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The Effect of Petrochemical Effluent on the Water Quality of Ubeji Creek in Niger Delta of Nigeria

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Abstract Water samples containing petrochemical effluents were evaluated for elemental contaminants along a kilometer distance in Ubeji Creek, a tributary of the Ubeji River in the Niger Delta of Nigeria. Twenty water samples were collected from six sites at various times. The water samples were analyzed for several physico-chemical parameters. Results showed wide varieties in temperature, pH, BOD, COD, dissolved and suspended solids as well as conductivity. The entire environment starting from the end-of-pipe source point was coated with black oily residue. Water quality parameters were very poor. The absence of fish and other aquatic lives, the high levels of Zn (2.4), Cr (0.24), Fe (63.44), Hg (4.24), Mn (2.49), and Pb (0.76) level (μg/L) confirm the toxic nature of Ubeji Creek. At the lower reaches, the mixing of effluent with brackish waters was not enough to support aquatic life, partly because of diminishing oxygen and toxic shock. Nevertheless, the study provides evidence to suggest that the water in Ubeji Creek is toxic. It also provides graphic data to suggest point source where effluents could be held for treatment or neutralization before being discharged into the aquatic environment.

Keywords Petrochemical effluents · Physico-chemical parameters · Water quality

Identification of effluents from industrial operations having diverse and significant environmental impacts in Niger Delta of Nigeria and evaluation of their impacts on the environment is of prime necessity. Data on the effects of petroleum effluents on aquatic life are few, although reports of homelands made desolate by oil pollution resulting in inter-ethnic conflicts exist (Benka-Coker and Ekundayo 1994; Amadi et al. 1996; Daniel-Kalio and Braide 2002; Ijah and Antai 2003; Simpson 2008). There is no doubt that petroleum has played an important role in the economy of the country, but over the past three decades, Niger Delta ecosystem has been subjected to destruction by petroleum product spillage and other effluents resulting from operational activities (Adeniyi and Afolabi 2002) with increase in processed petroleum products (effluents) that are discharged with little regard into aquatic environment. More than 90% of petrochemical plants in Nigeria are situated in the Niger Delta region (Essien and Antai 2005). In addition, most of them have low or no surveillance technologies of neutralizing oil effluents before disposal, leading to high level of pollutants in the environment (Li et al. 2005). Predicting the effects of these effluents is difficult because little is known of the basic biology of this tropical ecosystem (Benka-Coker and Ekundayo 1994; Osuji et al. 2004). New policies of industrial promotion and the trend towards privatization of government establishments especially Nigeria National Petroleum Company (NNPC) may accelerate environmental degradation by increased toxic levels of the pollutants. Some private enterprises have reported on the water quality of some impacted water bodies (Harrel 1985; Amadi et al. 1996). The qualities of these water bodies are marginal and in serious jeopardy. This is as a result of attempt at producing results that must be satisfactory to companies so as to sustain their contract agreements. In addition, sound strategies and monitoring methods for pollution control are lacking.

Gupta et al. (1981) reviewed a wide range of pollutants on test animals with increased temperature. Achuba and

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Osakwe (2003) reviewed the effects of oil pollution in a West African Environment. Wang et al. (1999), Essien and Antai (2005), reviewed the impacts of oil spills along the Nigerian coast. There is no report on a specific characteristics nature of pollutant in the oil with particularly reference to heavy metals. Therefore, the aim of the present study is to assess the impact of oil effluents on the water quality of Ubeji Creek by identifying and evaluating the levels of major elemental contaminants discharged into it. Ubeji is a remote village directly located behind a major petrochemical and refinery company. The landforms consist essentially of sedimentary basins and basement complex rocks (Ijah and Antai 2003). The implications of these rock formations allow permeability of fluids. The upper reaches of the Ubeji Creek runs alongside the petrochemical company, which was established in 1972. All the industrial wastes, untreated or minimally treated are discharged into Ubeji Creek, which runs immediately downstream from the end of pipe in a steep 0.5 m gradients. The wastes eventually end up in Ubeji River of which Ubeji Creek is a tributary. The petrochemical effluents heavily contaminate the shorelines, causing severe localized ecological damage to the near-shore community. The occupation of the human populations is mainly fishing and they depend on the creek as an outlet to the larger water. Therefore, the impact of the effluents cause serious toxic effects on the plankton on which the fishes depend.

