Physicochemical dynamics of the impact of paper mill effluents on Owerrinta River, Eastern Nigeria.

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Abstract: Industrial effluent discharge constitute major source of water pollution. Effects of effluent discharge from three paper mill industries on recipient Owerrinta River was determined by subjecting samples to standard physicochemical analysis. All values were within standard excepting the pH value of Effluent-II sample (3.92) and Total Suspended Solids values of all the effluent samples (84, 496, and 165mg/l), respectively. There were significant variations ($P < 0.05$) between effluents and river samples and within effluents and river samples respectively, for all the parameters. The values varied as follows: temperature (24.70 – 24.12 ^{0}C); pH (6.68 – 3.92); conductivity (64.67 – 0.02 µS/cm); Turbidities (259.00 – 16.00 NTU); Total Dissolved Solids (29.50 – 1.50 mg/l); Total Suspended Solids (496.00 – 2.02 mg/l); nitrate (NO_3^-) (19.10 – 0.08 mg/l); phosphate (PO_4^{2-}) (0.81 – 0.02 mg/l); sulphate (SO_4^{2-}) (34.00 – 0.06 mg/l); Biochemical Oxygen Demand (1.09 – 0.41 mg/l); Chemical Oxygen Demand (8.25 – 0.72 mg/l) and Oil and Grease (4.01 – 1.92 mg/l). Variations from River samples indicated impact from effluents discharge, while variations in effluents values implied the contributory pattern of the effluents to River quality. The River recovered from some parameter. Treatment of effluents to insignificant values will reduce the impact on River quality.

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Introduction

The introductions of contaminants through effluent and sludge to different environments can often over whelm the self-cleaning capacity of recipient ecosystems and thus result in the accumulation of pollutants to problematic or even harmful levels. An awareness of environmental problems and potential hazards caused by industrial wastewaters has prompted many countries to limit the discharge of certain toxic effluents. The raw wastewaters from pulp, paper and board mills can be potentially very polluting. Wastewaters have prompted many countries to limit the discharge of certain toxic effluents. The raw wastewaters from pulp, paper and board mills can be potentially very polluting. Indeed, a survey within the UK industry has found that their Chemical Oxygen Demand (COD) can be as high as 11 000 mg/L (Thompson et al., 2001). The amount of pollutant in pulp and paper mill effluent is measured in terms of two key parameters, Total Suspended Solids (TSS) and Biochemical Oxygen Demand (BOD) (OFIA, 2005).

Full access to safe drinking water to citizens living in developing countries was the decision of the United Nations Assembly of 10th November 1980. However, almost two decades after, over two billion people especially in the developing countries, lack safe water and sanitation (ODA, 1997). In Nigeria, especially in the Eastern region, the large scale pollution of streams and rivers is not only a major public health problem but also constitute a principal obstacle to socio-economic advancement and fight against poverty and malnutrition (Okpokwasili and Ogbulie, 1993). This problem has had its toll on aquatic species extinction and fish diseases of various consequences (Okpokwasili *et al*., 1995; Ogbulie and Okpokwasili, 1998).

Community based studies (Izuagba and Ogbulie, 1997) revealed that the use of natural water bodies for industrial and domestic waste disposal is expected to worsen in the nearest future. Previous studies have revealed that our sources of water are not only polluted by sewage but also by toxic discharge and emission from industrial and other sources (Okpokwasili et al., 1997). This is a serious source of concern considering the rapid population growth in the developing countries.

Owerrinta River provides water for domestic, industrial, and small scale agricultural irrigation practices in addition to fishery and recreational activities. This work therefore was aimed at determining the physicochemical characteristics of the paper mill industrial effluents and the recipient River samples and comparing the values to understand the contributions of individual paper mill industries in Owerrinta River quality and the River's ability to recover from the impact, to assist environmental regulatory agencies and other stake holders in controlling discharges from individual industries into the River for a sustainable environment and development.

Materials and Methods

Study area:

Owerrinta River is located within longitude $7^0$17'E and Latitude $5^0$18'N and serves as a recipient of effluents from three paper mill industries (Effluent I - Star paper mill, Effluent II- Apex paper mill, and Effluent III- Industrial paper mill) closely sited together, and provides sand for excavators, source of fishes and water for domestic uses.

