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Microbes and Mineral Elements in Oil Producing Areas of Ondo State, Nigeria

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Abstracts: Microbes and mineral constituents of oil producing areas of Ondo State vary from site to site. The highest of 240 x 10⁵ cfu/ml was recorded in Ayetoro compared with Sabomi having a low count record of 7x10³ cfu/ml. Mineral element ranges from the lowest of 1.15ppm and 2.13ppm in Seluwa and Gbawiyo to highest of 468.73ppm and 474.85ppm in Ayetoro and Seja for Ca; 0.24 and 3.52pp1m in areas like Sabomi and Araromi to 256.03ppm and 1185.34ppm in Ayetoro and Bijimi for Mg; 0.01 in Sabomi and Ilepete, Ayetoro, Ubale, Obeiji, Gbawiyo, Araromi, Abetobo, Pepe and Seluwa to 0.23 in Awoye, Ayetoro and Orioke for Mn; 0.07ppm in Ayetoro to 2.71 and 6.63ppm in Gbawiyo and Orioke for Fe; 0.01 in Igbokoda Jetty and Awoye, Ilepete, Ayetoro, Ubale, Obeiji, Gbawiyo, to 0.78ppm in Awoye and most stations studied for Lead (Pb). 0 values were recorded for PO4-P (ppm) in Ayetoro 1, Araromi, Bijimi and Sabomi to 0.49ppm in Awoye respectively. Other metal constituents in water samples are from the lowest of 64 ppm and 70.06 ppm in Gbawiyo and Awoye to highest of 440 and 400 ppm in Araromi and Obeiji for Cl; 0.1ppm in Awoye to 0.31 and 0.3ppm in Ilepete for Cr; 0.04 in Ayetoro, Gbawiyo, Araromi and Pepe to 0.11 and 0.1 ppm in Awoye respectively for Cd. Sabomi (control site) showed low levels of most metals except calcium (Ca) compared with these of oil producing sampling site studied thus suggesting the metal constituent infiltration from oil pollutants in this area.

Key words: Microbes · Mineral elements · Nigeria · Oil producing areas · Ondo State

INTRODUCTION

Oil exploration often affects many water bodies. Water is a natural resource that is needed by all living things. It is similarly a universal solvent, thus the study of ecology of oil producing areas in countryside as it affects water bodies is important because of the possible pollution of such area with petroleum hydrocarbon through oil spillage and its control. The effects of water pollution are not only devastating to people, but they can kill animals, fish and birds. Furthermore, the effects of water pollution pose a serious threat to society today and in the future. Thus there is need to keep our environment safe from pollution [1].

Oil spillage into water, affects the ecosystem and its components negatively. Some animals, such as birds, mammals and fish may and can be killed if they ingest oil. Many may die from eating oil contaminated prey. Birds may die if the oil costs their feathers. They can neither fly nor stay warm. Furthermore, when oil coats the feathers they can become sick and die. Oil and antifreeze impacts bad odor and leave a sticky film on the surface of water that kills animals and fish. So, our environment should be protected to avoid pollution from both microbial and chemical sources in nature [1]. Ilaje community which is an oil-producing area of Ondo State lies between latitudes 6° and 63' North and longitude 4°45' and 5°45' East. It was boarded on the south by the Atlantic Ocean, East by Delta State, North by Ikale Local Government and West by Ogun State. It is land area linked with many rivers undulating landscape and other adjoined zones with lowland in the coastal area. Contamination of source of drinking water is a common occurrence in the Niger Delta area of Nigeria where most of the water supply is derived from shallow and uncontained aquifers [2,3]. There is therefore the need for quick removal of oil from polluted environment.

Oil pollutants in an area becomes of concern because of some adverse effects on the ecology as earlier discussed, similarly some pollutant such as polycyclic aromatic hydrocarbons (PAHs) are a large and diverse group of chemicals having two or more aromatic rings and are a major components of petroleum hydrocarbons including bitumen [4]. PAHs have been detected in

Corresponding Author: A.O. Ajayi, Department of Microbiology, Adekunle Ajasin University, P.M.B 01, Akungba-Akoko, Ondo State, Nigeria commercial seafood in plant tissues and are capable of causing off-flavours in fish. PAHs are of special concern because of the carcinogenic nature of a number of members of this class of compounds [4]. Calcium is one of the contributors to hard water, it forms scale and hence undesirable in steam-raising generation plant. It can be normally removed by ions exchange operation. Magnesium is moderately toxic and it is found in almost all water supplies [5]. It is also a consistent of hardness. Lead is another common chemical pollutant highly toxic to humans and cams causes plumbism disease.

Copper (Cu) can constitute astringent taste and discoloration to water sources. Similarly, it can cause corrosion of pipe, fittings and utensils - through which it flow or has contact with. Manganese (Mn) is also highly toxic to humans and stains fixtures. Laundry TLV 0.05 Mg/I [5], while Iron (Fe) constitute a major aesthetic problem and not physiological because its high concentration may stain laundry and fixtures. Chloride can impact taste and affects the portability of water. It can be extremely corrosive as its molecular size is such that it can penetrate the protective oxide metal interface and react with steel structures [5]. The chloride content was determined using Mohr titration method with potassium chromate as indicator. This was a method adopted by Vogel [6]. The end point (at which the colour changes from bright yellow to orange) during titration of silver nitrate and sample give the value of the chloride content in milligrams per litre or (Mg/L) or ppm.

Previous investigations have shown that crude oil and other related organic pollutants can be degraded [7-10], but there is need for routine monitoring of our coastal water bodies [11]. In order to know the level of pollution and environmental degradation in the study area, an environmental impact assessment (E.I.A) study of the area should be carried out. The study of Munn [12], identified E.I.A as an activity designed to identify and predict the impact of project on the bio-geophysical programmes, operational procedures and to interpret and finally communicate the impact. The conservation of the biogeophysical component of the ecosystem is desirable for man's co-existence [15]. Thus there is need to monitor it's dynamics, for the sustenance of human and ecological development [11].

