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Evaluation and management of produced water from selected oil fields in Niger Delta, Nigeria

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ABSTRACT

Produced water which is the largest waste discharge from the production phase of oil gas wells has several components of toxic concern, ranging from heavy metals to soluble hydrocarbons. Management is normally aimed at minimizing or reducing the toxicity of discharged volumes. This study evaluated the physico-chemical properties and some trace metals constituents of ten produced water samples from five selected oil fields in Niger Delta to determine the extent of compliance with standards of discharge. The pH values ranged from 7.47 to 8.30; temperature ranged from 21.90 to 24.70°C; Alkalinity ranged from 49.00 to 340.00 mgL⁻¹; salinity ranged from 2700.00 to 4400.00 mgL⁻¹; turbidity ranged from 10.00 to 79.00; conductivity ranged from 126.50 to 198.00 μScm⁻¹; TDS ranged from 3200.00 to 7000.00mgL⁻¹; Mg²⁺ hardness ranged 47.00 to 100.00 mgL⁻¹; Ca²⁺ ranged from 94.00 to 200.00 mgL⁻¹. The concentrations of some trace metals like Zn, Cd, Cu, Pb, and Mn were within acceptable limits while others such as Fe, Cr and Ni are higher than the regulatory limit for nearshore. Most on the metals and physicochemical properties correlated positively showing strong association.

Keywords: produced water, oil fields, regulatory limit, management, Niger delta.

INTRODUCTION

Produced water is mainly salty water trapped in the reservoir rock and brought up along with oil or gas during production. It is a by-product of the production of hydrocarbons (oil and gas) from underground reservoirs. It consists of formation water, which is water naturally present in the reservoir, or condensed, water in gas production. Almost all offshore oilfields produce large quantities of contaminated water that can have significant environmental effects if not handled properly. Over the life of a well, the volume of water produced will exceed the volume of oil by

a factor of 3-6 times. The American Petroleum Institute estimates that in stripper oil well operations approximately nine barrels (378 gallons) of produced water are recovered for each barrel of oil [18]. Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities. This water is frequently referred to as connate water or formation water and becomes produced water when the reservoir is produced and these fluids are brought to the surface [9].

There is more in produced water than water and oil. In 1987, Neff described produced water for ocean discharge as containing up to 48 parts per million (ppm) of petroleum, because it has been in contact with crude oil in the reservoir rocks. There were also elevated concentrations of metals such as barium, beryllium, cadmium, chromium, copper, iron, lead, nickel, silver, and zinc including "small amounts of the natural radionuclides, radium226 and radium228 and several hundred ppm of non-volatile dissolved organic material of unknown composition which includes dissolved gases (hydrogen sulfide and carbon dioxide) [1,5].

When mixed with seawater, most physico-chemical features of produced water (low dissolved oxygen and pH, elevated salinity and metals) do not pose a hazard to water column biota, but in shallow, turbid waters, elevated concentrations of hydrocarbons may be detected in surface sediments up to about 1,000m from the discharge.

The discharge of produced water into the environment is becoming a serious concern because a wide range of pollutants which includes Hydrocarbons, inorganic salts, trace metals, production chemicals, and oil field chemical residues are also introduced into the environment.

Cline noted that produced waters from petroleum production operations are in most cases, more saline than sea water. Smith [14] has also confirmed the negative effects of produced waters on the Indonesian environment. However, studies have shown that where there is effective dilution, acute toxic effects of produce water are not expected to be found beyond 50m from the discharge point [10, 12]. Durrell [5] reported that oil companies operating in Norway have since the mid-1990s tried to develop efficient monitoring methods for discharged water.

Furthermore, the volume of produced water is expected to rise as many of the oil fields in the Niger Delta have aged and water conning is known to increase with the age of the field.

Metals are the main inorganic constituents thought to be of environmental concern. The most commonly studied metals are iron, cadmium, chromium, copper, lead, mercury, nickel, arsenic, and zinc. Due to different geological characteristics of the reservoirs, the results are characterized by considerable variability. For instance, gas fields usually provide higher values of heavy metals than oil fields; this is to say that the concentration of metals in produced water depends on the field, particularly with respect to the age and geology of the formation from which the oil and gas are produced. Produced water generated from mature fields has significantly less trace metal content than that from early production fields.

