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Characterization of Produced Water in Selected Oil Wells in Ughelli Delta State Nigeria

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ABSTRACT

The constituents of produced water that is being discharged to the environment has become of great concern in recent years due to its polluting effect. As such, this study assesses the presence of physiochemical parameters such as Total Dissolved Solids (TDS), Total Petroleum Hydrocarbon (TPH), Biochemical Oxygen Demand (BOD), presence of heavy metals, salinity, pH, temperature, Chemical Oxygen Demand (COD), Bicarbonate, Chloride etc. in produced water samples from different oil wells. The range of the levels of the physiochemical parameters are as follows; TDS: 20000ppm - 51600ppm; TPH: 32.54385ppm - 34.84466ppm; BOD: 0.0163mg/l - 0.032mg/l; Zinc: 0.12ppm - 0.4ppm; Iron: 0.39ppm - 0.4ppm; Copper: 0.05ppm - 0.15ppm; Chromium:0.3ppm; Cadmium: 0.06ppm; Lead: < 0.001ppm; Nickel: 0.85ppm - 1.17ppm; Salinity: 4950g/kg - 3300g/kg; pH: 8.10 - 7.84; Temperature: 26.7^{0}C - 27^{0}C; COD: 341mg/l - 354mg/l; Bicarbonate: 85mg/l - 90mg/l; Chloride: 3000mg/l - 2000mg/l. It was noticed that the amount of some various constituents exceeded their permissible limits. From the above studies is hereby recommended that carbon and mechanical filters should be installed between the first and second semi-permeable membrane sheets that are convolutely wound round the collector tube of the invention of Ernest Price (1980) so as to remove contaminants such as heavy metals, TDS, chloride and salt in cases of excessive pressure in which produced water gets to the surface pressure in which produced water gets to the surface.

Keywords: Produced water, Environmental pollution, Constituents, Physiochemical, Discharge

INTRODUCTION

Amyx *et al.*, (1960) discovered that crude oil bearing formations are generally permeated with fluids such as water, oil, gas or some combination of these fluids. During production of crude oil, these fluids are brought to the surface along with it which according to Mofat and Olof (1995), produced water is the largest volume by product or waste stream associated with oil and gas production. As in many cases, produced water is usually discharged to the environment with its consequent effect being environmental pollution. The effect is always due to the physical and chemical characteristics of the constituents, temperature, and content of dissolved organic material, humic acids, presence of other organic contaminants and internal factor (Frost *et al.*, 1998). In a country like Nigeria where rules and regulations are not effectively enforced, most of the oil and gas companies discharge untreated produced water to the environment. According to a research carried out by Environmental Rights Action (ERA, 1998) indicated that the refineries and terminals discharge largely untreated effluents (which include produced water) in Port Harcourt and Warri areas which are in the Niger Delta region.

According to U.S D.O.E. (2004) the physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Jackson and Myers (2002) asserted the fact that he quality of coal bed methane produced water varies with the original depositional environment, depth of burial, and coal type (Due to the chemical constituents of produced water, it has become of paramount importance to determine the composition its composition before discharging into the environment because of its toxicity. Studies indicate that the produced waters discharged from gas/condensate platforms are about 10 times more toxic than the produced waters discharged from oil platforms (Jacobs *et al.*, 1992).

U.S D.O.E. (2004) stated that the constituents in produced waters from conventional oil and gas production are as follows; dispersed oil, dissolved or soluble organic components, treatment chemicals, produced solids, scales, bacteria, metals, pH, sulphates and naturally occurring radioactive materials. Table 1 shows typical concentrations of pollutants in treated offshore produced water samples from the Gulf of Mexico (EPA 1993). These data were compiled by EPA during the development of its offshore discharge regulations and are a composite of data from many different platforms.

