GLOBAL JOURNAL OF ENGINEERING RESEARCH, VOL. 1, NO. 1, 2002: 51 -58

EFFECTS OF REFINERY EFFLUENT ON THE PHYSICO-CHEMICAL PARAMETERS OF STREAM WATER.

L. UYIGUE

(Received 30 July 2001; Revision accepted 14 December 2002)

ABSTRACT

Managing oil and gas industrial environment requires constant monitoring of the effluent discharges from such industries. The essence of such monitoring is to ascertain the level of compliance of such industries with the pollution control guidelines set by regulating agencies.

In this work, the effects of refinery effluent discharge on the physico-chemical parameters of the stream water has been studied, using treated effluent water discharged from the Port Harcourt Refinery into the Ekerekana Creek in Okrika as reference. Samples were collected at the discharge point into the Creek and subsequently at 500 metres and 1000 metres down stream.

The samples were analysed for physico-chemical parameters such as pH, TDS, TSS, COD, Oil and Grease, Temperature, Cations (Pb^{2+}, Fe (total), Cu^{2+}, Cr^{6+}, Ca^{2+}, and Mg^{2+}) and Anions (PO_4^{3-}, NO_3^-, SO_4^{2-} and Cl^-). The results showed that Oil and Grease, COD, Cations (Pb^{2+}, Fe (total)) and temperature were affected by dilution, and are stated as follows: oil and grease, 24 to 7mg/l; Iron (Fe (total)), 1.0 to 0.16 mg/l; lead (Pb^{2+}), 0.035 to 0.006 mg/l; COD, 7 to 1mg/l and temperature, 24.1 to 22.0°C.

Keywords: Effluent water, Concentration, Dilution, Physico-chemical parameter, Pollutant.

INTRODUCTION

Effluent water is often referred to as produced or waste water; such water contains fundamentally some quantity of substances in such a concentration that makes the water technically polluted (Madian et al, 1994). The sources of this water in the oil and gas industries comes from oil bearing formations, oil reservoirs and crude oil storage tanks. Other miscellaneous sources includes liquid discharges from production operations, accidental oil spills from leakages, deck drainages, and sour water stripper condensate. Others are contaminated process water, desalter water, caustic water and oily water from ships ballast (Jamaludin and Vandamme, 1994).

For about three decades now, the Niger Delta environment has experienced degradation due mainly to the discharge of noxious effluents both at fugitive points and pipe ends, by oil and gas industry operators. In the wake of a renewed environmental awareness on the negative impacts of such discharges on the environment, there is need to regularly assess the effluents so discharged. The essence of such assessment is to ascertain the level of compliance with the pollution control regulation, governed by the principal legislation of the Petroleum Act (1969) and enforced in Nigeria by the department of petroleum resources (DPR) and the federal ministry of environment (DPR, 1991).

Effluent water, if not treated will have some adverse effects on aquatic life, inhabitants and farmlands. It has been reported that heated effluent water increases the temperatures of the receiving river water body, leading to increased oxygen consumption of fish for metabolic processes, thereby decreasing oxygen concentration in water. The swimming speed of some fish species declines at higher temperatures, hence 19°C makes them

L. UYIGUE, Department of Chemical Engineering, University of Port Harcourt, Choba, Port Harcourt.

susceptible to predators and consequently reduces fish resistance to diseases (Harrison, 1990).

The presence of nitrogen and phosphorus in effluent water discharge has been found to encourage algae growth and presence of hydrocarbon can cause bacterial and fungal growth. This may lead to reduction in the population of plankton and undesirable fish infestation (Elf, 1993, Hilde and Stale, 1994).

The consumption of effluent water leads to infected concentration of heavy metal in human systems causing metabolic malfunctions. These metals are cadmium, chromium, mercury and lead. Also the consumption of fishes infected with mercury may result in the minamata disease. (Nwankwo and Irrechukwu, 1991).

Taste and odour of water contaminated with effluent water are usually found to be objectionable due to the presence of soluble hydrocarbons. Consequently, McKee (1972) predicted the solubility of modern gasoline in ground water to be in the range of 20 to 80 mg/l. The water was however found to be tasty at solubility range of 0.005mg/l to 0.5 mg/l. Nitrate also produces bitter taste in polluted water and may cause methemoglobinemia in infants under six months (Ajao et al, 1991).

