Quality Characteristics of an Oilfield Produced Waterand Its Recipient Discharge Pond

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Abstract

Oilfield produced water (oilfield wastewater) is a complex mixture of dissolved and particulate organic and inorganic chemicals including aromatic hydrocarbons and a few heavy metals in water which is generated duringcrude oil prospecting and processing.There is considerable concern about the aquatic disposal of produced water in the Niger Delta because of the potential danger of chronic ecological harm. It became necessary to carry out water quality analysis of raw produced water and its recipient pond for its quality characteristics before and after disposal. Produced water samples were collected from an onshore oil production platform and from a pond, into which the produced water is discharged fortnightly for a period of three months(January to March, 2018). These were analyzed for physicochemical parameters by standard methods and for heavy metals by flame absorption spectroscopy after digestion with 2 M HNO_3, Total Organic Carbon (TOC) and Total Petroleum Hydrocarbons (TPH) by gravimetric method after extraction with methanol followed by hexane. Average values of some physicochemical properties of the produced water such as Biological oxygen demands (BOD) was 19.5 mg/l, Turbidity ranged from 9.15- 23.80 NTU, and Chemical oxygen demand (COD) 36.8- 185.26 mg/l. Heavy metals such as Chromium 1.154 mg/l, Lead 0.2135 mg/l, Cadmium 0.106 mg/l, Nickel 0.084 mg/l all in January were above the allowable limit set by regulatory body in Nigeria. The Total organic carbon (TOC) ranged from 132.01-135.16 mg/l, Total petroleum hydrocarbon (TPH) ranged between 142.915-286.785 mg/l and 0.058-93.18 mg/l for polycyclic aromatic hydrocarbon (PAH). For the pond effluent, Turbidity 12.95-16.3 mg/l, COD 72.0- 86.4 mg/l, Chromium 0.8155 mg/l, Cadmium 0.073- 0.0425 mg/l, Nickel 0.0515-0.084 mg/l, were above the permissible limits. TOC ranged from 225.62-231.44 mg/l, TPH 83.1655-92.15145 mg/l and PAH 40.52-69.7005 mg/l. The dilution efficiency (%) of the pond water on the physicochemical constituents of oilfield produced water after discharge showed higher percentage in Conductivity (86.1µS/cm) in the month of February. TPH, Salinity, COD, BOD, were 67.9, 63.3, 55.7 and 50.8 mg/l respectively. In the month of March 54, 46.3 and 41.1 percent was recorded for Turbidity, TDS and TPH respectively. The highest negative values were recorded for PAH -69762 percent in March, and TDS-24693.4 percent in January. There is significant difference ($P>0.05$) in the Total suspended solid and Aluminum in the produced water and pond effluent. There was significant different ($P>0.05$) in Salinity, TDS, TSS, BOD, Conductivity, Nitrogen, Phosphate, PAH, Lead, Zinc Chromium, Copper and Cadmium in the produced water in the various months.

While there is significant difference (P>0.05) in Conductivity, Nitrogen, Phosphate, Aluminum, and Copperin the pond effluent. The results revealed that the oilfield produced water being discharged continuously without adequate treatments impacts the recipient pond negatively with its constituents and in turn could affect aquatic life and humans.

Keywords: Produced water, aromatic hydrocarbons, heavy metals, dilution efficiency.

Introduction

Oilfield produced water (produced water)is a complex mixture of dissolved and particulate organic and inorganic chemicals in water.Itis often generated during the production of crude oil and gas from onshore and offshore wells (Neff, 2002; Veil *et al*., 2004). The most abundant organic chemicals in most produced waters are water-soluble low molecular weight organic acids and monocyclic aromatic hydrocarbons. Produced water also includes formation water which is seawater or fresh water that has been trapped for millions of years with oil and natural gas in a geologic reservoir consisting of a porous sedimentary rock formation between layers of impermeable rock within the earth's crust (Collins, 1975).

Produced water represents the largest volume waste stream in oil and gas production operations on most oil production platforms (Stephenson, 1991; Krause, 1995). Produced water may account for 80% of the wastes and residuals produced from natural gas production operations (McCormack *et al*., 2001). In 2003, an estimated 667 million metric tons (about 800 million m3) of produced water were discharged to the aquatic environment from offshore facilities throughout the world.