Sample collection:

Samples were collected in triplicates with the aid of clean 1 liter water sampling cans. Collected samples were transported to the laboratory for analysis. Effluent and River samples were collected from discharge points before discharge into Owerrinta Point of Imo River for two years (2008 and 2009). River samples were collected thus: upstream – 100metres before the first discharge point; discharge point – 20metres after the third discharge point; and downstream – 100metres after the third discharge point.

Methodology:

The temperature, pH, conductivity, and turbidity were determined using digital meters. Total Dissolved Solids and Total Suspended Solids measurements were carried out by using the conductivity/total dissolved solids meter (HACH DR/2010 Spectrophotometer Hand Book, 1997). Nitrate, phosphate, and sulphate were determined by using a spectrophotometer with Nitra var 5 nitrate, Phosphor var 5 phosphate, and Sulfa var 4 sulphate reagents as described in the HACH Water Analysis Handbook (HACH, 1981). Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), and Oil and Grease were determined as described by the *Standard Methods for the Examination of Water and Wastewater* (APHA/AWWA/WPCF, 1985).

Statistical analysis:

The result was subjected to different statistical analyses and presentations by using tools ranging from T-test, Analysis of Variance (ANOVA), and Tukey Grouping, by the method of Statistical Package for Social Sciences (SPSS 16.0).

Results:

Table 1 shows the comparison of physicochemical parameters of effluents and stream samples with FEPA standards at Owerrinta Point of Imo River. All the values of the parameters were within FEPA standard excepting the value of pH of Effluent - II sample (3.92) that was acidic and the values of TSS of all the effluent samples (84, 496, 165mg/l) respectively.

Table 2 shows the temperature values between paper mill effluents and river water samples. There was significant variation in temperature ($P<0.05$) between the river and effluent samples. Upstream, Discharge point and downstream samples (Tukey group–A) were not significantly different because they fell within the same domain of mean values. While group–A was significantly different from group-B (Effluent II) and group–C (Effluent - I and III); and group–B (Effluent - II) was significantly different from group-C (Effluent - I and III) and vice versa, because they fell with different domains of values.

There was significant variation in pH ($P<0.05$) between the river and effluent samples. Group-A (Effluent II) was very acidic (pH= 3.92) and was significantly different from other groups. Group-B (Effluent - III) was significantly different from group-C, D and E (Effluent - I, Discharge point, and downstream samples) respectively and vice versa because they fell with different domains of values.

There was significant variation in Conductivity ($P<0.05$) between the river and effluent samples. Upstream, discharge point and downstream samples (Tukey group-A) were not significantly different because they fell within the same domain of values. Group-A was significantly different from group-B (Effluent - II), group-C (Effluent - III) and group-D (Effluent - I), while group-B was significantly different from group-C and group-D and vice versa. Conductivity was lowest in group-A (0.02 µS/cm) and highest in group-D (64.67 µS/cm).

There was significant variation in Turbidity ($P<0.05$) between the river and effluent samples. Upstream and downstream (group-A) were significantly different because they fell within the same domain of mean values. Group-A varied significantly from groups-B, C, D and E (Discharge point, Effluent - I, Effluent - III and Effluent - II) respectively, while group-B varied significantly from groups-C, D, and E respectively and vice versa. Turbidity was lowest in group-A (16.00 NTU) and highest in group-E (259.00 NTU).

There was significant variation in TDS ($P<0.05$) between the river and effluent samples. The upstream and downstream samples (Tukey group-A) were not significantly different because they fell within the same domain of mean values. Group-A was significantly different from group-B (Discharge point), group-C (Effluent - II), group-D (Effluent - III) and group-E (Effluent - I), and vice versa. TDS was lowest in group in group-A (2.10mg/l) and highest in group-E (29.50mg/l).