Oil remains a major effluent water pollutant when discharged on farmland. It increases aerobic condition in soil, thus reducing soil oxygen content. Hence transpiration and evaporation from soil is drastically reduced (Toogood and Rowell, 1977). Associated vegetation also show peculiar symptoms of leave yellowing, total chlorosis, premature abscission and necrotic spots. (Odu, 1981).

The pH value of the polluted soil may increase and brings it to neutral level irrespective of original status. Increase in the pollutant level may decrease the phosphorus level as in the case of Obagi. Total nitrogen may increase as well as potassium whilst calcium decreases (Elf, 1992).

Previous works done on physico-chemical analysis are widely reported in the literature but notable ones in the Niger Delta area are those of Obagi Creek and the Upomami flow station respectively (Elf, 1992, 1994). In the latter, three sampling points (SP1, SP2 and SP3), each 500 metres apart on the Upomami Creek were used for the study. The results showed that lead ions (Pb^{2+}), TSS, pH, Turbidity and TDS responded positively to dilution while other parameters, such as Copper ions (Cu^{2+}), Zinc ions (Zn^{2+}), Chromium ions (Cr^{6+}), Total iron (Fe), COD and BOD exhibited partial-dilution (Elf, 1994).

Effluent water from Obagi flow station was analysed for physico-chemical parameters such as Turbidity, BOD, COD, ammonium ions, oil and grease, phenolic compounds, salinity, TSS and total iron. The results showed that TSS and total iron exceeded their DPR limits (Elf, 1992).

EXPERIMENTAL

Prior to water sample collection the following controlling factors were noted, they are existing water quality, the rate of mixing, dilution, dispersion and the tidal influence.

Great dilution of the discharge effluent is expected at high tides than at low tides. Thus Ekerekana Creek is under tidal influence, it comes at about 4pm daily and return at night. The time of sample collection was when the tide was returning.

Samples were obtained at surface level from three linear points along the Ekerekana – Okrika Creek. One is at the effluent discharge point (WSP1), the second at 500 meters away from discharge point (WSP2) and another at 1000 meters away from discharge point (WSP3). While WSP1is to serve as control.

Collected samples from these three points were analysed in accordance with the department of petroleum resources (DPR) recommended test methods for physico-chemical parameters (DPR, 1991).

The physical parameters measured were sample pH and sample temperature using the pH meter. The pH meter was standardised using a buffer solution of pH 4, 7 and 10. The pH electrode was washed with distilled water and immediately immersed in a beaker containing the sample. The readings were taken from the pH meter (including the sample temperature).

The total dissolved solid (TDS), total suspended solid (TSS), chemical oxygen demand (COD) and oil and grease were measured by the chemical methods discussed here under.

(a) Total dissolved solid (TDS)

A porcelain dish was dried at 105°C in an oven for one hour and 50mls of sample was filtered into the pre-weighed porcelain dish using a 0.45 micron membrane filter.

The filtrate in the weighed porcelain dish was evaporated to dryness using an evaporating bath and the porcelain was dried again in the oven at 105°C for another one hour. The porcelain was subsequently reweighed.

$$\text{TDS (mg/l)} = \frac{((\text{weight of porcelain} + \text{Residue}) - (\text{weight of porcelain})) \times 10^6}{\text{Volume of sample}}$$

Precision = ± 0.001

(b) Total Suspended Solid (TSS)

With the aid of forceps, faintly marked membrane filter papers were dried in an oven at 105°C for one hour and placed in a dessicator to cool for another one hour. The membrane filter papers were weighed and weight recorded.

The weighed membrane filter paper was placed into a membrane filter paper holder and subsequently soaked with cleaned distilled water and tightened with the Millipore spanners. 50mls of sample was filtered using the 0.45 micron membrane filter and the membrane filter is further dried in an oven at 105°C for an hour, and placed in a dessicator for another one hour and reweighed.

$$\text{TSS(mg/l)} = \frac{((\text{weight of 0.45 membrane filter} + \text{Residue}) - (\text{weight of 0.45 membrane filter})) \times 10^6}{\text{Volume of sample}}$$

Precision = ± 0.001

(c) Oil and Grease

250mls of sample was measured into a separating funnel and 50mls of xylene was added. The mixture was thoroughly shakened so as to enable xylene mix with oil and grease.