Materials and Methods

Water samples were taken at six points along a 1-km distance of the creek. A reference point was taken before the discharge point (Site 0) this site was considered as a control point. An acid-cleaned, distilled water-rinsed containers fitted with string were used for collection of water. A 1 L container was lowered below water surface (about 5–10 inches) every 200 m. Temperature and pH (Corning PS pH meter, accuracy = 0.1) were recorded within 30 s in situ. Samples were stored on ice until arrival at laboratory. Aliquots were separated for the various tests and stored in a refrigerator at 2.5°C. Dissolved and suspended solids were determined by standard gravimetric procedures (Harrel 1985). Chloride, biological oxygen demand (5-day BOD) and chemical oxygen demand (COD) were determined by standard procedures (Achudume 2007). Strongly acidic or alkaline samples were neutralized to pH 7–8 before determination of BOD. Conductivity was determined with an electrolytic conductivity meter (Model MC-1, Mark V, by Electronic Switchgear, London).

For elemental analysis, water samples were acidified to a final concentration of 2% with nitric acid. Two samples were divided into two and portion of each half was spiked with known concentrations (0, 2.5, 5.0, and 10.0 ppm) of the 10 analytes in order to determined percent recovery. Unspiked samples, blanks and spiked samples were analyzed by Plasma Atomic Emission Spectroscopy (PAES). The PAES was standardized regularly once after analyzing five samples with matrix-matched standards (Inorganic Ventures, Lakewood, NJ). Standardization was verified with appropriate external standards (Spex Industries Inc., Edison, NJ). Analyte recovery in spiked samples ranged from 92% to 100%.

For analysis of mercury (Hg) in water samples, duplicate 50-ml sample aliquots were digested with sulfuric acid, nitric acid, potassium permanganate, and potassium persulfate at 95°C for 2 h. Elemental mercury was released from the digested samples by the addition of stannous chloride, amalgamated on silver wool, released by heating and measured by atomic absorption spectroscopy (AAS) using a Fisher Model HG-3 mercury analyzer (Spectro Products, Inc., North Haven, CT). The instrument was standardized regularly once after analyzing five samples with known concentrations of mercury (Spex Industries, Inc.) within the linear range of the instrument. Appropriate blanks and spiked samples were included in each run to verify standardization and determine percent recovery of Hg. Recovery in spiked samples was 98%–100%. The one-way analysis of variance (ANOVA) test was used to compare the mean values ± SD of elemental metals and for all parameters. Mean differences with $p < 0.05$ were considered statistically significant.

Results and Discussion

The concentrations (µg/L) of ten elements in water samples found in Ubeji Creek are presented in Table 1. Zinc, Fe, Hg, Mn concentrations in the water was elevated relative to most other sites. Lead and copper were moderate. The Fe concentration is very high followed by Hg in all the sites. Samples from sites 1, 2 and 3 had high levels of Zn, Fe, Hg and Mn (Fig. 1). In all the sites Fe and Mg concentrations were high.

Figure 2 shows the water temperature and pH at various sites in a progression from the end of pipe downstream to site 5 where thorough mixing of the effluents with brackish waters move on to the open bigger river. Figure 3 compares BOD and COD of each of the water samples in similar progression to site 5. Biological Oxygen Demand and COD in all sites were higher than recommended standards of effluent compliance limits 10 and 40 µg/L respectively for petrochemical plants for Nigeria surface waters as established by Federal Environmental Protection Agency (FEPA). Dissolved solids concentrations and suspended solids (Fig. 4) have high concentrations as also

Table 1 Concentration (μg/l) of 10 elements in water samples of Ubeji Creek Concentration (μg/l)