Industrial developments and growth in petroleum hydrocarbon exploration activities in Nigeria and all over the world has led to increased oil pollution in our environment [4]. This can result from accidental spillage during drilling, leakages of pipelines or through vanderlization. Similarly, some discharges or outburst of petrol from some oil tankers during accidents occasionally result in flow over land, vegetation and water surfaces, polluting the soil and water and posing serious ecological problems [3].

MATERIALS AND METHODS

Study Site: The study research was carried out in a sizeable riverine oil producing area of Ilaje community located on the southern part of Ondo State. This was a Delta region with most rivers drawing into the Atlantic Ocean. Sample was obtained from different sites in the four major kingdoms which constitutes Ilaje community namely Mahin, Ugbo, Etikan and Aheri Kingdom. The Local Government headquarters of Ilaje is at Igbokoda, Ilaje comprises of many towns and villages. Among the towns are Araromi seaside, Ode-Etikan, Abereke, Ayetoro, Bijimi, Ilepete, Obe-iji, Awoye, Ubales, Oghoye Awoye, Ayetoro, Gbawiyo, Abetobo, Pepe and Seluwa. Other areas covered were Sabomi, Iluagbo, Orioke, Ogogoro, Ehinmore, Seja, Asisa while Igbokoda also served as control site within these areas because the area is less prone to oil spillage or hydrocarbon pollutant from exploration sites.

Few communities visited in Eseodo Local Government that served as control site are Sabomi and Igbobini. But samples were collected mainly from Sabomi for some logistic reasons. Water and soil samples were collected from about 3 to 5 sampling site in areas visited depending on the accessibility and at a distance of about 100 meters apart based on the ecological zone thus they are designated sites 1 to 5 starting from the boat Jetty area apart from Ayetoro where the site was coded in opposite direction of Ayetoro 1 around the Ocean seashore down to Ayetoro 5 in the Jetty because that was our first starting point. Some samples were further coded a, b and c if in triplicate.

Methods of Sample Collection: Water samples were collected using sterile sample bottles of about 200ml in triplicates from each sample source. Similarly, sediment (soil) samples were obtained using sterile plastic nylon seals from sampling points where water was collected. An approximate of about 100 gram of soil samples were collected from each source and stored into a cold box (a containing ice) on board the boat (transport ferry). Similarly, some fish samples were obtained from the sampling sites for analysis. Temperature of the water was measured with the aid of a thermometer calibrated in degree centigrade (°C) during the period of collection.

The soil samples collected at sites from where water samples were obtained were also analyzed for some metal constituents to assess the environmental impact of pollutants on ecology and determine sites that could be of serious health threat or revealed to be ecologically devastated so as to know possible areas that can be given more attention during environmental monitoring and other ecological management schemes.

Laboratory Procedure

Microbiological Analysis: The water and soil samples obtained from the sampling sites were analyzed in the laboratory for some biological attributes. The microbial isolates recovered from these sources were characterized for identification purposes following some morphological and biochemical tests and occurrence at different sites in the oil producing riverine Ilaje community.

Culture Preservation: Microbial strains isolated were maintained on nutrient agar slants at 4°C. The stock culture was prepared in duplicates, one set serving as working cultures. They were sub-cultured every three months or when necessary. Nutrient agar, plate count agar, MacConkey agar and Eosin Methylene blue (E.M.B) agar were generally used during the study.

Mineral Elements Analysis: Water, soil, fish and economic plant sources were analyzed in the Laboratory for physical and chemical properties. The parameters determined include; pH, Electrical conductivity, calcium (Ca), Magnesium (Mg), Manganese (Mn), Iron (Fe), Copper (Cu), Lead (Pb), Phosphate (PO₄·P), Chloride (Cl), fluoride (Fl), Chromium (Cr), Cadmium (Cd) and hardness of the water samples was carried out in the Laboratory. Other physico-chemical parameters studied include total dissolved solid (TDS), Turbidity, Total suspended solid (TSS), Alkalinity. For the sediment (soil) samples apart from Ca, Mg, Cu, Mn, Fe, Pb, Cd and Cr determined, Nickel (Ni) composition of the sample sources was also analyzed.

Determination of Calcium (Ca) and Magnesium (Mg) Content: In determining the Ca and Mg content of the samples mehlich-3 extracts was used in preparing it with the samples and the resultant reading was taken on the Atomic absorption spectrophotometer (AAS). These were done by preparing some stock solutions and follow the sequence below:

- MIXED STOCK SOLUTION In a 1000ppm volumetric flask, add 8.00ml of 1000ppm of Ca and 1.60 ml of 1000pm Mg, Add 5.00ml of Mehlich-3 extractant. Dilute to 100ml with 1000ppm La or Sr solution (below). This solution contains 80ppm Ca and 16 ppm Mg.
- STRONTIUM, 1000PPM: Dilute 6.08g of SrCl₂ 6H₂O to 2 litres in a volumetric flask. Alternatively, make 1000ppm La solution by diluting 5.35g of LaCl_{3.}7H₂O to 2 litres.
- STANDARD PREPARATION: into 5 50-ml centrifuge tubes, add 38ml of 1000ppm Sr (or La) and 2.00ml of Mehlich-3 extraction solution and mix well. Then remove from the respective tubes O, 2.00, 4.00, 6.00 and 8.00, 12.0 and 16.0ppm. Ca; O, 0.800, 1.60, 2.40 and 3.20ppm.Mg.
- SAMPLE PREPARATION: Add 0.500ml of sample to a glass vial. Dilute with 9.50 of 1000 ppm Sr (or La).
- Read standards and samples on the AAS. The burner head should be rotated for Mg.
- Calculations: Determine concentration of sample from a standard curve (ppm).