Produced water can have different potential impacts depending on where it is discharged. For example, discharges to small streams are likely to have a larger environmental impact than discharges made to the open ocean by virtue of the dilution that takes place following discharge. It is therefore imperative to have adequate knowledge of the constituents and general characteristics of specific produced waters for regulatory compliance and for selecting management/disposal or effective treatment options such as secondary recovery to reduce toxicity before disposal.

Proper management of produced water should start from accurate estimation of the volume produced. However, the study by Veil and Clark [16] shows that there is still a lot of challenges on this even in the United States.

In Nigeria, although there has been no reported environmental disaster of high magnitude associated produced water disposal, it is nevertheless a known fact that much of this waste produced water is dumped in the environment, especially during drilling operation.

This study is aimed at determining the physico-chemical properties of produced water from selected oil fields in Niger delta, to determine the extent of compliance with standard and global best practices for disposal into the environment.

MATERIALS AND METHODS

2.1 Description of study area and sample collection.

The study area is Rivers state which lies on longitude 6°55′ 7°05′E and latitude 4°57′4° 48′N. It is one of the most significant areas in hydrocarbon production in the Niger Delta Nigeria. The work is limited to a few fields within the Niger Delta region. Samples of produced water were collected from onshore locations of Awoba, Cawthorne Channel, Obigbo, Agbarah, and Imo river oil fields in accordance with established guidelines and procedures. Measurement of temperature and pH were done at the sampling point due to sensitivity of their values, while the analyses of other parameters were done in the laboratory. While the conclusions reached in this work could have been helped by many more samples, time and finance limited sample collection to these few fields.

2.11 Chemical analyses of produced water samples.

The samples were analyzed quantitatively in laboratory for the following physico-chemical parameters, pH, temperature, Alkalinity, salinity, turbidity, electrical conductivity, Total Dissolved Solids (TDS) using a state of the art instrument for simultaneous multi-parameter measurement (U- 10, Horiba, LA-920, Kyoto, Japan). Mg^{2+} hardness, Ca^{2+} hardness, total hardness, and CO_2 were determined according to standard methods [8].

Trace metals such as Zn, Cd, Ni, Pb, Mn, and Fe associated with produced water were also determined using Atomic absorption spectroscopy (AAS).

RESULTS AND DISCUSSION

Table 1 is the result of physicochemical parameters of the produced water from the various fields.

Results obtained for pH varied between 7.54 and 8.30. These pH values are within allowable maximum limits for inland and near shore of 6.5 - 8.5 (table 3).

Akalinity values ranged from 49.00 to 340.00 mgL⁻¹ for samples from the various fields. The salinity values also ranged from 2600.00 to 4400 00 mgL⁻¹, the maximum limit set by the regulatory bodies for salinity as is 600.00 mgL⁻¹. The values obtained from the analysis of the produced water samples are far more than the maximum limit for inland and near shore. This is particularly worrisome as highly alkaline water often has high pH and contains elevated levels of dissolved solids/metals and also determines the ability of the water body to support algal growth and other aquatic life [4].

Turbidity ranged from 10.00 to 79.00 NTU for analyzed produced water samples. The limit set by regulatory body in Nigeria is 10NTU for inland and nearshore areas. All the samples have turbidity values above the set limit except samples from field OBI with turbidity of 10 NTU. Knowledge of turbidity variation in water measurement is of prime importance to water treatment operation because it is used in conjunction with other information to determine whether a supply requires special treatment by chemical coagulation and filtration before it may used for a public purpose [2].

Conductivity ranged from 126.50 to 198.00 μ Scm⁻¹. There is a relationship between the variables and conductivity which might be due to leaching of secondary salts and dissolved elements in the produced water samples [12].

The value of TDS ranged from 3200 to 7200 mgL⁻¹. These values are far higher than the regulatory limit of 2000 mgL⁻¹ for inland area. TDS a reflection of suspended and dissolved ions inherent in the produced water. It is an important indicator of the usefulness of water for various applications [15]. The concentration of the total dissolved solids which include heavy metals and dissolved salts, can be reduced by the installation of proper treating facilities.

Hardness of any water is caused by the presence of Calcium and Magnesium Carbonates. Total hardness, Magnesium and Calcium recorded for the produced water samples analyzed ranged from 141.00 to300.00 mgL⁻¹. The values of total hardness for the analyzed samples were significantly high; it was also observed that samples from the same geographical locations had closer range of values. This may have been influenced by the geological characteristics of the respective reservoirs. The effects of these high values of total hardness when discharged into any water body is that it can cause chocking and clogging in pipelines, formation of scales in boilers leading to wastage of fuel, overheating of boilers, scale deposition [6,17].

