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Physicochemical characteristics including heavy metals of oilfield wastewater from Etelebou oilfield location in Bayelsa state

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Abstract
Physicochemical properties and heavy metals of oilfield wastewater of Etelebou flow station in Bayelsa State was carried out for a period of 3-months. Oilfield wastewater samples from various pits (pit 1, pit 2, pit 3. Camp pit 1 and camp pit 2) in the station were analyzed using standard procedures. The physicochemical parameters analyzed and their ranges were; pH 6.55- 11.15, temperature 22.25-34.35ºC, turbidity 20 – 4742 NTU, TDS 163 – 6653 mg/l, TSS 28 – 4575.5 mg/l, COD 32.5 – 927.5 mg/l, BOD_5 16 – 443 mg/l, DO 0.6 – 6.15 mg/l, salinity 93.5 – 5147.5 mg/l, Conductivity 321 -11750 Us/cm, The range for heavy metals were chromium 0.09 to 0.16 mg/l, lead 0.47 to 1.01 mg/l, iron 1.63 to 5.62 mg/l, copper 0.01 to 0.03 mg/l and zinc 0.21 to 0.47 mg/l. Some physicochemical parameters and heavy metals observed during the study were statistically significant in some parameters and insignificant in other parameters. Some values obtained for the various parameters exceeded the recommended limits for effluent/wastewater before discharge. The study showed that the oilfield wastewater contains inorganic constituents that could be harmful if discharged into the surrounding soil or leached into groundwater. This could result to ecotoxicological problem in the environment.

Keywords: Oilfield wastewater, physicochemical parameters, heavy metals, ecotoxicology

Introduction
Oilfield wastewater is the most important waste among various types of wastewaters. This is majorly due to the wide range of pollutants that make up oilfield wastewater, which are difficult to degrade. Such pollutants include nitrogen oxides, volatile organic compounds, polycyclic aromatic hydrocarbons, carbon dioxide, sulfur dioxide, and heavy metals. Wastewaters containing these pollutants can harm groundwater reservoirs and other water resources if discharged improperly into the environment. As a result, these pollutants must first be cleaned from wastewater before being discharged into the environment (Aleruchi and Obire, 2018) [2].

During crude oil extraction activities, oil-related water is referred to as produced water or oilfield wastewater in oilfields and refineries. This water is regarded as one of the most significant aquatic wastes generated by the oil industry (Igunnu and Chen, 2014) [8]. It is critical to treat wastewater generated by crude oil activities, as this untreated wastewater may have an impact on the environment, soil, and groundwater and also on human health necessitating the need to deal with free crude oil, water, suspended particles, and other elements (Mohammed and Jasim, 2019) [9]. Many studies have shown that wastewater from oil fields can harm the ecosystem in a variety of ways (Al-Haleem *et al.*, 2010) [3] such as in Clay deflection owing to excess sodicity; plant dehydration and death due to an increase in soluble salts; aquatic environment damage due to a fall in oxygen level. The impact of chemical additives such as corrosion inhibitors and hydrogen sulfide (H_2S) scavengers on deep formation clogging by suspended solids, which results in an increase in injection pressure and a decrease in the flow rate of injected product water. Its composition ranges from simple to complex, implying that it is a mixture of dissolved and particulate organic and inorganic compounds rather than a single component. The properties of oilfield wastewater vary depending on a number of factors, including the field's geographical location, the depth and age of the geological formation, the extraction method, the geochemistry of hydrocarbon-bearing formations, the type of conducted hydrocarbon, and the chemical components of the reservoir. The composition of oily wastewater is strongly dependent on crude oil quality, the source of wastewater contaminants, and the operating conditions.

As a result, there was a significant variation in wastewater properties between investigations and a wide range of pollutants in varied concentrations. Apart from phenols, the most common mixtures in oil refinery wastewater and oilfield-produced water include oil and grease, which are a mixture of hydrocarbons such as BTEX (benzene, toluene, ethylbenzene, xylenes) (which have highly solubility features in water). Calcium and magnesium are also natural substances that cause hardness. The average COD concentration was 4000 mg/L, while according to Stearman (2014) [12], the COD content in oilfield generated water and oil refinery effluent was 21000 mg/L. Oilfield wastewaters are typically dumped into pits on land rigs. Pit burial is a low-tech, low-cost solution that eliminates the need to transfer waste away from the well site. The goal of this study was therefore, to determine the quantity of physicochemical and heavy metal constituents of oilfield wastewater deposited in the numerous pits in the Etelebou oilfield location in Bayelsa State of Nigeria.