The Following Calculation Applies:

Water sample/soil concentration $(\text{cmol} (+).\text{kg}^{-1}) =$ = ppm x 30 Eq.wt x Sample wt Where the equivalent weights (Eq.wts) are as follows Ca = 20.04Mg = 12.16

Note: The standards are scaled to provide the following approximate maximum soil. The following approximate maximum soil contents in cmol (+).kg⁻¹: Ca, 8 and Mg 2.6. Higher contents will require dilution.

Copper (Cu), Manganese (Mn) and Iron (Fe) analysis Standard Preparations of the Samples: With Mehlich-3 extracts also helps in determination of Cu, Mn and Fe constituents of the samples and taking the final reading on AAS as described below:

MIXED STOCK SOLUTION: To a 250ml volumetric flask, add 50.00ml of 1000ppm Mn, 50.00 ml 1000 ppm Fe and 1.00 ml of 1000pm Cu. Dilute to the mark with Mehlich-3 extractant. This solution contains 200 ppm Mn and Fe and 4.00 ppm Cu.

- STANDARDS: To 7 50-ml centrifuge tubes, add 50ml of Mehlich-3 extractant. Remove from the 5 respective tubes 0, 1.25, 2.50, 3.75, 5.00, 7.50 and 10.0 ml of liquid. Add the same amount of the mixed stock solution. These samples contain 0, 5.00, 10.00, 15.0, 20.0, 30.0 and 40.0ppm Fe and Mn and 0, 0.100, 0.200, 0.300, 0.400, 0.400, 0.600 and 0.800 ppm Cu.
- Read standards and undiluted sample extracts on the AAS.
- Calculations: Determine concentration of sample from a standard curve (ppm). The following calculations apply:

Sample concentration $(mg/1 \text{ or } mg/dm^3) = ppm X 10$

Sample concentration (ppm) = $\frac{ppm \times 30}{Sample wt.}$

Note: The standards are scaled to provide the following approximate maximum sample contents in ppm: Fe and Mn, 100; and Cu, 5. Higher contents will require dilution.

Mehlich-3 Extraction: The process of melich-3 extraction is stated bellows:

- Mehlich-3 extraction solution: In a 500ml polythene bottle, add ~250ml water, dissolve 69.45g NH₄F and 36.75 EDTA and make to 500ml. To a 10 liter jug, add about 8 liters of water and 200g NH₄NO₃. Add 40ml of the EDTA/NH₄F solution, 115 ml acetic acid and 8.2 ml of 70% nitric acid. Dilute to 10 liters. The pH should be 2.5 ± 0.1
- Using a 3.0ml scoop, weigh 3.0ml scoop, weigh 3.0 ml of soil in a 50ml centrifuge tube and record weight to the nearest 0.0g. NOTE: All centrifuge tubes and caps should be acid washed before use and stored under plastic. This method is very sensitive to Zn contamination.
- Add 30ml of Mehlich-3 extractant to a batch of 24 samples. Cap and shake for 5 minutes. Let stand for 10 minutes, then centrifuge.
- Repeat step 3 until all samples have been centrifuged. Be sure to stagger samples appropriately so that samples sit exactly 10 minutes between shaking and centrifugation.

Determination of Chloride Content: The chloride content was determined using Mohr titration method with potassium chromate as indicator. This was a method adopted by Vogel [6]. The end point (at which the colour

changes from bright yellow to orange) during titration of silver nitrate and sample give the value of the chloride content in milligrams per litre or (Mg/L) or ppm.

Modified EDTA Extraction Method Used to Quantify Lead (Pb), Cadmium (Cd) Chromium (Cr) and Related Metal: Dilute EDTA has been a preferred extractant for soils long before some other known methods. It was first proposed by Cheng and Bray [13] and subsequently advocated by Viro [14]. Different concentrations (0.01 to 0.1M) have been used in combination with buffered pH values of 4.6 to 9.0, although pH 7 appears to be a favourite. Different soil: extractant ratios and extraction times have been used. Clayton and Tiller [15] used a 7-d extraction with 0.1M EDTA at pH 6.0 for classification of soils with respect to the degree of contamination with Cd, Pb and Zn. This long extraction period is not suitable for routine analysis. The procedure describe below has been in use at the Macauley Land Use Research Institute for many of their trace element studies [16].

Reagent: 0.05M EDTA (PH7); dissolve 93.05g of EDTA (di-sodium salt) in approximately 4L of distilled and deionised water (DO). Adjust to pH 7.0 with 7M NH_4OH and make up to 5L with DD water.

Procedure:

- Weigh 5g of air-dried (<2mm) soil into a 125 Erlenmeyer flask and add 25ml of 0.05M EDTA solution.
- Shake for 1h at a speed of 120 cycles min⁻¹
- The samples were filtered through a Whatman No. 42 filter paper after shaking and analyze for metals by atomic spectroscopic

Comments: EDTA is generally useful extractant for many elements [16,17]. The above procedure is suitable for use with acid and calcareous soils. Merry and Tiller [18] found that Cd, Cu, Pb and Zn concentrations in plants growing on contaminated soils were related to the EDTA extracted metals from the soils. EDTA has also been shown to be one of the slightly better extractant Chromium (Cr).

Total Hardness: Two millimeters of buffer solution hardness is added to 100ml of the sample and swirled. 1 manver 2 hardness powder indicated was also added to the solution and swirled. The mixture was titrated against 0.800M EDTA until a change from red to pure blue was observed. It is then read and value expressed as mg/L

(CaCO₃) standard 500mg/L. Hardness of water is caused by multi-valent metallic cations, e.g. magnesium ions occur naturally.