Carbon (iv) oxide concentration for the produced water samples ranged from 10.00 to 87.00 mgL⁻¹. Although there is no regulatory standard for CO_2 . It is usually produced in waters through

biological oxidation of organic matter, particularly in polluted waters. Some of the produced water samples have high concentration of CO_2 .

Detailed trace metals analysis helps to establish the degree of produced water toxicity before discharge into the environment. Table 2 shows the concentration of most of the trace metals in produced water samples from the studied fields were below the regulatory limits. However, the concentration Fe, Cr and Ni are higher than the regulatory limit for nearshore.

Though Cr and Ni are micronutrients, their concentration at ppb level are toxic to aerobic microbes while soils containing 0.2 - 0.4% of Cr are considered infertile for agricultural purposes [4]. Excessive levels of Ni in the environment might be toxic to some soil fauna, like earthworms, which are adjuncts to the microflora in organic matter decomposition and may reduce heterotrophic activity of the microflora and thereby causing reduction of plant growth [13].

3.1 Management of produced water.

A mixture of performance standards for the disposal processes and regulations limiting discharges mandates the standards for treatment of produced water. Produced water must be either be reused or disposed off. It can be used as a source of water for waterfloods or pressure maintenance or pressure maintenance projects [14]. If reuse is not option, produced water is disposed of by discharge to the sea or injection underground. Standards of treatment for reuse are set by industry technical organizations. Standards for produced water disposal are determined by State, National and international regulatory bodies.

In Nigeria the main regulatory agency, the Department of Petroleum Resources (DPR) requires the constituents of produced water to be within the limits indicated in Table 3, while mandatory sampling, analysis and monitoring are as indicated in Table 4 for discharge into inland, near shore and offshore and rate of monitoring produced water parameters in Nigeria to monitor compliance with standards and global best practices before disposal. However, there are no medium and long term strategies and guidelines in place to achieve continuous reduction in permissible discharges until zero discharge is achieved. Dehydration units for the treatment of produced water are available at the terminals and disposal is mainly by the principle of dilution.

Table 1: Values of physico-chemical properties of produced water samples

Fields	Temp	pН	Alkalinity	Salinity	Turb	Cond	TDS	Mg Hard	Ca Hard	Total Hardness	CO ₂
CAW1	22.90	7.67	315.00	2700	18.00	148.10	6000	50.00	100.00	150.00	18.00
CAW2	23.40	7.54	285.00	2800	17.00	161.00	6500	49.00	98.00	147.00	10.00
CAW3	22.70	7.64	315.00	2600	20.00	148.00	3200	47.00	94.00	141.00	30.00
CAW4	23.20	7.81	270.00	3100	20.00	148.50	3700	50.00	100.00	150.00	20.00
AW1	22.40	7.89	237.00	3400	17.00	148.50	5100	83.30	166.60	250.00	45.00
AW2	22.70	7.67	251.00	3000	20.00	126.50	5150	51.00	102.00	153.00	34.00
AG1	24.70	7.89	340.00	4400	79.00	198.00	6270	85.00	170.00	255.00	79.00
AG2	21.90	7.67	315.00	3700	64.00	187.70	6100	100.00	200.00	300.00	87.00
OBI	22.40	8.30	49.00	3400	10.00	162.30	7000	49.00	98.00	147.00	19.00
IMR	22.70	7.47	286.00	2800	17.00	148.50	7200	47.00	94.00	141.00	17.00

Temp (°C), EC(µScm⁻¹), Turbidity (NTU), every other parameter is in (mg/L). All computations were done using Microsoft excel software.

Fields	Zn	Cd	Cu	Ni	Pb	Mn	Cr	Fe
CAW1	0.41	0.27	0.22	1.48	0.02	0.12	0.04	1.40
CAW2	0.40	0.10	0.22	0.76	0.01	0.18	0.03	1.40
CAW3	0.41	0.10	0.19	0.89	0.01	0.21	0.03	1.31
CAW4	0.42	0.20	0.22	0.94	0.01	0.16	0.04	1.37
AW1	0.32	0.26	0.31	1.51	ND	0.23	0.01	1.40
AW2	0.34	0.24	0.33	1.44	ND	0.20	0.01	1.34
AG1	0.61	0.60	0.43	2.48	0.01	0.44	0.02	1.25
AG2	0.59	0.64	0.36	1.90	0.01	0.44	0.02	1.27
OBI	0.42	0.19	0.31	0.98	0.01	0.23	0.03	1.90
IMR	0.49	O.21	0.32	1.24	0.01	0.26	0.02	1.90

