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Assessment of Saclux Paint Industrial Effluents on Nkoho River in Abia State, Nigeria

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Abstract

Water plays an important role in determining the quality of life on earth and yet this role is threatened by indiscriminate discharge of industrial effluents. The study aimed to assess the potential impact of industrial effluents from Saclux paint industry on the water quality of Nkoho River in Abia state, Nigeria. Water samples were taken at the effluent discharge point, upstream and downstream of the discharge point in the month of September, October and November, 2016 and geo-referenced using Garmin 76CSx Global Positioning system (GPS). The results showed that there were variations in the water quality characteristics in the different sampling time (September, October and November). Temperature, total solids (TS), suspended solids (SS), total dissolved solids (TDS), electrical conductivity (EC), turbidity and colour of the water samples were significantly higher ($p < 0.05$) at the mid-stream compared to the upstream and downstream in the month of September, but varied in the month of October and November, while hardness, nitrate, acidity, microbial load (TVC), total coliform, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were significantly higher ($p < 0.05$) at the upstream compared to midstream and down-stream in the different sampling time. Temperature (29.16-31.00°C), TS (3188.00-3973.70 mg/L), SS (2980.00-3848.67 mg/L), turbidity (119.43-131.47 NTU), pH (8.83-9.03), phosphate (99.23-120.13 mg/L) and phenol concentration (101.74-108.57 mg/L) of the effluent were above the Federal Ministry of Environment (FMEnv) limits, while SS, NTU, phenol, sulphate, phosphate, TVC, total coliform and EC of the water samples exceeded regulatory standards of FMEnv and WHO for surface water quality. The variations in the water quality parameters could be attributed to possible differences in the batches of paint produced at the different test time. It can be concluded from the study that the poor water quality might confer potentials hazards to aquatic life and end users.

Keywords: Effluent discharge; Water quality; Paint industry; Nkoho river

Introduction

The availability and quality of water always have played an important role in determining the quality of life. Water quality is closely linked to water use and to the state of economic development [1]. Most of the water bodies in the areas of the developing and developed world are the end points of effluents discharged from industries.

The present estimation of consumable water levels is placed at 1% with ground water levels also threatened by pollution [2,3]. Water pollution due to discharge of untreated industrial effluents into water bodies is a major problem in the global context [4]. The problem of water pollution is being experienced by both developing and developed countries. Human activities give rise to water pollution by introducing various categories of substances or waste into a water body. The common types of polluting substances include pathogenic organisms, oxygen demanding organic substances, plant nutrients that stimulate algal blooms, inorganic and organic toxic substances [5].

Waste water from industries and sewage spillages from burst pipes in urban centres are released into streams and wetlands which finally discharge in waterways and this can be the major cause of industrial pollution to water resources in the country and expose humans to toxic substances through drinking water.

In most developed and developing countries, rapid industrialization and man's constant quest for comfort as well as change in taste and fashion has resulted to various forms of advancement in science and technology [6]. This, in turn affects the environment significantly in various ways. In processing basic industrial raw materials to finished goods various harmful wastes, effluents and other toxic by-products are generated alongside the desired products. These toxic materials when discharged into the environment are capable of interfering with

environmental components as well as affecting man and other living components of the ecosystem. For instance, in areas where industrial waste effluents are discharged into surface waters, there is general reduction in the quality of such water and its ability to support aquatic life is equally reduced. Effluent is generally considered to be water pollution, such as the outflow from a sewage treatment plant facility or the waste water discharge from industrial facilities [7].

It is generally recognized that in many developing countries, industrial environmental standards are lacking, and where they do exist, the instruments of control are not efficient. This is largely explained by the absence of reliable and comprehensive system of monitoring of industrial emissions and enforcement of compliance with the industrial standards [8]. Pollution from industrial disposal and effluent discharges has become a serious environmental issue in many countries of Africa, Nigeria inclusive [9]. The ultimate recipient or end point of all forms of pollution is the natural water body [10].

Waste water is water affected in quality from various standard parameters set by anthropogenic influences. The liquid wastes

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discharged from domestic, industrial, agricultural and related sectors containing various kinds of contaminants can be found in waste water. Various constituents may be present in waste water. They can be rinsed waters, including residual acids, plating metals and toxic chemicals [11]. If the effluents are contaminated with toxic metals, it can compromise human health with acute and chronic diseases [12,13].

The waste water from agricultural fields is flowing through numerous water sources, as it may contain various organic matter and plant nutrients. Besides, these effluents may contain considerable amounts of potentially harmful substances and heavy metals like Fe, Cu, Zn, Mn, Cd, Cr, Pb etc. [14]. Paint industries pollute the environment through effluent discharge, gas emission and waste disposal in the form of organic and inorganic substances. Bhaluro and Adeko [15] and Lori et al. [16] recorded that of all the three forms of pollutants discharged by a paint industry, the effluents are by far the most significant due to its heavy metal compositions. The heavy metals have cumulative effects over the years; the presence of these heavy metals in the ecosystems has increased as a result of increase in industrialization process. Health problems such as genetic mutation, deformation, cancer, kidney problems etc., have been attributed to pollution by heavy metals.

Treatment of waste water prior to its discharge into the environment is desirable to avoid pollution. In Nigeria, the Federal Environmental Protection Agency (FEPA) now (FMEnv) has established guidelines and standards for industrial emissions and effluent discharges [17]. Industries are required by law to monitor their effluent to ensure compliance. This study examines the quality of effluent discharges from a paint processing plant of Saclux Paints Nigeria Limited, to investigate if it conforms to statutory standard for industrial effluent discharges by FMEnv as a regulatory agency to ensure sustainable environment.