There was significant variation in TSS ($P<0.05$) between the river and effluent samples. Upstream and downstream samples (Tukey group-A) were not significantly different because they fell within the same domain of mean values. Group A was significantly different from group-B (Discharge point), group-C (Effluent - I), group-D (Effluent -III), and group-E (Effluent -II), vice versa. TSS was lowest in group-A (1.8mg/l) and highest in group-E (496.0mg/l).

There was significant variation in nitrate ($P<0.05$) between the river and effluent samples. Upstream and downstream samples (Tukey group-A) were not significantly different because they fell within the same domain of mean values. While group-A was significantly different from group-B (Discharge point), group-C (Effluent - I), group-D (Effluent - II), and group-E (Effluent - III), group-B was significantly different from group-C, D, and E and vice versa. Nitrate was lowest in group-A (0.08mg/l) and highest in group-E (19.10 mg/l).

There was significant variation in phosphate (PO_4^{2-}) ($P<0.05$) between the river and effluent samples. Group-A varied significantly from groups-B, C, D, E and F and vice versa. Phosphate was lowest in group-A (0.02mg/l) and highest in group-F (Effluent - II) (0.8mg/l).

There was significant variation in sulphate ($P<0.05$) between the river and effluent samples. Upstream, discharge and downstream samples (Tukey group-A) were not significantly different because they fell within the same domain of mean values. Group-A was significantly different from group-B (Effluent - I), Group-C (Effluent - III), and group-D (Effluent - II), and vice versa. Sulphate was lowest in group-A (0.33mg/l) and highest in group-D (34.0mg/l).

There was significant variation in BOD_5 ($P<0.05$) between the river and effluent samples. Group-A (upstream) varied significantly from groups-B, C, D, E, and F (Discharge point, Downstream, Effluent III, Effluent II and Effluent I) respectively. BOD_5 was lowest in group-A (0.41mg/l) and highest in group–F (1.09mg/l).

There was significant variation in COD ($P<0.05$) between the river and effluent samples. Group-A (upstream) varied significantly from groups-B, C, D, E and F (Downstream, Discharge point, Effluent - I, Effluent - II and Effluent - III) respectively. COD was lowest in group-A (1.92mg/l) and highest in group-F (4.01mg/l).

There was significant variation in Oil and Grease ($P<0.05$) between the river and effluent samples. Group-A (upstream) varied significantly from groups-B, C, D, E, and F (Downstream, Discharge point, Effluent - III, Effluent - II and Effluent - I) respectively. Oil and grease was lowest in group-A (1.92mg/l) and highest in group-F (4.01mg/l).

Discussion:

The parameters as determined and shown in **Table 1** are those of effluents from industries and stream samples, and were compared with the guidelines for effluent discharge limitations (FEPA, 1991). The temperatures of the water samples and the effluent samples were within the <40^{o}C standard of FEPA. There was significant variation ($P <0.05$) between the mean values of the temperatures of effluent and water samples.

That temperatures of the upstream, discharge point and downstream water samples did not vary from each other and were lower than that of the effluent implied that the impact of the effluent could not elevate the temperature of the stream and the stream recovered quickly from the impact of the varied temperature of the effluents. This is in accordance with the reports of Sharples and Evans (1998) and Nwaedozie (2000).

There was significant variation between the effluent pH values and those of the water samples. The individual pH of each effluent (I, II and III) varied significantly which might be caused by the different chemical compositions of the effluents. The pH of the upstream water sample did not vary from the pH of the downstream butt both varied from the pH of the discharge point. The variation recorded with the discharge point might be due to the impact of the effluents discharged into the river at that point while the similarity in with the pH values of the upstream and downstream might be due to possible recovery of the stream from the impact of the effluents. This corroborates the reports of Odoemelam (1999).

The conductivity recorded significant variations between the stream samples and the effluent samples, though there was no variation within the stream samples while the effluent recorded variation in conductivity within the samples. This implied that the effluents contained higher levels of ionized salts from industrial activities than the stream samples, though the stream samples recovered from the impact of the effluent discharge. This corroborates the reports of Oluwande et al. (1983).

The turbidity measurement and analysis of stream samples and effluent samples showed significant variation. There was similarity between upstream and downstream samples while the samples varied from discharge point sample. This showed that the stream might have been recovered from turbidity levels of the different effluent samples. This corroborated the report of Sharples and Evans (1998).