Site	Cd	Zn	Cu	Cr	Fe	Hg	Mn	Co	Pb	Ni
0	0.00 ± 0.001	0.05 ± 0.00	0.001 ± 0.000	0.000 ± 0.00	0.2 ± 0.1	2.5 ± 0.1	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.001	0.00 ± 0.00
	(0.00–0.000)	(0.00–0.10)	(0.003–0.00)	(0.00–0.001)	(0.12–20.8)	(0.02–4.98)	(0.00–0.00)	(0.00–0.00)	(0.0.–0.02)	(0.00–0.00)
1	0.037 ± 0.001	5.14 ± 0.00	1.961 ± 0.008	0.18 ± 0.01	131.3 ± 1.3	5.7 ± 0.3	7.61 ± 0.12	0.19 ± 0.00	1.331 ± 0.037	0.24 ± 0.01
	(0.02–0.67)	(1.25–9.03)	(0.01–0.2.88)	(0.00–0.39)	(104.53–170)	(0.03–10.99)	(0.07–14.98)	(0.02–0.39)	(0.06–2.66)	(0.01–0.42)
2	0.031 ± 0.004	2.71 ± 0.02	0.888 ± 0.007**	*0.13 ± 0.07*NS	68.1 ± 0.6**	4.7 ± 0.0	2.26 ± 0.01**	0.18 ± 0.02NS	0.876 ± 0.004**	0.15 ± 0.01
	(0.01–0.062)	(0.04–0.48)	(0.06–1.76)	(0.01–0.25)	(67.02–70.4)	(0.05–3.94)	(0.20–4.36)	(0.00–0.29)	(0.48–1.46)	(0.01–0.29)
3	0.015 ± 0.003NS	0.85 ± 0.04*	0.527 ± 0.033*	0.15 ± 0.06NS	38.0 ± 0.1**	4.1 ± 0.1	0.35 ± 0.00**	0.12 ± 0.01*	0.363 ± 0.030**	0.04 ± 0.01*
	(0.00–0.31)	*(0.25–0.70)*	*(0.21–0.85)*	*(0.01–0.31)*	*18.77–56.56*	*(0.02–0.82)*	*(0.18–0.52)*	*(0.01–0.21)*	*(0.04–0.73)*	(0.00–0.08)
4	*0.018 ± 0.000*NS	*0.79 ± 0.00**	*0.465 ± 0.018**	*0.19 ± 0.02*NS	*16.9 ± 0.1***	*2.8 ± 0.00***	*0.21 ± 0.00***	*0.19 ± 0.01*	*0.408 ± 0.019***	0.06 ± 0.00*
	(0.02–0.29)	*(0.13–1.45)*	*(0.08–0.78)*	*(0.01–0.38)*	*(4.93–12.90)*	*(0.08–4.90)*	*(0.04–0.40)*	*(0.06–0.32)*	*(0.05–0.8)*	(0.03–0.09)
5	*0.040* ± 0.000	*2.56* ± 0.01	*0.589* ± 0.006**	*0.14* ± 0.06NS	*62.3* ± 0.2**	*3.4* ± 0.1**	*2.02* ± 0.01**	*0.10* ± 0.01*	*0.816* ± 0.007**	0.09 ± 0.02
	(0.02–0.08)	(0.04–5.08)	(0.01–0.99)	(001–0.28)	(34.63–90.4)	(0.68–6.10)	(0.02–4.04)	(0.02–0.19)	(0.30–1.82)	(0.00–0.04)

NS Non-significant decrease as compared to pair groups ($p > 0.05$)

Sample size = 6

Mean values ± standard deviation

Values in parentheses indicate the minimum and maximum levels

* Significant decrease as compared to Site 1 ($p < 0.05$)

