

IMPACT OF REFINERY EFFLUENT ON THE PHYSICOCHEMICAL PROPERTIES OF A WATER BODY IN THE NIGER DELTA

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Abstract. The physicochemical qualities of a refinery effluent and water and sediment of an effluent receiving water body were investigated. The treated refinery effluent contained very high concentrations of phenol (11.06 mg/l), oil and grease (7.52 mg/l), ammonia (8.52 mg/l), COD (91.76 mg/l), TDS (390.6 mg/l) and phosphate (6.2 mg/l), but low in sulphide, nickel, lead, copper and chromium, which were undetectable. High concentrations of phenol (5.13–16.38 mg/l), oil and grease (10.56–15.23 mg/l), and ammonia (4.31–13.17 mg/l) were observed in water and sediment samples respectively, at the point of effluent impact. A high concentration of sulphide (3.74 mg/l) was accumulated in the sediment at the point of impact of the refinery effluent, though it was undetectable in the effluent itself or water sample. The concentrations of these parameters as well as of phosphate, nitrate, zinc and COD declined progressively with distance from the point of impact but were still significantly higher than in control water and sediment in samples 1.5 km downstream from the point of impact. Higher concentrations of the pollutants were recorded in the dry season than rainy season except for phosphate and nitrate, which showed the reverse trend. Nickel, lead, copper, chromium and cyanide were neither detected in the effluent nor impacted water body.

Keywords. *contaminant concentrations, sediment accumulation, seasonal changes*

Introduction

Waste waters released by crude oil-processing and petrochemical industries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides, naphthylenic acids and other chemicals [22]. Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem [3, 4].

Various studies have shown positive correlation between pollutions from refinery effluents and the health of aquatic organisms. Previous observations [12] suggested a correlation between contamination of water and sediments with aromatic hydrocarbons from refinery effluents, and compromised fish health. An earlier study [14] demonstrated the accumulation of heavy metals with accompanying histopathology in *Oreochromis niloticus* exposed to treated petroleum refinery effluent from the Nigerian National Petroleum Corporation, Kaduna.

The Niger Delta is host to three of Nigeria's four refineries which generate large quantities of effluents daily. These effluents are discharged into natural water bodies after treatment. Though the compositions of the effluents are regulated by various laws, it is not known whether they comply with the legally accepted toxicant levels for refineries in Nigeria. Furthermore, the impact of these toxicants on the quality of the effluent receiving water body has not been investigated. The present study investigates

the quality of the refinery effluent and its impact on the physicochemical quality of Okrika arm of the Bonny River estuary, the body of water that receives the effluent discharged from the NNPC refineries in Port Harcourt.

Materials and methods

Description of the study area

The sampling stations investigated consist of five effluent receiving sites in the Okrika arm of the Bonny River estuary and the control site at Elechi Creek, all in the Niger Delta area. Sampling site I (S1), Ekerikana creek, is the effluent discharge point. Sampling sites II (S2), Okari Creek, and III (S3), Okrika station, are located 500 m and 1000 m respectively from sampling site I. Site IV (S4), Ogoloma, and site V (S5), Edemebiri, are located 500 m each on opposite sides of site III. Sampling site VI (S6), Elechi Creek, close to the University of Science and Technology Port Harcourt, is the reference (control) site, about 35 kilometers from the Okrika station. Human activities like fishing were observed in all the sampling stations except station I. All the stations also receive sewage input except station V (S5). The Okrika stations and Elechi creek of Bonny estuary are of brackish water type, and are mesohaline, with salinity values ranging from 14.4 to 19.1‰ with a mean value of 17.0‰±2.2.

Sample collection

Samples were collected once a month between July 1998 and March 1999. Composite water samples (sub-surface and middle depth) were collected at low tide with a 2 litre plastic hydrobios water sampler and transferred to clean 2 litre polyethylene containers and 250 ml capacity borosilicate glass bottles. Untreated effluent samples include the process waste water (PWW) derived from the refining process, the raw waste water (RWW) which is a combination of PWW and sewage that is channeled to the rotary bio-disk for treatment. Treated effluents include treated waste water (TWW) which is refinery effluent that has undergone both chemical and biological treatment to eliminate or reduce waste contents to acceptable levels, and the observation pond waste water (OPWW) which is a combination of treated waste water and non-processed waste water. These were collected in polyethylene containers and borosilicate bottles of the same capacity. They were rinsed several times with water or effluent samples at the point of collection. Sediment samples were collected with benthic sampler and transported in polyethylene bags. All samples were transported in ice chests and analyzed for pH and conductivity within 12 hours of collection. Other physicochemical parameters were analyzed later using refrigerated samples.