Table 1: Comparison of physicochemical parameters of effluents and stream samples with FEPA standards at Owerrinta Point of Imo River.

		STREAM SAMPLES			EFFLUENT SAMPLES			
PARAMETERS	A	B	C	I	II	III	FEPA STD	
Temperature ^{0}C	24.12	24.14	24.15	24.70	24.4	24.70	<40	
pH		6.68	6.35	6.67	6.22	3.92	6.13	6-9
Conductivity µS/cm		0.01	0.02	0.01	59.00	48.00	53.00	NA
Turbidity NTU	16.00	28.00	6.80	51.00	259	121	NA	
TDS mg/L		2.10	6.90	1.50	29.50	24.00	26.50	2000
TSS mg/L		4.80	17.00	2.02	84.00	496	165	30
NO_3^- ,,		0.09	2.00	0.08	3.40	8.50	19.10	20
PO_4^{2-} ,,		0.02	0.16	0.08	0.04	0.81	0.26	5
SO_4^{2-} ,,		0.33	1.00	0.06	19.00	34.00	30.00	500
BOD_5 ,,		0.41	0.66	0.78	1.09	1.02	0.48	50
COD ,,		0.72	1.24	1.22	4.77	8.25	6.97	NA
Oil and grease mg/L	1.92	3.22	2.01	4.01	3.91	3.77	10	

NA = Not availab

Table 2a: Physicochemical variations between paper mill effluents and river water samples

Sample	Temperature ^{0}C	pH	Conductivity µS/cm	Turbidity NTU	TDS mg/L	TSS mg/L
Upstream	24.12±0.026A	6.68±0.017E	0.13±0.06A	16.00±1.00A	2.10±0.10A	1.80±0.17A
Discharge point	24.14±0.026A	6.35±0.01D	0.02±0.01A	28.00±1.00B	6.90±0.20B	17.00±1.00B
Down Stream	24.13±0.025A	6.67±0.01E	0.02±0.01A	16.00±1.00A	2.10±0.10A	2.02±0.01A
Effluent I	24.70±0.100C	6.22±0.01C	64.67±6.66D	50.67±1.53C	29.50±0.17E	84.00±1.73C
Effluent II	24.40±0.173B	3.92±0.01A	47.00±1.00B	259.00±1.73E	24.00±0.50C	496.00±1.00E
Effluent III	24.70±0.100C	6.13±0.02B	52.00±1.00C	120.67±1.53D	26.50±0.50D	165.00±1.00D

At $P > 0.05$, Tukey grouping with same letters are not significantly different
At $P < 0.05$, Tukey grouping with different letters are significantly different.

Table 2b: Physicochemical variations between paper mill effluents and river water samples

Sample	Nitrate mg/L	Phosphate mg/L	Sulphate mg/L	BOD_5 mg/L	COD mg/L	Oil & Grease mg/L
Upstream	0.09±0.01A	0.02±0.01A	0.33±0.01A	0.41±0.01A	0.72±0.01A	1.92±0.01A
Discharge point	1.67±0.66B	0.16±0.01D	1.00±0.10A	0.66±0.01B	1.24±0.01C	3.22±0.01C
Down Stream	0.08±0.10A	0.08±0.01C	0.33±0.01A	0.78±0.01C	1.22±0.01B	2.01±0.01B
Effluent I	3.40±0.10C	0.40±0.01B	19.00±1.00B	1.09±0.01F	4.77±0.01D	4.01±0.01F
Effluent II	8.50±0.10D	0.81±0.01F	34.00±1.00D	1.02±0.01E	8.25±0.01F	3.91±0.01E
Effluent III	19.10±0.10E	0.26±0.01E	30.00±1.00C	0.97±0.01D	6.97±0.01E	3.77±0.01D

- At $P < 0.05$, Tukey grouping with different letters are significantly different.
- At $P > 0.05$, Tukey grouping with same letters are not significantly different.

