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Physicochemical Characteristics and Heavy Metals Assessment in Water and Sediments of Obodo Oilfield in Warri South Local Government Area of Delta State, Nigeria

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ABSTRACT: This study investigated the physicochemical characteristics and heavy metals levels in water and sediments of Obodo Oilfield in Warri South Local Government Area of Delta State using standard laboratory-approved APHA and ASTM methods. Results indicated traces of heavy metals present in the water and sediments. Temperature and TDS in the water samples were within the DPR established limits while TSS, Chemical Oxygen Demand, Salinity and Biochemical Oxygen Demand were higher than the control and well above the DPR established limits. The heavy metals present in the soil were all still within the permissible DPR limits, except for Cadmium which was higher than the control and DPR established limit. The results showed that the water and soil within the environment may have been considerably polluted and degraded by the operations of oil and gas production in the region. The study recommends that the activities of the oil and gas production companies be checked to ensure they are operating within the environmental standard regulations of the country and that the Government and necessary bodies should be proactive in checkmating illegal bunkering activities as they have become the major source of oil spills in the region.

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The Niger Delta in Nigeria is the largest wetland in Africa and the third largest mangrove forest in the world. The region is known for its richness in biodiversity as well as its oil and gas resources. Wetland ecosystems play a critical role in supporting the livelihoods of millions of people. At the same time, they are being degraded by unsustainable practices and a legacy of pollution and oil spills. The region is home to nearly 30 million people, and 60% depend directly on the food and natural resource provided by the environment – such as fish and clean drinking water – for their well-being (Ward, 2016). The Niger Delta is located in southern Nigeria, in the lower reaches of the Niger River, and extends between latitude 5°19″ 20.40″N to longitude 6°28″ 8.99″ E (Davies et al., 2009). The wetland is formed by the accumulation of sedimentary deposits transported by the Rivers Niger and Benue (World Bank, 1995), which discharge water, sediment and other loads across southern Nigeria, and beyond into the Atlantic Ocean. Over many years, the accumulation of sedimentary deposits has resulted in the formation of this complex and fragile delta with a rich biodiversity (Abam, 2001). The delta is majorly water, with thousands of creeks (Ikelegbe, 2006), and collectively, the delta accounts for 55% of all fresh water swamps in Nigeria (Umoh, 2008). Annual rainfall ranges from 3000 mm to 4500 mm, with a wet season between July and September, and a dry season from December to February. Average monthly temperature is 27°C (World Bank, 1995). The Niger Delta region consists of nine states, with over 30 million inhabitants, about 22% of Nigeria's population. The region is ethnically very varied. Ethnic groups include Bini, Efik, Ibibio, Ijaw,

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Isoko/Ukwani, Itsekiri and Urhobo. Despite its vast oil resources, the region remains poor with high levels of unemployment (Agbogidi and Ofuoku, 2006, Idemudia, 2009). Social issues presently confronting this region include cases of hostage taking, kidnappings and pipeline vandalization (Peterside, 2007, Watts, 2008). These are viewed as a response of the people to the perceived injustice in the distribution of socio-economic benefits of oil exploration and level of environmental pollution caused by oil production activities in the region. They believe that while local communities directly bear the environmental consequences of oil development, such as loss of biodiversity (Uluocha and Okeke, 2004, James et al., 2007, Phil-Eze and Okoro, 2009) and pollution of the water supply (Okoh et al., 1996), other regions of the country enjoy the economic benefits. Over the years, farming and fishing have been the main source of employment for most of the Niger Delta inhabitants. However, the environmental degradation elicited by oil and gas production have diminished farming and fishing activities in the region. These activities have rendered farming and fishing almost impossible in the region (Ebegbulem et al., 2013). Other forms of occupation include hunting, production of palm oil and palm kernel, distillers of gin from raffia palm and rubber tapping. Hunting has reduced drastically in the region due to deforestation caused by oil and gas exploration and production activities because animals are displaced from their habitat in the process. This in turn denies the local people of bush meat (Okpako, 2014). People whose occupations were rubber tapping and palm oil production have also been displaced from their jobs (Ojakorotu, 2009). Due to the environmental damage caused by oil and gas activities, the major occupations of the river side minorities have been decimated (Ebegbulem et al., 2013). More than 50 years of crude oil exploration and production in the Niger Delta region, has caused unquantifiable and inhuman devastation to the people of the region as the people are no longer engaged in their fishing, farming and hunting activities which were the mainstay of their economy (Chijioke et al., 2018). Large oil spills usually pollute coastal waterbodies, kill fishes and destroy agricultural crops and farm lands. The continuous impacts have caused major loses in productivity in fisheries and agricultural activities. Oil spills disrupt fishing and farming activities by polluting the water and causing fishes to either die or be displaced (Ebegbulem et al., 2013). In effect, the farmers and fishermen become unemployed as cleanup and remediation is not done at all. Another major environmental challenge hindering farming is gas flaring. Flares cause an elevation of temperature. The heat generated kills vegetation by suppressing the flowering of plants, in turn, preventing proper growth and decrease in production (Omohimoria et al., 2014). Crops planted close to flare sites experience retardation in their development because of high temperatures around flare sites (Dung et al., 2018). The Conoil Obodo field environment has over the years suffered considerable pollution and degradation from oil and gas exploration and production activities. Hence, the objective of this study is to investigate the physicochemical characteristics and heavy metals levels in water and sediments of Obodo Oilfield in Warri South Local Government Area of Delta State, Nigeria.