The chemicals of greatest environmental concern in produced water, because their concentrations may be high enough to cause bioaccumulation and toxicity, include aromatic hydrocarbons, some alkylphenols, and a few metals. There is considerable concern about the aquatic disposal of produced water, because of the potential danger of chronic ecological harm. Aquatic organisms near a produced water discharge may bioaccumulate metals, phenols, and hydrocarbons from the ambient water, their food, or bottom sediments. Upon discharge to the aquatic environment or water body, produced water dilutes rapidly, often by 100-fold or more within 100 m of the discharge.
In the Niger Delta, onshore oilfield production water is often discharged into nearby rivers or streams and is not documented. It is therefore necessary to conduct studies or the quality characteristics of production water and its recipient water body. The objective of this study therefore was to assess the level of physicochemical parameters of the oilfield processed water and the recipient discharge pond and also to determine the nature and extent of pollutants in the recipient water body.

Materials and Methods

Collection of Produced Water and Recipient Pond Water Samples

Produced water (oilfield wastewater) was collected from Ogbogu Flow Station; an onshore oil production platform located in Ogba Egbema Ndoni local government

Area (ONELGA) of Rivers State, Nigeria. The Produced water samples and recipient pond water samples were collected using 4 Litre capacity plastic bottles. Prior to the collection of the produced water the interior of the nozzle of the outlet biofilter was flushed for few minutes before collecting directly into the 4 litre plastic bottles. For the recipient water, 4 litre plastic sampling bottles were dipped few centimetres below the water level. The plastic bottles were appropriately labeled and stored in an ice packed cooler. The stored samples were immediately transported to the laboratory within 24 hours for processing and analyses. Samples were collected twice in a month (1^{st} and 3^{rd} week) for a period of three months (January, 2018 to March, 2018).

Physicochemical analysis of Produced Water and Recipient Pond Water Samples

Physicochemical analyses of theProduced water samples and recipient pond water sampleswere conducted according to standard procedures of APHA (1998) and ASTM (1999). The physicochemical parameters determined include pH, temperature,turbidity, total dissolved solids (TDS), total suspended solids (TSS), total dissolved solids (TDS), conductivity, salinity, conductivity, dissolved oxygen (DO), biological oxygen demand(BOD_5), chemical oxygen demand (COD), nitrogen, phosphate, total organic carbon (TOC), total petroleum hydrocarbon, total poly aromatic hydrocarbons (PAHs), and heavy metals such as nickel, lead, zinc, aluminum chromium, selenium, arsenic, copper, and cadmium.

The dilution efficiency (%) of the recipient pond water on the physicochemical constituents and on heavy metals of the produced water samples during each month was calculated using the equation of Alayu and Yirgu (2018)below.

$$\text{Dilution efficiency (\%)} = \frac{\text{Original value (Produced water)} - \text{Final value (Pond water)}}{\text{Original value (Produced water)}} \times 100$$

Statistical analysis was also conducted using Duncan Multiple Range test and Analysis of variance to determine whether there is significant difference between the physicochemical constituents of produced water and the recipient pond water and between the various samples collected during the various months.

Results

The result of the calculated average values of physicochemical constituents of oilfield produced water before and after discharge into the recipient pond is as shown in Table 1 below. The sum average for Temperature, pH, Total suspended solid (TSS), Dissolved oxygen (DO), Nitrogen, Phosphate, Total organic carbon (TOC), Polycyclic aromatic hydrocarbons (PAHs) were higher in the pond effluent than in the produced water. While the sum average for Biological oxygen demand (BOD), Chemical oxygen demand (COD), Total dissolved solid (TDS), Salinity, Turbidity, Conductivity and Total petroleum hydrocarbon (TPH) were higher in the produced water than in the pond effluent.

Statistical analysis showed thatexcept for the TSS, there is no significant different between the average values of the other physicochemical parameters in the produced water and the pond water.

Table 1: Average values of physicochemical constituents of oilfield produced water before and after discharge into pond.