Materials and Methods

Study area

This study was carried out in Nkoho at Ohokobe Afara-ukwu Main River which is situated in Umuahia North of Abia State in the South-Eastern part of Nigeria. The area is located in the lowland rainforest zone of Nigeria [18], which lies on Latitude 05°29′ to 05°42′ North and Longitude 07°29′ to 07°33′ East (Figure 1). The area has an average rainfall of 2,238 mm per year that is distributed over seven months rainy season period [19]. It has bimodal peaks, the first occurring in

Figure 1: Map of the study area.
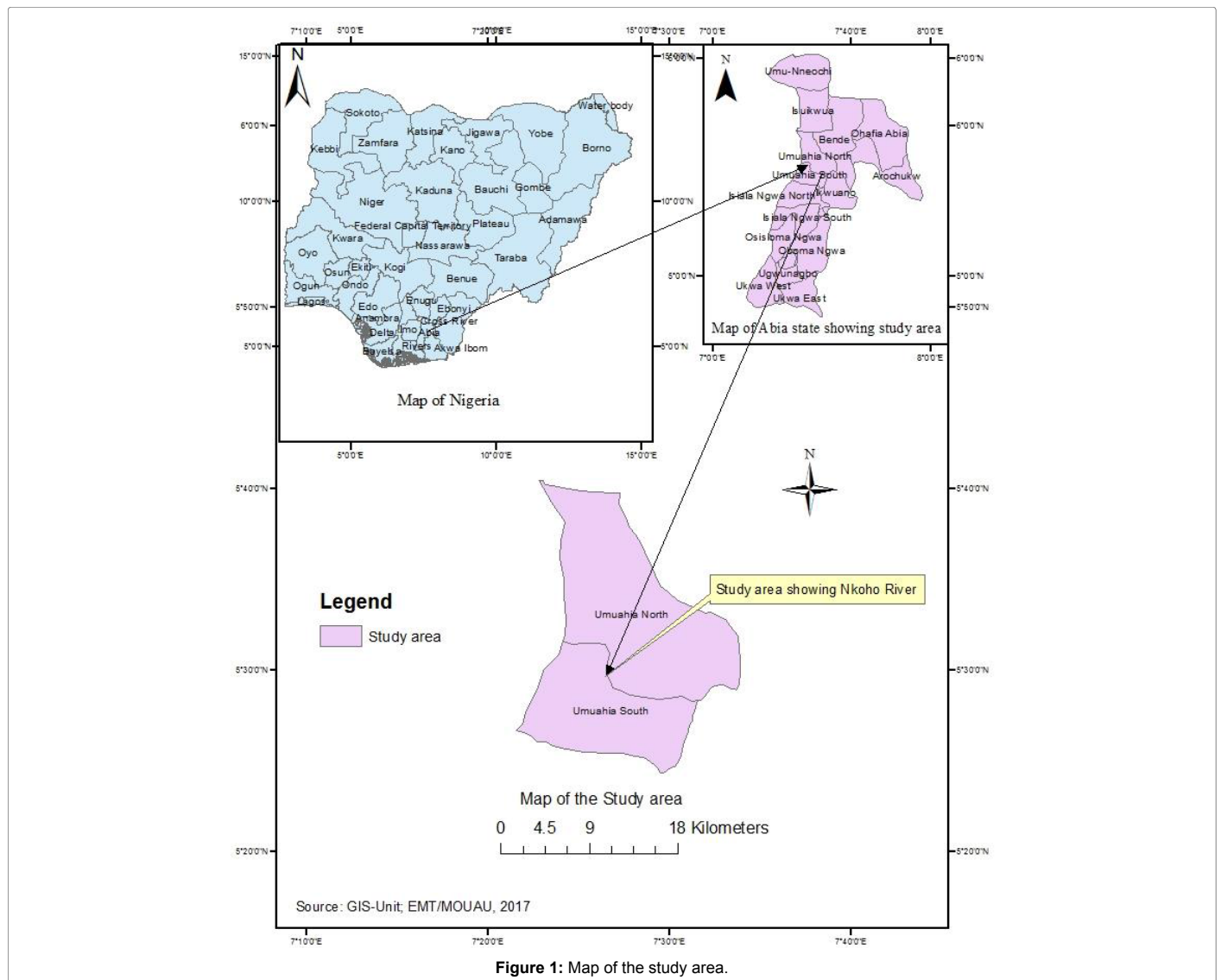
the month of June or July and the second occurring in the month of September. Its minimum and maximum temperatures are 23°C and 32°C, respectively and a relative humidity of 60-80% [20].

Sampling techniques

Sampling point was established and geo-referenced using Garmin Global Positioning system (GPS) at the effluent discharged point (N 05°29.702′ and E 007°29.084′), 100 m upstream (N 05°29.759′ and E 007°29.062′) and 100 m downstream (N 05°29.639′ and E 007°29.094′) of the discharge channel. Triplicate samples were collected for three months, starting from October-November, 2016. For each of the samples that were collected, parameters such as temperature, electrical conductivity (EC), turbidity, total solids (TS), suspended solids (SS), dissolved solids (TDS) and colour were analysed for physical parameters. Sulphate, nitrate, phosphate, alkalinity, acidity, pH, phenol, oil and grease were analysed for chemical parameters and dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), bacteria load, coliforms and *Escherichia coli* were also analysed for biological characteristics.

Physico-chemical sample analysis

The samples collected were analysed for parameters such as pH, temperature, electrical conductivity, turbidity and dissolved oxygen with shorter holding time with in-situ water quality analyser (Hannah Multimeter instrument H19829). Colours were determined with calibrated colour disc, total solids, suspended solids and dissolved solids were determined using the gravimetric method. Alkalinity and acidity were determined by standard methods for examination of water and waste water. Chloride was analysed according to the method of Association of Official Analytical Chemists [21]. Sulphate, nitrate and phosphate were determined spectrophotometrically.

Biological sample analysis

DO was determined using Wrinkler's method with azide modification following the description by APHA and BOD was analysed by subtracting the value of final concentration of DO (after 5 days of incubation at 20°C) from the concentration of initial DO. COD was measured by dichromate reflux method. Total plate count was determined according to the heterotrophic plate count method suggested by the American Public Health Association. Total coliform analysis was done using Most Probable Number (MPN).