MATERIALS AND METHODS

Study Area: The sampling was carried out at Conoil's Obodo oil field, in Warri South LGA of Delta State, Nigeria. The location is a riverine and swampy area of Obodo in Warri South Local Government Area of Delta State, Nigeria. The Obodo field is located in OML 150, a large block in Warri South LGA of Delta State, Nigeria. OML 150 comprises about 7 Itsekiri communities, viz Omadino, Opumami, Wakeinor, Ajasolor, Obodo, Iffie and Ijala. The oil wells in the field are linked to flow stations from where the oils are primarily treated and pumped into tank farms before they are then distributed to vessels. But currently, there is no production going on in the area because the tank farms were vandalized. Local production and oil bunkering by indigenes are also predominant in the area.

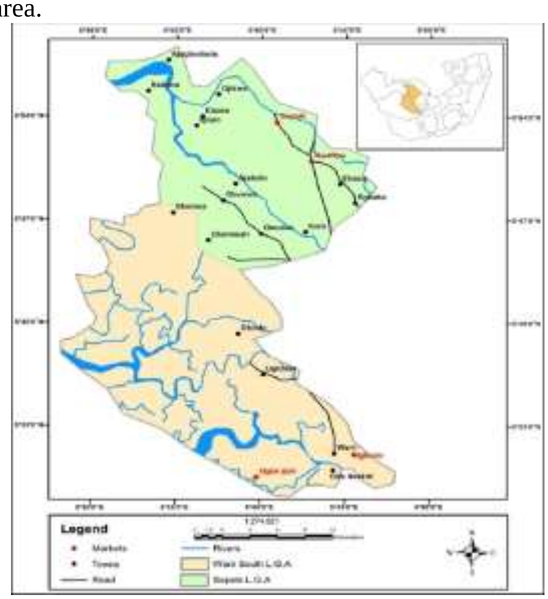

Fig 1: Map of Warri-South LGA and Sapele LGA showing the study area
(Source: ResearchGate)

Sample Collection: The water samples used for this analysis were collected from the above-mentioned location. A total of 3 water samples were collected directly from different points A, B and C within the location and a fourth sample which was the control sample was collected from a point D away from the location. The water samples were collected in 2L sterilized containers which were appropriately labelled before being taken to the laboratory. The water samples were subjected to the following tests using approved SM, APHA and ASTM methods: pH, conductivity, turbidity, total dissolved solid (TDS), total suspended solid (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), salinity, and heavy metal content. The soil samples used for this analysis were collected from different points A, B, C within the above-mentioned location, and a control sample D away from the location. The samples were collected at a depth of 0-30cm from the study location. The collected soil samples were carefully labeled for identification and stored in black polythene bags for onward transfer to the laboratory. At least 1kg (wet weight) of each sample was collected so that a minimum of 400g of the soil samples can be recovered after air-drying and removal of extraneous materials. The soil samples were then subjected afterward to the following tests using approved ASTM methods: pH, exchangeable cations and heavy metal content test.

Water pH: The pH of the water samples was determined in-situ.

Total Dissolved Solids (TDS): The TDS/Conductivity of the samples was determined in-situ.

