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Physicochemical characteristics including heavy metals of oilfield wastewater from Utorogu oilfield in Delta state

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Abstract
Oilfield wastewater has become a major pollutant in the environment as a result of oil and gas development. Toxic physicochemical components and heavy metals can be found in oilfield effluent. When oilfield wastewater is treated before being discharged into receiving bodies, its toxicity is lowered. Wastewater samples were collected using normal protocols during a six-month period at two-week intervals from three pits (pit 1, pit 2, and camp pit 1). The pH values ranged from 4.7-10.35, temperature 23.9 °C - 35.25 °C, turbidity (NTU) ranged from 3 – 324, TDS (Total Dissolved Solids) 12.5 - 18660 mg/l. Total suspended solids (TSS) values ranged from 3 - 548 mg/l. The values for Chemical Oxygen Demand (COD) in mg/1 ranged between 12 – 670.5 mg/l. The values of biological oxygen demand (BOD) 5 in mg/1 ranged from 12 – 116.5 mg/l. The mean values for dissolved oxygen (DO) in mg/1 ranged between 1.0 – 8.5 mg/l. Salinity values ranged between 16 - 19081 mg/l. Mean values for conductivity ranged between 44 -14673.5 µs/cm. The chromium concentration (mg/l) ranged between 0.001-0.503, Pb ranged from 1.939-2.577 mg/l, Fe ranged from 0.080- 3.221 mg/l, Cu ranged between 0.057-0.205 mg/l and zinc ranged from 0.230-2.000 mg/l. Some physicochemical characteristics, such as TDS, chemical oxygen demand, and heavy metals; chromium, iron, and copper, were found to be beyond the established limits, posing a risk to the environment.

Keywords: Oilfield wastewater, physicochemical constituents, heavy metals, environmental impact

Introduction

Oil and gas exploration and production (E&P) activities generate a lot of waste materials that requires management. These waste materials include produced waters or oilfield wastewater, spent drilling fluids, used drilling muds and drill cuttings. Oilfield wastewater is the largest wastewater source by volume generated during oil and gas extraction. Oilfield wastewater is the fluid (often called brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas and includes, where present, formation water, injection water, and any chemicals added downhole or during drilling, production or maintenance processes. Oilfield wastewater has a complex composition but its constituents can be broadly classified into organic and inorganic compounds. These include dissolved and dispersed oil components, grease, heavy metals, radionuclides, HF chemicals, dissolved formation minerals, salts, dissolved gases (including CO_2 and H_2S), scale products, waxes, microorganisms and dissolved oxygen (Fontenot *et al.*, 2013) [16]. Metal concentrations in produced water are usually higher than those found in sea water (Igunnu and Chen, 2014) [8]. The primary hydrocarbons which contribute to acute toxicity of OGPW are the aromatic and phenol fractions of dissolved hydrocarbons (Frost *et al*., 1998) [7].

Some oilfield wastewaters are managed on-site or within the oil and gas field using evaporation ponds or seepage pits. Recycling of produced waters for exploration and production operations within the oil and gas field is another primary means of produced water management. Some treatment may be required to render the water suitable for reuse in drilling or hydraulic fracturing. Another management strategy is the use of oilfield wastewater for dust suppression and deicing, though some states are looking more closely at this practice and restricting or removing this as an option. These management approaches are not subject to CWA NPDES permitting requirements if they do not involve discharge to surface waters. Wills (2000) [20] stated that oil field waste water is separated from hydrocarbons at the surface during drilling to remove as much oil as possible and then either discharged to the environment or injected back into the well.

During the oil - water- gas separation, the oil – water -gas mixture from the wells enters the manifold wellheads, which connects all the well lines. The wells are divided into low- and high-pressure line, leaving the manifolds the combined oil-water-gas enters the two-phase separators. A demulsifier (emulsion breaker) and an anti-scale are injected into the lines in between the manifold and the two-phase separators. In the two-phase separators the oil-water-gas mixture moves to the wash tank where separation of oil from water is achieved based on their densities, the gas enters the gas line and then is flared (Wemedo, 1995) [18].