The water was decanted, while the xylene-oil and grease mixture was ran into a glass tube. The xylene-oil and grease mixture was centrifuged for 10minutes and allowed to cool. The sample was read in a spectrophotometer in percentage. From the percentage, absorbance was read out in a chart and the concentration in parts per million (ppm) was determined from the graph.

$$\text{Oil + grease (mg/l)} = \frac{\text{ppm} \times (\text{volume of oil and grease + xylene mixture})}{\text{Volume of sample}}$$

Precision = ± 0.001

(d) Chemical Oxygen Demand (COD)

10mls of sample was homogenised for 5 minutes and 0.2ml was pipetted out into the COD vial. The cap was replaced tightly and the COD vial rinsed with distilled water and inverted several times for sample to mix with the vial.

The sample in the COD vial was heated in a COD reactor for one hour and removed to cool for another one hour also. The sample was taken to Hach DR/2000 for reading.

Precision = ± 0.001

(e) Cations and Anions

The concentrations of cations and anions in the sample were measured using the Direct Reading spectrophotometer (Hach DR/2000). The operation was based on program numbers and specific wavelengths using different powdered tablets.

RESULTS AND DISCUSSION

The results of the effluent water analysis

Cations/Anions	Program Number	Wavelength (nm)
Lead ions (Pb^{2+})	280	575
Copper ions (Cu^{2+})	135	560
Total Iron (Fe)	265	265
Chromium ions	90	540
(Cr^{6+})	160	800
Calcium ions (Ca^{2+})	150	850
Magnesium ions	490	890
(Mg^{2+})	780	620
Phosphate ions	355	500
(PO_4^{3-})	245	550
Sulphate (SO_4^{2-})		
Nitrate (NO_3^-)		
Chloride (Cl^-)		

Precision = ± 0.0001

are presented in the table and figures. Table 1 shows the results of the physical and chemical parametric measurements for surface water samples obtained from the three sampling points. Also shown in table 1 are the DPR compliance limits for inland and near shore areas.

Also, the spatial distributions of the surface water physico-chemical parameters for some selected parameters are presented in the figures. Figure 1 shows however, that temperature, chemical oxygen demand (COD), oil and grease are affected by dilution while pH is