Total Suspended Solids (TSS): The Total Suspended Solids (TSS) of the water samples was determined using Gravimetric (SM 2540-D) method. A well-mixed sample was filtered through a weighed standard glass fibre filter and the residual returned on the filter was dried to a constant weight in an oven at 103 to 105^0C. The increase in weight of the filter represents the Total Suspended Solid. This was reported in mg/l after calculation.

Chemical Oxygen Demand (COD): The Chemical Oxygen Demand was determined using the Coulometric (SM 5220-D) method. Select program for COD HR or LR depending on the COD vial concentration that was used. Place the COD vial adapter in the cell holder of the DR 3900 spectrophotometer. Insert reagent blank and zero. Place the vial containing the test sample in the adapter, and press read to give COD value in mg/L. Most organic and oxidizable inorganic substances present in water are oxidized by a boiling mixture of standard potassium dichromate acid standard solution. Dichromate is consumed in the oxidation of the organic matter, and the Chemical Oxygen Demand is determined calorimetrically, by measuring the increase in green color of the reduced chromium (Cr^{3+}) or the decrease in yellow color of the dichromate ($Cr_2O_7^{2-}$).

Biochemical Oxygen Demand (BOD): The BOD of the samples was determined using the Winkler's Dilution Method (SM 5210-B). The amount of oxygen consumed during a fixed period of 5 days is related to the amount of organic matter present in the original sample. Dissolved Oxygen of the samples was first determined using the Schott Gerate Dissolved Oxygen meter and then incubated for 5 days at 20^0C; and then measured again after a period of 5 days, with the BOD in mg/L determined from the following calculation and reported accordingly:

$$BOD_5 \text{ mg/l} / P = (D_1 - D_5) - (B_1 - B_5)\ x/y \quad (1)$$

Where, D_1 = Dissolved oxygen of the sample before incubation on day 1 (2nd sample); D_5 = Dissolved oxygen of the sample after incubation on day 5 (1st sample); B_1 = Dissolved oxygen of the blank before incubation (2nd blank); B_5 = Dissolved oxygen of the blank after incubation on day 5 (1st blank); P = Decimal volumetric fraction of sample used

$$\frac{30ml}{230ml} \frac{-}{-} \frac{volume\ of\ sample}{volume\ of\ aerated\ water}$$

x = % of seed in the diluted sample: y = % of seed in seed control bottle

Turbidity: The turbidity of the collected water samples was determined using the Nephelometric method (ASTM D1889). Rinse a clean sample cell with the solution to be measured. Three rinses with a small amount of sample will guard against sample contamination by dust or residue in the cell. Fill the sample with approximately 10ml of test sample. Dry the outside of the cell with a clean, lint-free cloth or tissue. Be particularly careful to make sure the bottom of the cell is clean and dry. Read the sample on the turbidimeter. Results are expressed in NTU (Nephelometric Turbidity Units).

Salinity: The method used for this analysis was the Argentometric Method (SM 4500-Cl-B). Directly titrate samples in the pH range of 7 to 10. Adjust sample pH to 7-10 with H_2SO_4 or NaOH if it is not in this range. For adjustment, preferably use a pH meter with a non-chloride type reference electrode. Add 1ml K_2CrO_4 indicator solution. Titrate with standard $AgNO_3$ titrant to a pinkish yellow end point. Be consistent in the end point recognition. Standardize $AgNO_3$ titrant and establish reagent blank value by the titration method outlined above. A blank of 0.2 to

0.3ml is used. Salinity is reported in mg/l after calculations using the formular:

$$mgCl^- / L = (A - B) x N x 35450 \div ml \text{ of sample}$$

Where = ml of titration for sample; B = ml titration for blank; N = Normality of $AgNo_3$

$$mgNacl / L = (mgCl^- / L) x 1.65 \quad (2)$$

Water Heavy Metal Content: Concentrations of the heavy metals; Lead (Pb), Zinc (Zn), Copper (Cu), Chromium (Cr) and Iron (Fe) were measured using Atomic Absorption Spectrophotometry (AAS) with Model No SM-3500.

Soil pH: Soil pH was measured by adopting the ASTM D 1293-99 and APHA 4500-H^+ B method. A soil suspension was prepared by mixing 10g air-dried soil sample with 10ml of distilled water, which was then stirred with a stirring rod for 20 minutes. The pH probe of the pH meter was then inserted and the pH values read.