Parameter(Mg/L)	**January**		**February**		**March**	
	Produced water	**Pond effluent**	**Produced water**	**Pond effluent**	**Produced water**	**Pond effluent**
Temperature (°C)	27.7	28.8	28.57	30.255	31.01	30.255
pH unit	7.65	7.82	8.48	6.89	7.485	7.505
Salinity	61.86	22.73	32.5	26.5	28.5	26.5
Turbidity (NTU)	23.8	16.3	9.15	12.95	31.9	14.55
Conductivity (µS/cm)	134.5	355.5	395	55	164	132
TDS	0.605	150	197.5	47	82	44
TSS	4.7	13.1715	1.167	11.9575	2.9205	11.3545
DO	1.99	2.37	2.675	2.405	3.33	3.76
BOD	19.04	9.37	3.0975	7.13	5.9135	6.7825
COD	185.26	82.03	100.8	72	36.8	86.4
Nitrogen	3.376	6.185	0.9645	3.4155	1.637	2.3005
Phosphate	0.546	0.813	0.1905	0.2145	0.1785	0.229
TOC	135.16	225.62	133.745	228.3	132.01	231.44
TPH	286.785	92.15145	213.765	83.555	142.915	83.1655
PAH	93.18	69.7005	0.455	67.727	0.058	40.52

The result of the calculated average values of heavy metal content of oilfield produced water before and after discharge into the recipient pond is as shown in Table 2 below.

Table 2: Average values of heavy metals of oilfield produced water before and after discharge into pond

Heavy metal(Mg/L)	**January**		**February**		**March**	
	Produced water	**Pond effluent**	**Produced water**	**Pond effluent**	**Produced water**	**Pond effluent**
Lead	0.2135	0.105	0.001	0.1035	0.001	0.1055
Zinc	2.110	1.513	0.012	1.431	0.060	1.513
Nickel	0.084	0.022	0.001	0.0515	0.001	0.084
Aluminum	0.135	0.087	0.112	0.0815	0.179	0.0805
Chromium	1.154	0.8155	0.001	0.249	0.001	0.4515
Selenium	0.001	0.001	0.001	0.001	0.001	0.001
Arsenic	0.001	0.001	0.001	0.001	0.001	0.001
Copper	0.042	0.053	0.001	0.013	0.009	0.013
Cadmium	0.106	0.073	0.001	0.018	0.001	0.0425

Chromium, Zinc, Lead were higher in January sampling in the produced water compared to the other months. The sum average in Aluminum was higher in the produced water than in the pond effluent. Lead, Zinc, Nickel, Chromium, Copper were higher in the pond effluent than in the produced water. Cadmium had the same value while arsenic and Selenium were below the level of detection. Significantly, there was no significant different between the produced water and the pond effluent except for Aluminum.

The concentration of heavy metalsinproduced water before and after discharge into pond is as shown in Figure 1. This is to illustrate the accumulation of heavy metals in the recipient pond in the month of February and March 2018. The notable heavy metals which accumulated in the recipient pond during this period were Zinc, lead, aluminum, chromium and nickel.

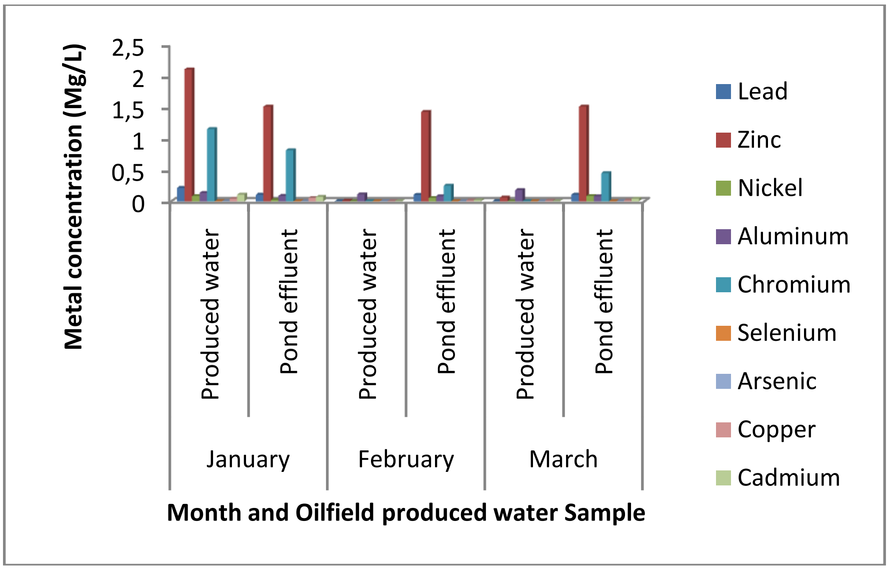

Fig 1: Heavy metal concentration inproduced water before and after discharge into pond

