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Assessment of Physicochemical Characteristics of Produced Water from Terminals of Some Oil Industry Facilities in Nigeria

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ABSTRACT: This study evaluated the physico-chemical characteristics, total hydrocarbon concentration (THC) and some heavy metal levels of produced water from terminals of two oil industry facilities in Nigeria, using standard methods. Appropriate sample bottles were used in the collection of samples for analyses of BOD, other physico-chemical characteristics, total hydrocarbon and heavy metals. The samples were preserved accordingly and transported to the laboratory in ice - packed coolers. The levels of the physico-chemical properties of produced water in the two locations, showed that mean temperature, pH, TDS, TSS, salinity and turbidity levels were: $24.40 \pm 0.35^{\circ}$ C - 25.50 $\pm 0.35^{\circ}$ C; $7.49 \pm 0.28 - 7.89 \pm 0.30$; 8428 ± 2332 mg/l - 9205 ± 2100 mg/l; 8.50 ± 3.40 mg/l $- 14.30 \pm 5.10$ mg/l; 6108 ± 1250 mg/l $- 7422 \pm 2280$ mg/l and 16.00 ± 5.00 NTU - 37.00 ± 9.60 NTU respectively. DO and BOD levels were respectively 3.07 ± 0.40 mg/l $- 3.29 \pm 0.40$ mg/l and 1.46 ± 0.38 mg/l $- 1.72 \pm 0.48$ mg/l. COD levels did not vary between the two locations. Mean TOC levels ranged between 0.05 \pm 0.02mg/l and 0.06 \pm 0.02mg/l while mean THC ranged between 4.72 \pm 1.59mg/l and 36.90 \pm 3.03mg/l. The levels of the nutrient characteristics of nitrate, phosphate and sulphate ranged as follows: NO₃⁻ (1.90 ± 1.16mg/l - 2.50 ± 0.26mg/l); PO₄³⁻ (0.52 ± 0.12mg/l - 1.07 ± 0.12mg/l) and SO_4^{2-} (14.40 ± 4.57mg/l – 21.70 ± 2.75mg/l). Levels of trace metals (Pb, Ni, V, Cd, Hg and Cr) were below detection limits. However, the concentration of Fe ranged between 0.53 \pm 0.11 mg/l 1.06 ± 0.26 mg/l. With the exception of salinity, TDS and TSS, the levels of other physico- chemical characteristics including the trace metals were within the permissible limits set out by Nigeria's Department of Petroleum Resources (DPR). © JASEM

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KEY WORDS: Physico- chemical characteristics, Produced water, oil terminals, Heavy metals, oil industry facility.

Introduction

Wastes of different types and characteristics are largely generated in the oil and gas industry. Of these, liquid wastes constitute a significant percentage.

In most crude oil-bearing formations, the rocks are generally permeated with fluids such as water, oil, gas or some combination of these fluids (Amyx *et al.* 1960).Water and other fluids in the reservoir, when brought to the surface, constitute the produced water.

It is, by far, the largest volume byproduct or waste stream associated with oil and gas production (Mofat and Olof, 1995). Indeed, both intentional and unintentional discharges of produced waters have been associated with oil production.

Although attention on environmental degradation has always been focused on oil spillage, there is abundant

evidence to show that much of the degradation comes from petroleum related facilities and installations (Ibiebele, 1986; Dessel and Omuka, 1994 Mofat and Olof, 1995 and Obunwo *et al.*, 2006).

An investigation 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.

This study is thus aimed at assessing the physicochemical characteristics of produced water from terminals of some oil industry facilities in the Niger Delta, Nigeria and to compare the data obtained with standards set out by the regulatory bodies in the country, since both intentional and unintentional discharges of produced waters have been associated with oil production. 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). The researchers 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.

In Nigeria, studies by Oboh *et al.*, (2009), noted that discharged produced waters had high metal ions and total hydrocarbon concentrations. Okoro (2010), on the other hand, demonstrated that produced water discharges in near shore environment in the Niger Delta led to substantial accumulation of hydrocarbons and microorganisms up to 500m from discharge points. Isehunwa and Onovae (2011) observed that the produced water discharged into the environment in the studied areas had high levels of oil and grease as well as TDS and TSS.

The coastal aquatic ecosystems of the Niger Delta region of Nigeria have of recent received much attention because of the considerable man-mediated perturbations these fragile environments have been subjected to. In this study, two key oil centres in the Niger delta region, Warri and Port Harcourt, were chosen as the sampling areas. Produced waters from a number of oil industry facilities in these areas were sampled.

MATERIALS AND METHODS

Samples of produced water were obtained from two (nearshore) terminals in Port Harcourt and Warri of the Niger Delta. Sampling was done in accordance with established guidelines and procedures (APHA, 2005). Samples for BOD analysis were collected in amber glass bottles while samples for other physicochemical parameters were collected in plastic containers. Samples for hydrocarbon analysis were collected in 1litre glass bottles. For measurements of heavy metal levels, few drops of concentrated nitric acid were added to the produced water collected in sample bottles. Sampling was carried out monthly for 12 months (January – December, 2012), to cover both wet and dry season periods.

In situ measurements of pH, temperature, conductivity, dissolved oxygen and turbidity were carried out with the thermometer and pH, conductivity/TDS, DO and Turbidity meters respectively. Analyses of other parameters, Salinity, Total Dissolved Solids (TDS), Total Suspended

Solids (TSS), Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD₅), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Anions (phosphate, sulphates and nitrates), Metals (Chromium, Copper, Iron, Lead, Zinc, Nickel, Cadmium, Mercury and Vanadium) and Total Hydrocarbon Concentration (THC), followed standard methods (APHA, 2005) in the laboratory.