Soil Exchangeable Cations: The total exchangeable cation is the sum of exchangeable Ca, Na, K, Mg, Al, determined by Atomic Absorption Spectrophotometer after extraction. 5g of each air-dried soil sample was weighed into 25ml of ammonium acetate. The ammonium acetate was prepared by dissolving 72.09g of the acetate in 1000ml of distilled water. 3M of ammonium hydroxide was added to raise the pH of the prepared acetate to pH 7. An atomic absorption spectrophotometer was then used to determine the values for the various cations in mg/L. Mg/L values of Ca, Mg, K, Na and Mn were determined and converted to meq/L.

$$CEC = EA + TEB \quad (3)$$

Where CEC = Cation Exchange Capacity; EA = Exchangeable Acidity; TEB = Total Exchangeable Bases

Soil Heavy Metal Content: 1.0g of each sample was contacted with 10ml of concentrated HCL and Nitric acids mixture in the ratio 3:1 (i.e., 7.5ml HCL and 2.5ml HNO_3). The mixture was swirled and kept in the fume cupboard. The samples were digested on hot plate stirrer at 60^0C until cessation of white fumes. After cooling for 10 minutes, 10ml of deionized water was added and filtered using separating filter paper. The filtrates were analyzed using atomic absorption spectrophotometer. Heavy metal absorbance detected at various wavelengths were mainly for Chromium, Cadmium, Nickel, Lead, Zinc, Copper, Manganese and Iron.

RESULTS AND DISCUSSIONS

Surface Water Samples Results: The results of the surface water samples collected and analyzed are shown in table 1. The pH values of all the samples collected at points A, B, C and control point D varied between 5.37 to 6.48. This range shows the water samples are rather acidic and may not be recommended for drinking because according to the Environmental Protection Agency (EPA), water's safe pH for drinking spans between 6.5 and 8.5. The samples contained Dissolved and Suspended Solids in varying amounts. Dissolved solids naturally increase water's conductivity, and from the results, sample A had the highest conductivity because it contained the highest amount of total dissolved solids. According to World Health Organization, TDS level less than 300mg/L is considered as excellent for drinking, between 300 and 600 mg/L is good, 600 – 900 is fair, 900 – 1200 is poor and TDS level more than 1200 mg/L is unacceptable. From the results, this also confirms that samples A, B and C are unsafe for any form of human consumption. Chemical Oxygen Demand (COD) reflects the level of pollution and contamination present in the water samples. It increases as concentration of organic matter increases. The mean Chemical Oxygen Demand for samples A, B and C was 108mg/L which was above the control of 21 and the DPR limit of 40, and so indicates high amount of organic matter are present in them. This may be due to oil spills from bunkering activities, decaying plant matter, industrial effluent discharges and human waste pollution from inhabitants. Turbidity measures the relative clarity of water. The cloudier the water, the higher its turbidity. This reflects why sample A registered the highest turbidity. Also, it was seen that samples A, B and C had high levels of salinity; but sample A had the highest level which implied that it had the highest concentration of dissolved salts present in it. Heavy metal traces of ($<$ 0.01 mg/L) of Pb, Zn, Cu, Cr and Fe were evident in samples A, B, C and D. This is because heavy metals are known to be naturally occurring compounds, but are introduced in large quantities in different environmental compartments through anthropogenic activities associated with oil exploration and production. Low heavy metal accumulation has been reported in Nigerian water bodies in a previous study by (Omoigberale and Ogbeibu, 2007). Due to its high toxicity to aquatic life and man, heavy metals have been used as an indicator of pollution (Omoigberale and Ogbeibu, 2005). Oshienemen et al., (2018) in his study stressed that oil spill impacts on communities are numerous and thereby needs the government and or the oil-related companies to involve the community members in decision making.

Table 1: Physicochemical Characteristics and Some Heavy Metals in Water Samples from Obodo Oilfied in Warri South Local Government Area of Delta State, Nigeria