The oil as crude flows out of the wash tank into another tank called Storage Tank, from where the crude is taken to the expedition line, the water now as oil field waste water flows into a buffer tank and as the waste water leaves the wash tank into the buffer tank flocculants (water clarifier) is injected into it which then makes the water to appear soapy. Before the waste water enters the buffer tank, it passes through a shimmer, which skims off oil from the water. The water is retained in the buffer tank for some time, where more oil is removed from the water and separated. The oilfield wastewater flows in WEMCO (Last stage of treatment) where further extraction of oil from the water is achieved. All extracted oil flows into the API-pit from where they enter the expedition line (Wemedo, 1995) [18].

The waste water now leaving the WEMCO is regarded as treated oilfield water, part of the treated oil field waste water flows into the filters from where it is injected back into the wells to enhance oil recovery. The remaining treated wastewater is either discharged into sea, where operation is offshore (Obire and Amusan, 2003) [12] or into pits (ponds) where operation is onshore (DPR, 1991; Obire and Wemedo, 1996; Wills, 2000) [13, 12, 20].

However, as the treated water lies in the waste pit, more oil can be skimmed off and biological agents can help to purify it naturally (Wills, 2000) [20]. While in the pit, the oil field waste water could contaminate the soil environment as result of overflow or seepage from faulty pits. The oil-water-gas separation process is a continuous process except the flow station is shut down. The goal of this research is to determine the physicochemical components and heavy metals of oilfield wastewater from the various pits in Utorogu land rig

Materials and Methods

The Study Area

Utorogu field is an oil and gas field located in the western Niger Delta within the West African sub region. The field has been in production for over twenty years. Utorogu also houses the first integrated Gas Plant that supplies gas to various parts of the country. The study areas are Land rig. There are various Pits, Pit 1 is the first pit to the right after entering the gate in the Rig site, Pit 2 is the next pit as one move on. Camp pit 1 is the first pit on entry into the camp.

Collection and Determination of Samples

At each sampling point, the water samples were collected using a specially prepared pail. The pail was rinsed with the samples before collection from each pit point. The samples were put in a properly labelled plastic bottles for Physicochemical analysis and heavy metals. Representative's portions of the oil field wastewater samples were collected in two weeks interval for 6 months. In collecting the samples air space was left in the bottle to facilitate mixing by shaking. Aseptic technique was adopted to eliminate sample contamination. Physicochemical analysis including heavy metals was determined using standard procedures. The physicochemical parameters analyzed include; pH, temperature, turbidity, total dissolved solids, total suspended solids, biological oxygen demand, chemical oxygen demands, salinity, conductivity and dissolved oxygen.

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 0.45-micron 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

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

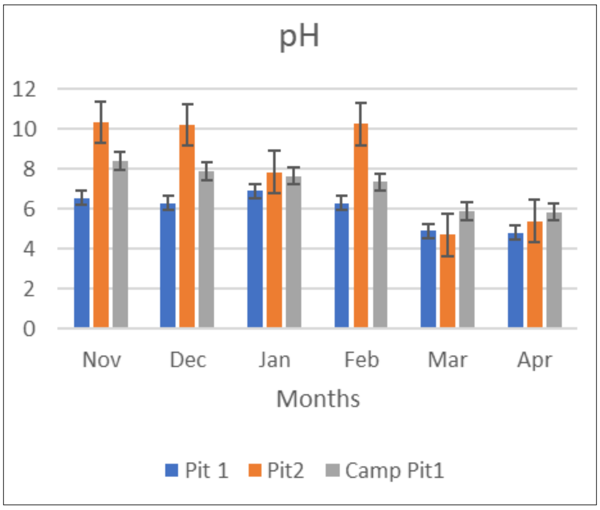
The two-way ANOVA was used to enable detection of significant differences between locations, periods examined and if there was an interaction between locations and periods. Post-hoc analysis using Tukey test indicated where actual significant difference occurred either for location or period.