Water and sediment analysis

An HACH conductivity/TDS meter (Loveland, CO 80539) was used for conductivity and total dissolved solids determination. An HACH pH meter was used for pH determination. An HACH DR/2000 spectrophotometer was used for determination of dissolved oxygen, biochemical oxygen demand, nitrate, ammonia, sulphate and phosphate. An HACH COD reactor was used for chemical oxygen demand determination. All analyses were carried out following the procedures of HACH chemical company (1996). Phenol, oil and grease, alkalinity, chloride/salinity, sulphide and cyanide were measured by methods adapted from *Standard methods for the examination of water and wastewater* [1]. A Perkin Elmer 3100 atomic absorption spectrophotometer (Boston, MA 02118-2512, USA) was used for the determination of the heavy metals including nickel

(Ni), lead (Pb), zinc (Zn), iron (Fe), copper (Cu), and chromium (Cr). Sediment samples were air-dried by thinly spreading on a clean laboratory bench surface at room temperature, and brought to a relatively homogenous state by thoroughly mixing, and sieving with 2 mm mesh before being treated. In the case of fresh samples, large stones and roots were picked out before mixing and weighing. Moisture determination of duplicate samples of the sediment was carried out for dry weight correction. The sediment samples were then prepared (extraction method) for the various physicochemical determination following procedures of Stewart *et al.* [21].

Results

Composition of refinery effluent

The physicochemical qualities of the major effluents generated in the Port Harcourt refineries were investigated, and the level of contaminants estimated. The concentration of the most significant pollutants in the various refinery effluents are shown in *Table 1*.

Process waste water (PWW) is water that is intended to come into contact with hydrocarbons or treating chemicals at a refinery. Raw waste water (RWW) is a combination of PWW and sewage. Treated waste water (TWW) is refinery effluent which has undergone both chemical and biological treatment to eliminate or reduce waste contents to acceptable levels. The observation pond waste water (OPWW) is a combination of treated waste water and non-process waste water. Values represent the mean of seven samples collected over a period of seven months.

PWW contained the highest concentrations of oil and grease (26.42 mg/l), phenol (90 mg/l) and conductivity (1179.4 $\mu\text{S cm}^{-1}$), and significant quantities of BOD (75.3 mg/l), COD (155.3 mg/l), and ammonia nitrogen (22.35 mg/l). RWW on the other hand contained higher concentrations of BOD (216.0 mg/l), COD (232.1 mg/l) ammonia-nitrogen (26.01 mg/l) as well as the nutrient compounds namely phosphate (15.4 mg/l), nitrate-nitrogen (1.91 mg/l) and sulphate (30.31 mg/l) than the PWW. Treated waste

Table 1. *The physicochemical quality of Port Harcourt refinery effluents (mg/l)*

Parameters	PWW	RWW	TWW	OPWW
pH	07.93	8.3	6.03	8.47
conductivity ($\mu\text{S cm}^{-1}$)	1179.4	1146	774	495.2
BOD	75.3	216	22.08	5.28
COD	155.3	232.1	26.68	91.76
oil and grease	26.42	12.48	4.27	7.52
ammonia (N)	22.35	26.01	13.52	8.52
nitrate (N)	01.53	1.91	1.64	0.754
phosphate	01.11	15.4	6.81	6.21
salinity	19.52	18.62	16.92	13.1
phenol	90	69.112	1.84	11.06
sulphide	<0.01	<0.01	<0.01	<0.01
cyanide	<0.01	<0.01	<0.01	<0.01
sulphate	13.91	30.31	39.08	30.74
TDS	383.6	335.4	209.23	390.6
nickel (Ni)	<0.001	<0.001	<0.001	<0.001
lead (Pb)	<0.01	<0.01	<0.01	<0.01
zinc (Zn)	0.186	0.187	0.11	0.11
iron (Fe)	0.214	0.297	0.203	0.241
copper (Cu)	<0.001	<0.001	<0.001	<0.001
chromium (Cr)	0	0	0	0

water (TWW), showed a reduction in the level of virtually all the parameters observed in RWW, though significant concentrations of phenol (1.84 mg/l), oil and grease (4.27 mg/l), ammonia-nitrogen (13.52 mg/l), BOD (22.08 mg/l) COD (26.68 mg/l) and sulphate (39.08 mg/l) persisted. The OPWW contained high concentrations of the following parameters including COD (91.76 mg/l), oil and grease (7.52 mg/l), phenol (11.06), TDS (390.6 mg/l) and iron (0.241 mg/l) which were observed to be higher than in the TWW. Other parameters remained fairly constant while ammonia nitrogen and BOD showed reduction in concentration. Sulphide, cyanide, nickel, lead, copper and chromium were not detected (<0.001 mg/l) in the refinery effluents before and after treatment.