Materials and Methods

The Study Area

The Etelebou flow station is a land rig which is located in Bayelsa State. This land rig belongs to Shell Petroleum Development Company of Nigeria (SPDC), and it is one of the oilfields feeding the Nigeria Liquefied Natural Gas (NLNG), Bonny Island, Rivers State. The oilfield wastewater that is being generated is usually discharged into various pits designated as pit 1, pit 2, pit 3 camp pit 1 and camp pit 2.

Collection and Determination of Samples

Oilfield wastewaters were collected from various pits on monthly basis for three months (November, December, and January). Standard scientific procedures and containers were used to collect samples and preserved in an ice packed cooler. Fast changing parameters such as pH, temperature, turbidity, total dissolved solids, total suspended solids, salinity and conductivity were determined *in situ* while others such as dissolved oxygen, biological oxygen demand and chemical oxygen demands were determined *ex situ*. Procedures described in Standard Methods for the examination of water and wastewater analysis by APHA (1998) were adopted.

Heavy metals analyzed were chromium (Cr), lead (Pb), iron (Fe), copper (Cu) and zinc (Zn). Sample for heavy metal determination were preserved with concentrated Nitric Acid (NHO3). Heavy metal analysis was carried out using Atomic Absorption Spectrophotometric method. The samples were digested with Nitric Acid (HNO3) followed by Filtration through a 0.45µm membrane filter. The resultant filtrate was aspirated onto the equipment and analyzed for Zinc, Chromium, Copper, Lead and Iron. The equipment has automatic reading capability. The model of the equipment is an Analyst 700 (Perkins Elmer precisely) test method ASTM D- 1068-88. The sample was atomized into the flame and irradiated by the light from a source, this source emitted radiation specific to the element being analyzed. The absorption of the radiation by the atomized sample is directly proportional to the concentration of the element. The quantitative relationship is expressed by the Beer-Lamberts Law.

A= a b c: where a- Absorption; b- Cell path length; c- Concentration

This test method determines total recoverable and dissolved metals in water samples in the range from 0.05-5.0mg/l for samples with concentrations within the linear limit while those with lower concentrations are concentrated to fall within the limits or recorded as "less than the instrument detection limit''. The procedure involves the following steps (a) Instrument optimization (b) Instrument calibration (c) Sample analysis.

Statistical Analysis

The two-way ANOVA was used to enable detection of significant differences between locations, periods examined and if there was an interaction between locations and periods. Post-hoc analysis using Tukey test indicated where actual significant difference occurred either for location or period.

Results

The pH values are presented in Fig.1. Pit 1 pH values ranged from 7.55 to 7.75, the month of December recorded the least pH value while the highest value was recorded in November. In pit 2, the pH values ranged from 8.55 to 11.15, the least value was recorded in November while the highest was in December. Pit 3 pH values ranged between 8 to 9.85, the least value was recorded in January while the highest value was recorded in December. Camp pit 1 and Camp pit 2 recorded pH range of 6.8 to 8.8 and 6.55 to 7.7, respectively. Both pits recorded lowest pH values in the month of November and highest values in the month of December. There was significant difference ($P \leq 0.05$) between the various pits but there was no difference in the months.

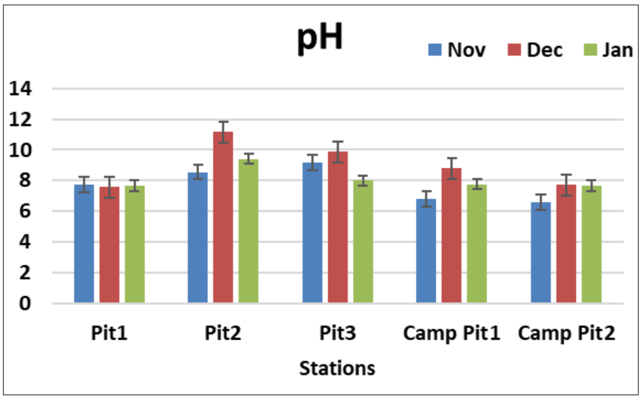

Fig 1: Mean pH of the various pits in Months

The temperature values obtained are presented in Fig. 2. Values obtained from pit 1, pit 2 and pit 3 ranged from 22.6°C to 32.2°C, 22.25 to 34.35 and 22.25 to 33.4°C, respectively. the least temperature values in the pits were obtained in the month of November while the highest temperature values were recorded in the month of December. For Camp pit 1, the temperature values obtained ranged from 22.65 to 28.65°C. Camp pit 2 recorded range of 22.6 to 31.8°C. Camp pit 1 and 2 recorded least temperature values in November while the highest for Camp pit 1 was obtained in January and December for Camp pit 2. There was no significant difference between the various pits, but the values between the months were significantly different at $P \leq 0.001$.