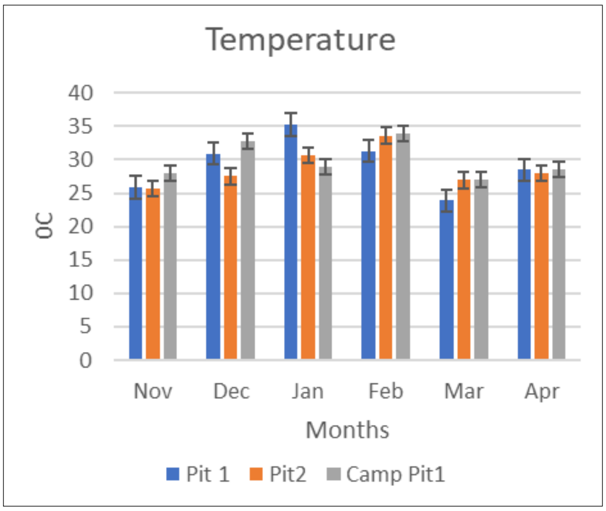
Results

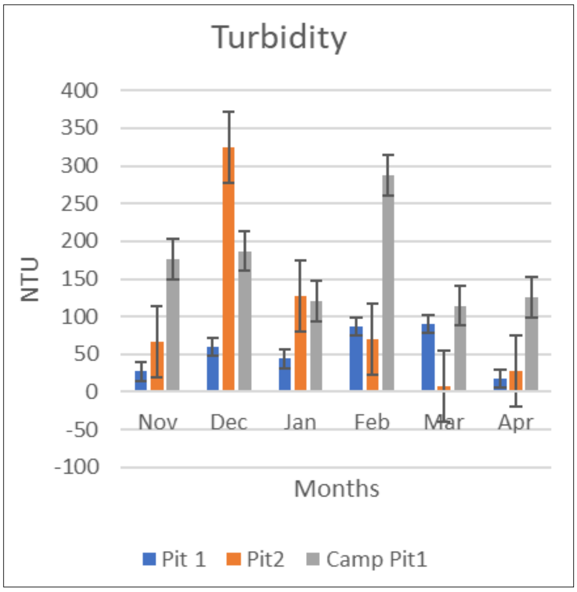
Figure 1 shows the values for the physicochemical parameters of the oilfield wastewater from individual pits in Utorogu, while Table 2 shows the ANOVA results. Pit 1, pit 2, and Camp pit 1 had pH ranges of 4.8 to 6.9, 4.7 to 10.35, and 5.85 to 8.4, respectively. Pit 2 had the highest pH value in the month of November and least value in March in pit 2. The pH values were significantly different ($P<0.05$) between the pits. The temperature in °C ranges for pit 1, pit 2, and camp pit 1 were 23.9-35.25 °C, 25.7-33.6 °C, and 27-33.9 °C, respectively, with the highest value in camp pit 1 in the month of January while the least value was recorded in the month of March in pit 1. There was no significant difference in the Temperature between the pits. The turbidity in NTU range were 15-90, 3-324, and 114.5- 287 for pit l, pit 2, and camp pit 1, respectively with the highest of 324 in pit 2, statistically there was no difference.