Contaminant levels at the point of impact of the effluent

The average level of contaminant in the effluent receiving water body within ten meters around the point of effluent discharge, henceforth referred to as the point of impact (POI), is shown in *Table 2*.

Higher concentrations of oil and grease (10.56 mg/l), ammonia nitrogen (4.31 mg/l), phenol (5.13 mg/l) and COD (41.19 mg/l) were observed in the water sample at the POI of the effluent than the OPWW. The concentrations of zinc and sulphate were lower in the water sample than in the OPWW while sulphide and lead were not detected. The concentration of oil and grease (15.23 mg/l), ammonia nitrogen (13.17 mg/l) and phenol (16.38 mg/l) in the sediment samples were much higher than observed in both the river water samples and the OPWW. High levels of sulphide (3.74 mg/l) was observed in the sediments at the POI and represents a significant observation considering that sulphide was neither detected in any of the refinery effluents nor in the river water sample at the point of impact. Zinc was also concentrated many times in the sediment above the values seen in the river water sample and the OPWW.

Variations in the physicochemical properties of water and sediment samples

The physicochemical properties of the effluent receiving water body were evaluated for a distance of approximately 1.5 km from the point of impact of the effluent for 9 months. Mean phenol concentration of 5.13 mg/l was observed at the POI (S1), decreasing rapidly to about 0.006 mg/l at station 5 (about 1.5 km away). The phenol concentration at the control, not impacted water body, station 6 (approximately 35 kilometers away), was approximately 0.001 mg/l (*Fig. 1*).

Table 2. Comparative chemical quality of the observation pond waste water, water and sediment samples from the point of impact of the Port Harcourt refinery effluents

parameter (mg/l)	OPWW	samples from the point of impact (POI)		FEPA effluent limitations guideline (1991) mg/l
		water sample	sediment sample	
BOD	5.28	2.76	ND*	10.00
COD	91.76	41.19	ND	40.00
oil and grease	7.52	10.56	15.23	10.00
ammonia (N)	8.52	4.31	13.17	0.20
phenol	11.06	5.13	16.38	0.50
sulphide	<0.01	<0.01	3.74	0.20
lead (Pb)	<0.01	<0.01	0.01	0.05
zinc	0.11	0.05	0.21	NI
phosphate	6.21	0.06	0.14	NI

*ND: not done; NI: not indicated. Values with the 'less than' (<) sign were below detection level.

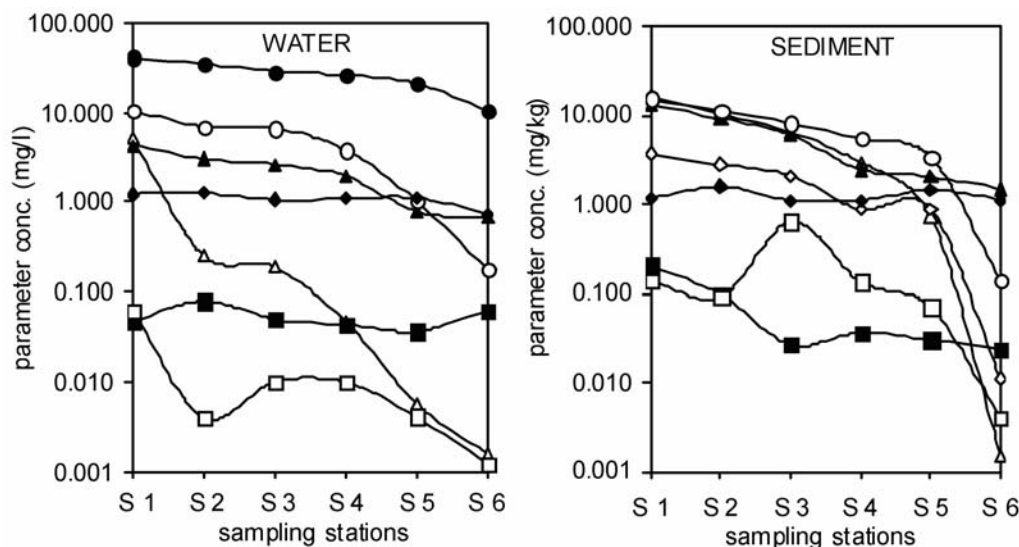


Figure 1. Changes in the concentration of $\text{NH}_4\text{-N}$ (\blacktriangle), nitrate-N (\blacklozenge), sulphide (\diamond), phosphate (\square), oil and grease (\circ), COD (\bullet), zinc (\blacksquare) and phenol (\triangle) in water and sediment obtained along the course (Stations S1-S5) of a refinery effluent polluted water body and from a control site (Station S6)

