

Laboratory Analysis of the Chemical Properties of an Oil Polluted Ecosystem in Imutu, Delta State, Nigeria

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Abstract: This research work was undertaken to determine the extent of oil pollution on a polluted site of Niger-Delta area of Nigeria by investigating the concentration of physicochemical characteristics properties like pH, Total Dissolved Solid, Electrical Conductivity, Oil and Grease and presence of heavy metals like Nickel, Cadmium, Chromium, Cobalt, Copper, Lead, Iron, Zinc, Arsenic in the collected soil samples from different sampling locations were determined. Environmental Guidelines and Standards for the Petroleum Industry in Nigeria was used to determine if the test result falls within the acceptable limit. Test result indicated that, lead, copper, chromium cobalt, zinc, cadmium, nickel and arsenic were within acceptable limits whereas electrical conductivity, oil and grease, and iron were found to be very high and above specified limits. Test result indicated that electrical conductivity increased from 1320 to 3525 ($\mu\text{S}/\text{cm}$) with highest value seen with sample from 100m from highly polluted site and lowest in highly polluted soil sample. Total dissolved solid also increased from 690 to 1760 (mg/l) with the highest with soil sample at 100m from highly polluted site and lowest soil sample at 1m depth from highly polluted soil surface sample. Oil and grease and Ph also follow the same trend. Therefore in order to assess the effect of pollution on ecosystem, the chemical analysis of the concentration of the pollutant at the site should be employed.

Keyword: chemical analysis, Electrical conductivity, oil pollution, physicochemical properties, TDS.

1.0 Introduction

On land, crude oil spills have caused great negative impact on food productivity. For example, a good percentage of oil spills that occurred on the dry land between 1978 and 1979 in Nigeria, affected farmlands in which crops such as rice, maize, yams, cassava plantain were cultivated. Crude oil affects germination and growth of some plants. It also affects soil fertility but the scale of impact depends on the quantity and type of oil spilled. Spilled petroleum hydrocarbons in the environment are usually drawn into the soil due to gravity until an impervious horizon is met, for example bedrock, watertight clay or an aquifer. Poor miscibility of crude oil accounts for accumulation of free oil on the surface of ground water and this may migrate laterally over a wide distance to pollute other zones very far away from the point of pollution. Industrial and municipal discharges as well as urban run-offs, atmospheric deposition and natural seeps also account for petroleum hydrocarbon pollution of the environment. It is worthy of note that groundwater is one of the many media by which human beings, plants and animals come into contact with petroleum hydrocarbon pollution. Crude oil and petroleum are complex mixtures of several polycyclic

Contamination of soil arising from spills is one of the most limiting factors to soil fertility and hence crop productivity. Report revealed that thirteen years after the Exxon Valdez oil spill in Prince William Sound, the toxic effects are still being felt due to the remaining bulk of the less-weathered subsurface oil [4]. A random sampling of underground fuel storage tanks conducted by U.S. Environmental Protection Agency (USEPA) in the United States revealed about 35% leaks in these tanks (United Press International, 1986). The major concern with crude oil spill has been its contamination of ground water, and the subsequent clean up.

Crude oil pollution of the environment may arise from oil well drilling production operations, transportation and storage in the upstream industry, and refining, transportation, and marketing in the downstream industry. It could also be from anthropogenic sources [1].

Sources of petroleum and its products in the environment will also include accidental spills and from ruptured oil pipelines [2]. One of the major fates of spilled petroleum oil in the coastal environment is its incorporation into the sediments. Problems associated with the study and remediation of the polluted ecosystem can be very expensive. The legal problems related to compensation in terms of assigning monetary reward may bring serious controversy. This study is therefore undertaken to determine the extent of oil pollution on a polluted site by investigating the physicochemical characteristics and microbial qualities of some specified selected parameters.

aromatic compounds and other hydrocarbons [3].

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2.0 Materials and Methods

Sampling:

All the collected samples were preserved in accordance with guidelines and International Standards. All other QA/QC procedures relevant to sample collection, custody and analyses were strictly adhered to. (APHA 1995; ASTM, 1979). The crude oil sample was obtained from Burutu oil field, Nigeria. Analysis of the Physicochemical properties like pH, Total Dissolved Solid, Electrical Conductivity, Oil and Grease and presence of heavy metals like Nickel, Cadmium, Chromium, Cobalt, Copper, Lead, Iron, Zinc, Arsenic were carried on the polluted soil samples. Due diligent were taken to prepare the samples for specified test as indicated below:

Physico-chemical analysis: *ph/temperature (apha 460), conductivity (apha 145), and TDS (apha 208d)*: These chemical properties were determined electrometrically with a multi- parameter data logger (Hanna model HI991300).