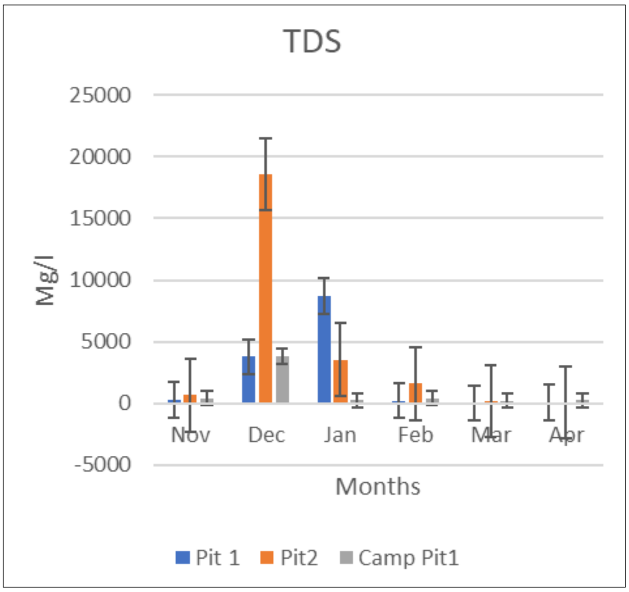
However, the highest value of turbidity was noted in the month of December while the least value was in the month of March in pit 2. The overall range TDS (Total Dissolved Solids) in mg/l at different pits were 23-8690 mg/l, 12.5-18660 mg/l, and 222-3820 mg/l, with the maximum recorded in pit 2 in the month of December, while the least value was observed in the month of March in pit 1. Total suspended solids (TSS) in mg/1 ranged from 3 to 91, 5 to 414, and 116 to 548 for pit 1, pit 2 and camp pit1, respectively, with the maximum value in camp pit 1 in the month of November, the least value was noted in the month of April in pit 1. There was significant difference between the values in the pits. The range values for Chemical Oxygen Demand (COD) in mg/1 were 20-177, 12-355, and 25-670.5, for pit 1, pit 2 and camp pit 1, respectively, with the highest value in camp pit 1in the month of April and least in February in pit 1. Biological oxygen demand (BOD)5 in mg/1 range and mean values for the pits were 21.5-88, 12-103.5, 29-116.5, respectively, for pit 1, pit 2, and camp pit 1, with camp pit 1 having the highest value in camp pit 1 in the month of April and least value in November in pit2. The values were significantly different between the pits. The dissolved oxygen (DO) in mg/1 range values for the locations were 3.35-7.7, 3.95-8.5, and 1.0 – 5.25 for pit l, pit 2, and camp pit l, respectively. highest value of dissolved oxygen was observed in pit 2 in the month of April and least in February in camp pit 1. The salinity in mg/1 range for the pits were 16-1509, 27-19081, and 28-710, respectively, for pit l, pit2, and camp pit l, with the maximum in pit 1 in the month of December and least value in the month of March in pit 2. The range of values for pit l, pit 2, and camp pit 1, conductivity in µs/cm was 47-14673.5, 108-6469.5, and 44-6916.5, respectively; the greatest mean value was in pit 2 in the month of January and least value in pit 2 in the month of November, March and April.

Chromium, Lead, Iron, Copper, and Zinc were among the metals tested in the oil field wastewater samples gathered (Table 1). Pit l, 0.001-0.503 mg/l, pit 2, 0.005–0.405 mg/l, and camp pit 1, 0.005–0.412 mg/l for chromium content (mg/l). Pit 2 recorded the highest mean value. For pit l, pit 2, and camp pit l, the lead in mg/l range values were 1.939–2.335 mg/l, 1.967–2.377 mg/l, and 2.179–2.577 mg/l, respectively. The greatest mean value was in pit 1. For pit l, pit 2, and camp pit l, the range values of iron (mg/l) were 0.742-2.000 mg/l, 0.561–2.392 mg/l, and 0.080–3.221mg/l, respectively. The greatest mean value was in pit 1. For pit l, pit 2, and camp pit l, the range values of copper (mg/l) were 0.071- 0.205 mg/l, 0.094– 0.105 mg/l and 0.057– 0.110 mg/l, respectively. The greatest mean value was in camp pit 1. For pit l, pit 2, and camp pit l, the range and mean values of zinc (mg/l) were 0.155-0.921 mg/l, 0.230-2.000 mg/l, and 0.203-1.566 mg/l, respectively. The highest mean value was in pit 2 and camp pit 1.









