IMPACT ASSESSMENT OF INDUSTRIAL EFFLUENT ON WATER QUALITY OF THE RECEIVING ALARO RIVER IN IBADAN, NIGERIA.

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ABSTRACT

Alaro River is receiving industrial effluent as a point source. The water quality of the river upstream and downstream after the point of effluent discharge was assessed with the view of determining the effect of industrial effluent on the water quality of the river. The water samples were analyzed for dissolved oxygen (DO), pH, alkalinity, electrical conductivity, total solid (TS), chloride, sulphate, phosphate and heavy metals (Pb, Mn, Ni, Cd, Cr and Cu). The average levels of the parameters upstream were: pH (7.8 ± 0.5); DO (7.0 ± 1.3 mg/L); alkalinity (405 ± 103 mg $CaCO_3$/L); TS (328.8 ± 106.7 mg/L); chloride (474.8 ± 154.1 mg/L); sulphate (2.3 ± 0.7 mg/L); phosphate (0.175 ± 0.026 mg/L); Pb (0.023 ± 0.001mg/L); Mn (0.169 ± 0.009 mg/L); Ni (0.011 ± 0.003 mg/L); Cd (0.004 ± 0.002 mg/L); Cr (0.003 ± 0.001 mg/L) and Cu (0.005 ± 0.001 mg/L). Much higher average levels of alkalinity (744 ± 80 mg $CaCO_3$/L); total solids (1379 ± 389 mg/L); chloride (1126 ± 83 mg/L); sulphate (16.4 ± 13.9 mg/L); phosphate (4.62 ± 2.07 mg/L); Pb (0.14 ± 0.03 mg/L); Mn (0.456 ± 0.190 mg/L); Ni (0.03 ± 0.03 mg/L); Cd (0.01 ± 0.001 mg/L); Cr (0.021 ± 0.007 mg/L); Cu (0.0923 ± 0.035 mg/L) and lower average levels of pH (6.5 ± 0.5) and DO (0.63 ± 0.93 mg/L) were obtained downstream. The levels of most parameters in the effluent exceeded the effluent guideline for discharge into surface water. River's recovery capacities for the water quality parameters were fairly good and ranged between 36 and 90 %.

Keywords: Alaro River; Industrial effluent; Water quality; Pollution; Nigeria

1. INTRODUCTION

One of the most critical crises in developing countries is the lack of adequate treatment of drinking water. Rivers, streams, wells, and borehole water are usually used as supplements for the scarce pipe borne water for drinking with little or no treatment. Drinking such water has led to the outbreak of epidemics such as cholera and other water related diseases on several occasions (Frontiers, 1996; USFDA, 1993; Adesina, 1986). The supply of water in several cities is limited, and in many cases, water supply is chronically insufficient for the inhabitants. Despite the inadequacy of water supply, the management and conservation of the available water bodies is generally poor. Industrial growth is fast increasing globally and so also is the water demand for industrial productions or processes. This has put more pressure on the limited available water resources. Water bodies are also constantly used as receptacles for the untreated waste water or poorly treated effluents accrued from industrial activities, which has rendered many water bodies unsuitable for both primary and/or secondary usage.

In advanced countries, environmental monitoring agencies are more effective and environmental laws are strictly followed. General environmental quality monitoring is compulsory and the monitoring of the quality of water resources is done on a regular basis (Neal and Robson, 2000; USEPA, 2000; Robson and Neal, 1997; USEPA, 1996; USEPA, 1995; USGS, 1995, USEPA, 1991). As a result, any abnormal changes in the environmental or water quality can easily be detected and appropriate action taken before the outbreak of epidemics.

The case is quite the opposite in many developing countries. Environmental laws where there are any, are rarely observed. Industrial growth and its associated environmental problem such as soil, plant, and air contamination is fast increasing (Fakayode and Onianwa, 2002; Onianwa and Fakayode, 2000). Reports of general water quality contaminations in several cities in Nigeria abound (Olajire and Imeokparia, 2001; Biney et al., 1994; Onianwa, 1993) yet, little is known about the effect of effluent discharge as a point source on the water quality of numerous rivers and streams in the country. Literature on the recovery capacity studies from pollutional loads or stress, a significant parameter in determining the degree of self -purification ability of rivers is also sparse or limited.

The present study investigates the effect of the industrial effluent as a point source on the water quality of a receiving Alaro River in Oluyole Industrial Estate in Ibadan, Nigeria**.** Ibadan is the second largest and the second most populated city in Nigeria with an estimated population of 4 million. In addition, the effluent was also sampled and analyzed to evaluate the level of compliance with the effluent quality guideline for discharge into surface water. The study further determined the recovery capacity of Alaro River from the effluent pollutional load.