Other parameters including ammonia nitrogen, oil and grease, and COD showed similar patterns of variations, with highest values observed at the point of effluent impact and declining rapidly up to a distance of 1.5 km from the POI. The concentrations of these parameters at the control point S6, approximately 35 km upstream of the impacted water body were significantly lower ($p < 0.05$) than at the impacted sites. Phosphate and nitrate-N also showed significant decrease in concentration along the course of the impacted water body, but in a less dramatic manner than observed for the other parameters. Zinc showed little or no variation along the course of the impacted water body, with the average values obtained not significantly different from those obtained at the control station S6. Regression analyses of the curves confirm the above observations and showed very strong correlation between concentration and distance from the point of impact for COD, phenol and $\text{NH}_4\text{-N}$ ($R^2 > 0.96$) strong correlation for oil and grease ($R^2 \approx 0.93$), low correlation for nitrate and phosphate ($R^2 \approx 0.63$) and no correlation for zinc ($R^2 = 0.05$).

The pattern of variation in the concentrations of the sediment quality parameters was generally similar to those observed for the water samples. However, the absolute concentrations of the parameters were higher in the sediment (sometimes up to 10 times) than in the water samples. Significant differences ($P < 0.05$) were also observed in the concentration of sediments parameters obtained from the least impacted area and control sites, exceeding tenfold in the cases of phenol, oil and grease and sulphide. The most significant difference in sediment quality parameter was observed for phenol which showed over 300 fold difference between S5 and S6. Another conspicuous case was that of sulphide which, though not detected in any of the refinery effluents or the impacted water sample was found in significant concentrations in the sediment samples and up to 1 mg/l even at a distance of 1.5 km away from the POI. While the concentration of phosphate in the sediment was generally much higher in the impacted water body than the control sampling station, no clear relationship between concentration and distance from the point of impact was observed. Zinc concentration in the sediment showed a more predictable decline from S1 to S5 ($R^2, 0.75$) while nitrate-

nitrogen on the other hand showed no relationship whatsoever between distance and concentration (R^2 , 0.0073). Other water and sediment quality parameters investigated including DO, BOD, conductivity, chloride, alkalinity, sulphate, pH, temperature and iron did not show significant difference between the impacted and non impacted sampling stations. Nickel, lead, copper, chromium and cyanide, were not detected in the water and sediment samples of either the impacted or non impacted water bodies.

Seasonal changes in physicochemical parameters

Clearly visible seasonal changes in the concentration of the various water quality parameters were also observed. Generally higher concentrations of the respective parameter were observed in the dry season (December, January, February and March) than in the rainy season (July, August, September, October and November) (Figs. 2, 3 and 4). At the POI (Station 1, Fig. 2), phenol showed a seven fold increase in concentration from a relatively low value of 1.007 mg/l in July (the peak rainy season month) to 7.41 mg/l in December (the peak dry season month). A similar trend was observed for stations S2–S6.

However, when the mean value for the dry season months (December to March) were compared to the rainy season months (July to November), statistically significant differences were observed only in stations S1, S2, S3 and S6 ($P < 0.05$). A comparable seasonal trend was observed in the concentration of COD, $\text{NH}_4\text{-N}$, chloride, zinc, iron, DO, BOD, and oil and grease in the refinery effluent impacted water body (S1–S5) and the non impacted control station (S6). Chloride showed the most consistent variation in concentration with season, with significant differences ($P < 0.05$) observed in every one of the six stations sampled. The cases of phosphate and nitrate are worth noting in that they exhibited significantly higher concentrations in the rainy season than the dry season in contrast to the other parameters. Statistically significant seasonal variations in the concentration of the sediment quality parameters were also observed at some of the stations, but these differences were not as evident as in the water samples.