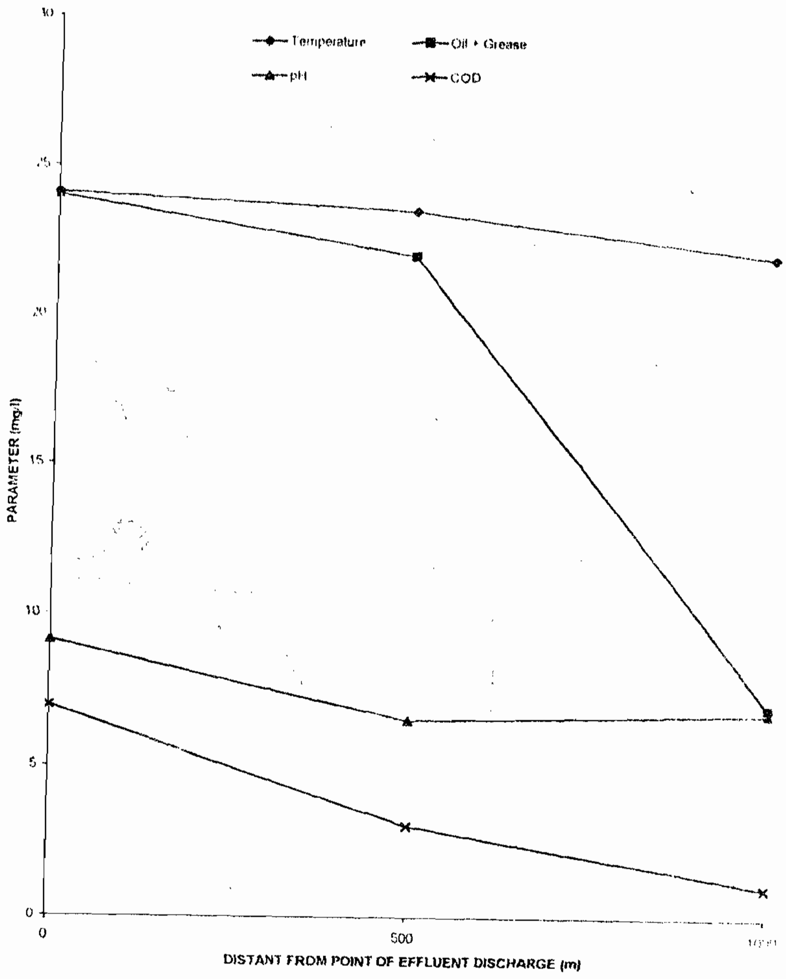

FIGURE 1: SPATIAL DISTRIBUTION OF SELECTED PHYSICO-CHEMICAL PARAMETERS MEASURED AWAY FROM POINT OF EFFLUENT DISCHARGE

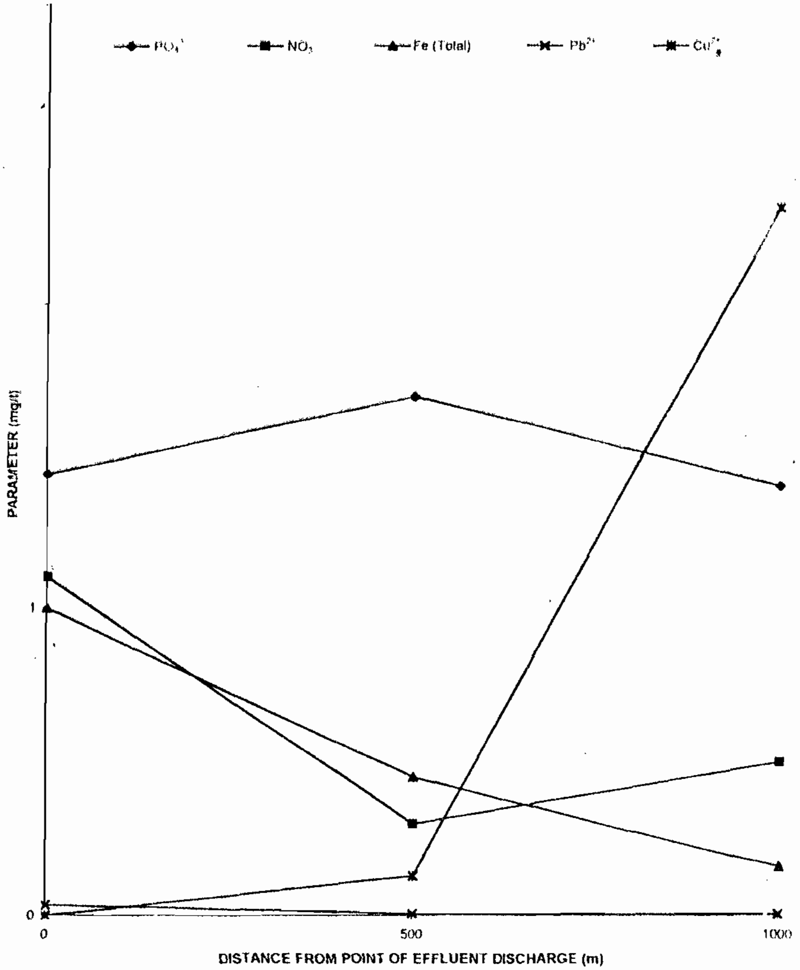

FIGURE 2: SPATIAL DISTRIBUTION OF SELECTED CHEMICAL PARAMETERS MEASURED AWAY FROM POINT OF EFFLUENT DISCHARGE

unaffected. The reason being that, the receiving stream water apart from being mildly acidic, hydrogen ion (H^+) concentration remains constant no matter the volume of the water.

Figure 2 shows that Total iron (Fe) and lead ions (Pb^{2+}) are affected by dilution while nitrates (NO_3^-) and phosphates (PO_4^{3-}) may be said to be partially diluted since the concentration at 500m sample point is lower than that at 0m sample point. Copper ions (Cu^{2+}) is however unaffected by dilution. Figure 3 shows that chloride (Cl^-), magnesium ions (Mg^{2+}), calcium ions (Ca^{2+}) and sulphate (SO_4^{2-}) are undiluted.