RESULTS

Water Samples: Table 1 shows the total bacterial and coliform counts during the rainy season in the month of June. The total bacterial count ranged from 3 x 10^3 cfu/ml in Ilepete to 200×10^3 cfu/ml in Awoye. Similarly for the control sites the lowest recorded was 2 x 103 cfu/ml and highest was 7 x 10^3 cfu/ml both at different sites of Sabomi via Igbobini. The coliform counts of the study sites for rainy season in the month of June also range from low counts of 0 and 1 x 10^2 cfu/ml in areas like Odofado, Ayetoro and Bijimi to a high counts up to 44 and 45 x 10^2 cfu/ml in Odeetikan and Abereke, respectively. Table 2 also shows the microbial load of the microorganisms during the dry season. The bacterial count ranged from low of 5 x 10^5 cfu/ml in Abereke 1 to a high of 81×10^5 cfu/ml in Ayetoro. The coliform counts also varied from low counts of 6 x 10^3 cfu/ml in Awoye 1 to 48×10^3 cfu/ml in Ode-Etikan. Statistically mean counts of coliforms for all the sample sites were significantly lower than the total bacterial counts based on feacal pollution level (Table 1).

Table 1: Total bacterial and coliform counts in some sample stations studied during rain season (Month of June)

| Study site | | | Controlled site | | | | |
|--------------------|--|---|--------------------|--|---|--|--|
| Sampled stations | Total bacterial count (cfu/ml x 10 ³) | Coliform count (cfu/ml x 10 ²) | Sampled stations | Total bacterial count (cfu/ml x 10 ³) | Coliform count (cfu/ml x 10 ²) | | |
| Awoye 1 | Swarmy organisms | 3 | Sabomi 1 | 2 | - | | |
| Awoye 2 | 200 | 8 | Sabomi 2 | 5 | 4 | | |
| Awoye 3 | 30 | - | Sabomi 3 | 7 | - | | |
| Awoye 4 | 10 | 2 | Iluagbo | 6 | 4 | | |
| Awoye 5 | Swarmy | - | Total (Mean count) | 20/4 = 5 | 8/4 = 2 | | |
| Ilepete 1 | 30 | 17 | | | | | |
| Ilepete 2 | 3 | 1 | | | | | |
| Ayetoro 5 | 13 | 1 | | | | | |
| Odofado | 3 | - | | | | | |
| Bijimi 1 | 8 | - | | | | | |
| Bijimi 2 | Multiple | 2 | | | | | |
| Bijimi 3 | 8 | 1 | | | | | |
| Abereke 1a | 91 | 41 | | | | | |
| Abereke 1b | 96 | 44 | | | | | |
| Abereke 2a | 72 | 36 | | | | | |
| Abereke 2b | 89 | 37 | | | | | |
| Abereke 3 | 174 | 100 | | | | | |
| Odeetikan | 24 | - | | | | | |
| Odeetikan 1b | 20 | 4 | | | | | |
| Odeetikan 2a | 46 | 34 | | | | | |
| Odeetikan 2b | 55 | 45 | | | | | |
| Odeetikan 3a | 13 | 8 | | | | | |
| Odeetikan 3b | 36 | 31 | | | | | |
| Total (Mean count) | 1021/23 = 44.39 | 415/23 = 18.04 | | | | | |

| Table 2: Total bacterial and coliform | counts of water samples during dry season (Month of February) | |
|---------------------------------------|---|-------------------------------|
| Sample code | Total bacterial count (cfu/ml x 10 ⁵) | Coliform count (cfu/ml x 103) |
| Ayetoro 1 | 62 | 16 |
| Ayetoro 2 | 20 | 40 |
| Ayetoro 3 | 81 | 17 |
| Awoye 1 | 48 | 6 |
| Awoye 2 | 16 | 20 |
| Awoye 3 | 60 | 18 |
| Ilepete 1 | 50 | 20 |
| Ilepete 2 | 70 | 31 |
| Ilepete 3 | 30 | 24 |
| Abereke 1 | 5 | 44 |
| Abereke 2 | 28 | 36 |
| Abereke 3 | 40 | 46 |
| Odeetikan 1 | 24 | 20 |
| Odeetikan 2 | 62 | 48 |
| Odeetikan 3 | 52 | 8 |
| Total (Mean count) | 648/15 = 43.2 | 394/15 = 26.27 |

| Table 3: Metal Constituent and Hardness of Water from oil producing areas of Ondo State Physico-Chemical Parame | ameters of water samples |
|---|--------------------------|
|---|--------------------------|