Statistical analysis

The data collected from this study were subjected to Analysis of Variance (ANOVA) using Statistical Package for Social Sciences (SPSS). Means were calculated and compared. One-way analysis of variance was used to find the levels of significance of the considered parameters. A further mean separation using mean plots to analyze the inequality in means across the sample locations was done. Results obtained were compared with values recommended as international minimum standards by FMEnv [22] and WHO [23], for domestic and aquatic uses respectively. Mean values of the water parameters over the stipulated time in the different locations was differentiated using Fisher's Least Significant Difference (F-LSD) at p-value less than 0.05 ($p < 0.05$) as statistically significant.

Results and Discussion

Results of laboratory analysis of the paint industrial effluent from the Paint industry into Nkoho river water are shown in Table 1. From the results as shown in the table, there were variations in the quality characteristics of the effluent in the different sampling time (September, October and November) as well as in the quality characteristics of the river water samples at the different sampling points. The paint effluent showed significant variations ($p < 0.05$) in its quality over time. The effluent temperature was 29.16°C, 31.00°C and 30.83°C in the month of September, October and November, respectively, while the pH was 8.87, 9.03 and 8.83 in the same sampling periods. The oil contents of the effluents were 4.19% (w/w), 4.29% (w/w) and 4.09% (w/w). Turbidity of the effluent was 119.43 NTU, 131.47 NTU and 126.23 NTU.

The total solids content of the paint industrial effluent was 3.188% (3188.00 mg/L) in September, 3.73% (3731.33 mg/L) in October and 3.973% (3973.70 mg/L) in November. Similarly, the suspended solids were 112.33 mg/L (0.112%), 207.0 mg/L (0.207%) and 210.0 mg/L (0.210%) in September, October and November respectively. These results show that there were variations in physical characteristics of the paint effluents at the different times of sampling (September, October and November). The variations in the physical characteristics of the effluent at the different sampling times could be attributed to the fact that the effluent discharges represented wastes from different batches of paint production. In this regard, the contribution of the wastes at any point in time may be a function of the type of paint manufactured at that time.

Effluent Samples	September	October	November	FMENV	WHO
Temperature (°C)	29.16 ± 0.28	31.00 ± 0.00	30.83 ± 0.28	25	23.50
TS (mg/L)	3188.00 ± 5.29	3731.33 ± 9.29	3973.70 ± 10.21	500	500
SS (mg/L)	2980.00 ± 7.21	3848.67 ± 7.09	3703.70 ± 12.74	50	50
TDS (mg/L)	208.00 ± 3.46	246.67 ± 2.30	270.00 ± 3.60	2000	<2000
EC (µS/cm)	226.00 ± 2.00	231.00 ± 2.00	221.67 ± 3.21	-	400
Turbidity (NTU)	119.43 ± 1.61	131.47 ± 1.65	126.23 ± 0.28	1.0	5.00
Colour (TCU)	13.93 ± 0.15	15.80 ± 0.20	13.03 ± 0.05	15.0	15.0
Oil & grease (mg/L)	4.19 ± 0.02	4.29 ± 0.03	4.09 ± 0.09	10	10
pH	8.87 ± 0.05	9.03 ± 0.05	8.83 ± 0.05	6-9	7.0-8.5
Sulphate	492.93 ± 3.9	63.97 ± 1.13	524.87 ± 2.13	500	200
Nitrate	8.54 ± 0.09	8.58 ± 0.13	9.13 ± 0.21	20	10
Phosphate	99.23 ± 3.2	111.20 ± 2.42	120.13 ± 2.13	5	5
Alkalinity	11.24 ± 0.2	11.17 ± 0.18	11.73 ± 0.03	-	200
Acidity	4.39 ± 0.03	4.45 ± 0.02	4.19 ± 0.03	NS	NS
Phenol	101.74 ± 2.78	187.20 ± 4.15	108.57 ± 2.49	0.5	0.5

<0.01: Implies that the values were below the minimum detectable limit of 0.01; SD: Standard Deviation.

Table 1: Values of Mean ± SD for parameters measured for the effluent physic-chemical characteristics (Source: FEPA and WHO [17,23]).

Notwithstanding the variation in the physico-chemical characteristic of the effluents over time, there were variations in the effluent quality relative to that allowable by regulations. Compared with regulatory standards of the federal Ministry of Environment (FMENV) the temperature of the effluents were within acceptable range (25-30°C). The pH however, went beyond the 6.5-8.5 limits and recorded 8.83 to 9.03. The total solid (TS) content was in the range of 3188 mg/L to 3973.7 mg/L, and was found not to conform to regulations since it exceeded the 2000 mg/L acceptable limit for effluent discharged into river. High solid content of effluent discharge into river is undesirable as it may contain organic and inorganic solids which reduce light penetration hence reducing the ability of microorganisms in the recipient water body (algae) to photosynthesize.

The high solid content of the effluents manifested in high level of turbidity which ranged from 119.43 NTU (September) to a peak of 131.47 NTU (October), while November effluent recorded 126.23 NTU. This manifestation could be indicative of need to dilute the paint effluents further before discharge into the Nkoho River. Also, the suspended solid was in the range of 2980 mg/L to 3703.7 mg/L which failed the standard regulation (50 mg/L). The suspended solids, as filterable materials in the surface water temperature since they absorb heat from sunlight. The effluents showed low acidity which fluctuated over time with readings 4.39 (September), 4.45 (October) and 4.19 mg/L (November), respectively.

The low acidity confirmed the high pH recorded earlier and was confirmed by the relatively high alkalinity which was in the range of 11.17 to 11.73 mg/L. The level of sulphate in the effluent was found to be high. The sulphate levels were ranged between 492.93 mg/L and 524.87 mg/L between the months of September to November.

The range of the values obtained in this study agrees with the high to moderate levels of PO_4^{3-} in southern Nigeria Rivers [24]. Although phosphates are not toxic and do not represent a direct threat to animals and other organisms, they do represent a serious indirect threat to water quality [25].