Discussion

Phenol is one of the major pollutants found in refinery effluents. It was found in large concentrations in both the PWW and the RWW. The major sources of phenol in the petroleum refinery PWW are the thermal and catalytic cracking processes. The observed values for phenol of 1.84 mg/l and 11.06 mg/l in the TWW and OPWW respectively were much higher than the 0.5 mg/l [9] or 0.1 mg/l [8] recommended for refinery effluents. High phenol concentration in the TWW was probably associated with the very high concentrations in the RWW that goes in for biological treatment in the rotary bio-disk which probably exceed the design limit. This does not however account for the much higher levels of phenol in the OPWW which was six times higher than in the TWW. This high concentration may be traced to large quantities of non process waste water (NPWW) which is channeled into the observation pond without treatment. Current observations show that the NPWW consist of product tank drains and spent caustic water as well as storm runoffs which contain large quantities of waste matters especially phenol (12.75 mg/l). Phenols have been observed to be very toxic to fish and other aquatic organisms and has a nearly unique property of tainting the taste of fish if present in marine environment in concentration ranges of 0.1 to 1.0 mg/l [5, 6, 20]. The toxic concentration for fishes may range from < 0.1 to > 100 mg/l, depending on the chemical nature of the phenol, the fish species and the developmental stage, with embryo-larval stages being

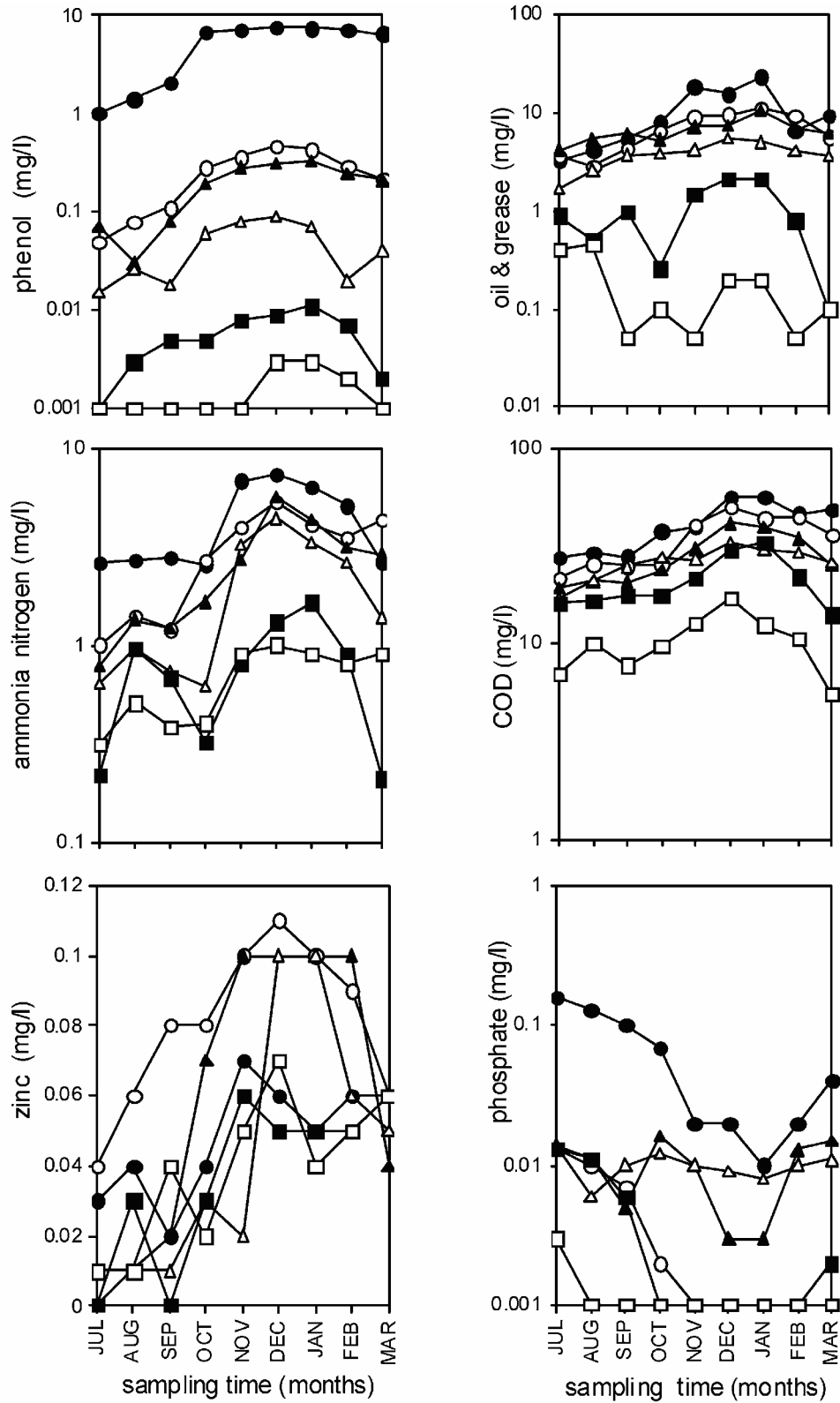


Figure 2. Seasonal variations in physicochemical parameters of water samples obtained from different sites along a refinery effluent impacted water body (●: station 1; ○: station 2; ▲: station 3; △: station 4; ■: station 5), and a non-impacted control water body (□: station 6)