| | | | | 1 | | · | | | | | | 1 | | |
|-----|---------------|-------------------|--------|--------|-------|-------|-------|-------|-------|-------|----------|-------|-------|----------|
| | Station | Electrical | Ca | Mg | Mn | Fe | Cu | Pb | P04p | Cl | Fluoride | Cr | Cd | Hardness |
| | Code | Conductivity (mS) | (ppm) | (ppm) | (ppm) | (ppm) | (Ppm) | (ppm) | (ppm) | (ppm) | (ppm) | (ppm) | (ppm) | (ppm) |
| 1. | Awoye 1 | 18.00 | 344.4 | 245.09 | 0.23 | 0.40 | 0.092 | 0.78 | 0.08 | 70.06 | 0.7 | 0.19 | 0.1 | 212 |
| 2. | Awoye 2 | 18.00 | 356.00 | 201.21 | 0.15 | 0.40 | 0.092 | 0.37 | 0.49 | 100 | 0.1 | 0.12 | 0.09 | 198 |
| 3. | Awoye 3 | 13.50 | 338.22 | 232.55 | 0.15 | 0.32 | 0.076 | 0.78 | 0.09 | 80.04 | 0.5 | 0.21 | 0.11 | 187 |
| 4. | Awoye 4 | 18.00 | 342.66 | 130.27 | 0.15 | 0.48 | 0.092 | 0.78 | 0.01 | 103 | 0.9 | 0.26 | 0.06 | 228.18 |
| 5. | Ilepete 1 | 6.00 | 112.15 | 136.68 | 0.07 | 0.73 | 0.076 | 0.37 | 0.02 | 88 | 0.1 | 0.31 | 0.08 | 200 |
| 6. | Ilepete 2 | 11.50 | 123.23 | 135.90 | 0.07 | 0.23 | 0.076 | 0.78 | 0.01 | 152 | 0.1 | 0.26 | 0.08 | 208.26 |
| 7. | Ilepete 3 | 8.50 | 121.01 | 135.59 | 0.07 | 0.32 | 0.076 | 0.78 | 0.01 | 132 | 0.3 | 0.21 | 0.07 | 420 |
| 8. | Ilepete 4 | 11.00 | 120.28 | 132.46 | 0.15 | 0.15 | 0.076 | 0.78 | 0.03 | 92 | 0.5 | 0.3 | 0.05 | 364 |
| 9. | Ayetoro 1 | 11.00 | 166.15 | 224.34 | 0.15 | 0.32 | 0.076 | 0.37 | 0 | 112 | 0.3 | 0.21 | 0.09 | 800 |
| 10. | Ayetoro 2 | 26.00 | 397.50 | 256.03 | 0.23 | 0.32 | 0.092 | 0.37 | 0.01 | 144 | 1 | 0.19 | 0.07 | 540.02 |
| 11. | Ayetoro 3 | 23.00 | 468.73 | 245.75 | 0.15 | 0.40 | 0.107 | 0.78 | 0.01 | 84 | 0.2 | 0.22 | 0.06 | 180 |
| 12. | Ayetoro 4 | 22.50 | 433.10 | 71.56 | 0.07 | 0.40 | 0.107 | 0.78 | 0.02 | 200 | 0.7 | 0.17 | 0.04 | 200 |
| 13. | Ayetoro 5 | 2.00 | 64.89 | 53.65 | 0.07 | 0.15 | 0.076 | 0.78 | 0.02 | 116 | 0.1 | 0.24 | 0.08 | 580 |
| 14. | Ayetoro 6 | 1.50 | 44.99 | 20.16 | 0.15 | 0.07 | 0.072 | 0.37 | 0.03 | 120 | 0.3 | 0.15 | 0.06 | 184.1 |
| 15. | Ubale 5a | 0.50 | 12.31 | 19.87 | 0.07 | 1.84 | 0.076 | 0.78 | 0.04 | 176 | 0.4 | 0.22 | 0.07 | 124 |
| 16. | Ubale 3b | 0.20 | 11.46 | 15.03 | 0.07 | 2.55 | 0.076 | 0.37 | 0.06 | 95 | 0.2 | 0.14 | 0.05 | 122 |
| 17. | Obaji 4b | 1.00 | 10.54 | 4.83 | 0.07 | 0.88 | 0.076 | 0.37 | 0.12 | 400 | 0.2 | 0.23 | 0.06 | 160 |
| 18. | Gbawiyo 3b | 0.11 | 2.13 | 6.43 | 0.07 | 1.84 | 0.092 | 0.37 | 0.04 | 64 | 6 | 0.24 | 0.04 | 88.6 |
| 19. | Gbawiyo 1b | 0.16 | 3.07 | 10.36 | 0.07 | 2.71 | 0.076 | 0.37 | 0.68 | 224 | 0.8 | 0.17 | 0.08 | 850 |
| 20. | Araromi 1b | 0.47 | 54.57 | 20.75 | 0.15 | 0.15 | 0.61 | 0.37 | 0.05 | 1.80 | 0.1 | 0.26 | 0.04 | 196 |
| 21. | Araromi 2b | 0.60 | 48.67 | 3.52 | 0.15 | 0.40 | 0.076 | 0.37 | 0 | 440 | 0.3 | 0.14 | 0.00 | 204.24 |
| 22. | Araromi | | | | | | | | | | | | | |
| | (3b Atlantic) | 17.00 | 215.07 | 5.84 | 0.07 | 0.32 | 0.61 | 0.78 | 0 | 96 | 0.2 | 0.19 | 0.05 | 600 |
| 23. | Abetobo 1b | 0.16 | 3.11 | 4.83 | 0.07 | 0.88 | 0.061 | 0.78 | 0.01 | 242 | 0.6 | 0.21 | 0.06 | 56 |
| 24. | Pepe 3 | 0.15 | 26.57 | 3.81 | 0.07 | 2.08 | 0.076 | 0.78 | 0.05 | 184 | 0.1 | 0.22 | 0.04 | 140.4 |
| 25. | Seluwa | 0.05 | 1.83 | 3.95 | 0.07 | 0.88 | 0.061 | 0.78 | 0.01 | 92 | 0.4 | 0.19 | 0.08 | 60 |