Table 3: Dilution efficiency (%) of pond water on physicochemical constituents of oilfield produced water after discharge.

Parameter	Month		
	January	February	March
Salinity (Mg/l)	63.3	18.5	7
Turbidity (NTU)	31.5	-41.5	54.4
Conductivity (µS/cm)	-164.3	86.1	19.5
TDS (Mg/L)	-24693.4	76.2	46.3
TSS (Mg/L)	-180.2	-924.6	-288.8
DO (Mg/L)	-19.1	10.1	-12.9
BOD (Mg/L	50.8	-130.2	-14.7
COD (Mg/L)	55.7	28.6	-134.8
Nitrogen (Mg/L)	-83.2	-254.1	-40.5
Phosphate (Mg/L)	-48.9	-12.6	-28.3
TOC (Mg/L)	-66.9	-70.7	-75.3
TPH (Mg/L)	67.9	60.9	41.8
PAHs (Mg/L)	25.2	-14785.1	-69762.1

The dilution efficiency (%) of pond water on the physicochemical constituents of oilfield produced water after discharge into the recipient pond in three months is as shown in Table 3.

Negative values shows that the constituents were concentrated in the pond.Salinity, TPH, were not concentrated in the various months of sampling while TSS, Nitrogen, Phosphate, TOC were concentrated in the all the months of sampling. Other physicochemical parameters were concentrated in one month or the other.

The dilution efficiency (%) of pond water on the heavy metal content of oilfield produced water after discharge into the recipient pond in three months is as shown in Table 4 below. Negative values shows that the metals were concentrated in the pond. Heavy metals concentrated in the various months include Copper. Aluminum was not concentrated in the months of sampling while other heavy metals were concentrated in one month or the other.

Table 4: Dilution efficiency (%) of pond water on heavy metals of oilfield produced water after discharge into pond.

Heavy metal	**Month**		
	January	**February**	**March**
Lead (Mg/L)	50.8	-10250	-10450
Zinc (Mg/L)	28.3	-11825	-2421.7
Nickel (Mg/L)	73.8	-5050	-8300
Aluminum (Mg/L)	35.6	27.2	55.0
Chromium (Mg/L)	29.3	-24800	-45050
Selenium (Mg/L)	0	0	0
Arsenic (Mg/L	0	0	0
Copper (Mg/L)	-26.2	-1200	-44.4
Cadmium (Mg/L)	31.1	-1700	-4150

Discussion

The average value for temperature pH, Total suspended solid (TSS), Dissolved oxygen (DO), Nitrogen, Phosphate were higher in the pond effluent than in the produced water but where still within the permissible limit (DPR, 2002; WHO, 1999) both nationally and internationally and there was no significant different except for the TSS. The higher values in the TSS in the pond effluent suggests that wastes are being added to the pond effluents from other sources apart from the produced water that is being discharged into it, such as rainstorm deposition or runoffs from the surrounding. This is in agreement with the findings of Eunice *et al*., 2017.
The moderate value in DO in the pond effluent indicates the ability to support aquatic life and attributed to the presence of degradable organic matter. The DO average value 2.37-3.76, was lower than that reported by Uzoekwe and Oghosanine 2011. They reported DO of 5.93 mg/l for receiving water body.
High concentration of Phosphates and nitrogen in the pond effluent could be as a result of runoff from agricultural site. Phosphate levels in the effluent receiving water

body have been reported earlier to be associated with the refinery operation because of the changes in its concentration from the point of refinery effluent (Otokunefor and Obiukwu, 2005). Though the values for the phosphate and nitrogen are within limits in the study, accumulation over time could result to eutrophication and blue baby syndrome for nitrate. Eunice *et al.*, 2017 also reported levels of phosphate that complied with FEPA limit (FEPA, 1991).