2. MATERIAL AND METHODS

The industries in the Oluyole Industrial Estate range from agrochemical, paper mill, and pharmaceutical to metal works, construction, foods, and packaging industries. The effluents from the industries in the estate were connected by a network of canals and channeled directly into Alaro River as a point source (see Figure 1). Effluent (EFF) was collected as a composite sample at the point of discharge (PD) into the river at 15 minutes interval over a period of four hours. At each time of effluent collection, two separate set of samples were collected, one for the determination of heavy metals and the second for the determination of other physico-chemical parameters. The point of discharge was chosen as a reference point. Water upstream (UPS) were sampled at four sampling locations before the point of effluent discharge at a distance of 250 m apart. Water samples were also collected downstream after the point of discharge (APD) of the effluent at ten different sampling locations at 250 m intervals. At each sampling location, the surface water sample was collected at the middle of the river and stored in a clean polyethylene bottles that have been prewashed with nitric acid and thoroughly rinsed with deionized water.

The water chemical analysis was done using standard analytical methods of water analysis (Trivedi and Goyal, 1986; APHA-AWWA-WPCF, 1985; USEPA, 1979). Non-conservable parameters such as, temperature, pH, and electrical conductivity (EC) were determined at the time of sampling in the field. The pH of the sample was measured with a pH meter that has been previously calibrated with buffer solutions and conductivity was measured with a conductivity meter calibrated with potassium chloride solution. Dissolved oxygen (DO) was determined by Winkler's titration. The dissolved oxygen contents of the effluent or water samples were fixed on the field by addition of manganous sulphate solution and alkali-iodide-azide reagents to the sample. The samples were transported to the laboratory where the samples were titrated with a standard sodium thiosulphate solution. Total solid (TS) was determined gravimetrically by evaporating a known volume of water sample to dryness in a preweighed crucible on a steam bath at 105^oC. Sulphate (SO_4^{2-}) was determined by a turbidimetric method. 20 mL of the buffer solution (made from magnesium chloride, sodium acetate, potassium nitrate, and acetic acid), and a spoonful of barium chloride crystal was added to a known volume of the sample and stirred on a magnetic stirrer for one minute. The barium sulphate turbidity was then measured with a UV-visible spectrometer at 420nm. Alkalinity was determined by titrating a known volume of water sample with 0.10M HCl. Chloride (Cl^-) was analyzed by titration of a known volume of water sample with standardized 0.014N mercuric (II) nitrate solution. Phosphate (PO_4^{3-}) was determined colorimetrically by ascorbic acid-molybdenum blue method (APHA-AWWA-WPCF, 1985).

Heavy metal was determined by digesting a known volume of water sample with analytical grade HNO_3. The digested sample was filtered into a 20 ml standard flask, made up to the mark with distilled-deionized water and stored in a nitric acid prewashed polyethylene bottle in the refrigerator prior to the chemical analysis. The water extracts were analyzed for metals (Pb, Mn, Ni, Cd, Cr, and Cu) by atomic absorption spectrometer. Each sample was analyzed in duplicate and the average of the results reported. General laboratory quality assurance measures were always observed to prevent sample contamination and instrumental errors. The water used throughout the experiment was doubly distilled in an all glass distiller before it was deionized. Wavelengths setting of the spectrometers used were done daily by the standard instrumental procedure and other equipment used were always calibrated against reference standards