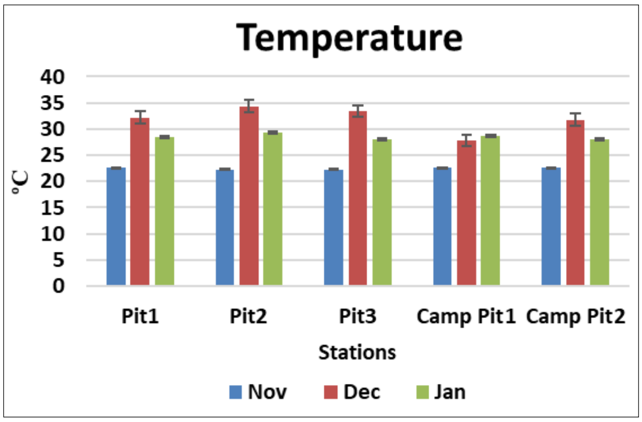

Fig 2: Mean Temperature of the various pits in Months

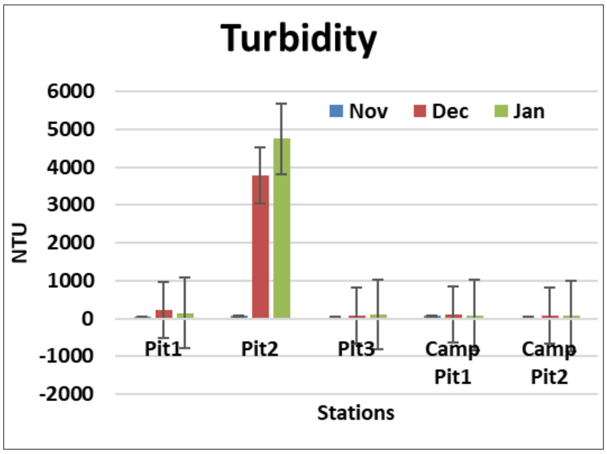

Fig 3: Mean Turbidity of the various pits in Months

The turbidity values presented in Fig. 3 showed that pit 1 values ranged between 48 to 222 NTU, lowest value was obtained in November while the highest was recorded in December. Pit 2 ranged between 77 to 4742 NTU, lowest value of turbidity was observed in November while the highest value was in January. Pit 3 values ranged between 20 to 108 NTU, lowest value was obtained in November and highest in January. Camp pit 1 and 2 ranged between 75.5 to 111.5 and 29 to 72 NTU, respectively. The lowest values in both camps were recorded in November while the highest were in December. There was significant difference at P≤0.05 between the pits.

The TDS obtained from the various pits are presented in Fig. 4. The TDS values ranged between 163.5 to 4930 mg/l, 1986 to 6653 mg/l, 186.5 to 1346 mg/l, 239-256 mg/l and 163 to 297 mg/l in pit 1, pit 2, pit 3, Camp pit 1 and Camp pit 2, respectively. Pit 1, pit 2, pit 3 and camp pit 2 recorded lowest values in November while lowest value for camp pit 1 was recorded in December. The highest values in pit 2 and camp pit 2 were obtained in December. Pit 1, pit 3 and camp pit1 recorded highest values in January. Values obtained in the various pit and in the months were statistically not significant.

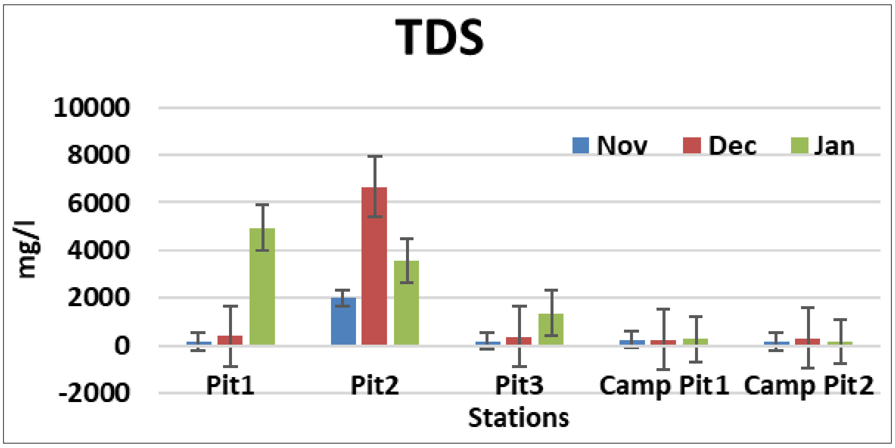

Fig 4: Mean TDS of the various pits in Months

TSS obtained from the various pits ranged from 50.5 to 154 mg/l, 93 to 4575.5mg/l, 28 to 123 mg/l, 96.5 to 122 mg/l and 45 to 93 mg/l in pit 1, pit 2, pit 3, camp pit 1 and camp pit 2, respectively. The lowest TSS values in all the sampling pits were observed in the month of November. Highest TSS values were obtained in December for pit 2, camp pit 1 and camp pit 2 while pit 1 and pit 3 recorded its highest TSS values in January (Fig. 5).