Total organic carbon (TOC) and Polycyclic aromatic hydrocarbon (PAHs) were also observed to be high in the pond effluent than in the Produced water. This could be as a result of continuous discharge and accumulation over time. Total petroleum hydrocarbon and PAHs observed in the study are known to be toxic to aquatic life. The concentration of PAHs was higher in this study compared to the range of 0.040 to about 3 mg/l reported by Neff *et al.*, 2011.

The COD, BOD, and Turbidity of the produced water discharged into the pond effluent did not meet the effluent limitation standard set by DPR and FMEnv for refinery effluent in Nigeria. The COD was also high in the pond effluent. COD and BOD in the produced water indicate that the water was highly polluted. Uzoekwe and Oghosanine (2011) also recorded high COD and BOD values in samples collected from discharge point than water receiving body.

TDS was 0.605-197.5 mg/l in the produced water compared to 2440 mg/l reported by Neff et al. (2011) in produced water. The TDS sum average value was higher than that of the pond water but was within the permissible limit in both samples. High TDS can result in low oxygen levels and be toxic to freshwater biota in receiving waters (Boelter *et al*., 1992) implying that aquatic life could be threatened.

The conductivity in the produced water was higher than in the pond effluent. Conductivity gives an indication of the amount of total dissolved solid in water (Yilmaz and Koc, 2014).

Turbidity values of both produced water and pond effluent were above the WHO (1999) standard. The high turbidity could be as a result of high amount of suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter accumulated during industrial processes and from runoffs.

Heavy metals such as Lead, Zinc, Nickel, Chromium, and Copper were higher in the pond effluent than in the produced water. There is no significant different between the heavy metals in the produced water and the pond effluent except for Aluminum which was higher in the produced water than in the pond effluent. The value of the Aluminum in produced water reported by Neff et al (2011) was higher 1.03 mg/l than the value in this study 0.112-0.179 mg/l. Cadmium had similar value while arsenic and selenium were below the level of detection. Some of the heavy metals such as chromium, Lead, Cadmium, Nickel were observed to be high in January and were above the set limit by regulatory bodies. This could be as a result of inadequate treatment. In the pond effluent, chromium (January), cadmium, Nickel (February and March) were traced above permissible limit. High concentration according to Adeniyi and Okediyi (2004) could be traceable to other sources. Toxic metals and radionuclides dissolved in formation water can be potential hazard (Obire and Amusan, 2003).

The dilution efficiency of the pond water revealed the level of concentration of various physicochemical constituents of the oilfield produced water and its implications. TSS, Nitrogen, Phosphate, TOC were concentrated in the all the months of sampling which indicates the ability to impact receiving water body. Higher concentration of nutrients may stimulate microbial and phytoplankton growth in the

receiving water body (Rivkin *et al.*, 2000; Khelifa *et al.*, 2003).High turbidity can cause potential problems for water purification processes (Igbinosa and Okoh, 2009) and aquatic lives affected. TDS in high concentration could be threatening to aquatic life and it can also causes changes in taste, excessive scaling in water pipes, water heaters boilers and household appliances. High conductivity gives an indication of the amount of total dissolved solid in receiving water bodies (Yilmaz and Koc, 2014).
High concentration in BOD and COD indicates organic and inorganic pollution respectively which are harmful to aquatic life. According to Neff (2002), some produced water contains chemicals that are highly toxic to sensitive marine species even at low concentrations. PAH is of great environmental concern in produced water, it may cause bioaccumulation and toxicity.
Produced water when discharged to shallow, enclosed coastal water or when discharge is of low density, produced water chemicals may remain high for long enough to cause ecological harm.
High concentration of heavy metals may accumulate in sediments near the produced water discharge which may harm bottom living biological communities.

Conclusion

The results revealed that the pond water is impaired with the continuous discharge of the produced water without adequate treatment. It is therefore recommended that regulatory bodies should monitor the treatment of oilfield produced water before its discharge to receiving water.

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