Both parameters were above the permissible levels for treated effluents in Nigeria and World Bank guidelines. Also the phenol content of the effluent was detected to be in the range of 101.74 mg/L to 187.20 mg/L and was highest in the month of October. However, the nitrate level in the effluent was found to be on the low side ranging from 8.54 mg/L to 9.13 mg/L all of which fell within acceptable limits. Although, most of the chemical composition of the sampling points did not meet acceptable limit set by various regulatory bodies. This presented the paint industry effluent as potential source of high pollutant for surface water and other environments.

On the whole, it was observed that the paint industrial effluents failed the standard regulatory limits in terms of physical characteristics

prior to discharge into the recipient water of Nkoho River as discussed in considerations of the results of physical characteristics of the water sample.

The results of the physical water quality characteristics of water samples from Nkoho River are shown in Table 2. The result show variations in the physical properties of the water upstream before the point of effluent discharge into the river (mid-stream) and the downstream waters. There were slight and insignificant variation in the temperature of the upstream water samples in the three sampling times of September, October and November with values of 28.67 ± 0.29°C, 29.83 ± 0.28°C and 29.33 ± 0.58°C, respectively. Similarly, slight variations were recorded in the temperature of the water at effluent discharge point which recorded 29.00 ± 0.00°C, 30.17 ± 0.76°C and 29.67 ± 0.58°C for the same period. It was also observed that at the downstream region of the sampling points, the temperature readings was 28.67 ± 0.29°C, 29.17 ± 0.28°C and 29.33 ± 0.58°C for the same period of September, October and November, respectively. From this, it was observed that all the water samples conformed well to the permitted temperature range for surface water [23]. The temperature of river water is reported to be an important index as it governs the biological species in the water and their activities to a large extent [26]. Also other reports show that the higher aquatic orders such as fish are affected drastically not just by temperature but also by temperature dependent parameters like dissolved oxygen (DO).

The turbidity of water samples from the Nkoho River showed variation between the upstream control water sample (7.27 ± 0.12 to 7.80 ± 0.30 NTU), the midstream which received the effluent directly (16.67 ± 0.23 to 22.67 ± 0.83 NTU) and the downstream water (16.00 ± 0.17 to 18.13 ± 0.55 NTU). The water samples at the effluent receiving point (mid-stream) and the downstream water beyond the point have turbidity values well beyond the recommended level for surface water (5 NTU) as set by the World Health Organization [23].

However, the upstream water sample prior to the discharge of the effluent had much lower level of turbidity (7.27-7.80 NTU), notwithstanding the relatively lower turbidity level, the control water failed the turbidity test. This was attributed to possibly contamination of the water before the effluent was discharged into the river at the upper locations in the river course. River water is open to receive soil washout from slopes into the water sometimes including animal and human faeces, carcass of dead wild animals etc., high turbidity is not desirable in surface water as it leads to restriction in light penetration processes such as flocculation and filtration which increases cost of purification. DWAF [27] reported that high turbidity is associated with microbial contamination as high turbidity makes it difficult to disinfect water properly. Muoghalo and Omocho [28] observed that highly turbid water is disqualified as source of water for domestic use in the community. On the whole, the discharge of paint industrial effluent

Parameters	September			October			November			FMENV	WHO
	Upstream	Midstream	Downstream	Upstream	Midstream	Downstream	Upstream	Midstream	Downstream		
Temperature (°C)	28.67 ± 0.29ᵃ	29.00 ± 0.00ᵃ	28.67 ± 0.29ᵇ	29.83 ± 0.28ᵃ	30.17 ± 0.76ᵃ	29.17 ± 0.28ᵃ	29.33 ± 0.58ᵃ	29.67 ± 0.58ᵃ	29.33 ± 0.58ᵇ	25	23.50
TS (mg/L)	302.67 ± 0.58ᵃ	489.00 ± 2.00ᶜ	434.00 ± 2.00ᵇ	337.00 ± 6.24ᵃ	503.33 ± 1.52ᶜ	470.00 ± 2.64ᵃ	344.33 ± 4.93ᵃ	492.33 ± 6.51ᶜ	452.62 ± 2.08ᵇ	500	500
SS (mg/L)	190.33 ± 1.15ᵃ	312.00 ± 1.73ᵇ	274.00 ± 2.00ᵃ	207.00 ± 4.58ᵃ	308.67 ± 2.51ᵃ	286.67 ± 1.15ᵃ	210.00 ± 3.61ᵃ	330.67 ± 2.52ᶜ	309.33 ± 3.51ᵃ	50	50
TDS (mg/L)	112.33 ± 0.58ᵃ	177.00 ± 3.61ᵇ	160.00 ± 2.00ᵃ	130.00 ± 1.73ᵃ	194.67 ± 2.30ᵇ	183.33 ± 1.52ᵇ	134.33 ± 5.69ᵃ	161.67 ± 4.04ᵇ	143.33 ± 5.51ᵃ	2000	<2000
EC (µS/cm)	139.33 ± 1.53ᵃ	187.67 ± 1.53ᶜ	166.67 ± 1.16ᵇ	147.33 ± 2.08ᵃ	208.00 ± 2.00ᶜ	180.67 ± 2.51ᵇ	160.33 ± 2.08ᵃ	199.33 ± 2.31ᶜ	188.33 ± 0.58ᵃ	-	400
Turbidity (NTU)	7.27 ± 0.12ᵃ	16.67 ± 0.23ᶜ	16.00 ± 0.17ᵇ	7.80 ± 0.30ᵃ	22.67 ± 0.83ᶜ	18.13 ± 0.55ᵇ	7.63 ± 0.45ᵃ	18.13 ± 0.29ᵇ	17.67 ± 0.12ᵇ	1.0	5.00
Colour	5.87 ± 0.12ᵃ	7.13 ± 0.06ᶜ	6.43 ± 0.06ᵇ	5.97 ± 0.05ᵃ	7.23 ± 0.05ᶜ	6.43 ± 0.11ᵇ	6.17 ± 0.12ᵃ	6.90 ± 0.17ᵇ	6.23 ± 0.12ᵃ	15.0	5.0

a,b,c: Mean value with the same alphabet are not significantly different; < 0.01: Implies that the values were below the minimum detectable limit of 0.01; SD: Standard Deviation.