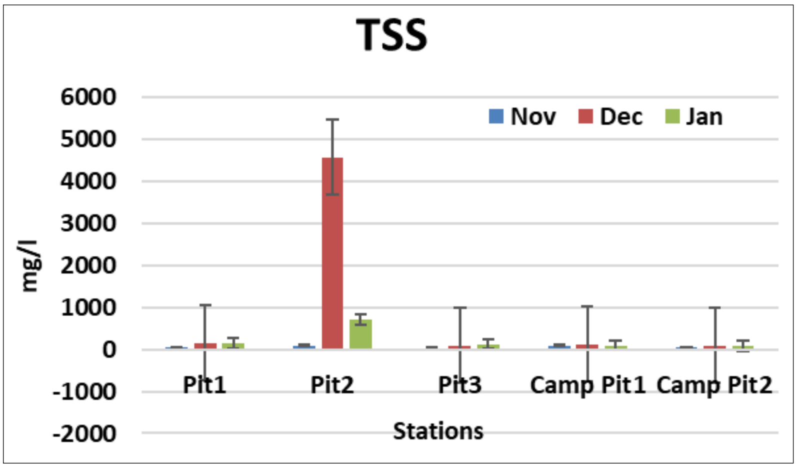

Fig 5: Mean TSS of the various pits in Months

Figure 6 showed the COD obtained from the various pits. Pit 1 COD values ranged from 64 to 372 mg/l, pit 2 ranged between 38.5 to 927.5 mg/l, pit 3 ranged from 32.5 to 328.5 mg/l, camp pit 1 ranged from 103.5 to 355.5 mg/l and camp pit 2 ranged from 99 to 556 mg/l. The lowest and highest values were observed in November and December, respectively in all the pits apart from camp pit 2 was lowest value was recorded in December and highest value in January.

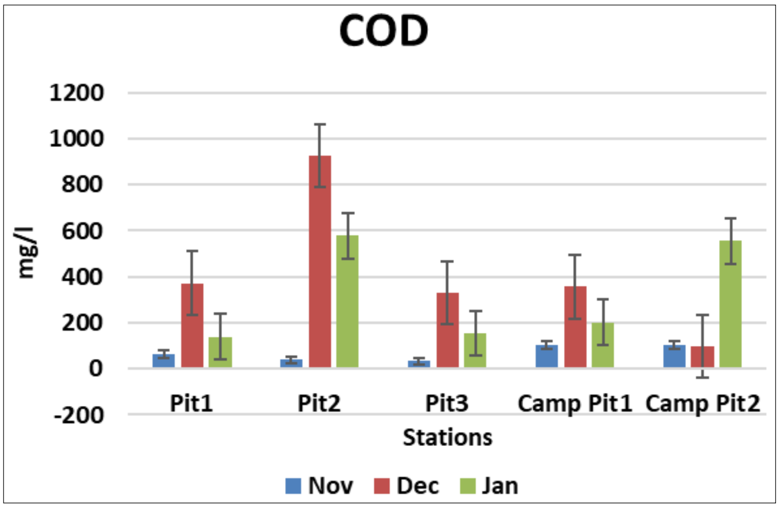

Fig 6: Mean COD of the various pits in Months

The BOD values obtained in this study are presented in Fig. 7. Pit 1 had a range of 29 to 65 mg/l, pit 2 ranged between 18 to 95mg/l, pit 3 ranged from 16 to 66.5 mg/l, camp pit 1 ranged from 49.5 to 77.5 mg/l and camp pit 2 ranged from 50 to 443 mg/l. The lowest BOD values were observed in the month of November in all the pits. Highest value of BOD was recorded in pit 1 and camp pit 2 in December while pit 2, pit 3 and camp pit 1 recorded its highest value of BOD in the month of January.