The TDS that was recorded between the mean values of the effluents and the mean values of stream water samples indicated higher dissolved solutes in paper mill effluents than the water samples. The mean values of the upstream and downstream were the same but varied from the value of the discharge point sample which might be probably due to the impact of the effluent discharge at the point and possible recovery of the river at downstream. This is in line with the work of Odoemelam (1999) and Colodey and Wells (1992).

The TSS values of the effluents recorded variations with the stream water samples similar to the TDS and might inferences. This is in line with the report of Colodey and Wells (1992).

The sulphate values of the effluents varied significantly with the mean values of the stream water samples. This might imply higher dissolved sulphate solutes in the effluent than the stream samples. These high values of sulphate in effluent did not influence the value of the discharge point and subsequently the value of the downstream probably due to natural ability of the river to recover from the impact. This is supported by the report of Anyam (1990).

The values of nitrate of effluents and the mean values of river water samples showed significant variation between effluents and river water samples, variations within effluent samples and variations within River samples, though the value of the upstream sample did not vary from the value of the downstream samples. These variations might imply that there were higher values of nitrate in effluents than the stream sample, and that the higher value indicated in discharge point over the upstream and downstream values might be due to the impact of effluent discharge from the paper mill industry. While the similarity in the values of upstream and downstream indicated possible recovery of the river from the impact of the effluent discharge. The values of the effluent varied in this pattern: Effluent III >Effluent II > Effluent I, implying that this was the contributory pattern of nitrate to the river. This report is in accordance with that of Beecroft and Oladimeji (1987).

The values of phosphate of effluent and the values of river samples showed significant variation between effluent and river samples. The value of phosphate in Effluent - I was less than the values at discharge point and downstream. This implied the major phosphate in river were Effluent II an Effluent III. The value of downstream was higher than the upstream value indicating possible non-recovery of the river at the point from impact of phosphate discharges from effluents. The values of the effluent varied in this pattern: Effluent II > Effluent > Effluent I, implying that this was the contributory pattern of phosphate to the river. This is in conformity with the report of Odoemelam (1999).

The five – day Biochemical Oxygen Demand (BOD_5) indicated that there were significant variations in BOD_5 of effluents and river samples, variations within the river samples and variations within the effluent samples. The values in the river showed the following trend; downstream > discharge point > upstream. This implied possible rise in BOD_5 due to the effluent discharges at the discharge point and further increase recorded at downstream probably due to discharges from drainages that empty into the river and other human activities. The trend in the values of BOD_5 effluents showed: Effluent I > Effluent II > Effluent III which might imply that it was the contributory pattern of organic materials into the river. This corroborates the works of Sharples and Evans (1998).

The records of Chemical Oxygen Demand (COD) indicated that there was a significant variation in COD of effluent and river samples, variations within the river effluents and variation within the effluent samples. The values in the river showed the following trend: discharge point > downstream > upstream. This implied that high COD recorded at discharge point might be due to high chemical discharge at the point and the rivers gradual recovery at the downstream. The trend in the values of COD of effluents showed: Effluent II > Effluent III > Effluent I which may mean that it was the contributory pattern of chemicals into the River. This corroborates the works of Sharples and Evans (1998), and Sial et al. (2006).

The values of oil and grease analysis shared significant variations in oil and grease values of effluents and River samples, variations within the River samples and variations within the effluent samples. The values in the River showed the following trend: discharge point > downstream > upstream. This implied that high oil and grease recorded at discharge point might be due to high oil spill, leakages, and discharge of spent oil from generator engines, machines, vehicles, and tanks. This is in conformity with the report of Otokunefor and Obiukwu (2005). The trend in the values of oil and grease of effluents showed: Effluent I > Effluent II > Effluent III which might imply that it was the contributory pattern of oil and grease into the River. This corroborates the work of Sial et al. (2006).

Conclusion

The research work revealed the impact of the paper mill effluents from the three paper mill industries on the Owerrinta River. Though the impact might not be conclusive by comparison of values of parameters with local and international water and effluent regulatory standards, the dynamism of the River values exposed the impact and the River's natural ability to contain with the impact from the industries. Treatment of effluent has not reduced the impact of the discharges on the empirical quality of water bodies which might expose organisms to toxic effects.

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