Table 4: Metals constituents in water samples from oil producing areas and controlled sites

| s/n | Station Code | Ca (ppm) | Mg (ppm) | Cu (ppm) | Mn (ppm) | Fe (ppm) | Pb (ppm) | Elect.cond (mS) | PO4P (ppm) | pН | Temp. |
|-----|----------------|----------|----------|----------|----------|----------|----------|-----------------|------------|------|-------|
| 26. | Bijimi 1a | 377.71 | 1185.34 | 0.034 | 0.17 | 0.79 | 0.42 | 39.00 | 0.07 | 6.52 | 28 |
| 1. | Bijimi 1b | 347.66 | 1057.63 | 0.034 | 0.09 | 0.86 | 0.33 | 37.00 | 0.03 | 6.68 | 31 |
| 2. | Bijimi 2 | 148.14 | 478.76 | 0.018 | 0.09 | 0.09 | 0.24 | 15.00 | 0 | 6.6 | 30 |
| 3. | Sabomi 1a | 3.11 | 0.33 | 0.018 | 0.17 | 0.55 | 0.24 | 0.10 | 0 | 6.45 | 30 |
| 3 | Sabomi 1b | 2.21 | 0.24 | 0.034 | 0.09 | 0.40 | 0.24 | 0.02 | 0 | 6.35 | 29.5 |
| 4. | Sabomi 2a | 3.31 | 0.63 | 0.63 | 0.01 | 0.63 | 0.15 | 0.05 | 0 | 6.59 | 29.5 |
| 5. | Sabomi 2b | 2.71 | 0.65 | 0.034 | 0.09 | 0.63 | 0.24 | 0.15 | 0 | 6.54 | 30 |
| 6. | Sabomi 3 | 3.31 | 0.65 | 0.018 | 0.09 | 0.71 | 0.018 | 0.16 | 0 | 6.55 | 29.5 |
| 7. | Iluagbo | 5.49 | 2.63 | 0.034 | 0.09 | 0.32 | 0.15 | 0.08 | 0 | 6.82 | 30 |
| (a) | Ayetoro A1 | 369.69 | 1081.58 | 0.101 | 0.17 | 0.86 | 0.51 | 27.00 | 0.04 | 6.63 | 24.2 |
| 8. | Ayetoro A2 | 40.98 | 112.15 | 0.034 | 0.09 | 0.17 | 0.15 | 6.50 | 0 | 6.26 | 25 |
| 27. | Ilepete 1 | 313.64 | 933.90 | 0.09 | 0.42 | 0.63 | 0.068 | 37.50 | 0.02 | 6.59 | 27.3 |
| 9. | Ilepete 2 | 309.64 | 909.95 | 0.034 | 0.09 | 0.17 | 0.15 | 6.50 | 0 | 6.53 | 26.8 |
| 10. | Igbokoda Jetty | 1.15 | 0.82 | 0.01 | 0.00 | 0.23 | 0.08 | 0.04 | 0.03 | 6.2 | 30 |
| 28. | Orioke 1 | 395.17 | 1069.58 | 0.06 | 0.23 | 6.63 | 0.27 | 37.00 | 0.27 | 0.27 | 28.5 |
| 11. | Ogogoro 1 | 449.36 | 1066.35 | 0.04 | 0.15 | 5.23 | 0.27 | 36.00 | 0.14 | 6.52 | 27.5 |
| 12 | Ehinmore | 219.68 | 411.98 | 0.88 | 0.07 | 0.88 | 0.18 | 12.50 | 0.15 | 6.61 | 29 |
| 13 | Seja 1 | 474.85 | 1088.98 | 0.08 | 0.15 | 6.40 | 0.27 | 35.00 | 0.21 | 6.40 | 28.5 |
| 14 | Asisa | 128.27 | 1037.27 | 0.06 | 0.15 | 7.10 | 0.37 | 27.00 | 0.22 | 6.60 | 27.5 |

In Table 3, the ranges for metal constituents are from the lowest of 1.15ppm, 1.83ppm and 2.13ppm in Seluwa and Gbawiyo 3b to highest of 468.73ppm and 474.85ppm in Ayetoro 3 and Seja for Ca; 0.24 and 3.52ppm in areas like Sabomi and Araromi to 256.03ppm and 1185.34ppm in Ayetoro 2 and Bijimi 1a for Mg; 0.01 in Sabomi 2a and Ilepete 1,2 3,Ayetoro 4,5 Ubale 5a, 3b Obeiji 4b Gbawiyo 3b, 1b Araromi 3b, Abetobo 1b, Pepe 3 and Seluwa to 0.23 in Awoye 1, Ayetoro 2 and Orioke for Mn; 0.07ppm in Ayetoro 6 to 2.71 and 6.63ppm in Gbawiyo 1b and

Table 5: Metals in soil from oil producing areas of Ondo State

| s/n | Station Code | Ca (ppm) | Mg (ppm) | Cu (ppm) | Mn (ppm) | Fe (ppm) | Pb (ppm) | Ni (ppm) | Cd (ppm) | Cr (ppm) |
|-----|--------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 15. | Pepe 1 | 6.08 | 3.10 | 2.28 | 71.3 | 188.60 | 0.07 | 0.1 | 0.02 | 0.19 |
| 16. | Gbabijo 1 | 4.83 | 2.90 | 0.82 | 219.90 | 194.47 | 0.11 | 0.16 | 0.04 | 0.12 |
| 17. | Ayetoro 2 | 4.85 | 3.20 | 2.78 | 153.90 | 201.00 | 0.1 | 0.13 | 0.03 | 0.18 |
| 18. | Abetobo 1a | 3.57 | 2.10 | 1.58 | 97.65 | 196.44 | 0.09 | 0.17 | 0.04 | 0.15 |
| 19. | Araromi 1 | 2.56 | 0.41 | 0.77 | 17.38 | 165.10 | 0.05 | 0.11 | 0.02 | 0.1 |
| 20. | Araromi 1 A | 8.21 | 3.05 | 0.98 | 143.78 | 187.06 | 0.07 | 0.15 | 0.02 | 0.15 |
| 21. | Gbabijo | 3.57 | 2.55 | 0.88 | 110.26 | 193.32 | 0.1 | 0.13 | 0.01 | 0.18 |
| | | | | | | | | | | |