Table 1: Produced Water Characteristics Following Treatment

Constituent	Concentration after BPTLevel Treatment (mg/L)[a]	Concentration after BATLevel Treatment (mg/L) – Gas Flotation Treatment[b]
Oil and grease	25	23.5
2-Butanone	1.03	0.41
2,4-Dimethylphenol	0.32	0.25
Anthracene	0.018	0.007
Benzene	2.98	1.22
Benzo(a)pyrene	0.012	0.005
Chorobenzene	0.019	0.008
Di-n-butylphthalate	0.016	0.006
Ethylbenzene	0.32	0.062
n-Alkanes	1.64	0.66
Naphthalene	0.24	0.092
p-Chloro-m-crescol	0.25	0.010
Phenol	1.54	0.54
Steranes	0.077	0.033
Toluene	1.901	0.83
Triterpanes	0.078	0.031
Total Xylenes	0.70	0.38
Aluminium	0.078	0.050
Arsenic	0.11	0.073
Barium	55.6	35.6
Boron	25.7	16.5
Cadmium	0.023	0.014
Copper	0.45	0.28
Iron	4.9	3.1
Lead	0.19	0.12
Manganese	0.12	0.074
Nickel	1.7	1.1
Titanium	0.007	0.004
Zinc	1.2	0.13
Radium 226 (in pCi/L)	0.00023	0.00020
Radium 228 (in pCi/L)	0.00028	0.00025

[a]BPT = best practicable technology, [b]BAT = best available technology, Source: EPA (1993)

As a result of the negative effects discharge of produce water has on the environment, this research intends to;

i.) Characterize produced water based on its composition.

ii.) Identify the impacts of produced water to the environment.

iii.) Suggest management techniques that could be more efficient and effective for produced water in Niger Delta.

GEOLOGIC SETTING

The study area lies between longitude $6^0$03'E to $6^0$28'E and latitude $5^0$21'N to $5^0$46'N.The study area is Ughelli, Delta State. The subsurface geology of the Niger Delta basin to which Ughelli belongs is well established. The basin fill is made up of three Formations, namely from the oldest to the youngest Akata, Agbada and Benin Formations. The Akata formation is composed of continuous shale and about 10% sandstone. The shale is believed to be over pressured and under-compacted. It ranges from Eocene to Recent and was deposited under marine conditions. Agbada Formation comfortably overlies the Akata Formation (C.S Nwajide, 2006; Murat,1970; Asseez, 1979; Short *et al*., 1967). It is a parallic sequence of alternating shale and sandstone with variable age ranging from Eocene in the north to Pliocene/Pleistocene in the south, and Recent in the Delta surface. Its lateral equivalent at the surface, the Ogwashi-Asaba Formation and Ameki Formation are of Eocene - Oligocene age. The continental Miocene-Recent Benin Formation conformably overlies the Agbada Formation. It is composed of 90% sands and about 10% shale/clays; the sand ranges from gravelly, coarse to fine grained (Akpoborie *et al*., 2011).

LITERATURE REVIEW

A number of studies have been conducted in the USA on produced water from different oil and gas platforms (Neff, 1998; Jacobs *et al*., 1992; Cox 1992 and Cline 1998). It was observed that waters discharged from gas and condensate platforms were far more toxic than the produced waters discharged from oil platforms. They also noted that produced water contained varying concentrations of Barium, Beryllium, Cadmium, Chromium, Copper, Iron, Lead, Nickel, Silver, Zinc as well as small amounts of natural radioactive materials. Studies have shown that if there is effective dilution, acute toxic effects of produced water are not expected to be fond beyond 50m from the discharge point. This is the reason Durrell *et al.,* (2000) reported that oil companies operating in Norway have since in the mid- 1990s tried to develop efficient monitoring methods for discharged water.

In Nigeria, Oboh *et al* (2009), noted that discharged produced waters had high metal ions and total hydrocarbon concentrations. While Okoro (2010) asserted the fact that produced water discharges in near shore environment in the Niger Delta led to substantial accumulation of hydrocarbon and microorganisms up to 500m from discharge points. Isehunwa and Onovae (2011) made some observations that produced water discharged into the environment in some had high levels of oil and grease as well as total dissolved solids (TDS) and total suspended solids (TSS).

Although in Nigeria, there has been no reported environmental disaster of high magnitude associated with produced water disposal but it is a known fact that much of the waste produced water is dumped in the environment, especially during drilling operations. Emam *et al* (2014) carried out an evaluation on the characteristics of offshore oilfield produced water. He discovered that some common characteristics such as specific gravity, salinity, TDS, and some ions such as sodium and chloride of oilfield produced water are increased as the depth of the oilfield increases.