** Highly significant as compared to Site 1 ($p < 0.005$)

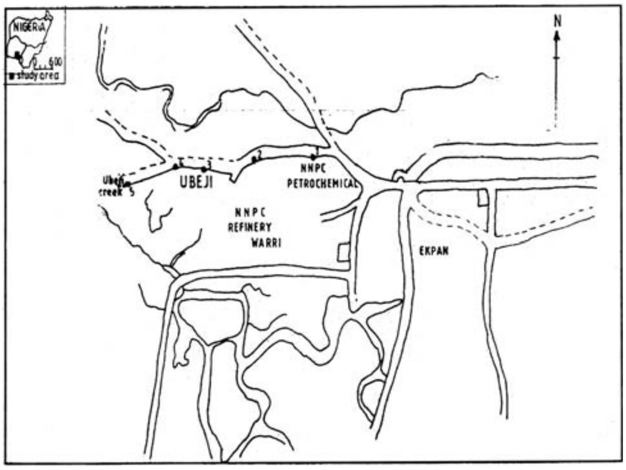

Fig. 1 Location of sample areas in Ubeji creek

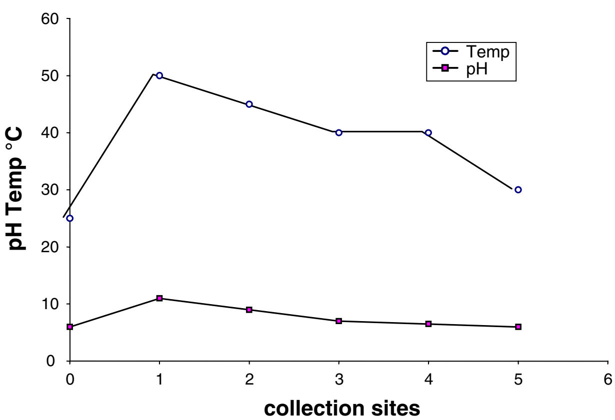

Fig. 2 Temperature and pH of water samples

observed for chloride from site 1 to 3 (Fig. 5). At sites 2, Cu, Fe, Mn and Pb concentrations had highly significant increases of these metals compared to site 1.

The following physical descriptions of individual sites also highlight important sample characteristics. Site 0, the source of the reference sample, is immediately upstream from the end of pipe. This site is characterized with heavy concentration of the mangrove area showing overlaps of black oily frontal scarp and narrow creek end. At the extreme end, children swim in the water. There were small fish, crabs and other crustaceans. The concentration of all elements was at zero level except for Hg whose concentration was slightly observed but well below the concentrations from areas highly contaminated. Site 1 was the first effluent point and was characterized by oily coated shoreline. Liquid wastes were discharged directly into an open water body through a small pipe. The effluent contained oily films and the smell was not different from crude oil. Fish and other aquatic life were absent from this site and at each site downstream to Ubeji River. Vegetation was

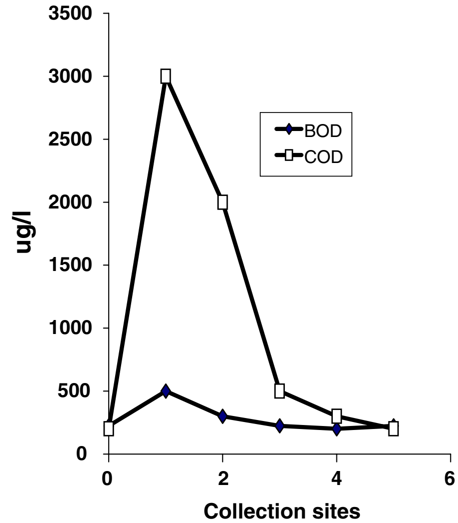

Fig. 3 Biological oxygen demand (*BOD*) and chemical oxygen demand (*COD*)