Table 2: Values of Mean ± SD for parameters measured for the physical characteristics of the river water (Source: FEPA and WHO [17,23]).

into the Nkoho River increased the already slightly high turbidity of the water to a much higher and undesirable levels.

Total solids in the river water at points before the discharge of paint industrial effluent were 302.67 ± 0.58 mg/L, 337.00 ± 6.24 mg/L and 344.33 ± 4.93 mg/L in the month of September, October and November, respectively, but increased to 489.00 ± 2.00 mg/L, 503.33 ± 1.52 mg/L and 492.53 ± 6.51 mg/L at the point where the effluent was discharged. However, the values recorded at the downstream point were 434.00 ± 2.00 mg/L, 470.00 ± 2.64 mg/L and 452.62 ± 2.08 mg/L. It was observed that the total solids in the river water was below the 500 mg/L permitted by regulatory bodies [22,29] but the recipient of the discharged increased the solids beyond the permissible level. However, which reduced at the downstream to levels higher than that from the initial (control) water solid contents before the paint effluent discharge.

The reduction in the solids downstream could be attributed to self-purification of the river. Wasserman et al. [30] observed similar reduction and attributed it to physiochemical reactions such as sedimentation, coagulation, fixation as well as possible oxidation and precipitation.

Similarly, both the total dissolved solids (TDS) and suspended solids (SS) varied in line with the total solids as described above. In the upstream (control) water sample, the dissolved solids were 112.33 ± 0.58 mg/L (September), 130.00 ± 1.73 mg/L (October) and 134.33 ± 5.69 mg/L (November), respectively. While the midstream water (discharged point) recorded 177.00 ± 3.61 mg/L (September), 194.67 ± 2.30 mg/L (October) and 161.67 ± 4.04 mg/L (November) as against the downstream sample which had 160.00 ± 2.00 mg/L (September), 183.33 ± 1.52 mg/L (October) and 143.33 ± 5.51 mg/L (November). In each case, highest solid values were recorded in the month of October which corresponds with the onset of dry season. The relatively high value recorded in the dry season was attributed to the decreased water volume which possibly reduced water flow thus having more particles in the water at any given time within the periods.

In general, variations existed in the physical characteristics of the Nkoho river water between the control water sample and the water polluted following discharge of paint industrial effluent. Secondly, there were variations of significant differences in the physical characteristics of the water samples at the different sampling times of September, October and November. Interestingly, the physical properties of the Nkoho river water failed to meet the regulatory specification prior to effluent discharge into it. This was attributed to possible pollutants which occur at the upper part of the river course before the water flowed down to the test sampling points. From the result, the physical characteristics values generally did not meet the standard qualification as water source for domestic use.

Table 3 shows the chemical properties of Nkoho river water and effluents in the months of September, October and November, 2016. The upstream water sample varied significantly with the midstream water sample which received direct discharge of the effluents as well as the downstream water. Similarly, there were variations of significant differences ($p < 0.05$) in the chemical properties of the effluents in the different months. The effluents showed low acidity which fluctuated over time with readings 4.39 (September), 4.45 (October) and 4.19 mg/L (November), respectively.

The low acidity confirmed the high pH recorded earlier and was confirmed by the relatively high alkalinity which was in the range of 11.17 to 11.73 mg/L. The level of chlorides and sulphate in the effluent was found to be high. The chloride level was in the range of 243.2 mg/L to 262.33 mg/L while sulphate levels were ranged between 492.93 mg/L and 524.87 mg/L between the months of September to November.

Both parameters were above the permissible levels for treated effluents in Nigeria and World Bank guidelines. Also the phenol content of the effluent was detected to be in the range of 101.74 mg/L to 187.20 mg/L and was highest in the month of October. However, the nitrate level in the effluent was found to be on the low side ranging from 8.54 mg/L to 9.13 mg/L all of which fell within acceptable limits. Although, most of the chemical composition of the sampling points did not meet acceptable limit as set by various regulatory bodies. This presented the paint industry effluent as potential source of high pollutant for surface water and other environments.