Umudi (2011) obtained samples from four areas in the Niger Delta and ran analysis on each of them. He found out that the metal concentration of iron, zinc, nickel, cadmium and lead were higher than the accepted limits of World Health Organization (WHO) and National Environment Standard and Regulation Enforcement Agency (NESREA) while only a few contents like copper, chromium and manganese were within acceptable limits. A study was done by Frost et al (1998) on the physical and chemical properties of produced water constitutes, like temperature, content of dissolved organic material, humic acids, and presence of organic contaminants etc. He concluded that these numerous variables determine the actual impacts of produced water discharge to the environment. Brown (1957) related the level of impact which produced water has on the environment to the different constituents which it is made of. Constituents like dispersed oil, dissolved oil, chemicals, produced solids, scales, metals, sulphates, bacteria etc. were observed to cause environment degradation.

MATERIALS AND METHODS

Two samples (A and B) of produced water were obtained from different oil wells in Ughelli, Delta State Nigeria and carefully contained in well sealed amber glass bottles. A fresh water which is to serve as a base for comparison was also obtained. Sampling was done in accordance with established guidelines and procedures (APHA, 2005). Samples were analysed in the laboratory for determine the presence of different organic and inorganic components.

Physiochemical Analysis:

Basic sediment and water (BS &W) and oil was determined by inserting two test tubes containing samples A and B into a centrifuge which was set to spin for 10mins after which the different percentages of the components were calculated. pH and Temperature were analysed electrometrically using a multi- parameter photometer. Electric Conductivity (EC) and Total Dissolved Solids Determination were determined with a dipstick in a process in which were diluted with 99ml of distilled water because the concentration of samples was too high.

Amount of chloride present was measured through a titration process. Potassium chromate ($K_2Cr_2O_2$) and silver nitrates ($AgNO_3$) were used the reagents used and the quantity of chloride was calculated for using the Equation (1) below;

$$Cl\left[{}^{mg}\!/_{l}\right] = \frac{(A-B)*1000}{ml\ of\ sample} \quad (1)$$

A = ml $AgNo_3$ used for titrating sample; B = 0.2ml $AgNO_3$ used for titrating.

Salinity of the samples was simply gotten by Cl x 1.65 (g/kg), where Cl is the amount chloride present. Total Petroleum Hydrocarbon (TPH) was determined using gas chromatography before which an extraction process was carried out using a separating funnel. Dissolved Oxygen (DO) was measured electrometrically with a DO meter. Biochemical Oxygen Demand (BOD) which is dependent on Dissolved Oxygen (DO) was calculated for using the following Equation (2);

$$BOD = \frac{DO_0 - DO_5}{percentdilution} \quad (2)$$

DO_0= Dissolved oxygen for day zero; DO_5=Dissolved oxygen after 5days

Total Organic Carbon (TOC) was determined through a titration process in which 0.5M of potassium dichromate was added and then 20ml of conc. Sulphuric acid were added to the samples. 0.25M Ammonium FAS was consequently used to titrate to final end point. The Equation (3) was used to calculate for TOC.

$$TOC\,(mg) = \frac{V_b - V_s * M * 160}{ml\,of\ sample} \quad (3)$$

V_b = ml of Ferrous Ammonium Sulphate used for blank; V_s = ml of Ferrous Ammonium Sulphate used for sample; M = Molarity of Ferrous Ammonium Sulphate

Amount of Heavy Metals present in the samples was determined using Atomic Absorption Spectrophotometer (AAS). Also, the amount of bicarbonate present in the samples was determined through a titration process. The quantity was calculated using Equation (4);

$$HCO_3({}^{mg}\!/_{l}) = \frac{1000 * N\ of\ H_2SO_4 * volume\ of\ acid\ used}{ml\ of\ sample} \quad (4)$$

HCO_3= Hydrogen carbonate ion; N= Molarity number of H_2SO_4

Chemical Oxygen Demand (COD) was measured through titration method in which 10ml of 0.25M $K_2Cr_2O_7$ added to the water samples. The quantity of COD was calculated for using Equation (5);

$$COD[{}^{mg}\!/_{l}] = \frac{(V_b - V_s) * N * 16000}{ml\ of\ Sample} \quad (5)$$

V_b= volume of blank; V_s=volume of sample; N= molarity number of $K_2Cr_2O_7$

RESULTS AND DISCUSSIONS

The results of the analysis of the produced water samples are presented in Table 2. It also shows the permissible limits allowed for each of the constituents of the produce water sample.

i) Temperature: Difference between samples is not much and it is also within the range of the permissible limit and the fresh water sample as shown in Fig. 1.

ii) pH: The acidity of the produced water samples is within the permissible limits but it is higher than that of the fresh water as shown in Fig. 2.

iii) Electrical Conductivity: From Fig. 3 below, it is clearly indicated that produced has a very high electrical conductivity compared to that of fresh water.