The increased concentrations (undilution) for some of these parameters may be due to the presence of slightly soluble residual impurities in the receiving stream water body, arising from leaching due to stream water contact with rocks and soils as well as human excreta and salt water intrusion, as in coastal areas (Harrison, 1990). The possible implication of this

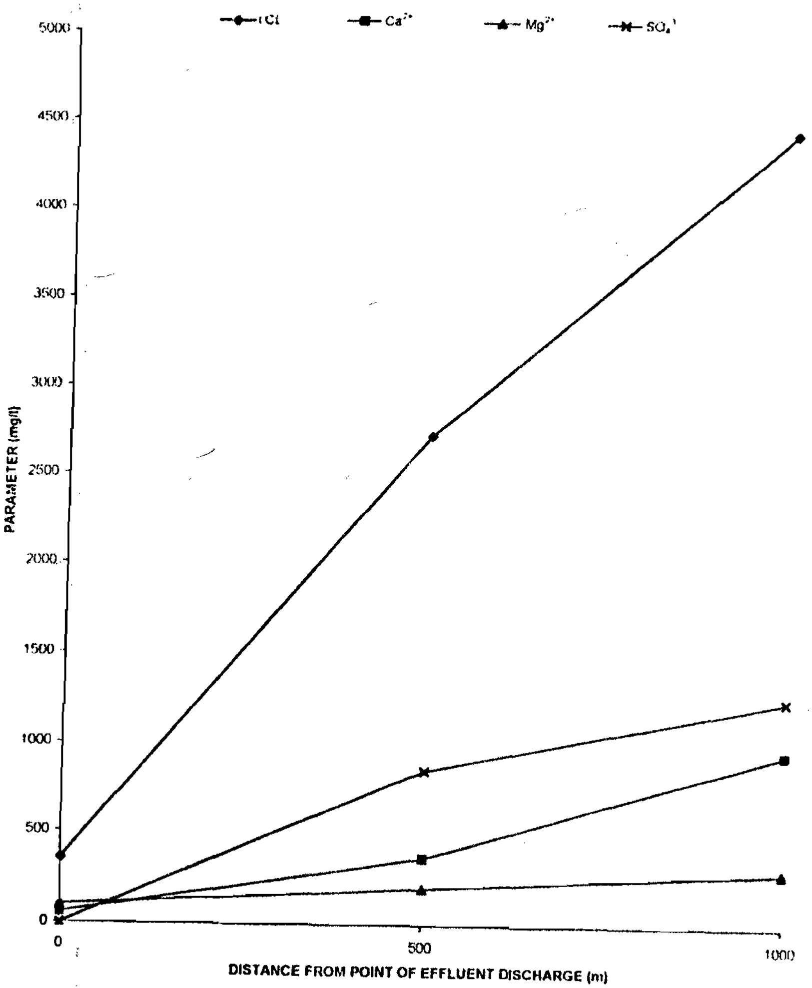

FIGURE 3: SPATIAL DISTRIBUTION OF CHEMICAL PARAMETERS MEASURED AWAY FROM POINT OF EFFLUENT DISCHARGE

phenomenon is a severe environmental problem such as hardness of water.

Apparently therefore, the results of this work obtained in the table and figures are at variance to the findings for Obagi Creek and Upomami flow station (Elf, 1992, 1994) except for total iron (Fe) that responded positively to dilution for both Ekerekana and Obagi Creek. This variance may be due to existing water body quality for the different creeks.

Consequently, the undiluted physico-chemical parameters (see table 1) of the effluent discharge along the creek such as pH, total dissolved solid (TDS), total suspended solid (TSS), calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}) and chloride (Cl^-) may be apparently due

TABLE 1: RESULTS OF PHYSICO-CHEMICAL ANALYSIS OF EFFLUENT WATER FROM THREE SAMPLING POINTS

S/No	PARAMETERS	DPR COMPLIANCE LIMITS MAXIMUM FOR ANY CONSERVATIVE 30-DAY PERIOD		WSP1 (0m)	WSP2 (500m)	WSP 3 (1000m)
	(A) Physical	Inland Area	Near shore Area			
1	pH	6.5 – 8.5	6.5 – 8.5	9.16	6.54	6.8
2	Temperature (°C)	35	40	24.1	23.5	22.0
	B(i) Chemical					
3	TDS (mg/l)	2000	5000	2360	13,120	22,220
4	TSS (mg/l)	30	50	154	176	316
5	Oil and Grease (mg/l)	10	20	24	22	7
6	COD	40	No limit	7	3	1
	(ii) Cations					
7	Pb^{2+} (mg/l)	0.05	No limit	0.035	0.007	0.006
8	Fe (Total) (mg/l)	1.00	-do-	1.00	0.45	0.16
9	Cu^{2+} (mg/l)	1.5	-do-	ND	0.13	2.32
10	Cr^{6+} (mg/l)	0.03	-do-	ND	ND	ND
11	Ca^{2+} (mg/l)	200	-do-	100	200	300
12	Mg^{2+} (mg/l)	150	-do-	60	364.5	951.71
	(iii) Anions					
13	PO_4^{3-} (mg/l)	20	No limit	1.43	1.69	1.39
14	NO_3^- (mg/l)	50	-do-	1.1	0.3	0.5
15	SO_4^{2-} (mg/l)	400	-do-	<0.01	850	1250
16	Cl^- (mg/l)	600	-do-	355.06	2728.01	4451.53