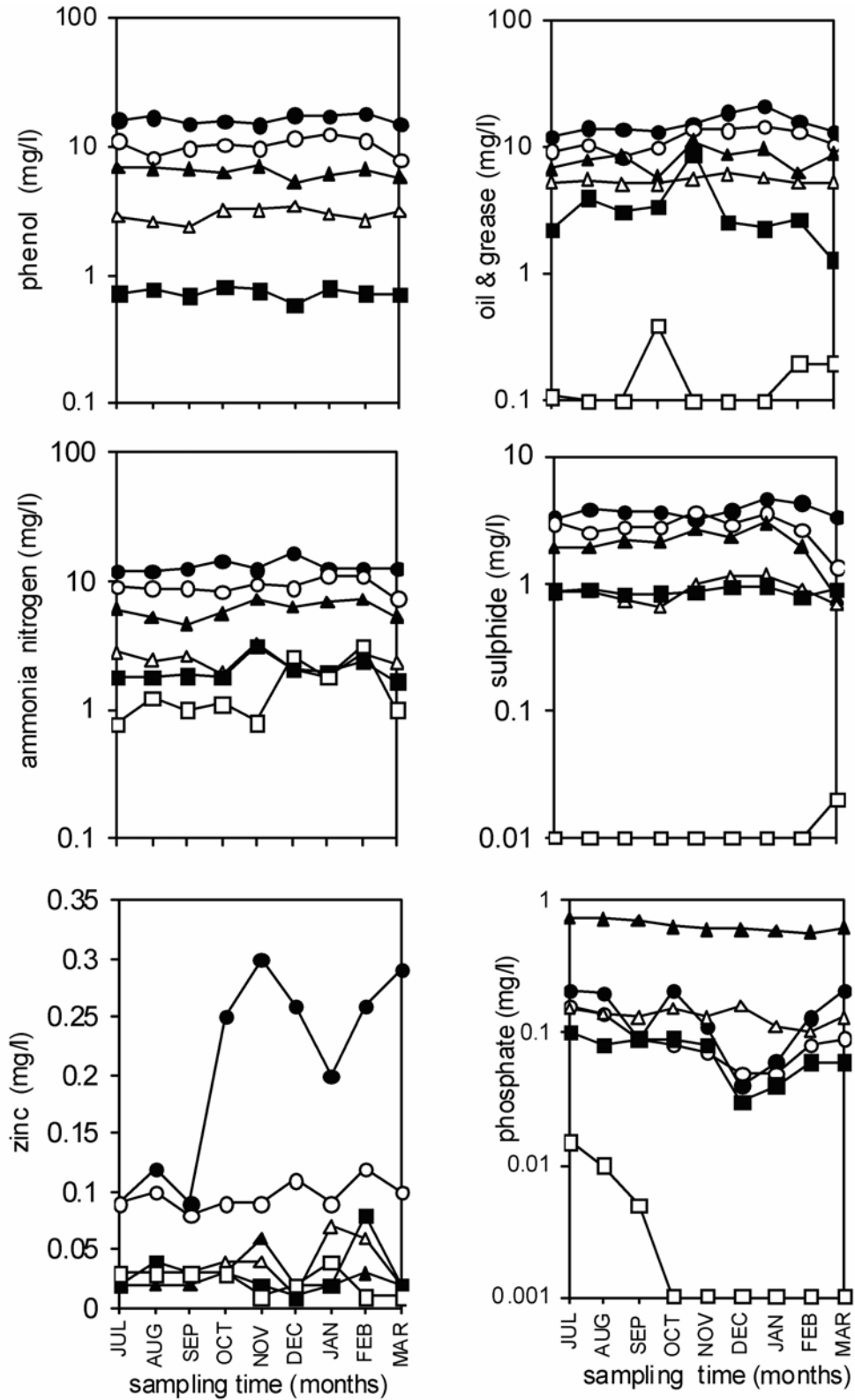


Figure 3. Seasonal variations in physicochemical parameters of sediment samples obtained from different sites along a refinery effluent impacted water body (●: station 1; ○: station 2; ▲: station 3; Δ: station 4; ■: station 5), and a non impacted control water body (□: station 6)