Table 2. Physiochemical characteristics of produced water at oil wells in Ughelii, Delta State.

S/N	Physiochemical Parameters	Units	Sample A	Sample B	Fresh Water	Permissible Limit
1	Temperature	^{0}C	26.7	27	26.7	30
2	pH	-	8.10	7.84	4.23	6 - 9
3	E-Conductivity	mS/m	44200	120700	248	-
4	COD	mg/l	341	354	-	30
5	TOD	mg//	1400	2200	-	-
6	BOD	mg/l	0.0163	0.032	-	5
7	Salinity	g/kg	4950	3300	37.95	0.0
8	DO	mg/l	5.77	5.52	3.90	5
9	Cl	mg/l	3000	2000	23	250
10	TDS	ppm	20000	51600	243	500
11	Bicarbonate	mg/l	85	90	-	180 – 240
12	Zinc (Zn)	ppm	0.12	0.4	0.03	3.0
13	Iron (Fe)	ppm	0.39	0.4	0.27	0.5
14	Copper (Cu)	ppm	0.05	0.15	0.01	2.0
15	Chromium (Cr)	ppm	0.3	0.3	0.20	0.5
16	Cadmium (Cd)	ppm	0.06	0.06	0.05	0.005
17	Lead (Pb)	ppm	<0.001	<0.001	<0.001	0.01
18	Nickel (Ni)	ppm	0.85	1017	<0.001	0.05
19	TPH	ppm	32.54385	34.84466	0.00	0.00
20	BS	-	0	17	-	-
21	W	-	47	83	100	100
22	O	-	53	-	-	-