Parameters	September				October				November				FMENV	WHO
	Upstream	Midstream	Downstream	Effluent	Upstream	Midstream	Downstream	Effluent	Upstream	Midstream	Downstream	Effluent		
Hardness mg/L	22.48 ± 0.03[c]	13.03 ± 0.11[a]	14.86 ± 0.04[b]	62.54 ± 0.22	25.01 ± 0.16[c]	13.43 ± 0.07[a]	15.64 ± 0.41[b]	63.97 ± 1.13	23.60 ± 0.87[c]	12.93 ± 0.23[a]	15.67 ± 0.30[b]	66.23 ± 0.15	200	100
Sulphate	330.93 ± 2.04[a]	412.33 ± 3.40[c]	367.90 ± 2.00[b]	492.93 ± 3.9	314.07 ± 13.59[a]	391.00 ± 4.19[c]	349.70 ± 1.50[b]	501.03 ± 4.08	311.07 ± 11.16[a]	399.33 ± 20.25[c]	350.97 ± 4.45[b]	524.87 ± 2.13	500	200
Nitrate	13.71 ± 0.43[c]	10.21 ± 0.06[a]	12.86 ± 0.09[b]	8.54 ± 0.09	16.64 ± 0.16[c]	11.34 ± 0.34[a]	12.52 ± 0.60[b]	8.58 ± 0.13	17.97 ± 0.92[c]	12.83 ± 0.25[a]	12.53 ± 0.23[a]	9.13 ± 0.21	20	10
Phosphate	37.61 ± 1.23[a]	60.73 ± 0.89[b]	59.09 ± 0.84[b]	99.23 ± 3.2	47.23 ± 1.78[a]	71.30 ± 2.26[c]	65.13 ± 0.75[b]	111.20 ± 2.42	41.00 ± 4.50[a]	73.67 ± 2.45[c]	66.93 ± 0.92[b]	120.13 ± 2.13	5	5
Alkalinity	0.49 ± 0.03[a]	1.09 ± 0.04[c]	0.78 ± 0.03[b]	11.24 ± 0.2	0.74 ± 0.12[a]	0.84 ± 0.05[a]	0.78 ± 0.02[a]	11.17 ± 0.18	0.63 ± 0.06[a]	0.73 ± 0.06[a]	0.67 ± 0.06[a]	11.73 ± 0.03	-	200
Acidity	5.83 ± 0.06[c]	5.51 ± 0.03[b]	5.40 ± 0.02[a]	4.39 ± 0.03	6.47 ± 0.01[c]	5.03 ± 0.07[a]	6.92 ± 0.04[b]	4.45 ± 0.02	6.13 ± 0.02[c]	5.09 ± 0.02[a]	5.87 ± 0.01[b]	4.19 ± 0.03	NS	NS
Chloride	35.23 ± 1.25[a]	121.10 ± 2.21[c]	84.43 ± 1.60[b]	243.20 ± 1.38	42.07 ± 0.46[a]	121.77 ± 1.19[c]	87.30 ± 1.13[b]	256.47 ± 6.81	38.70 ± 0.36[a]	120.97 ± 2.25[c]	89.67 ± 1.12[b]	262.33 ± 3.86	250	250
Phenol	0.35 ± 0.02[a]	1.12 ± 0.04[c]	0.96 ± 0.02[b]	101.74 ± 2.78	0.49 ± 0.03[a]	1.31 ± 0.03[c]	1.03 ± 0.01[b]	187.20 ± 4.15	0.40 ± 0.04[a]	1.41 ± 0.50[c]	0.85 ± 0.03[b]	108.57 ± 2.49	0.5	0.5
pH	6.47 ± 0.06[a]	6.90 ± 0.01[c]	6.77 ± 0.06[b]	8.87 ± 0.05	6.53 ± 0.05[a]	7.03 ± 0.11[c]	6.77 ± 0.05[b]	9.03 ± 0.05	6.43 ± 0.06[a]	6.83 ± 0.06[c]	6.67 ± 0.12[b]	8.83 ± 0.05	6-9	7-8.5
Oil & grease	0.03 ± 0.01[a]	0.07 ± 0.01[b]	0.05 ± 0.01[ab]	4.19 ± 0.02	0.03 ± 0.00[a]	0.09 ± 0.02[b]	0.03 ± 0.01[a]	4.29 ± 0.03	0.02 ± 0.01[a]	0.09 ± 0.02[b]	0.02 ± 0.01[a]	4.09 ± 0.09[a]	10	10

[a,b,c]Mean value with the same alphabet are not significantly different; < 0.01: Implies that the values were below the minimum detectable limit of 0.01; SD: Standard Deviation.

Table 3: Values of Mean ± SD for parameters measured for the Chemical Characteristics of the River in mg/L (Source: FEPA and WHO [17,23]).

Recorded values for hardness of the water was higher for upstream (22.48 mg/L) as against 13.032 mg/L (midstream) and 14.86 mg/L for downstream. Although, recorded values for water hardness were within the permissible limits of 100 mg/L [17] for both portable water and water for domestic uses.

The alkalinity level of the upstream was in the range of 0.49 to 0.63 mg/L, while the effluent polluted water at the entry point (midstream) recorded 0.73 to 1.09 mg/L and the downstream recorded 0.67 to 0.78 mg/L respectively. On the other hand, the acidity levels were relatively higher in the upstream with a range of 5.83 mg/L to 6.47 mg/L as against 5.03 to 5.51 in the midstream and 5.40 to 5.92 for the downstream.

Sulphates and phosphates in the water samples varied significantly. In the upstream, the point before the entry of the paint effluents, the values obtained for sulphate were 330.93 mg/L (September), 314.07 mg/L (October) and 311.07 mg/L (November). Phosphate was 37.61 (September) 47.23 (October) and 41.00 mg/L (November). On the other hand, values of sulphates and phosphates recorded at the midstream were 412.33 (September), 391.00 (October) and 399.33 mg/L (November), respectively. The corresponding values for phosphates were 60.73 (September), 71.30 (October) and 73.67 mg/L (November). This result show that both sulphate and phosphates increased in the water following pollution by the paint industry effluents. The sulphates content of the polluted water was found to be higher than the 300 mg/L and 500 mg/L levels permitted by World Health Organization and FEPA for portable water.

Similar observation was made in the nitrate levels of the water samples. Both the upstream and the point of effluent discharge were found to have nitrate levels above the 10 mg/L allowable levels. In addition, the phenol levels of all the samples had higher values than the 0.02 mg/L permitted for water for domestic use by WHO standards. Oil and grease content of the Nkoho River at all the test points and periods were all below the 10 mg/L limit set by regulation. However, there was slightly higher value (0.07 ± 0.01 to 0.09 ± 0.02 mg/L) at the effluent discharge point of the river water. The upstream (control) water sample had a range of 0.02 ± 0.01 to 0.03 ± 0.01 mg/L while the downstream had a range of 0.02 ± 0.01 to 0.05 ± 0.01 mg/L. The general low oil and grease content of the water samples was attributed to hydrophobicity relationship of oil and water wherein there is repulsion of one by the other and vice versa.

Table 4 shows the biochemical and biological characteristics of Nkoho River water sample and the effluent contaminant. The results showed that there were variations in the values of the quality parameters of the river water sample at the different sampling points and there variations underscore the impact of the paint industry effluent pollution on the river water.