PH Value determination: A 4 parts pH measuring system was used for ph determination namely: a ph sensing electrodes, electronic circuit that translate the signal into readable reference for the user and the sample being measured. A 9 volt battery was connected to the ph meter, the cover was adjusted to desired view angle, the meter was switch on and the mode was set to ph position, this activated the liquid crystal display, the cable was connected to the BNC input and the electrode was conditioned in buffer 7.0 solution until the LCD is stable (30 sec) the temperature control was adjusted to ambient temperature, the buffer and the samples was allowed to come to this ambient temperature ,the calibration control was adjusted in such a way that the LCD showed the value of buffer 7.0 at 250°F,the electrode was then rinsed with buffer 4.0, blot dry and immersed in buffer 4.0 when the LCD is stable (30sec) the slope control was adjusted to make LCD show the value of 4.0 solution, the system has now been calibrated to read sample with different ph values. The electrode was the rinsed with a small portion prepared crude sample, blot dry and immerse in the sample. This was repeated for measuring the ph value of all the prepared crude samples.

Electrical conductivity (EC) determination: A saturated paste of samples of crude oil was prepared. The electrical conductivity of the sample was determined electrometrically with a calibrated electrical conductivity meter.

Heavy Metals Determination (AAS): Samples were pre-treated with 2ml conc. HNO₃ per litre of sample. The equipment was conditioned by auto-zeroing it with distilled water and with conc. HNO₃. The pre-treated sample was analysed for heavy metals using the

appropriate hollow cathode element of each metal of interest at the appropriate wavelength, lamp current, band-pass, and background correction.

Oil and Grease Determination (ASTM D 3921): About 100ml acidified sample (pH 2) was measured into a graduated glass bottle. 4ml of an organic solvent was added to the sample and the bottle vigorously shook for 2mins. The contents of the bottle were emptied into a separating funnel and shook vigorously. The stopper of the funnel was intermittently opened to release pressure build up. The contents of the funnel were allowed to settle. The bottom layer of the solution was transferred into a clean beaker using glass funnel previously stuffed with cotton wool and 1g anhydrous sodium sulphate at the aperture of the glass funnel to absorb water.

Density determination: 50 ml pycrometer (density bottle) was rinsed with distilled water and dry with acetone, the mass of empty pycrometer was measured and recorded using analytical balance, the pycrometer was then filled with distilled water, the stopper was inserted and the stopper hole was also filled with distilled water, it mass was measured recorded, the pycrometer was then filled with distilled water and dry with acetone, the pycrometer was the filled to the brim with the crude oil sample, the pycrometer was then hanged in thermostat bath at the given temperature and was allowed for a few minutes to reach equilibrium, the pycrometer was the removed from the bath, wipe dry and weigh on an analytical balance, the density of oil sample was obtained as

$$D = \frac{M_W}{V_M}$$

Where D = density (lb/bbl), M_W = Molecular weight (lb) and V_M = volume (bbl)

Determination of specific gravity 60°F : The sample was prepared and transferred into a clean gravitometer cylinder, the gravitometer was then lowered gently into the sample and it was sealed, it was then depressed to about two scale division into the liquid and then it was sealed, sufficient time was then allowed for the gravitometer to become completely stationary and for air bubbles to surface, when the gravitometer finally comes to rest and floating freely, the Gravitometer was read to the nearest scale division, the correct reading is that point on the gravimeter scale at which the liquid cut the scale. The point was determined by placing the eye slowly below the level of the liquid and raising it slowly unto the surface until a disturbed eclipse appears to be a straight- line crossing the gravimeter scale. Note that for conversion of specific gravity at laboratory temperature (°F) to value at 60 °F, the equations below were used

$$SG = \frac{\rho_F}{\rho_W}$$

Where SG = Specific Gravity (dimensionless), ρ_F = Density of fluid (kg/m^3) and ρ_W = Density of water (kg/m^3).

API gravity determination: The sample was prepared and transferred into a clean gravitometer cylinder, the gravitometer was then lowered gently into the sample and it was sealed, it was then depressed to about two scale division into the liquid and then it was sealed, sufficient time was then allowed for the gravitometer to become completely stationary and for air bubbles to surface, when the gravitometer finally comes to rest and floating freely, the Gravitometer was read to the nearest scale division, the correct reading is that point on the gravimeter scale at which the liquid cut the scale. All the samples for ph measurement were maintained at 60°F , and the ph was calculated from the correlation.

$$^\circ\text{API} = \frac{141.5}{SG @ 60^\circ\text{F}} - 131.5$$

3.0 Result and Discussion

Test results from analysis of the soil samples as specified are indicated in the tables below:

Table 1: Physicochemical Analysis of highly polluted soil surface sample

| S/N | Parameter | Test result |
|-----|-------------------------|-------------|
| 1 | pH | 7.64 |
| 2. | TDS (mg/l) | 710 |
| 3. | EC ($\mu\text{S/cm}$) | 1400 |
| 4. | Oil and Grease (mg/l) | 33452 |
| 5. | Nickel (mg/l) | 0.001 |
| 6 | Cadmium (mg/l) | <0.001 |
| 7 | Chromium (mg/l) | <0.001 |
| 8 | Cobalt (mg/l) | <0.001 |
| 9 | Copper (mg/l) | 0.002 |
| 10 | Lead (mg/l) | 0.002 |
| 11. | Iron (mg/l) | 18.47 |
| 12 | Zinc (mg/l) | 0.078 |
| 13 | Arsenic (mg/l) | <0.001 |