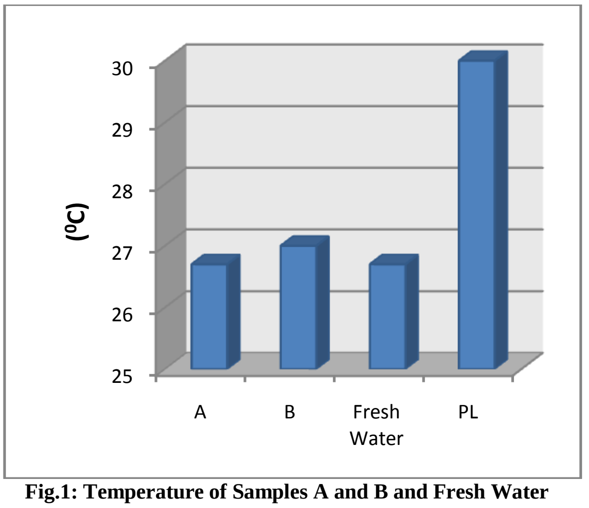

Fig.1: Temperature of Samples A and B and Fresh Water

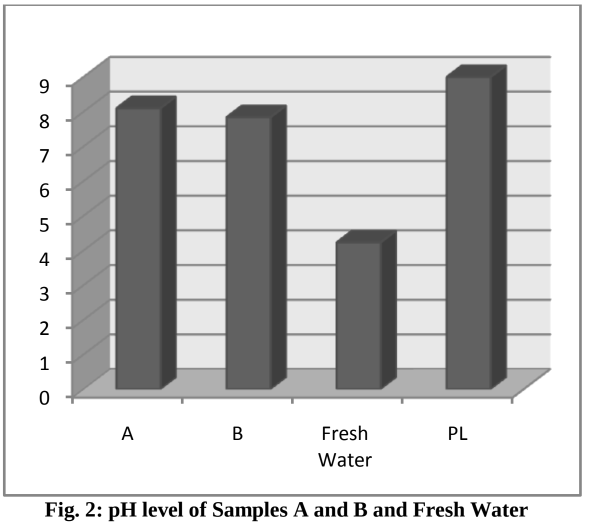

Fig. 2: pH level of Samples A and B and Fresh Water

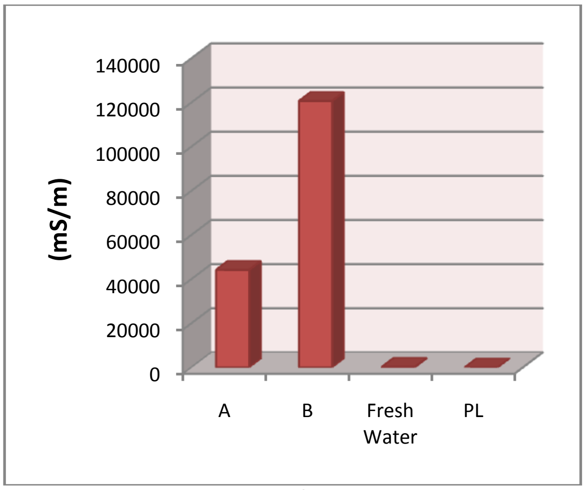

Fig. 3: Electrical Conductivity of Samples A and B and Fresh Water

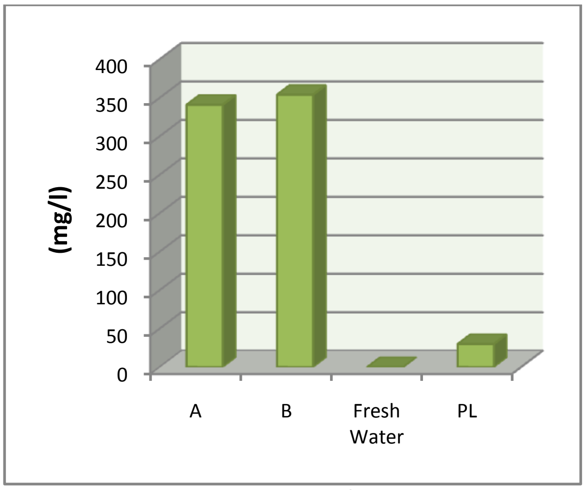

Fig. 4: Chemical Oxygen Demand of Samples A and B and Fresh Water

iv) Chemical Oxygen Demand (COD): From Fig. 4, it is indicated that sample B has a higher amount of organic compounds than sample A meaning that sample B has a higher organic pollutants than sample A.

v) Total Oxygen Demand (TOD): Sample B has a higher amount of TOD, this means it has higher amount of oxygen that will aid combustion which is indicated in Fig. 5.

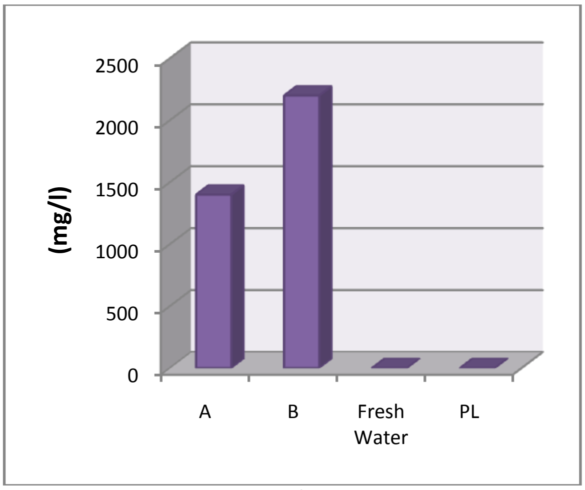

Fig. 5: Total Oxygen Demand of Samples A and B and Fresh Water

vi) Biochemical Oxygen Demand (BOD): Fig. 6. Shows that sample B has a greater amount of BOD than sample B. This means sample B has enough dissolved oxygen needed by aerobic biological organisms to break down organic materials present in it.

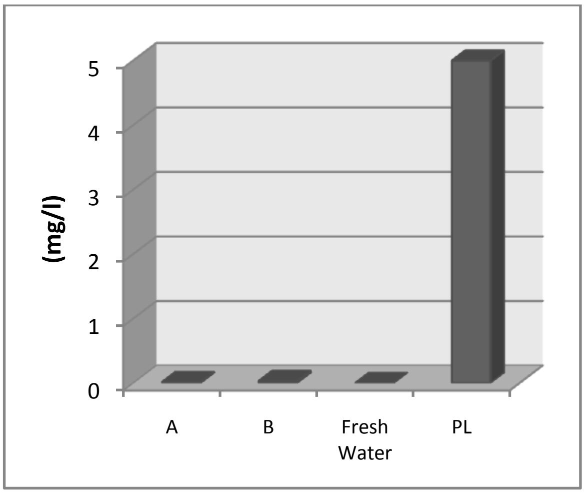

Fig. 6: Biochemical Oxygen Demand of Samples A and B and Fresh Water

vii) Salinity: The level salinity in the produced water samples (A and B) is very high compared to that of fresh water. This simply implies that produced water has a higher dissolved salt content than fresh water. Also, the quantity is far higher than the permissible limit. This is shown in Fig. 7.