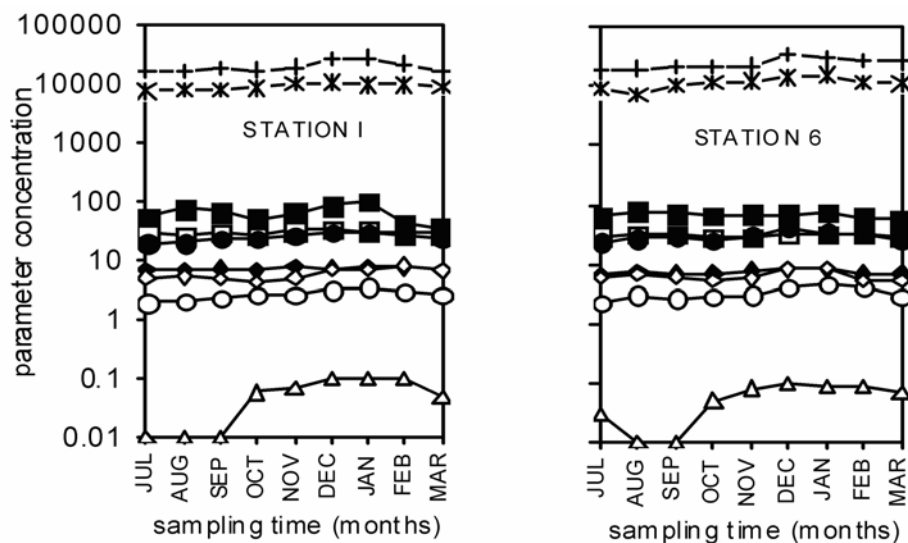


Figure 4. Seasonal variations in nine physicochemical parameters of water samples obtained from the effluent discharge point (station 1) and non-impacted control water body (station 6) seemingly unaffected by the effluent. +: conductivity ($\mu\text{S cm}^{-1}$); *: chloride (mg/l); ■: alkalinity (mg/l); ●: sulphate (mg/l); ○: BOD; ◆: pH; ◇: DO; □: temperature ($^{\circ}\text{C}$); Δ: iron (mg/l)

many times more susceptible than adults [7]. The concentration range of phenol in the sediments (18.02–0.58 mg/l) from the point of impact of the effluent up to a distance of 1.5 km down. Untreated refinery effluents generated by the refinery include the process waste water (PWW) derived from the refining process, and the raw waste water (RWW) which is a combination of PWW and sewage that is channeled to the rotary bio-disk for treatment. The treated effluents include treated waste water (TWW) which is refinery effluent that has undergone both chemical and biological treatment to eliminate or reduce waste contents to acceptable levels, and the observation pond waste water (OPWW) which is a combination of treated waste water and non-processed waste water stream, and is likely to have both acute and chronic effects on the marine organisms, especially the bottom feeders within the impacted areas. Verbal evidence from local fishermen suggests that the area around the point of discharge of the effluents is devoid of fishes and hence no fishing activity is carried out there anymore. Unpublished data also show a dramatic reduction in the number of viable microorganisms found in both water and sediment at the point of impact.

The NPWW was also responsible for the increased concentration of oil and grease in the OPWW and hence for the high level of this contaminant in the effluent receiving water body. The average concentrations of oil and grease in water and sediment (10.56 and 15.23 mg/l, respectively) at the point of discharge were found to be higher than the maximum permissible limit of 10 mg/l for the effluent. In effect, the water quality at the point of effluent discharge may be considered to be similar to an improperly treated effluent that is in need of further treatment action in order to reduce the contaminant concentrations to acceptable levels. Petroleum hydrocarbons have been observed to be toxic to aquatic life. It has been observed [16] that a water-accommodated fraction of crude oil or dispersed crude oil water-accommodated fraction increased the activity of gill citrate synthase, LDH, and hepatic ethoxyresorufin-O-deethylase (EROD) at a concentration of 14.5 mg/l. Lipophilic hydrocarbons have been observed to accumulate

in the membrane lipid bilayers of microorganisms and interfering with their structural and functional properties [19]. Grant & Briggs [10] concluded that hydrocarbons are the most significant cause of toxicity in sediment samples obtained from around a North Sea oil platform contaminated by large piles of oil based drill cuttings and that polar organic compounds, sulphides and ammonia are of much lower significance. The high oil and grease concentration observed in the effluent receiving water body in this study, in combination with other pollutants, could be responsible for the depletion of the fish and other aquatic life at the point of impact of the effluent.