The microbial load of the effluent was found to be much lower (2.17×10^2) cfu/mL than those of the water samples which was in the range of 2.91×10^6 to 3.45×10^6 cfu/mL for upstream, 2.90×10^6 to 2.07×10^6 cfu/mL for mid-stream and 3.03×10^6 to 2.49×10^6 cfu/mL for downstream respectively. The result further show that the microbial load of the effluent fluctuated from 2.17×10^2 cfu/mL in September, 2.00×10^2 cfu/mL in October and 2.33×10^6 cfu/mL for November while that of the river water samples decreased linearly from September to November. The bacteria load was highest in the upstream water 3.45×10^6 cfu/mL prior to the effluent contamination (midstream) 2.90×10^6 cfu/mL than in the downstream section 2.93×10^6 cfu/mL for the month of September and same was observed to be 3.01×10^6, 2.31×10^6 and 3.03×10^6 cfu/mL for upstream, mid-stream and downstream respectively for the month of October as against the effluent value of 2.00×10^6 cfu/mL and for the month of November, the effluent value was 2.33×10^6 cfu/mL as against 2.91×10^6, 2.07×10^6 and 2.49×10^6 cfu/mL for upstream, mid-stream and downstream water respectively.

Similar trend was also observed in the coliform count which showed Most Probable Number (MPN/100 mL) of 38.33 (upstream), 15.33 (midstream) and 13.33 (downstream) respectively in September. For October, 18.33 (upstream), 12.33 (midstream) and 17.00 (downstream). While for November, 2.91 (upstream), 2.07 (midstream) and 2.49 (downstream).

The low bacteria presence in the effluent as 1.67, 2.33 and 2.67 for September, October and November respectively was attributed to the unfavourable environment of the effluent which probably caused inhibition in the growth and multiplication of bacteria in the effluent polluted water relative to the control water sample (upstream). Olaoye and Oladeji [31] observed that paint industries releases large quantities of waste some of which are hazardous into the environment with the attendant health problems and ecological imbalance as well as bioaccumulation in aquatic organisms.

Dissolved Oxygen (DO) of the paint industry effluent was higher than the acceptable benchmark of 20 mg/L for treated effluents before discharge into the environment, with mean values of 23.93 mg/L to 25.37 mg/L (September-November). Also, the DO levels of the river water samples were higher than the acceptable limits for aquatic life (6.8 mg/L) and for recreational water quality (7.5 mg/L) in accordance with the government regulatory body [17]. In general, DO levels less than 5 mg/L are stressful to most aquatic organisms. Most fish die at 1-2 mg/L. However, fish can move away from low DO areas [32]. The result implies that the water is safe and can support aquatic life.

In the same sense, the BOD of the control river water samples varied between 6.63 mg/L in the rainy season (September) and 5.43 mg/L in the dry season (November). The effluent polluted river water sample

Parameters	September				October				November				FMENV	WHO
	Upstream	Midstream	Downstream	Effluent	Upstream	Midstream	Downstream	Effluent	Upstream	Midstream	Downstream	Effluent		
TVC x 10⁶ (cfu/mL)	3.45 ± 0.04ᵇ	2.90 ± 0.10ᵃ	2.93 ± 0.03ᵃ	2.17 ± 0.04	3.01 ± 0.02ᵇ	2.31 ± 0.03ᵃ	3.03 ± 0.07ᵇ	2.00 ± 0.05	2.91 ± 0.03ᶜ	2.07 ± 0.03ᵃ	2.49 ± 0.03ᵇ	2.33 ± 0.57	-	-
Total coliform MPN/100 mL	38.33 ± 2.88ᵇ	15.33 ± 2.30ᵃ	13.33 ± 1.15ᵃ	1.67 ± 0.57	18.33 ± 1.53ᵇ	12.33 ± 1.53ᵃ	17.00 ± 3.00ᵇ	2.33 ± 0.57	31.67 ± 2.88ᵇ	13.00 ± 1.73ᵃ	14.67 ± 3.06ᵃ	2.67 ± 0.57	0	-
DO (mg/L)	8.77 ± 0.12ᵃ	10.30 ± 0.10ᵇ	8.97 ± 0.15ᵃ	23.93 ± 0.1	9.17 ± 0.32ᵃ	9.97 ± 0.15ᵇ	9.87 ± 0.32ᵃ	1.33 ± 0.5	9.80 ± 0.20ᵇ	9.67 ± 0.12ᵃ	8.87 ± 0.15ᵃ	25.37 ± 0.5	7.5	5
BOD (mg/L)	6.63 ± 0.11ᵃ	8.00 ± 0.34ᶜ	6.27 ± 0.05ᵇ	16.50 ± 0.2	5.80 ± 0.30ᵃ	8.97 ± 0.21ᶜ	6.70 ± 0.17ᵇ	15.33 ± 0.7	5.43 ± 0.12ᵃ	7.13 ± 0.21ᵇ	5.90 ± 0.17ᵇ	19.03 ± 0.2	30	
COD (mg/L)	40.13 ± 0.75ᵃ	61.87 ± 0.30ᶜ	46.07 ± 0.25ᵇ	85.93 ± 2.4	33.77 ± 0.46ᵃ	61.73 ± 3.87ᶜ	48.17 ± 0.25ᵇ	92.83 ± 1.5	43.07 ± 0.25ᵃ	59.50 ± 1.31ᶜ	45.01 ± 0.64ᵇ	84.00 ± 1.0	100	200
E. coli x 10² (cfu/mL)	7.00 ± 1.73ᵃ	4.33 ± 0.57ᵃ	7.667 ± 0.57ᵇ	1.67 ± 0.57	3.67 ± 0.58ᵃ	2.67 ± 0.58ᵃ	3.33 ± 0.58ᵃ	1.33 ± 0.57	4.00 ± 1.73ᵃ	2.67 ± 1.15ᵃ	3.00 ± 1.00ᵃ	1.67 ± 0.5	0	-

a,b,cMean value with the same alphabet are not significantly different; < 0.01: Implies that the values were below the minimum detectable limit of 0.01; SD: Standard Deviation.

Table 4: Values of Mean $\pm$ SD for parameters measured for the Biochemical and Biological characteristics of the River (Source: FEPA and WHO [17,23]).

had BOD values of 8.00 mg/L (September), 8.97 mg/L (October) and 7.13 mg/L (November). Both the control water sample and the polluted samples did not meet the acceptable limit of 4-5.0 mg/L for surface water.