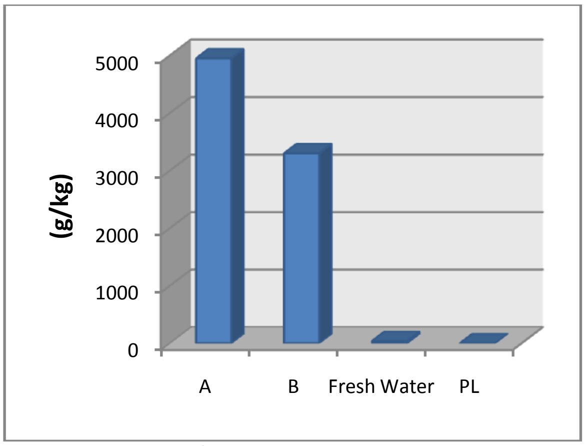

Fig. 7: Salinity of Samples A and B and Fresh Water

viii) Dissolved Oxygen (DO): It can be seen that samples A and B have higher amount of dissolved oxygen than what is present in the fresh water sample. This is indicated in Fig. 8.

ix) Chloride: Fig. 9. shows that the difference between the amount of chloride present in produced water samples (A and B) and that of the fresh water is very high and it is also higher than the permissible limits.

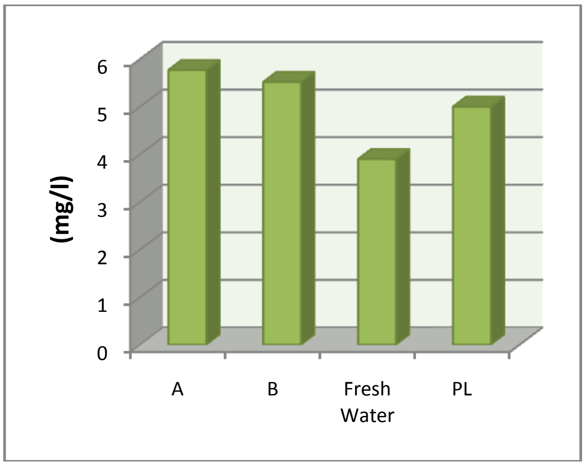

Fig. 8: Dissolved Oxygen of Samples A and B and Fresh Water

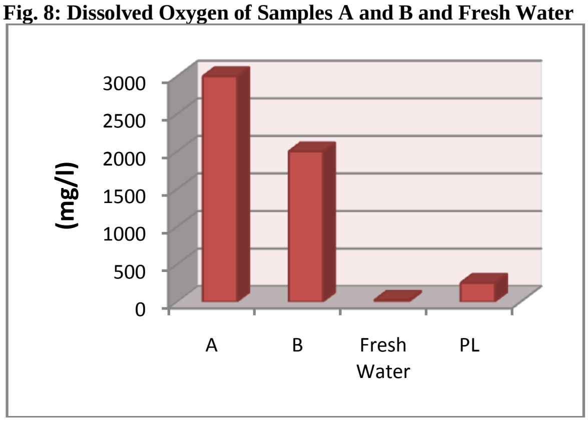

Fig. 9: Amount of Chloride present in Samples A and B and Fresh Water

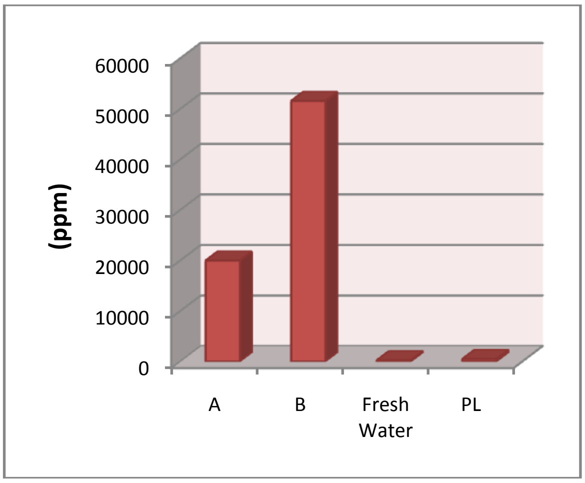

Fig. 10: Total Dissolved Solids present in Samples A and B and Fresh Water

x) Total Dissolved Solids (TDS): Fig. 10. shows that the produced water samples have a very high amount of TDS which far exceeds present in fresh water and the permissible limit. This is shown in Fig. 10.