Table 2: concentrations of trace metals in produced water samples in ppm

Table 3: Effluent Limitations for Inland/Nearshore Oil and Gas Installations for Oily Waste Water

Effluent characteristic	Inland area	Nearshore	Offshore
pH	6.5-8.5	6.5-8.5	No limit
Temperature °C	25	30	-
Oil/Grease content	10	20	40
Salinity	600	2,000	No limit
Turbidity	>10	>15	-
Total dissolved solid	2,000	5,000	-
Total suspended solids	>30	>50	-
Chemical oxygen demand	10	125	-
Biochemical oxygen demand	10	125	-
Lead	0.05	No limit	-
Iron	1.0	No limit	-
Copper	1.5	No limit	-
Chromium	0.03	0.05	-
Zinc	1.0	5	-
Sulphide mg/1	0.2	0.2	0.2
Sulphate (SO4-) mg/1	200	200	300
Mercury mg/1	0.1	-	-
Turbidity	10 NTU	10 NTU	10 NTU

Source: Environmental Guidelines And Standards for the Petroleum Industry in Nigeria (EGASPIN 2000).

Table 4. Stipulated rate of monitoring for produced water parameters in Niger delta

Effluent characteristic	Monitoring frequency
рН	
Temperature	
Electrical Conductivity	
Salinity as chloride	Once per week for production platforms, Tank-farms and terminals
Oil and grease	
Total Organic Carbon (TOC)	
Total Dissolved Solid (TDS)	
Biochemical Oxygen Demand (BOD)	
Chemical Oxygen Demand (COD)	
Dissolved Oxygen	
Phenols	
Sulphide	Once per month
Ammonia	
Total Phosphorus	
Heavy Metals	
Total Coliform Bacteria	
Hydrocarbon compounds e.g. Naphthalene, Benzene and Xylene	Once per year as requested by DPR

	Temp	pН	Alkalinity	Salinity	Turb	Cond	TDS	Mg Hard	Ca Hard	T. Hard	CO_2	Zn	Cd	Cu	Ni	Pb	Mn	Fe	Cr
Temp	1.00																		
pН	0.00	1.00																	
Alkalinity	0.37	-0.77	1.00																
Salinity	0.39	0.49	-0.01	1.00															
Turb	0.43	0.00	0.49	0.82	1.00														
Cond	0.37	0.37	0.20	0.79	0.84	1.00													
TDS	0.04	0.10	-0.27	0.26	0.14	0.37	1.00												
Mg Hard	-0.02	0.14	0.27	0.78	0.78	0.69	0.12	1.00											
Ca Hard	-0.02	0.14	0.27	0.78	0.78	0.69	0.12	1.00	1.00										
T. Hard	-0.02	0.14	0.27	0.78	0.78	0.69	0.12	1.00	1.00	1.00									
CO_2	0.10	0.10	0.35	0.81	0.91	0.72	0.03	0.93	0.93	0.93	1.00								
Zn	0.33	-0.05	0.37	0.63	0.85	0.87	0.35	0.54	0.54	0.53	0.67	1.00							
Cd	0.16	0.05	0.36	0.82	0.92	0.76	0.36	0.87	0.87	0.87	0.93	0.83	1.00						
Cu	0.21	0.27	-0.02	0.85	0.70	0.57	0.50	0.67	0.67	0.67	0.74	0.58	0.81	1.00					
Ni	0.35	0.09	0.39	0.80	0.86	0.62	0.26	0.78	0.78	0.78	0.85	0.64	0.91	0.83	1.00				
Pb	0.00	-0.13	0.21	-0.31	-0.15	-0.16	0.10	-0.20	-0.20	-0.20	-0.23	-0.11	-0.04	-0.33	0.08	1.00			
Mn	0.18	0.07	-0.67	0.80	0.90	0.80	0.30	0.76	0.76	0.76	0.89	0.85	0.88	0.83	0.76	-0.41	1.00		
Fe	-0.28	0.26	-0.67	-0.23	-0.51	-0.20	0.56	-0.45	-0.45	-0.45	-0.51	-0.10	-0.39	0.02	-0.38	-0.08	-0.21	1.00	
Cr	0.15	0.05	0.00	-0.36	-0.24	0.00	-0.17	-0.49	-0.49	-0.49	-0.47	0.03	-0.34	-0.67	-0.45	0.49	-0.46	0.06	1.00

Table 5. Pearson's correlation coefficient matrix (r) for physicochemical characteristics and some heavy metal contents in produced water.