Parameters	Range	Mean	STD	SE	Control	DPR Limits
pH	6.36-6.48	6.41	0.05	0.03	5.37	6.5 – 8.5
Temp. ^{0}C	25-25.6	25.2	0.26	0.15	25.5	26.0
Total Dissolved Solids	1184-1843	1432	292.5	168.9	25	2000
Total Suspended Solids	1.00-57.0	23	24.39	14.08	< 1.0	< 30% of the receiving medium
Chemical Oxygen Demand	54-150	108	40.1	23.15	21	40
Salinity (Cl^-)	505-1046	716	236.2	136.37	15.5	600
Turbidity	4.51-14.0	8.22	4.14	2.39	10.1	< 10% of the receiving medium
Conductivity	2234-3478	2701	553.15	319.35	46	N/A
BOD	10.42-26.98	19.64	6.89	3.98	4.86	10.0
Pb^{2+}	<0.01	< 0.01	<0.01	<0.01	< 0.01	0.05
Zn^{2+}	<0.01	< 0.01	<0.01	<0.01	< 0.01	0.03
Cu^{2+}	0.01	0.01	0	0	< 0.01	1.50
Cr^{6+}	<0.01	< 0.01	<0.01	<0.01	< 0.01	0.03
Total Iron (Fe^{2+} + Fe^{3+})	0.09-0.43	0.31	0.15	0.09	0.28	1.00

Explanation: mg/l – Milligram Per Liter, NTU – Nephelometric Turbidity Units, µs/cm – Microsiemens Per Centimeter

Involving the community will give an insight to vital needs of the community, which will be imbibed in the structure of the infrastructural compensation.

Soil Samples Results: The analytical results of soil samples collected at points A, B and C from the study location are presented in table 2. The pH range of the soil samples from points A, B, C and D varied between 6.33 and 7.81, with sample C having the highest pH value of 7.81. The variation in pH may be as a result of the soil type, soil texture and mineral content, since they were collected from different locations in the area. Wang Ying et al., (2013) in a study conducted in Momoge Wetland of China confirmed that Crude oil contamination can significantly increase the soil pH up to 8.0, and reduce available phosphorus concentrations in the soil. The Exchangeable Cations are also a function of the soil type, soil pH and soil organic matter content. In a study carried out by Abii and Nwosu in 2009 in Eleme in Rivers State of the Niger-Delta Area of Nigeria, they found out that the fertility status of the soils in the region is reduced as the oil makes most of the essential nutrient unavailable for plant and crop utilization. Also, it is evident from table 4 that the soil samples are contaminated with heavy metal traces of Chromium, Cadmium, Nickel, Lead, Zinc, Copper, Manganese and Iron. These heavy metals occur naturally in soils through natural processes such as the weathering process of underlying rocks. Oil spillage is another contributing factor to the presence of heavy metals in soils. The general increase of heavy metal content in the soil has been largely attributed to oil spillage. When spills occur, heavy metal pollution of the soil is caused by metals present in the crude especially copper, nickel, cadmium, zinc, chromium and lead. These heavy metals cause severe damage to the soil and plants when they are highly concentrated. It has been observed that the pollution caused by heavy metals does not only result in adverse effects on various parameters relating to plant quality and yield, but also causes changes in the size, composition and activity of the microbial activities (Yao and Huang, 2003).

Table 2: Physicochemical Characteristics and Some Heavy Metals in Soil Samples from Obodo Oilfied in Warri South Local Government Area of Delta State, Nigeria

Parameters	Range	Mean	STD	SE	Control	DPR Limits
pH	6.3-7.81	6.89	0.66	0.38	6.91	6.5 - 8.5
Exchangeable Cations	8.21-281	129.16	108.1	62.41	28.56	N/A
Cr^{6+}	1.23-5.20	3.34	1.63	0.94	1.00	100
Cd^{2+}	1.8-2.35	2.16	0.22	0.13	1.75	0.80
Ni	1.33-15.98	14.82	1.11	0.64	10.78	35
Pb^{2+}	0.55-3.64	1.79	1.33	0.77	2.70	85
Zn^{2+}	26.20-70.00	43.26	355.02	204.97	51.40	140
Cu^{2+}	7.03-14.28	9.77	12.10	6.99	3.78	36
Mn^{2+}	16.90-43.75	26.70	12.10	6.99	16.05	N/A
Total Iron (Fe^{2+} + Fe^{3+})	1350-3903	2657.67	1043.19	602.27	1329	N/A

Explanation: Kg – Kilogram, mg/kg – Milligram Per Kilogram, meq/100g – Milliequivalent Per One Hundred Gram

Conclusion: There is no doubt that the operations involved in producing oil and gas degrade the environment and damage the quality of soil, air, and water. The region's damaged ecosystem is a result of a lack of rigorous adherence to current environmental protection rules and regulations as well as the failure of governmental and non-governmental organizations to enforce these laws. It is vital to understand the repercussions of these oil and gas activities on water and soil, and methods for mitigating them, in order to improve the environment and socioeconomic life and wellness of the people in the region.

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