xi) Bicarbonate: Fig. 11. Shows that ample B has a higher amount of bicarbonate than sample A, this simply means that sample B has higher amount of carbonic acid which contains the ion hydrogen carbonate. Also it value is lower than the permissible limit.

xii) Heavy Metals: Fig. 12. shows the result of different trace metals present and some not present in each of the samples. All of the above indicate the presence of heavy metals except for lead. Lead read negative for all the samples, indicating the absence of lead. Nickel also read negative in the fresh water sample indicating its absence.

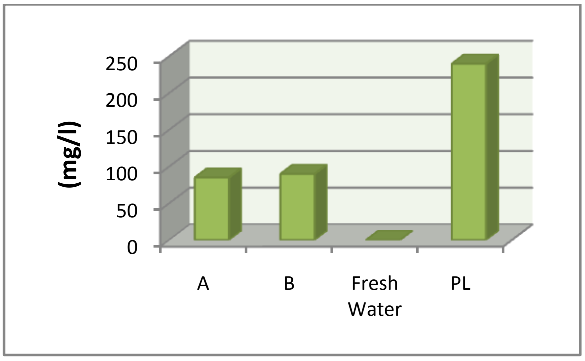

Fig. 11: Amount of Bicarbonate present in Samples A and B and Fresh Water

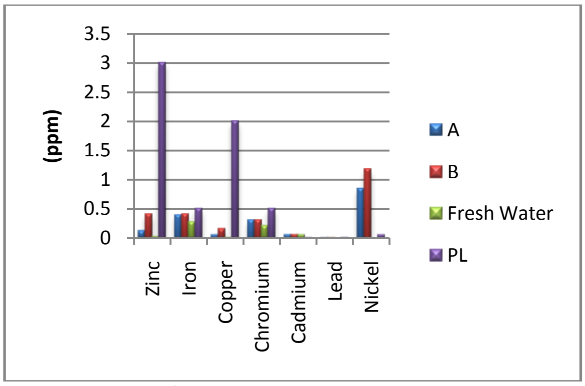

Fig. 12: Amount of Heavy Metals present in Samples A and B and Fresh Water

xiii) Total Petroleum Hydrocarbon (TPH): Fig. 13. shows the different hydrocarbon present in sample A. This graph shows counts against minutes. The final results recorded that sample A has a total number of petroleum hydrocarbon to be 32.54385.

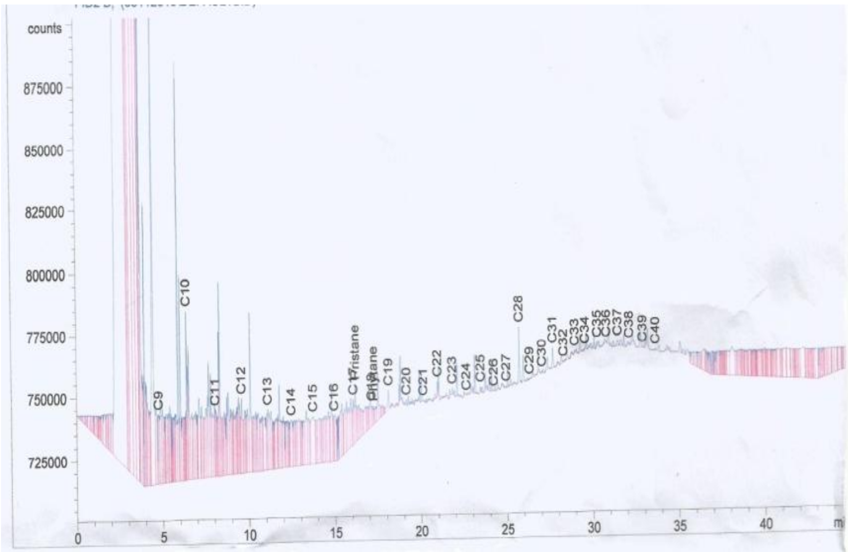

Fig. 13: Amount of Total Petroleum Hydrocarbon present in Sample A

Fig. 14. Shows counts against minutes indicating the number of hydrocarbons present in the sample. The sum total of petroleum hydrocarbon recorded is 34. 84466.

