (b) differences in concentrations of the predominant ions can be explained as resulting from mining or agricultural activities; (c) because nitrate is not naturally present in the waters, the agricultural activities can be related to contamination processes. In this area, nitrate could be due to leakages from municipal sanitary systems in the villages, and to the use of fertilizers (Ding *et al.*, 2003).

Hydrogeochemistry of groundwater

Piper diagrams are a type of trilinear diagram widely used in hydrogeology as they illustrate the hydrochemical

characteristics of groundwater by representing the concentration of anions and cations in separate triangular diagrams (Piper, 1944; Freeze and Cherry, 1979). Geochemically, similar waters are clustered in clearly defined areas, indicating, for example, water mixture phenomena, precipitation and dissolution (Beatriz *et al.*, 1998).

All water samples, groundwater and surface water, collected near the landfill have been plotted in a Piper diagram (Fig. 3). It can be observed that waters, except MBB2, show contents that are higher in sulfate than in bicarbonate and chloride; and with respect to cations, the calcium content is higher than that of magnesium and potassium and sodium. MBB2 contains higher bicarbonate and sulfate than chloride. All water samples except MBB2 are located in the same zone of the diagram where the water type is

sulfate calcium, permanent hardness (Ding *et al.*, 2003).

Based on the interpretation of the Piper diagram, the following hydrogeochemical

and hydrogeological considerations can be assumed:

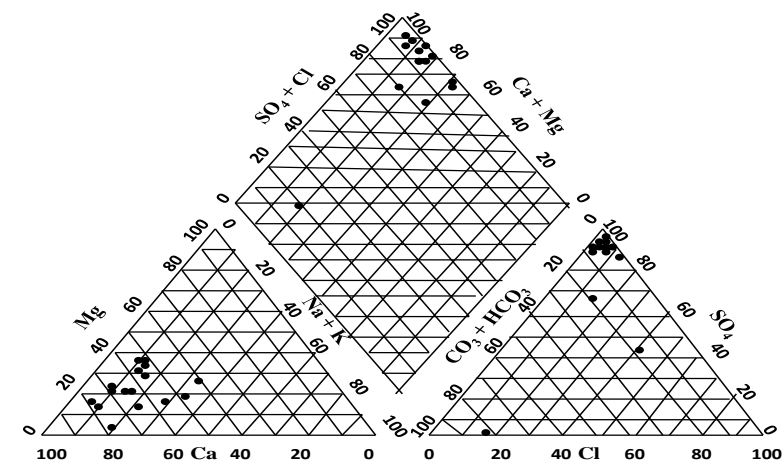


Fig. 3: Trilinear diagrams of major ions in the water samples.

(a) Hydrogeochemical variations of groundwater are greater in anion than in cation contents and indicate that mining of the oil shale and disposal of its tailings have modified and enhanced the anion differences. (b) The compositions of groundwater, surface water and leachate are very similar, indicating that they link with each other hydraulically and hydrogeochemically. (c) The highest sulfate concentration in waters may be explained by oxidization of sulfide, which is high in tailings (Ding *et al.*, 2003).

PAHs distribution in soil and water

Polycyclic aromatic hydrocarbons (PAHs) are persistent worldwide organic pollutants. It is reported that more than 200 aromatic hydrocarbons are carcinogenic compounds some of which are PAHs (Wang *et al.*, 1993).

The results are consistent with those of some researchers who found that the PAHs

are sorbed by organic matter in sediment or soil (Naes, 1997; Ding *et al.*, 2003). Therefore, soil should be included in groundwater remediation, as it is the secondary pollution source to groundwater in many cases, because of the potential leaching of the sorbed organic pollutants. When methods were applied to determine the source of PAHs (Zhan *et al.*, 1998; Pichaya *et al.*, 1998; Naes, 1997; Onuska, Davides, 1991), the results showed that the PAHs found in soil came from oil shale waste. In the soil (MBA4 and MBB4), 2–4 cyclic PAHs were the dominant species. (Ding, *et al.*, 2003).

CONCLUSIONS

The analyses revealed that the soil and groundwater samples were contaminated to various degrees by several chemicals or pollutants from the oil shale tailings. The major environmental problems associated with the site were acidification of soil and groundwater, high content of heavy metals

and sulfate in soil and groundwater; and organic contamination of soil, in particular, finding of carcinogenic Benzo[*a*] pyrene and other PAHs. The environmental conditions at the site permit leachate generation and easy transport of contaminants.

Geochemical analysis showed that soil and groundwater contamination was significantly observed to be from the oil shale waste disposal sites. The nearer the sampling sites to the tailing, the heavier was the contamination of the soil and groundwater. The different water samples all had similar chemical characteristics.

PAHs were retained mostly in the soil, and consisted of mainly naphthalene, fluorene, phenanthrene and anthracene. Results indicated that the source of the PAHs was also the oil shale tailings.

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