Table 6: Metals in soil from oil producing areas and control sites

| | | Ca | Mg | Cu | Mn | Fe |
|-----|-------------------------|-------|-------|-------|--------|-------|
| s/n | Station Code | (ppm) | (ppm) | (ppm) | (ppm) | (ppm) |
| 1 | Sabomi® | 0.97 | 0.21 | 1.18 | 7.8 | 179.5 |
| 2 | Sabomi 1b [©] | 0.15 | 0.11 | 0.57 | 3.7 | 108.1 |
| 3 | Sabomi 2b [©] | 0.23 | 0.09 | 0.53 | 2.0 | 167.3 |
| 4 | Sabomi 3 [©] | 12.48 | 3.78 | 1.15 | 35.9 | 166.3 |
| 5 | Iluagbo © | 0.58 | 0.20 | 0.31 | 9.2 | 115.5 |
| 6 | Ilepete 1 | 9.20 | 20.70 | 0.80 | 296.6 | 115.1 |
| 7 | Ilepete 2 | 8.16 | 21.10 | 0.59 | 283.5 | 143.6 |
| 8 | Bijimi 2 | 8.20 | 16.20 | 0.50 | 370.4 | 153.1 |
| 9 | Bijimi 1a | 8.74 | 29.00 | 1.56 | 193.1 | 154.1 |
| 10 | Ayetoro A1 | 7.78 | 20.70 | 1.37 | 320.0 | 134.6 |
| 11 | Ehinmore 1b | 7.10 | 16.30 | 0.31 | 237.73 | 187.0 |
| 12 | Igbokoda 2 [©] | 2.40 | 0.33 | 0.39 | 19.21 | 540 |
| 13 | Orioke 2 | 3.35 | 8.20 | 0.38 | 43.68 | 1720 |
| 14 | Asisa 2a | 7.05 | 18.70 | 0.32 | 300.76 | 1960 |

Legend: [©]: Control sites

Table 7: Metals constituents in aquatic organisms of oil producing areas

| s/n | sample | Fe (ppm) | Cu (ppm) |
|-----|---------------|----------|----------|
| 1 | Crab | 579.72 | 126.321 |
| 2 | Crayfish | 114.34 | 45.878 |
| 3 | Tilapia | 1572.55 | 27.84 |
| 4 | Flat fish | 133.37 | 42.95 |
| 5 | Long fish | 260.81 | 32.91 |
| 6 | Water hyacine | 1185.38 | 78.65 |

Orioke for Fe; 0.01 in Igbokoda Jetty and Awoye 2, Ilepete 1, Ayetoro 1,2,6,Ubale 3b, Obeiji 4b, Gbawiyo 3b, 1b, 2b to 0.78ppm in Awoye and most stations studied for Lead (Pb) in the first phase of the research (Table 5); 0 value was recorded for PO4-P (ppm) in Ayetoro 1, Araromi 2b, 3b, Bijimi and Sabomi to 0.49ppm in Awoye 2 respectively (Table 3 and 5). Sabomi and Igbokoda Jetty is control site.

The values obtained for other metal constituents in water samples are from the lowest of 64 ppm and 70.06 ppm in Gbawiyo 3b and Awoye 1 to highest of 440 and 400 ppm in Araromi 2b and Obeiji 4b for Cl; 0.1ppm in Awoye 2, Ilepete 1,2, Ayetoro 5, Araromi 1b and Pepe 3 to 1.0 and 0.9ppm in Ayetoro 2 and Awoye 4 for Fluoride;

0.12 ppm in Awoye 2 to 0.31 and 0.3ppm in Ilepete 1 and 4 for Cr; 0.04 in Ayetoro 4, Gbawiyo 3b, Araromi 1b and Pepe 3 to 0.11 and 0.1 ppm in Awoye 3,1 respectively for Cd. Similarly the total hardness of the sampled site range from the lowest of 56 and 60 ppm in Abetobo 1b and Seluwa to a high of 850 and 800 ppm in Gbawiyo 1b and Ayetoro 1 respectively (Table 3).

The temperature of the surface water determined onsite at the point of water sample collection also varied generally from the lowest of 23°C to 33°C. It was however assumed that climatic conditions might have influence on this based on sunlight intensity and period of sampling collection.

The estimate of metal constituents of the study area is as shown in Table 2. This range from a low of 2.56 cmol/kg, 0.41 cmol/kg, 0.77 ppm, 17.38 ppm, 165.10 ppm and 0.05 ppm in Araromi 1 to 8.21 cmol/kg in A.I.A (Araromi 1A); 3.10 and 3.05 cmol/kg in Pepe 1 and A.I.A; 2.78 ppm in Ayetoro 2; 219.90 ppm in Gbabijo 1; 201 ppm in Ayetoro 2; 0.11 ppm in Gbabijo 2 for Ca, Mg, Ca, Mn, Fe and lead (Pb), respectively (Table 5).

Further work done on sediments of oil producing sites and control site where oil contaminants are not experienced is as shown in Table 4. The values range from 0.15 cmol/kg (Ca) in Sabomi 1b, 0.09 cmol/kg Mg) in Sabomi 2a, 0.31 ppm (Cu) in Iluagbo/Ehinmore, 2.0 ppm in Sabomi and 108.1 ppm (Fe) in Sabomi 1b to a high of 12.48 cmol/kg in Sabomi 3, 29.00 cmol/kg in Bijimi 1a, 320.0 ppm in Ayetoro A1 and 1960 ppm in Asisa 2a for Ca, Mg, Cu, Mn and Fe respectively. It should however be noted at this junction that Sabomi which is a control site among the studied oil producing sampling sites have relatively low levels of most metals analyzed except calcium (Ca) whose salt can constitute hardness in this area.

Table 7 reflects the metal constituents of various aquatic organisms of oil producing areas. This include representation of crustacean like crab, fish and crayfish and an aquatic plant namely water hyacine. The two major metals that these samples were analyzed of were Iron (Fe)

and Cupper (Cu). The study shows that Fe value range from 114.34 ppm in crayfish to a high of 1572.55 ppm and 1185.38 ppm in Tilapia fish and water hyacine respectively (Table 7).