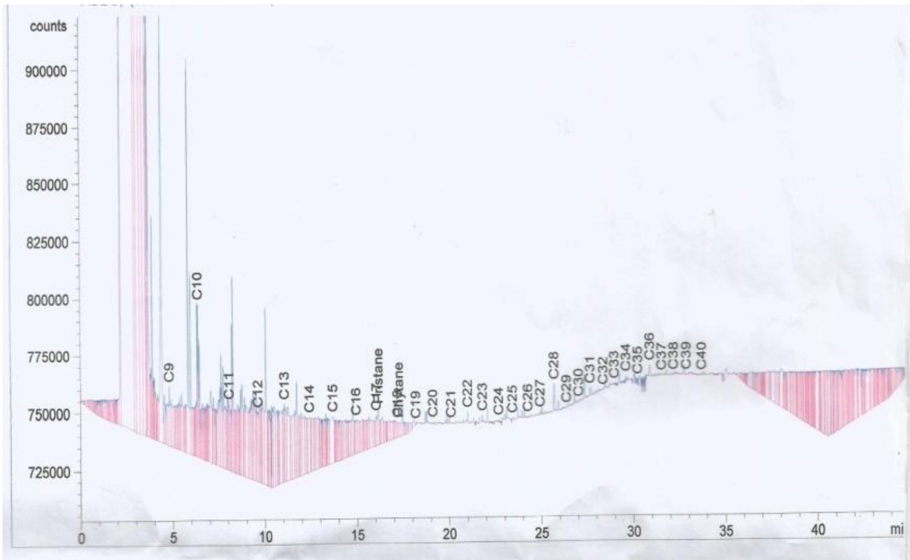

Fig. 14: Amount of Total Petroleum Hydrocarbon present in Samples B

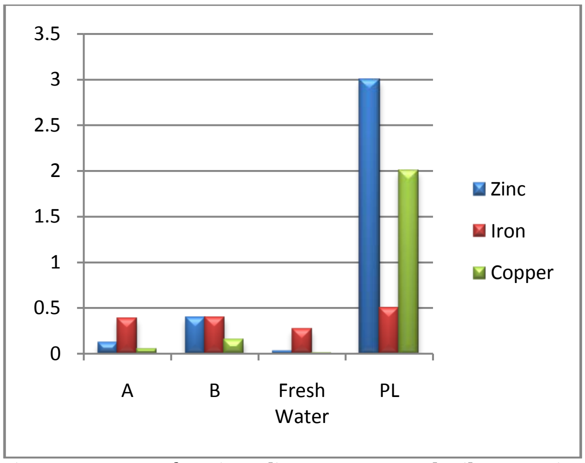

Fig. 15: Amount of Basic Sediment, Water and Oil present in Samples A and B and Fresh Water

xiv) Basic Sediment and Water (BS&W) and Oil: Fig. 15. shows the percentage of the substances present in each of the sample. For sample A, water and oil were present; while sample B had basic sediments and water present and then the fresh water had only water present.

CONCLUSION AND RECOMMENDATIONS

From the physiochemical analysis carried out on the samples, it was noticed that the constituents of produced water from different oil wells vary. Also, it was noticed that the quantities of the various constituents in the produced water exceeded the permissible limits.

As the produced water is mostly discharged to the environment, it is of utmost necessity that it should be treated properly till its constituents get to the permissible limits so that it would not pollute the environment in a bid to ensure sustainable development. In view of this, some recommendations as to how produced water can be effectively be managed so that it can have minimum negative impact on the environment while its usefulness is maximally utilized. The recommendations are as follows;

i.) Produced water should be adequately treated using some technologies like hydro clones, biological aerated filters, adsorption etc. These technologies will help reduce components like dispersed oil, heavy metals, soluble organics etc.

ii.) Produced water management schemes should include proper reuse options, like irrigation, industrial use, and domestic use.

iii.) Produced water disposal should be regulated by bodies like Federal Environmental Protection Agency (FEPA) and Department of Petroleum Resources (DPR) and other agencies to enable an environmentally safe discharge.

iv.) There should be strict regulations on how much produced water that should be discharged into the environment and also, companies should be made to pay fines when these regulations are violated.

v.) Activated carbon and mechanical filters should be installed between the first and second semi-permeable membrane sheets that are convolutely wound round the collector tube of the invention of Ernest Price (1980) so as to remove contaminants such as heavy metals, TDS, chloride and salt in cases of excessive pressure in which produced water gets to the surface.

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