NOTE: ND = NOT DETECTED

to the presence of residual pollutants in the Ekerekana creek.

CONCLUSION

The reduction in concentration of physico-chemical parameters such as lead ions (Pb^{2+}), phosphate (PO_4^{3-}) and nitrate (NO_3^-) along the creek surface to such a level lower than the DPR compliance limits, indicates that the Ekerekana creek has very low potential for the above parameters.

The unusual increase in the concentration of other physico-chemical parameters such as TDS, TSS, calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}), sulphate (SO_4^{2-}) and chloride ions (Cl^-) along the creek surface may be attributed to existing residues of these impurities at Ekerekana Creek water body.

Consequently, the effluent water discharge from the Port Harcourt Refining Company (PHRC) may be said to be of acceptable quality than that of the creek.

NOMENCLATURE

DPR	=	Department of Petroleum Resources
TDS	=	Total Dissolved Solid
SP1	=	Sample Point One
SP2	=	Sample Point Two
SP3	=	Sample Point Three
TSS	=	Total Suspended Solid
COD	=	Chemical Oxygen Demand

BOD	=	Biological Oxygen Demand
WS	=	Water Sample
WSP1	=	Water Sample Point One
WSP2	=	Water Sample Point Two
WSP3	=	Water Sample Point Three
DR	=	Direct Reading
SPE	=	Society of Petroleum Engineers
PHRC	=	Port Harcourt Refining Company Limited.

REFERENCES

Ajao, E. A., Oyewo, E. O. and Orekoya, T. , 1991. The Effect of Oil Formation Water on some Marine Organisms. SPE Conference Proceedings. 80-81.

Department of Petroleum Resources (DPR). 1991. Environment Guidelines and Standards for the Petroleum Industry in Nigeria. Ministry of Petroleum Resources, Lagos. 5 - 120.

Elf Petroleum Nigeria Limited. 1994. Effluent Water sampling and Monitoring of Physico-chemical Parameters at Upomami Creek and Discharge Point. 1-15.

Elf Petroleum Nigeria Limited. 1992. Effluent Water sampling and Monitoring of physico-chemical Parameters at Obagi Flow Station. 1-20.

Elf Petroleum Nigeria Limited. 1993. Environmental Evaluation Report for Odhiage Spillage Point. (OML-58). Vol . 1 & 11. 15-42.

Harrison, R.M., 1990. Pollution: Causes, Effects and Control Royal Society of Chemistry, Cambridge. R. M Harrison 2nd Edition. 99-125.

Hilde, R. and Stale, J., 1994. Determination of produced water contaminants in the marine environment. SPE Jakarka 27151:479-484.

Jamaludin, A.K.M. and Vandamme, L.M. 1994. Produced Water Management in the Canadian Petroleum Industry. SPE Jakarta. 27133: 353-364.

Madian, E.S., Tarwanto, M., Snavely, E.S. and Jan, R.J. 1994. Treating of Produced Water and the Giant Arun Field. SPE Jarkata. 27130: 335-344.

McKee, J.E. 1972. Gasoline in Ground Water. Journal of Water Pollutant Control Federation. 44: 293-302.

Nwankwo, J. N. and Irrechukwu, D.O. 1991. Problems of Environmental Pollution and Control in Nigeria Petroleum Industry. SPE Conference Proceedings 102-107.

Odu, C.T.J. 1981. Proceedings from Seminar on: The Petroleum Industry and the Nigeria Environment VI. 143-152.

Toogood, J.A. and Rowell, M. J., 1977. Reclamation Experiments in the Fields in Reclamation of Agricultural Soil after Oil Spill. Part 1: Research J A. Toogood Edition. 34 - 64.