3.12 Correlation analysis:

Pearson correlation coefficients for the data were evaluated to determine the level of inter-metal association and the values are shown in Table 5. Elemental pairs Zn/Cd (r = 0.83); Zn/Cu (r = 0.58); Zn/Ni (r = 0.64); Zn/Mn (r = 0.85); Cd/Cu (r = 0.81); Cd/Ni (r = 0.91); Cd/Mn (r = 0.88); Cu/Ni (r = 0.83); Cu/Mn (r = 0.83); Ni/Mn (r = 0.76); Pb/Cr (r = 0.49) significantly correlated with each other, suggesting that each paired elements have identical source or chemical phenomena, whereas the rest of the elemental pairs are poorly or not correlated with each other. The association of Cu with Ni and Cd with Ni in produced water may strengthen terrigenous sources or geo-chemistry [9]. Metals show correlation with the physico-chemical characteristics. Pairs such as Zn/sal., Cd/sal., Cu/sal, Ni/sal, Zn/turb., Cd/turb., Cu/turb., Ni/turb., Mn/turb., Zn/ cond., Cd/cond., Cu/cond., Ni/cond., Mn/cond., Zn/T.hard., Cd/T.hard., Ni/T. hard. Mn/T.hard. have strong positive correlation with each other suggesting their Physico-chemical associations. Cu/ TDS, Fe/TDS show moderate positive correlation with each other, whereas the rest of the metals and physico-chemical parameters either show negative correlation or are not correlated.

CONCLUSION

This study has shown that some physico - chemical properties of produced water from some of the Niger Delta oil fields are higher than the stipulated regulatory limit for discharge into the environment, Total dissolved solids, total suspended solids and some other parameters are still very high, continuous discharge of these produced water without adequate treatment will further damage our fragile environment. It is therefore recommended that adequate treatment, monitoring and re-use for irrigation or as industrial process water plan for produced water in the Niger Delta be put in place to ensure compliance with best global practices.

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REFERENCES

[1] Brendehaug, J. et al., A Preliminary Study, in *Produced Water*, J.P. Ray 1992.

[2] Clair, N.S. Perry, L.M. and Gene, F.P.. Chemistry of Environmental engineering and science: 5th ed. **2003**, McGraw- Hill companies Inc.

[3] Cline J.T. API Produced Water Management Technical Forum and Exhibition, **1998**. Lafayette, LA, USA.

[4]. Duffus, J.H. Environmental Toxicology. 2^{nd} ed. **1980**, Edward Arnold Publishers Limited, London. P 21 – 103.

[5] Durell G. et al., **2000**. 5th SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production. 26-28 June **2000**. Stavanger, Norway.

[6] Egereonu, U. Dike, R. Journal of Chemical Society Nigeria 2007 32:59-166

[7] Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN 2000).

[8] Franson, M.A.. Standard Methods for the Examination of Water and Wastewater. 14th ed. **1995.**, New York, USA, p150-152.

[9] Joel, O. F.et al., Journal. Applied Sci. Environ. Management. 2010, 14 (2) 37 - 41

[10]Johnsen, S. et al., Seventh SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, **2004**, Calgary, Society of Petroleum Engineers, Richardson, Texas.

[11] Neff, J. M. Elsevier Applied Science Publishers, 1987, London p. 469-538.

[12] Onojake M.C. et al., J. Water Qual Expo Health 2011, 3:91–99

[13] Osuji, L.C. and Onojake, C.M. Chemistry and Biodiversity. 2004. 1:1708 - 1715.

[14] Smith J.P. et al., Environmental Toxicology and Water Quality. 1998. 13(4): 323-336.

[15] Tobonimi, J.K.I. et al., Sciencia. Africana. 2010, 9: 154 - 165

[16] Veil, J. A. and Clark, C.E. SPE, Presented at the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Rio de Janeiro, **2010**

[17] World Health Organization. *Guidelines for drinking water quality*. 2nd ed. **1998**, p188.

[18] Yang, M. and Nel, T. SPE Annual Technical Conference and Exhibition, **2006.** San Antonio, Texas, USA.