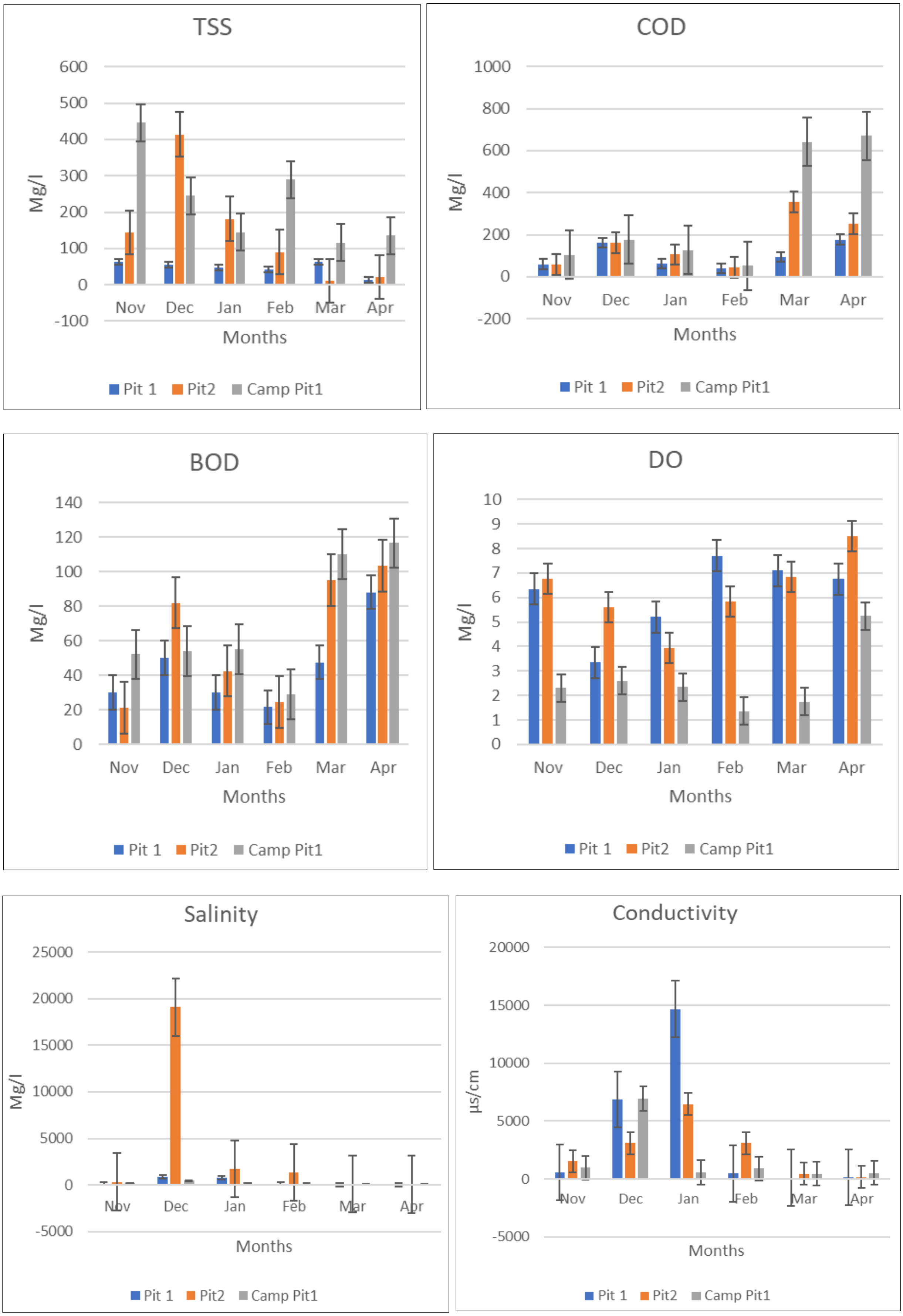


Fig 1: Physicochemical Parameters of the oilfield wastewater from individual pits

Table 1: Heavy Metal from the Various pits in Utorogu

Heavy Metals (mg/l)	Pit1 (mg/l)	Pit2 (mg/l)	Camp pit1
Chromium (mg/l)	0.001- 0.503	0.005 -0.405	0.005- 0.412
Lead (mg/l)	1.939 – 2.335	1.967 – 2.377	2.179 – 2.577
Iron (mg/l)	0.742 – 2.000	0.561 - 2.392	0.080 - 3.221
Copper (mg/l)	0.071 – 0.205	0.094 – 0.105	0.057- 0.110
Zinc (mg/l)	0.921 – 0.155	0.230 – 2.000	0.203 - 1.566