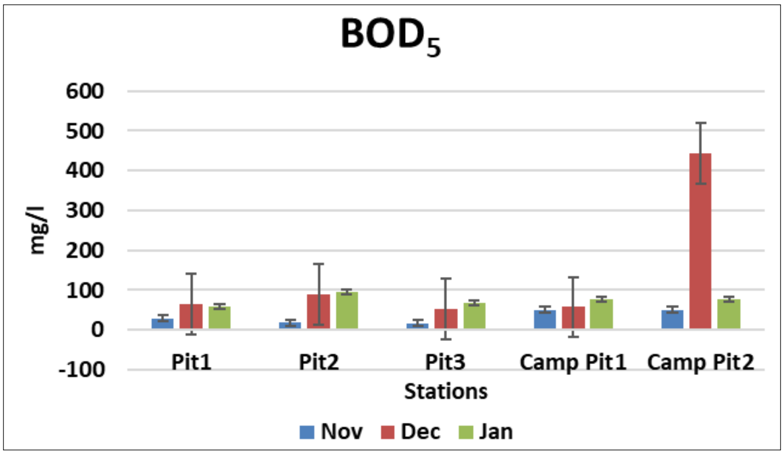

Fig 7: Mean BOD of the various pits in Months

DO values obtained ranged from 0.9 to 5.4 mg/l for pit 1, 2.35 to 4.6 mg/l for pit 2, 3.4 to 6.15 mg/l for pit 3, 0.85 to 4.9 mg/l for camp pit 1 and 0.6 to 4.91mg/l for camp pit 2. The lowest values were recorded in January in all the pits except camp pit 2 which recorded lowest value in December. The highest values were recorded in the month of November in all the pits except for pit 3 which recorded highest in December (Fig. 8).

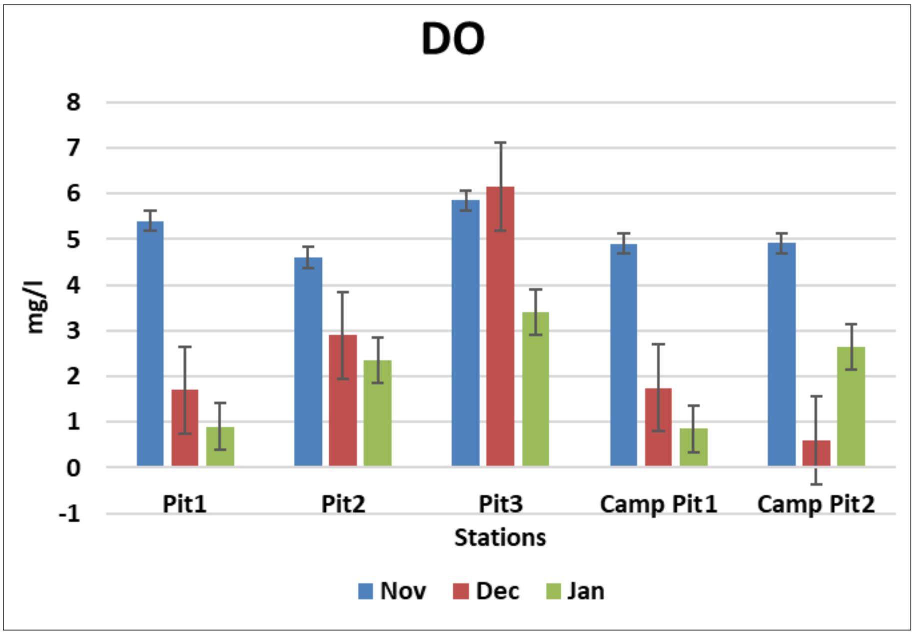

Fig 8: Mean DO of the various pits in Months

Salinity obtained in the study areas are recorded in Figure 9. Pit 1 ranged from 109 to 2795.5 mg/l, pit 2 ranged from 1020.5 to 5147.5 mg/l, pit 3 ranged from 126.5 to 976.5 mg/l, camp pit 1 ranged from 93.5 to 148.5 mg/l and camp pit 2 ranged from 98 to 5138.5 mg/l. The lowest values were observed in November in all the pits apart from camp pit 1 and camp pit 2 which recorded the lowest in January and December. The highest salinity values were obtained in January for pit 1, pit 3 and camp pit2. Pit 2 and camp pit 1 recorded highest value of salinity in December and November, respectively.