RESULTS AND DISCUSSION

The results of the physico-chemical values at the two terminals as well as the permissible standards in Nigeria (DPR, 2002) are presented in Table 1. The mean pH values ranged between 7.49 ± 0.28 and 7.89 ± 0.30 ; the higher pH being recorded at the Warri terminal. Although, there was no significant difference (p<0.05) in pH at the different terminals, the apparent difference might have arisen from inherent geochemical properties of the formations. The pH values were, however, within permissible limits (6.5 - 8.5), implying that during the chemical treatment of the formations during production, pH was not adversely impacted.

Similarly, temperature, TOC, THC, nutrient parameters and the oxygen- related characteristics did not vary widely and were within the permissible limits. This trend is largely attributed to the large volume of water within the recipient environment which brings about massive dilution of the discharged produced water.

The mean TDS values indicated that higher levels were recorded at the Port Harcourt terminal (9205 \pm 2100mg/l) than at the Warri terminal (8428 \pm 2332mg/l). These levels are, however, higher than the permissible limits (5000mg/l) for nearshore area. The leaching of secondary salts might be contributory to the high levels of TDS in the produced water (Onojake, 2011). Discharge of such produced water with high levels of TDS into freshwater systems has the potential of affecting activities in the aquatic environment (Tubonimi *et al.*, 2010).

Mean salinity values were also higher at the Port Harcourt terminal $(7422 \pm 2280 \text{mg/l})$ than at the Warri terminal $(6108 \pm 1250 \text{mg/l})$. Salinity values at the two terminals were significantly different (p>0.05) and were also higher than the permissible limit (2000 mg/l). These results are in good agreement with earlier studies (Otto *et al.*, 1990; Jacobs *et al.*, 1992 and Cline, 1998) which had indicated that most produced waters were more saline than sea water.

On the other hand, although both levels exceeded the permissible limits (<15.0NTU), mean turbidity levels were higher at the Warri terminal (37.00 ± 9.60)

NTU) than at the Port Harcourt terminal (16.50 \pm 5.00NTU).

Mean Total Hydrocarbon Concentrations (THCs) varied widely at the two terminals. Concentration at the Warri terminal (36.90 ± 3.03 mg/l) was markedly higher than that at the Port Harcourt terminal (4.72 ± 1.59 mg/l) and also exceeded the permissible limit (20.0mg/l). Factors that affect the concentration of hydrocarbon in produced water include density, interfacial tension and type/efficiency of chemical treatment (Ali, *et al.*, 1999). These factors might be responsible for the marked variation of THC at the two terminals.

Although high levels of metal ions have been reported in produced water in a Nigerian oil facility

(Oboh *et al*, 2009), there was no evidence of high metal levels in the terminals of the two oil facilities in Port Harcourt and Warri during the study period. With the exception of Fe, the metal levels were generally below the detection limits of the Atomic Absorption Spectrophotometer (0.001mg/l). The mean Fe levels at the two terminals were Port Harcourt (1.06 \pm 0.26mg/l) and Warri (0.53 \pm 0.11mg/l). It had been reported (Vittt *et al*, 2003) that the concentration of metals in produced water was field specific and related to the age and geology of the rock formation from which the oil and gas were produced. We thus attribute the high Fe level at the Port Harcourt terminal to the geology of the rock formation there.

TABLE 1 : Physico-chemical	characteristics of produced water at Port Harcourt and			
Warri terminals				

<i>ai</i>	Warri terminals					
S/no	Parameter	Port Harcourt terminal	Warri terminal Mean	Permissible limits		
		Mean	Witchi	mints		
1	pН	7.49 ±0.28	7.89 ± 0.30	6.5 - 8.5		
2	Temperature °C	25.50 ± 0.35	24.40 ± 0.35	30		
3	TDS (mg/l)	9205 ± 2100	8428 ± 2332	5000		
4	Salinity(mg/l)	7422 ± 2280	6108 ± 1250	2000		
5	Turbidity (NTU)	16.00 ± 5.00	37.00 ± 9.60	<15		
6	DO (mg/l)	3.07 ± 0.40	3.29 ± 0.40	N.A		
7	BOD ₅ (mg/l)	1.72 ± 0.48	1.46 ± 0.38	125.0		
8	COD (mg/l)	3.91 ± 1.32	3.91 ± 1.32	125.0		
9	TSS (mg/l)	8.50 ± 3.40	14.30 ± 5.10	<50		
10	Nitrate (mg/l)	1.90 ± 1.16	2.50 ± 0.26	N.A		
11	Phosphate (mg/l)	0.52 ± 0.12	1.07 ± 0.12	N.A		
12	Sulphate (mg/l)	21.70 ± 4.57	14.40 ± 4.57	200.0		
13	THC (mg/l)	4.72 ± 1.59	36.90 ± 3.03	20.0		
14	Fe (mg/l)	1.06 ± 0.26	0.53 ± 0.11	N.A		
15	Zn (mg/l)	BDL	0.05 ± 0.01	5.0		
16	Cu (mg/l)	BDL	BDL	N.A		
17	Cr (mg/l)	BDL	BDL	N.A		
18	Pb (mg/l)	BDL	BDL	N.A		
19	Ni (mg/l)	BDL	BDL	N.A		
20	Cd (mg/l)	BDL	BDL	N.A		
21	V (mg/l)	BDL	BDL	N.A		
22	Hg (mg/l)	BDL	BDL	N.A		

Conclusion: The data of the physico-chemical characteristics on produced water discharged at the two terminals indicate that the aquatic environments of the oil facilities are not adversely affected by metal pollution. Desalination facilities may have to be installed to reduce the salinity of the discharged produced water.

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