Table 2: Physicochemical Analysis of soil sample @ 1m depth at highly polluted site

| S/N | Parameter | Test result |
|-----|-------------------------|-------------|
| 1 | . pH | 7.40 |
| 2. | TDS (mg/l) | 690 |
| 3. | EC ($\mu\text{S/cm}$) | 1320 |
| 4. | Oil and Grease (mg/l) | 5200 |
| 5. | Nickel (mg/l) | 0.001 |
| 6 | Cadmium (mg/l) | <0.001 |
| 7 | Chromium (mg/l) | 0.002 |
| 8 | Cobalt (mg/l) | <0.001 |
| 9 | Copper (mg/l) | <0.001 |
| 10 | Lead (mg/l) | 0.002 |
| 11. | Iron (mg/l) | 12.680 |
| 12 | Zinc (mg/l) | 0.078 |
| 13 | Arsenic (mg/l) | <0.001 |

Table 3: Physicochemical Analysis of soil sample @ 100m from highly polluted site

| S/N | Parameter | Test result |
|-----|-------------------------|-------------|
| 1 | . pH | 6.72 |
| 2. | TDS (mg/l) | 1760 |
| 3. | EC ($\mu\text{S/cm}$) | 3525 |
| 4. | Oil and Grease (mg/l) | 1980 |
| 5. | Nickel (mg/l) | <0.001 |
| 6 | Cadmium (mg/l) | <0.001 |
| 7 | Chromium (mg/l) | 0.023 |
| 8 | Cobalt (mg/l) | <0.001 |
| 9 | Copper (mg/l) | 0.002 |
| 10 | Lead (mg/l) | 0.006 |
| 11. | Iron (mg/l) | 12.680 |
| 12 | Zinc (mg/l) | 0.057 |
| 13 | Arsenic (mg/l) | <0.001 |

Table 4: Physicochemical Analysis of Film of Crude on nearby Water Surface

| S/N | Parameter | Test result |
|-----|-------------------------|-------------|
| 1 | . pH | 3.80 |
| 2. | TDS (mg/l) | 1640 |
| 3. | EC ($\mu\text{S/cm}$) | 3204 |
| 4. | Oil and Grease (mg/l) | 1424 |
| 5. | Nickel (mg/l) | <0.001 |
| 6 | Cadmium (mg/l) | <0.001 |
| 7 | Chromium (mg/l) | 0.113 |
| 8 | Cobalt (mg/l) | <0.001 |
| 9 | Copper (mg/l) | <0.001 |
| 10 | Lead (mg/l) | 0.006 |
| 11. | Iron (mg/l) | 0.574 |
| 12 | Zinc (mg/l) | 0.139 |
| 13 | Arsenic (mg/l) | <0.001 |

Results of the different samples from the different sampling locations of highly polluted soil surface, soil sample at 1m depth at highly polluted site, soil sample at 100m from highly polluted site and Film of Crude on nearby Water Surface are presented in tables (1 – 4).

Test result indicated that heavy metals; lead, copper, chromium cobalt, zinc, cadmium, nickel and arsenic were within acceptable limits whereas electrical conductivity, oil and grease, and iron were found to be very high and above specified limits as shown in tables (1-4).it was noted that electrical conductivity increased from 1320 to 3525 with highest value seen with sample from 100m from highly polluted site (table 2) and lowest in highly polluted soil sample (table 1). This is due to the fact that electrical conductivity is a function of level of contamination at the polluted site, the higher the level of spill the lower the electrical conductivity. The Total dissolved solid also increased from 690 to 1760 with the highest with soil sample at 100m from highly polluted site (table 2) and lowest soil sample at 1m depth from highly polluted soil surface sample(table 3).this follow from the electrical conductivity, the higher the electrical conductivity the higher the Total Dissolved Solid. The oil and grease value increased from 33452 to 1980 with lowest value in highly polluted soil sample (table 1) and lowest in soil sample at 100m from highly polluted site (table3). This is due to high concentration of contaminant at highly polluted site than other selected sites.PH ALSO increased from 7.40 to 3.80 with highest at highly polluted site (table 1)and lowest at Crude on nearby Water Surface sample.

Conclusion

When hydrocarbons are released into the environment (Ecosystem), their effects should be minimized as much as possible; this can be accomplished through a trough chemical/laboratory analysis of the contaminants at the polluted site, so as to reduce its long term threat to all forms of life. Immediate remediation technology should also be carried out to restore affected areas to base – line level. Due diligence to be adhered to for continuous monitoring to validate the effectiveness of mitigation.

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