The Cu content of this aquatic organisms also range from 7.86 ppm and 27.84 ppm in water hyacine and Tilapia fish respectively to a high of 126.321 ppm in crab Table 5), thus showing the ability of this organisms to accumulate some chemicals or heavy metals from the oil producing areas of which could constitute some health problems in case of excess consumption or if adequate care is not taken.

DISCUSSION

This study shows the occurrence of microbes (Tables 1 and 2) in relation to variations in some physicochemical parameters of oil producing riverine areas of Ondo state which has some ecological implications [14,16]. Table 1 shows the total bacterial and coliform counts during the rainy season in the month of June. The total bacterial count ranged from 3 x 10³ cfu/ml in Ilepete to 200 x 10³cfu/ml in Awoye. Similarly for the control sites the lowest recorded was 2 x 103 cfu/ml and highest was 7 x 10^3 cfu/ml both at different sites of Sabomi via Igbobini. The coliform counts of the study sites for rainy season in the month of June also range from low counts of 0 and 1 x 10² cfu/ml in areas like Odofado, Ayetoro and Bijimi to a high counts up to 44 and 45 x 10^2 cfu/ml in Odeetikan and Abereke, respectively. The control site, however, showed coliform value that varied from low counts of 0 to 4×10^2 cfu/ml (Table 1). Similarly for the dry season. The bacterial count ranged from low of 5 x 10^5 cfu/ml in Abereke 1 to a high of 81 x 10^5 cfu/ml in Ayetoro. The coliform counts also varied from low counts of 6 x 10^3 cfu/ml in Awoye 1 to 48 x 10^3 cfu/ml in Ode-Etikan. Value of coliforms mean counts for all the sample sites were significantly lower than the total bacterial counts based on pollution level from domestic sources (Table 1). Coliform bacteria serves as indicator for feacal pollutants.

There was high level of conductivity in areas like Seja, ogogoro, Orioke and Ayetoro due to the presence of enormous amount of ionizable materials that enhance passage of electric current (Table 3). Many complex stations like Awoye, Ayetoro Bijimi, Ilepete, Orioke, Ogogoro Ehinmore and Seja showed high level of calcium content above the stipulated maximum permissible level of 200 ppm in some sampled areas, which is undesirable as it influence or causes hardness of water or scaling of pipes in case of pipeline network systems. This is consistent with previous studies [19,20].

Some areas in Awoye, Ayetoro, Bijimi, Orioke, Ogogoro, Seja, Asisa and Ehinmore exceeded the maximum permissible level of Magnesium of 150 ppm ft. Excess of this element can equally cause hardness in water and impact taste with gastrointestinal irritation. The manganese and copper (Cu) level for all study sites are within permissible level be below 0.5 ppm and 1.5 ppm respectively. The current standard is maximum of 0.05 ppm [5]. However all the areas studied during the course of this research were found to exceed that level permissible for lead which shows some potent dangers in the oil producing areas of Ondo State and possibility of even reducing refining in case this is the source. The phosphate PO, P. level also varies from site to site, the range obtainable in these areas could still favour agricultural products in case of farming in these areas.Other chemical parameters like chloride (Cl) and Fluoride (FI) are within permissible range in the study area. The maximum allowable for Chloride which could also be an antigenic determinant is within safe limit, more so the water sources may not be always used for drinking purposes.Chromium (Cr) and cadmium (Cd) can cause toxicity in water, furthermore cadmium affects metabolism and may substitute for Ca^{2+} in the bone structure resulting to itai-itai disease observed in Japan a serious crippling condition (TJV. O.O mg/l) [5]. Nearly all the site sampled and analyzed for this elements contain some traces of this elements in minute qualities but can also constitute some hard in certain areas with high as shown in Table 1 & 2. Some riverine areas like Ayetoro and Gbawiyo off shoot the maximum permeable level of 500mg/ for total hardness, however few others as exceeded the 100mg/L total hardness as shown in Table 1.

In the soil samples of all areas visited some metal elements constituents were determined. These include Ca, Mg, Ca, Mn, Fe, lead (Pb), Ni, Cd and Cr. However high range of 219.90 ppm (Manganese (Mn) in Gbabijo 1 and 201 ppm of Iron Fe in Ayetoro 2 is alarming because it exceeds the maximum permissible level of 1.0ppm and 0.5 ppm for Mn and Fe respectively. Other sites involved can be observed in table 3. During the study Igbokoda Jelly, Iluagbo and Sabomi which are near Igbobini in Eseodo riverine area was used as control site. Analysis result in Sabomi showed low levels of most metals except calcium (ca) compared with these of oil producing sampling site studied thus suggesting the metal constituetant infiltration from oil pollutants and related matters in oil producing areas of Ondo State. This study reveal high level of some heavy installs like Iron (Fe) and copper (Cu) in some aquatic organisms from these oil producing areas showing the possibility of biomagnification or accumulations of these metals. Example is 1572.55 ppm of Iron (Fe) In Tilapia fish which is one of the edible foods commonly consumed by people. The study of Nweke et al., [17] shows that many microorganisms are known to degrade a wide range of organic compounds to harmless substances [18]. However, additional contamination with heavy metals present the activity of heterotrophic microorganisms, impacting both their physiology special problems for bioremediation [17]. Plant specie, water hyacine analyzed for metal components also show high range of Iron (Fe) at 1185.35ppm demonstrating possibility of some plants especially crops or agricultural products accumulating heavy metals as a result of pollutants which may signal an inherent danger unless positive measures are taken to minimize sources of these pollutants. The copper contents exceeding 1.5 ppm permissible level for all the aquatic organisms tested is significant health wise because it gives astringent taste, discolor and corrode pipe, fittings and utensils [5, 21].

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