Considering that natural waters typically contain little ammonia, usually in concentrations below 0.1 mg/l, and that the FEPA and DPR recommended maximum permissible limits in refinery effluents are 0.2 mg/l, the concentration of ammonia in the effluent, water and sediment of 0.21 to 16.8 mg/l were considered to be very high. Concentration of ammonia as low as 0.08 mg/l have been observed to reduce the swimming performance of coho salmon, an effect attributed to metabolic challenges as well as depolarization of white muscle [25]. Another study [23] observed a median lethal concentration (LC50) value of 0.045 mg/l for unionized ammonia (NH₃-N).

Other parameters that were significantly elevated in the water and sediment samples of the impacted water body are zinc, sulphide and phosphate. The concentration of zinc in the sediment is worthy of note as it increased from a basal level of approximately 0.025 mg/l at control sites to about 0.3 mg/l at the point of impact at the peak dry season month of November. Toxicity identification studies have indicated that zinc may be the primary cause of toxicity in certain contaminated aquatic systems [2]. High concentrations of zinc have been observed to be specifically toxic to an aquatic insect *Ranatra elongata* (1.658–2.853 mg/l), and in the microtox test system (1.35 mg/l) [18]. The case of sulphide is very interesting because it was not detected in the effluent nor water samples from the effluent receiving water body, but was found in significant concentrations in the sediment of the impacted water body. This highlights the important role of the sediment as a sink for toxic materials contained in the effluents. As observed earlier [24], contaminants from land-based sources introduced into surface waters rapidly become scavenged by suspended particles that tend to settle to the bottom where they become highly concentrated. The concentrations of phenol, oil and grease, and ammonia were also observed to be higher in the water and sediment at the point of impact than in the effluent from which they were derived. A number of factors may be responsible for this, including evaporation of water resulting in concentration of the toxicants to higher levels than found in the effluent and accumulation over time of trace concentrations of sulphide and other contaminants from the effluent over the 20 year period of operation of the refinery.

The COD value of the effluent discharged into the Okrika River did not meet the effluent limitation standard set by FEPA and DPR for refinery effluents in Nigeria largely as a result of the high COD values of the NPWW which was channeled without treatment into the observation pond. While the graded reduction in the COD values indicated an input from the refinery effluent mainly, the unpredictable distribution of BOD values on the other hand suggest input from different sources, the most important of which could be the faecal waste deposition by the surrounding communities.

Seasonal variations were observed in the concentrations of various water quality parameters, including those whose concentrations were related or unrelated to refinery effluent discharge. While most of the parameters showed higher concentrations during the dry season when water volume is reduced to its minimum two parameters namely, phosphate and nitrate showed reduced concentrations. Phosphates and nitrates are

components of agricultural fertilizers commonly used by farmers in the Niger delta area. These fertilizers may be leached into the rivers during the rainy season and thus account for the increased concentration in the Bonny river estuary during the rainy season. Phosphate level in the effluent receiving water body have been observed earlier to be associated with the refinery operation because of the changes in its concentration from the point of refinery effluent. The observed increase in concentration during the rainy season suggests an additional source of this nutrient in the Bonny river estuary, namely the surrounding farmlands. It was noted that urban storm water runoff is a major source of contaminants to southern California's coastal waters and responsible for detectable toxicity in the Ballona creek which drains a highly urbanized watershed [2].

This study has shown that refinery effluent discharged into the Okrika arm of the Bonny River estuary resulted in the presence of high concentrations of pollutant in the water and sediment. The toxicants have been shown to be present in concentrations which may be toxic individually to different aquatic organisms. Pollution of the aquatic ecosystem poses a serious threat to aquatic organisms and ultimately the entire ecosystem. The long term impact of refinery effluent discharge into the Bonny River estuary is not known. An eleven year study of the 1989 Exxon Valdez oil spill revealed that though the contaminants were rapidly eliminated by weathering [15], toxicity of sediments remained at a few heavily polluted locations around the Prince William Sound Alaska, which persisted ten years after the spillage [11]. A recent study [17] has shown that hydrocarbon may remain buried in sediment for up to 30 years without major alteration in concentration. Furthermore, the complex combination of toxic substances that are simultaneously present in refinery effluents may act synergistically and therefore impose a higher toxicity burden on the ecosystem than may be predicted in laboratory studies on individual toxicants [13]. Continued discharge of improperly treated effluent may further compound the worsening environmental problem of the Bonny River estuary, and the delicate ecological balance of the Niger Delta basin. An early resolution of the problem of treatment of the NNPC refinery effluent is therefore imperative in order to save the effluent receiving water body from further degradation.

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