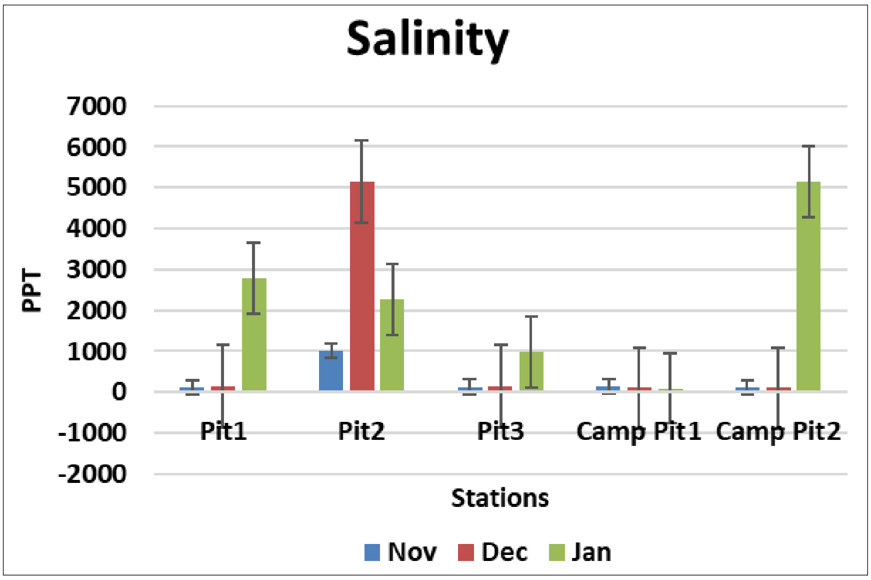

Fig 9: Mean Salinity of the various pits in Months

The conductivity values recorded in the study area are shown in Fig. 10. Pit 1 ranged from 321 to 9270 Us/cm, pit 2 ranged from 3555 to 11750 Us/cm, pit 3 ranged from 365.5 to 2385 Us/cm, camp pit 1 ranged from 483 to 538 Us/cm and camp pit 2 ranged from 329 to 612 Us/cm. the least values were recorded in the month of November in the various pits. Pit 1, pit 3, and camp pit 1 recorded highest values of conductivity in January while pit 1 and camp pit 2 recorded highest values in December.

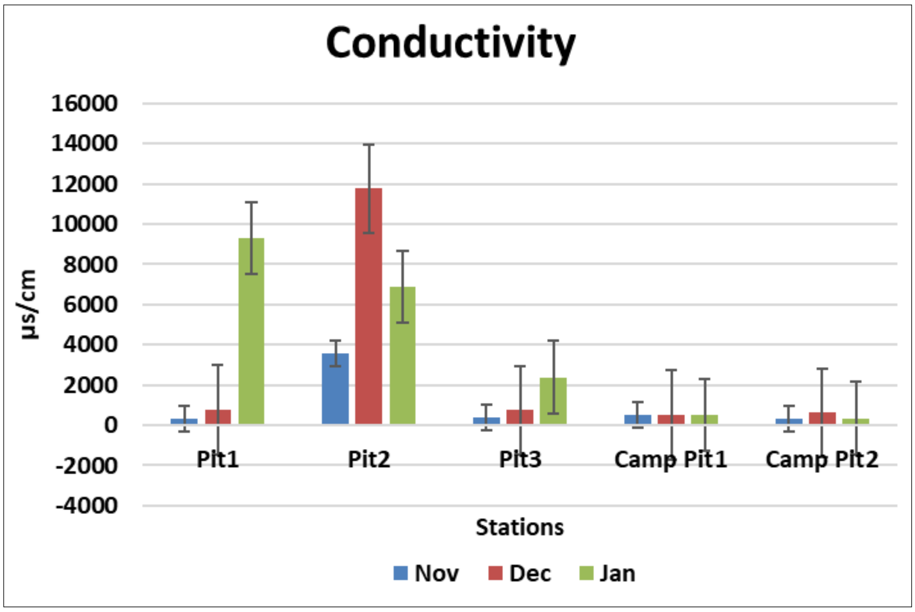

Fig 10: Mean Conductivity of the various pits in Months

The mean value of heavy metals obtained in the various pits are presented in Table 2. The heavy metals analyzed were chromium, lead, iron, copper and zinc. Pit 2 recorded the least value of 0.09 mg/l of chromium and the highest value of 0.16 mg/l in pit 3 and camp pit 1. Lead recorded the least value of 0.47 mg/l in camp pit 1 and highest value of 1.01 mg/l in camp pit 2. Iron was lowest in pit 3 (1.63 mg/l) and highest in camp pit 2 (2.659 mg/l). For copper, the least value of 0.01 mg/l was recorded in camp pit 2 and highest value of 0.03 mg/l in pit 3. Pit 3 recorded the lowest value of 0.21 mg/l of zinc and highest value of 0.47 mg/l in pit 2 and camp pit 2.