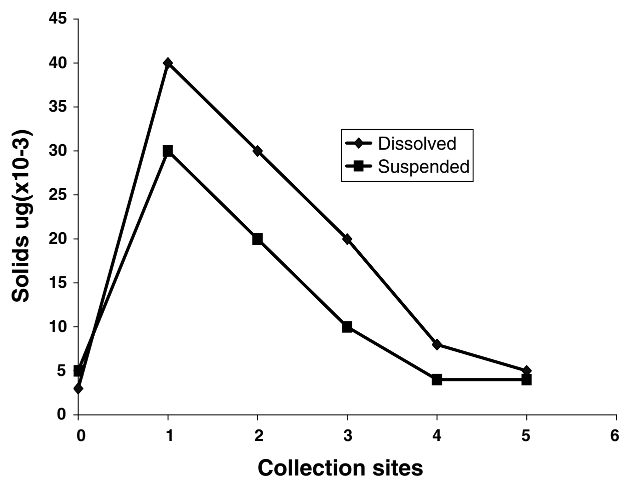

Fig. 4 Dissolved and suspended solids in water sample

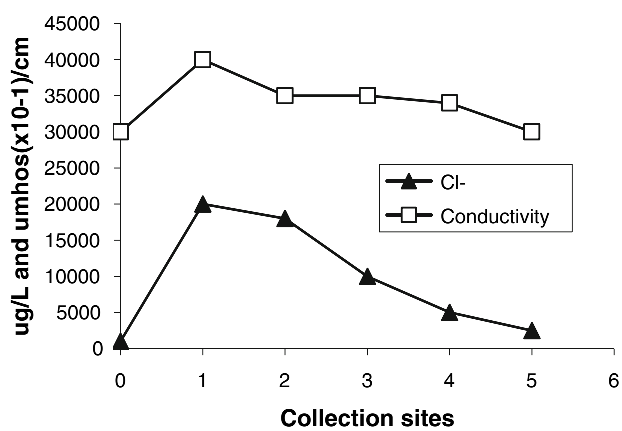

Fig. 5 Total Chloride concentrations (μg/mL) and conductivity (μmhos/cm) in water samples

sparse compared to Site 0. This site showed signs of damage from the black coated surrounding. All the elements were elevated relative to other sites. Site 3, the concentration of the elements started to decrease while the surrounding areas remained coated with black oily surface. There were no fish and no sign of other aquatic life. Site 4 was further observed to decrease in the elemental contents. Temperature and pH were normal relative to Site 0. BOD and COD were among the lowest recorded. Site 5 was the last point of sampling, a few distances downstream to Ubeji River. At the site, the water level was high with low water current. The chloride level was low. No remarkable concentrations of elements were detected, but a slight increase in water and Hg concentrations suggests some input from the tributaries. Elemental concentrations were not remarkably different from the previous site. Small fish were seen from Ubeji River jumping above the water surface if they swam into the mixing point, and some dead fish were seen floating on the surface of the water. These were the first fish observed in 1-km reach of Ubeji Creek during the study.

The nature of the effluent from the petrochemical company is characterized by visible signs which include black coated environment, oil films on water surface, high water temperature, partial deforestation of vegetation, especially the mangrove forest and the observed high levels of some physio–chemical parameters. For example, despite the gradual mixing of the effluent in the brackish water that in ordinary circumstance would result in dilution, assimilation and/or neutralization, the concentrations of all the parameters and various elements were remarkably high at all sites. The sudden increases of the elements at Site 1 suggest strongly this effluent as a source of many cations (Table 1). In particular, were the concentrations of Zn, Fe, Hg, and Mn that suggest the effluents may contain many other cations that may adversely impact on living organism in the water environment. Generally, there is an attenuation of measured parameters after Site 0 indicating some capacity for assimilation and perhaps dilution by converging tributaries. Nevertheless, comparing these effluents to the Canadian Environmental Quality Standards (2003), Redondo and Platonov (2009) Ubeji Creek is a toxic environment. Though a number of laws already exist in the Nigeria oil industry most of them provide the framework for oil exploration and exploitation. However, only some of these laws provide guidelines on the issues of pollution.

In impact studies following oil spill (Daniel-Kalio and Braide 2002; Osuji et al. 2004; Achudume 2007) the reports concluded that mangrove plant communities are important breeding ground for marine organism. It is therefore, not surprising with the continuous absence of fish and other aquatic organism in Ubeji Creek. The high water temperatures are also not surprising. Most brackish water organisms, fishes in particular, will not survive long-term exposure to a temperature of 35°C and higher (Khan et al. 2001; Achuba and Osakwe 2003) at least in part because of diminished levels of dissolved oxygen. Furthermore, those fish that have acclimatized to cooler environments as a result of mangrove canopy, suffer from thermal shock when they come in contact with water that is 5°C higher than that of their normal surroundings. The thermal shock may lead to death of fish in prolonged contact.