Table 2: Summary Table for ANOVA between Pits in each location (**Utorogu)**

Parameter	Location (F-values)	Time (F-values)	Location (Tukey Test)	Time (Tukey Test)
pH	6.43*	5.74**	Pit2<Pit3<Camp Pit1	Nov<Dec=Feb=Jan<Apr=Mar
Temperature	0.40ns	5.11*	Camp Pit1=Pit2=Pit1	Feb<Jan=Dec=Apr<Nov=Mar
Turbidity	3.62ns	1.41	Camp Pit1=Pit2=Pit1	Dec=Feb=Jan=Nov=Mar=Apr
Total Dissolved Solids	1.02ns	2.37	Pit2=Pit1=Camp Pit1	Dec=Jan=Feb=Nov=Mar=Apr
Total Suspended Solids	4.73*	1.63	Camp Pit1<Pit2<Pit1	Dec=Nov=Feb=Jan=Mar=Apr
Biological Oxygen Demand	4.73*	13.40***	Camp Pit1<Pit2<Pit1	Apr<Mar<Dec<Jan=Nov=Feb
Chemical Oxygen Demand	3.43ns	3.58*	Camp Pit1=Pit2=Pit1	Apr=Mar=Dec=Jan=Nov=Feb
Salinity	1.39ns	1.19ns	Pit2=Pit1=Camp Pit1	Dec=Jan=Feb=Nov=Mar=Apr
Conductivity	0.66	2.66ns	Pit1=Pit2=Camp Pit1	Jan=Dec=Feb=Nov=Mar=Apr
Dissolved Oxygen	16.87***	2.43ns	Pit2=Pit1<Camp pit1	Apr=Mar=Nov=Feb=Dec=Jan

KEY: Ns = Not Significant; * = ($p<0.05$); ** = ($p<0.01$); *** = ($p<0.001$)