Generally speaking, there were significantly different (p<0.05) variations in the biochemical and biological quantity of the Nkoho river water before and after pollution by the paint industry effluents. It was observed that the paint industry effluent impacted negatively on the biochemical and biological quality of the river water. This negative impact was attributed to the poor quality of the effluent discharged into the river. However it was noted that the river water quality was not good enough before the discharge of effluent into the water. Therefore, the effluent simply worsened the already low quality of the Nkoho river water.

COD values conveyed the amount of dissolve oxidizable organic matter including non-biodegradable matter present in it. The high COD value in the sample effluent recorded determines that the effluent had high organic load [33]. Low level of COD recorded across the river course could therefore suggest that there may not be direct influence of effluent discharge to the river and also that such a river is good for irrigation, domestic and aquatic life.

From the result of the tables, the BOD values were less than the standards. It was reported that natural water with the BOD values of 4 mg/L is considered to be slightly polluted with organic matter, but safe for drinking. Stream keeper's field guide [17] reported that unpolluted natural waters should have a BOD of 5 mg/L or less. Raw sewage may cause increase in BOD values up to 150 to 300 mg/L. Biological Oxygen Demand (BOD) test is useful in determining the relative waste loading and higher degree therefore indicates the presence of large amount of organic pollutant and relatively higher level of microbial activities with consequent depletion of oxygen content.

According to WHO [34], low NO_3^- could be due to low effect of agricultural runoff, refuse dump runoff or contamination by human and animal waste.

Presence of chloride ion in Nkoho River agrees with the report of Walakaria [35], that chloride is commonly found in streams and freshwater. However, there was a sharp increase after the effluent discharge in the midstream value of chloride. Such variation may be due to increase in discharge of effluent from the paint industry or agriculture and domestic activities along the river.

The phosphate (PO_4^{3-}) levels varied along the sampling points and time (September-October) having a relatively higher values. The range of the values obtained in this study agrees with the high to moderate levels of PO_4^{3-} in southern Nigeria Rivers [24]. Although phosphates are not toxic and do not represent a direct threat to animals and other organisms, they do represent a serious indirect threat to water quality [25].

The pH however, went beyond the 6.0-9.0 and 7.0-8.5 limits respectively for both FMEnv and WHO standards for the effluents and recorded 8.83 to 9.03. The study revealed that the pH values of the river appeared to be slightly acidic as it had values that ranged from 6.43-7.03 and within the permissible limit of FMEnv and WHO standard. It was also observed that the pH of all the effluents was greater than 8.5 (pH>8.5) which indicates that the water is hard. The reduction in pH level of the river is probably due to the organic waste that is discharged into some parts of the river. The pH can be decreased by the carbon dioxide released by the bacteria breaking down the organic wastes [36]. It can also be due to the fact that the areas this occurred are used as a urinal. The urine contains uric acid that can increase the acidity of water [37]. Carbon dioxide dissolves in water to form carbonic acid. Although this is weak acid, large amounts of it will lower the pH and when waters with low pH values come into contact with certain chemicals and metals, this often makes them more poisonous than normal.

The highest value of EC was measured in the effluent of the month of October (231.00 µScm⁻¹) and at ranges from 139.33 ± 1.53 µScm⁻¹ to 147.33 ± 2.08 µScm⁻¹ for the river water and was generally low in all the points and effluents compared to WHO and FMEnv permissible limit. The low EC along the river can be attributed to the dilution effect and other natural processes along the river. Similar result was observed by Akpan-Idioka et al. [38].

However, there was a significant variation in the EC values among the locations of the river. Since the TDS and EC are indices for salinity hazard in water [39]. The EC values confirmed the low level of TDS in the river water. The result also implies that the river water is palatable for domestic and agricultural use.

Turbidity in water is caused by the presence of suspended matter such as clay, silk, finely divided organic. The entire river course sampling points and the effluents recorded a high turbidity above WHO and FMEnv standards. The river did record a high turbidity values as it affects fish and aquatic life by interference with sunlight penetration. Water plants need light for photosynthesis. If the suspended particles block out light, photosynthesis and the production of oxygen for fish and aquatic life will be reduced. If light levels get too low, photosynthesis may stop altogether and algae will die [40].

Apparent colour is the colour of the whole water sample and consists of colour from both dissolved and suspended components. The presence of colour in water does not necessarily indicate that the water is not potable. Colours in natural waters can originate from decomposition of organic matter and discharge of certain waste [35].

Conclusion

From the results of the study, effluent and water samples were above the permissible criteria by different regulatory bodies as it affects its physicochemical and biological quality. The poor quality of the paint industry effluent was seen as an indication of non-treatment or improper treatment of the effluents prior to its discharge into the Nkoho River. Secondly, there were variations in the constituents of the effluents at the different test times (September, October and November) and these variations were attributed to possible differences in the batches of paint produced at the different test time.

The discharge of effluents into the river caused changes in the quality of the river water. As was observed that the physicochemical characteristics of the Nkoho river water before the entrance of the effluent, did not meet the acceptable criteria for surface water. However, the entrance of the paint effluents aggravated the already poor water quality of the river. It was also observed that the water quality characteristics, varied with sampling points (up-stream, mid-stream and down-stream) and with sampling time (September, October and November).

It was finally observed that the poor quality of the water occasioned by the further deterioration following the entrance of the paint industry effluents, confer potentials of health hazards to users of the water. This raises strong public health concerns and challenge to appropriate environmental authorities to address without delay.

Recommendations

The results suggest that the effluents being discharged into the Nkoho River have considerable negative effects on the water quality in the recipient water body. The consistent discharge of the untreated or poorly treated effluents increases the load of nutrients and pollutants entering the river and this will continue to increase and further diminish the quality of water. It is therefore recommended that careless disposal of wastes should be discouraged and there is need for the industry to install a waste treatment plant with a view to treat wastes before being discharged into the river. There is also need for regulatory agencies like Federal Ministry of environment (FMEnv), Department of Petroleum Resources (DPR), National Environmental Standards and Regulatory Agency (NESRA) and the likes to closely monitor effluents from industries before its discharge.

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