Table 1: Mean values of heavy metal content in the various pits in Etelebu oil rig location

Heavy Metals	Pit 1	Pit 2	Pit 3	Camp pit 1	Camp pit 2
Chromium (mg/l)	0.13	0.09	0.16	0.16	0.14
Lead (mg/l)	0.51	0.63	0.63	0.47	1.01
Iron (mg/l)	5.62	4.96	1.63	3.19	2.659
Copper (mg/l)	0.02	0.02	0.03	0.03	0.01
Zinc (mg/l)	0.26	0.47	0.21	0.30	0.47

Table 2: ANOVA between pits in Etelebu oil rig location

Parameter	Location (F-values)	Time (F-values)	Location (Tukey Test)	Time (Tukey Test)
pH	6.32*	4.27ns	Pit 2 < Pit 3 = Camp Pit 1 < Pit 1 = Camp Pit 2	Dec = Jan = Nov
Temperature	0.88ns	50.04***	Pit 2 = Pit 3 = Pit 1= Camp Pit 2 = Camp Pit 1	Dec < Jan < Nov
Turbidity	3.93*	1.16ns	Pit2=Pit1=Camp Pit 1 = Pit 3 = Camp Pit 2	Jan = Dec = Nov
Total Dissolved Solids	3.10ns	1.15ns	Pit 2 = Pit 1= Pit 3= Camp Pit 1 = Camp Pit 2	Jan = Dec = Nov
Total Suspended Solids	1.49ns	1.08ns	Pit 2 = Pit 1= Camp Pit 1 = Pit 3 = Camp Pit 2	Dec = Jan = Nov
Biological Oxygen Demand (BOD_5)	1.21ns	1.66ns	Camp Pit 2 = Pit 2 = Camp Pit 1 = Pit 1= Pit 3	Dec = Jan = Nov
Chemical Oxygen Demand	1.38ns	3.83ns	Pit 2 = Camp Pit 2 = Camp Pit 1 = Pit 1 = Pit 3	Dec = Jan = Nov
Salinity	1.33ns	1.79ns	Pit 2 = Camp Pit 2 = Pit 1 = Pit 3 = Camp Pit 2	Jan = Dec = Nov
Conductivity	3.18ns	1.29ns	Pit 2 = Pit 1= Pit 3 = Camp Pit 1 = Camp Pit 2	Jan = Dec = Nov
Dissolved Oxygen	2.83ns	10.81**	Pit 3 = Pit 2 = Camp Pit 2 = Pit 1 = Camp Pit 1	Nov < Dec = Jan