The presence of high levels of cations in the effluents appears to be the result of inefficient process before discharge. Gross contamination could be reduced through resource recovery, a process that would, in turn, be economically favorable. The data suggest that a point source discharge within the company premises could be created where effluents could be held for treatment or combined for neutralization and cooling. With this, the high concentrations of toxic elements such as Zn, Fe, Hg, and Mn could be reduced. Similarly, the high water temperature, pH, BOD and COD might be as simple as holding for aerobic treatment.

References

Achuba FI, Osakwe SA (2003) Petroleum-induced free radical toxicity in African catfish (*Clarias gariepinus*). Fish Physio Biochem 29:97–103. doi:10.1023/B:FISH.0000035905.14420.eb

Achudume AC (2007) Assessment of farmland sediments after flooding in Ubeji land in Niger delta of Nigeria. Environ Monit Assess 135:335–338. doi:10.1007/s10661-007-9653-y

Adeniyi AA, Afolabi JA (2002) Determination of total petroleum hydrocarbons and heavy metals in soils within the vicinity of facilities handling refined petroleum. Environ Int 28:79–82. doi:10.1016/S0160-4120(02)00007-7

Amadi A, Abbey SD, Nma A (1996) Chronic effects of oil spill on soil properties and microflora of a rainforest ecosystem in Nigeria. Water Air Soil Pollut 86:1–11. doi:10.1007/BF00279142

Benka-Coker MO, Ekundayo JA (1994) Effects of an oil spill on soil physico-chemical properties of a spill site in the Niger delta area of Nigeria. Environ Monit Assess 36:93–104. doi:10.1007/BF00546783

Daniel-Kalio LA, Braide SA (2002) The impact of accidental oil spill on cultivated and natural vegetation in a wetland areas of Niger delta. Nigeria J Hum Environ 31:441–442

Essien JP, Antai SP (2005) Negative effects of oil spillage on beach microalgae in Nigeria. J Microbiol Biotechnol 21:567–573. doi:10.1007/s11274-004-3910-9

Gupta PK, Khangarot BS, Durve VS (1981) The temperature dependence of the acute toxicity of copper to freshwater pond snail *Viviparus bengalensis* L. Hydrobiologia 83:461–464. doi:10.1007/BF02187041

Harrel RC (1985) Effects of a crude oil spill on water quality and macrobenthos of a southeast Texas stream. Hydrobiologia 124:223–228. doi:10.1007/BF00015238

Ijah UJJ, Antai SP (2003) Removal of Nigerian light crude oil in soil over a 12-month period. Int Biodeterior Biodegradation 51:93–99. doi:10.1016/S0964-8305(01)00131-7

Khan AA, Coppock RW, Schuler MM (2001) Effects of multiple exposures of small doses of Pembina cardium crude oil and diesel in rats. Arch Environ Cont Toxicol 40:418–424. doi: 10.1007/s002440010192

Li H, Zhang Y, Zhang CG, Chen GX (2005) Effect of petroleum-containing wastewater irrigation on bacterial diversities and enzymatic activities in a paddy soil irrigation area. J Environ Qual 34:1073–1080. doi:10.2134/jeq2004.0438

Osuji LC, Adesina SO, Obute GC (2004) Post-impact assessment of oil pollution in Agbada west plain of Niger delta. Chem Biodiver 1:1569–1578. doi:10.1002/cbdv.200490117

Redondo JM, Platonov AK (2009) Self-similar distribution of oil spills in Europea coastal waters. Environ Res Lett 4 01 4008 doi: 10.1088/1748-9326/4/1/014008, online at stacks.iop.org/ERI/4/01 4008

Simpson S (2008) In Nigeria 'oil war', militants step up attacks. www.csmonitor.com/2008/10/07/nigeria_conflit_a_warning_for-big_oil_in_iraq_ accessed September 21, 2008

Summary of Existing Canadian Environmental Quality Guidelines (2003) http://www.ccme.ca/assets/pdf/el_062.pdf. Accessed December 2003

Wang Z, Fingas M, Page DS (1999) Oil spill identification. J Chromatography A 843:369–411. doi:10.1016/S0021-9673(99)00120-X