Discussion

In this study, the pH value recorded lowest mean value in pit 2 in the month of March. The highest value was recorded in pit 2 in the month of November. The pH values in the various pits were significantly different. Similar results were recorded by Aleruchi and Obire (2018) [2] while evaluating the quality characteristics of an oilfield produced water and its recipient discharge point. The measure of pH does not have a major health or sanitary effect except for excessive values that indicate the acidity or alkalinity of the water. These may have organoleptic consequences. The pH level is also important for the life expectancy of fish. The range suitable for fisheries is considered to be 5.0 to 9.0 (FEPA, 1991) [6]. All the pits are within the set standard by WHO. Temperature observed in the course of this study showed values were within the limits set by FEPA (1991) [6] with placed a limit of 35°C. The spatial spreading of temperature over the wastewater in the pits is prejudiced by; amount of insulation received and nature of surface (Ogamba *et al*., 2015) [14] including the dissolved oxygen concentration. The highest temperature mean recorded in Utorogu was observed in pit 1 in the month of January, while pit 1 recorded the least value in the month of March. There was no significant difference in the temperature between the various pits. This study temperature had a narrow range which shows that it will have little or no effect in the survival of microorganisms as a wide range of fluctuation in temperature can result in reducing or eliminating some microorganisms from that environment. Turbidity of water is as a result of extraneous substances on it, the more those substances exist in that environment, the more turbid the environment. Turbidity values obtained in the course of this study had a wide range of fluctuation. Turbidity is directly proportional to TSS and TDS (ECM, 2006). The highest turbidity of was recorded in pit 2 in December and the lowest was recorded in pit 2 in the month of March. The low values of turbidity observed 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 was attributed to the amount of rainfall, and probably the hydrocarbon content in the oilfield wastewater during the period of sampling. Mean values obtained for Total dissolved solids (TDS) were within a wide range. Total dissolved solids are a measure of the solutes dissolved in the solution (water). TDS is directly proportional to turbidity. The highest mean of TDS was recorded in pit 2 in the month of December, while the lowest was observed in March in pit 1, however there was no significant difference between the pits. Total dissolved solid recorded in the study were generally above the limit of 500mg/l specified by SON (2007) and permissible and desirable criteria for water quality in Nigeria as specified by Ademoroti (1996) [1]. Low total dissolved solid suggest low nutrients especially cations and anions. According to Amangabara and Ejenma (2012) [3], high total dissolved solid indicates the level of cations and anions in such water Values obtained for the Total suspended solids lowest value was obtained in pit 1 in the month of April and highest value obtained in camp pit 1 in the month of November and was significantly different. The amount of TSS values in the pits indicates the level of wastes being added from sources other than the generated water being discharged into it, such as rainfall depositing or runoffs from the surrounding area. Total suspended solids provide information about inorganic (silts, clays, etc) and organic composition (algae, zooplankton, bacteria, and detritus) in a water body that are carried along via runoff (Rim-Rukeh and Agboz, 2013) [17]. Total suspended solid also provide information on the microbial load of a water body (Prekeyi *et al*., 2015) [15]. Basically, high total suspended solid has adverse effect on aquatic organisms especially fisheries. Values obtained for biological oxygen demand (BOD5) were within a slightly large range of values. The lowest was in pit 2 in the month of November and the highest was in camp pit 1 in the month of April. The values obtained in the various pits were different statistically. The limit by FEPA (1991) [6] is 10mg/l, values obtained in this study were well above this limit. Chemical oxygen demand recorded highest mean value in camp pit 1 in the month of April while the lowest value was recorded in pit 1 in February. The chemical oxygen demand concentration at the three sampling points was above the permissible limit of WHO and NESREA standards for effluent discharges to surface water (WHO, 1996; NESREA, 2009) [19, 11]. Values for Salinity recorded during the course of this study were high and also had a wide range of fluctuation. The highest was in pit 2 in the month of December, while the lowest was recorded in the months of November, March and April in pit 2. Statistically, salinity values obtained were not significantly different. A highly saline environment containing a high level of NaCl (Sodium chloride) contributes to corrosion (Wemedo, 1995) [18]. Conductivity is a measure of dissolved ions in solution and its directly proportional to the number of dissolved substances in solution, thus conductivity is directly proportional to TDS and vice versa. The highest mean obtained for conductivity was from pit 1 in January, camp pit 1 recorded the lowest mean value of conductivity in the month of April. Dissolved oxygen value obtained was within a narrow range, with lowest in camp pit 1 in the month of February and highest in pit 2 in the month of April and were significantly different statistically. Dissolved oxygen is a measure of the level of O_2 dissolved in the sample, levels lower than 2.0mg/l result in environmental stress (Clerk 1986) [4]. Dissolved Oxygen values obtained were well above this limit. Heavy metals are known to have serious health and environmental concerns. Some of the roles and effects of heavy metals have been comprehensively documented by Izah *et al*. (2016) [9, 10], Izah and Angaye (2016) [9, 10]. On pollution perspective, heavy metals can enter the surface water resources through several routes including runoff from soil erosion, direct discharge of wastes into the water and other anthropogenic activities in the water resources including dredging. According to standards set by DPR (1991), Chromium (Land rig is - 0.03, swamp (no limit). Results obtained for recorded higher mean value in all the sampling points as compared to the DPR standard. DPR (1991) and FEPA (1991) [6] limit for lead are 0.05mg/l. Pit 1 and camp pit 1 showed higher values above the set limits. Iron values obtained were above limit set by DPR (1991) which set standards of l.0mg/l. all the sampling points recorded high values above the set limit. However, pit 1 recorded the highest mean value which was followed by camp pit 1 and the pit 2. Copper values obtained from this study were within DPR (1991) limit of 1.5mg/l. FEPA (1991) [6] limit is 0.05mg/l, they were also below this limit considering their overall mean values apart from camp pit 1 which mean was slightly above the FEPA limit. DPR (1991) and FEPA (1991) [6] limit for zinc for Land Rig is l.0mg/1 and for swamp Rig is 5.0mg/l. Values obtained for Land Rigs were below limit. However, pit 2 and camp pit 1 recorded higher values than pit 1.

Conclusion

The purpose of this study was to assess the physicochemical parameters and heavy metal contents in Utorogu oilfield wastewater (the principal discharge from a drilling and exploitation field location) in Delta State. The data gathered in this investigation revealed substantial variances and fluctuations in some pits, as well as moderate or narrow variations in others. This study revealed the characteristics of physicochemical parameters in distinct pits. Analysis of the physicochemical elements of oilfield wastewater is critical to minimizing the environmental impact on receiving environment.

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