Key: ns-not significant, *-P≤0.05, **- P≤0.01, ***- P≤0.001

Discussion

The present study has revealed the physicochemical constituents of oilfield wastewater from various pits in Etelebou oilfield location. In pit 1 the least pH value was recorded in the month of December while the highest value was recorded in November. In pit 2, the least pH value was recorded in November while the highest was in December. Pit 3 pH values showed that the least value was recorded in January while the highest value was recorded in December. Camp pit 1 and Camp pit 2 recorded lowest pH values in the month of November and highest values in the month of December. There was significant difference between the various pits but there was no difference in the months. The pH values of the wastewater were within the alkaline range in all the months and in the five samples analyzed. Pit 2 and 3 values observed exceeded the recommended limit of 8.5 (DPR, 1991) [5] however, pits 1, camp pit 1 and 2 were all within the permissible range of 6.5 and 8.5 allowed for wastewater before discharge (FEPA, 1991) [7]. Study of pH of the wastewater was important because high alkaline pH above the standard limit (8.5) encourages corrosion, and growth of microorganisms whose activities also accelerate corrosion. The least temperature values in the pits 1, 2 and 3 were obtained in the month of November while the highest temperature values were recorded in the month of December. Camp pit 1 and 2 recorded least temperature values in November while the highest for Camp pit 1 was obtained in January and December for Camp pit 2. There was no significant difference between the various pits, but the values between the months were significantly different. Temperatures observed during the study period were within physiological temperature ranges and did not exceed the 35 ^{O}C acceptable limit for wastewater discharge (FEPA 1991) [7]. Temperature is a crucial component in determining the survival of microorganisms in a given habitat, and various bacteria flourish at different temperatures. The temperatures recorded in this study were in the mesophilic range, indicating that more mesophilic microbes would survive in the wastewater. The degree of temperature variation is a significant aspect in the influence of temperature. A large temperature range impacts organism survival and, in the case of microbes, can drastically alter their numbers, whereas a narrow temperature range has little or no influence on the living systems. The turbidity showed that pit 1 lowest value was obtained in November while the highest was recorded in December. Pit 2 lowest value of turbidity was observed in November while the highest value was in January. Pit 3 lowest value was obtained in November and highest in January. Camp pit 1 and 2 lowest values were recorded in November while the highest were in December. There was significant difference between the pits. The low values of turbidity observed in the month of November in the various pits in the study area could be attributed to the season, which was observed to be a dry season. Higher level of turbidity recorded in December and January was attributed to the amount of rainfall, and probably the hydrocarbon content in the oilfield wastewater during the period of sampling. The turbidity values recorded in this study were far higher than the values recorded by Aleruchi and Obire (2018) [2] for the Ogbogu flow station oilfield wastewater. The TDS obtained from the various pits showed that Pit 1, pit 2, pit 3 and camp pit 2 recorded lowest values in November while lowest value for camp pit 1 was recorded in December. The highest values in pit 2 and camp pit 2 were obtained in December. Pit 1, pit 3 and camp pit1 recorded highest values in January. Values obtained in the various pit and in the months were statistically not significant. The high TDS in this study could be related to concentration of solute in the wastewater. The lowest TSS values in all the sampling pits were observed in the month of November. Highest TSS values were obtained in December for pit 2, camp pit 1 and camp pit 2 while pit 1 and pit 3 recorded its highest TSS values in January. The increased TSS values in the pits indicate that wastes are being added from sources other than the generated water being discharged into it, such as rainfall depositing or runoffs from the surrounding area. This is consistent with findings of Eunice *et al*., (2017) [6]. The lowest and highest values of COD were observed in November and December, respectively in all the pits apart from camp pit 2 which lowest value was recorded in December and highest value in January. The lowest BOD values were observed in the month of November in all the pits. Highest value of BOD was recorded in pit 1 and camp pit 2 in December while pit 2, pit 3 and camp pit 1 recorded its highest value of BOD in the month of January. The permissible BOD limit allowed by FEPA (1991) [7] for effluent before discharge was $10mg^{-}l$ and all the values observed in all the samples analyzed were far above the recommended limit. COD and BOD in the wastewater indicate that the water was highly polluted. Uzoekwe and Oghosanine (2011) [13] also recorded high COD and BOD values in samples collected from discharge point than water receiving body. The lowest values of DO were recorded in January in all the pits except camp pit 2 which recorded lowest value in December. The highest values were recorded in the month of November in all the pits except for pit 3 which recorded highest in December. In secondary wastewater treatment, it is recommended to have at least 2 mg/L of dissolved oxygen to avoid dead zones in the biological floc by keeping the critical bacteria alive, instead of dying and settling out of the treatment mixture. In this study, the dissolve oxygen values were higher than 2mg/l except for pit 1 and camp pit1 in January. Dissolved oxygen is an extremely important characteristic of water quality for any application (hydroponics, environmental sampling, fish farming, aquariums, brewing, etc) including wastewater and wastewater treatment. In this way, DO should always be monitored during secondary treatment and effluent discharge to ensure safe levels for sanitation and the external environment. The lowest values of salinity were observed in November in all the pits apart from camp pit 1 and camp pit 2 which recorded the lowest in January and December. The highest salinity values were obtained in January for pit 1, pit 3 and camp pit2. Pit 2 and camp pit 1 recorded highest value of salinity in December and November, respectively. Salinity is a measure of the sodium chloride concentrations of the environment. High sodium chloride concentrations contribute to high alkaline pH, which in turn may encourage corrosion of metals (Obire and Wemedo, 1996) [11]. The least values of conductivity were recorded in the month of November in the various pits. Pit 1, pit 3, and camp pit 1 recorded highest values of conductivity in January while pit 1 and camp pit 2 recorded highest values in December. The heavy metals analyzed were chromium, lead, iron, copper and zinc. The high values obtained in the heavy metals could be as a result of inadequate treatment. High concentration according to Adeniyi and Okediyi (2004) [1] could be traceable to other sources. Toxic metals and radionuclides dissolved in formation water can be potential hazard (Obire and Amusan, 2003) [10].

Conclusion

In conclusion, the present research revealed the presence of inorganic constituents and physical parameters including heavy metals in the wastewater. Some physicochemical parameters and heavy metals observed during the study were statistically significant in some parameters and insignificant in others. Some values obtained for the various parameters exceeded the recommended limits for effluent/wastewater before discharge. The study showed that the oilfield wastewater contains inorganic constituents that could be harmful if discharged into the surrounding soil or leached into groundwater. This could result to ecotoxicological problem in the environment. Constant monitoring of physicochemical parameters and heavy metals in oilfield wastewaters and required treatment of the wastewater is therefore necessary to ensure allowable limits in oilfield wastewater before discharge into various pits in land rig oilfield locations.

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