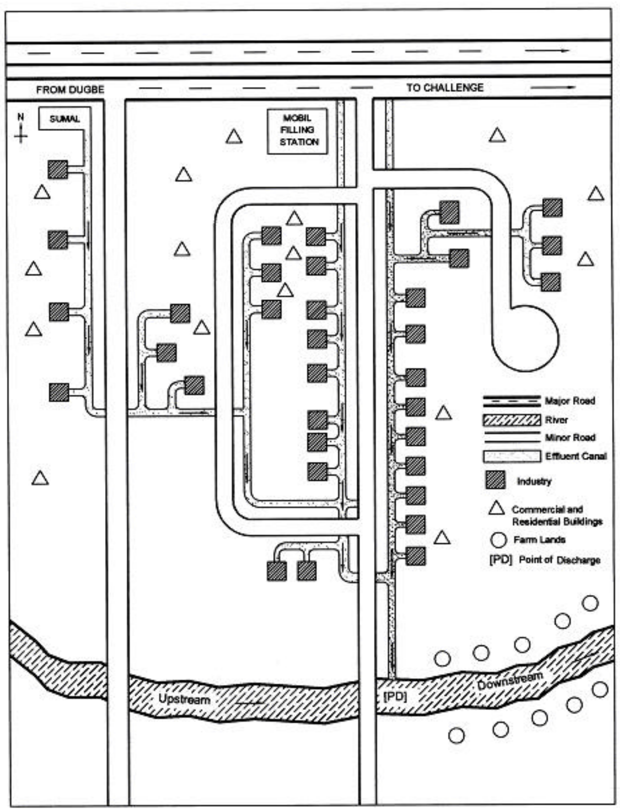

Figure 1. Layout of the Oluyole Industrial Estate, Ibadan, Nigeria

3. RESULTS AND DISCUSSION

Alaro River was a clean, clear and free flowing river before the point of the discharge of the effluent. After the point of discharge, the river became gray-black, stagnant with offensive odour. Table I shows the average levels of pH, DO, alkalinity, EC, chloride, sulphate, phosphate, and TS with distance at the sampling points. The degree of contamination as a result of effluent discharge was estimated by the accumulation factor (AF), the ratio of the average level of a given parameter downstream after the point of effluent discharge to the corresponding average level upstream (Table II).

Table I: Levels of pH, dissolved oxygen (DO), alkalinity, electrical conductivity, chloride, sulphate, phosphate and total solids at various sampling points

Sampling Point	Distance (m)	pH	DO (mg/L)	Alkalinity (mg $CaCO_3$/L)	EC ($\Omega^{-1}cm^{-1}$)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	PO_4^{3-} (mg/L)	TS (mg/L)
UPS4	1000	8.2	6.9	520	3400	279.9	1.6	0.19	230
UPS3	750	7.2	5.4	450	7300	559.8	3.2	0.17	440
UPS2	500	7.8	7.2	370	5600	629.8	2	0.14	245
UPS1	250	8.1	8.5	280	6800	429.9	2.3	0.20	400
Average upstream		7.8	7.0	405	5775	474.8	2.3	0.18	328.8
*STDEV		0.5	1.3	103	1737	154.1	0.7	0.03	106.8
EFF	0	5.4	0.0	940	22000	1279.6	52	88.10	2655
APD1	250	5.5	0.0	880	20000	1259.6	45	8.44	1995
APD2	500	6.2	0.0	840	18000	1240	32	7.47	1755
APD3	750	6.3	0.0	790	14000	1169.6	27	6.26	1735
APD4	1000	6.4	0.0	780	13000	1149	15	5.41	1535
APD5	1250	6.7	0.0	750	13000	1134	12	4.99	1445
APD6	1500	6.7	0.0	740	13000	1127	11	4.26	1290
APD7	1750	6.8	0.8	700	12000	1070	10	2.81	1220
APD8	2000	6.9	1.1	670	12000	1059.7	4	2.63	1140
APD9	2250	6.9	1.9	650	12000	1042.7	4	2.37	915
APD10	2500	7.1	2.5	640	12000	1009.4	4	1.82	760
Average downstream		6.5	0.63	744	13900	1126	16.4	4.62	1379
*STDEV		0.5	0.93	80	2807	83	13.9	2.27	389

*Standard deviation (±)

The temperatures of the water upstream and downstream were normal with no significant difference. The average temperature obtained upstream and downstream of 27.5 ^{o}C was about the values of the ambient air temperatures. The pH levels upstream ranged from 7.2 to 8.2, with an average level of 7.8. These pH values were normal for unpolluted fresh water (Kudryavtseva, 1999; Chernyavskaya et al., 1993). The acidity of the effluent was low (pH 5.4) compared to the pH of water upstream. Low pH of the effluent could be attributed to mineral acids such as hydrochloric, nitric, phosphoric and/or sulphuric acids which are essential reagents or raw materials in many industries. Discharge of the effluent into the river resulted to a decrease in pH levels of the water downstream. The pH level was 5.5 at APD1 and 6.2 at APD2. The level of pH 6.9 at APD9 was still slightly acidic and lower than the pH levels obtained upstream. pH has profound effects on water quality. It affects the metals solubility, the alkalinity, and hardness of the water. Aquatic organisms are also affected by pH because most of their metabolic activities are pH dependent (Wang et al., 2002; Chen and Lin, 1995; Morgan and McMahon, 1982; Haines, 1981).

Table II: Accumulation factors and percentage recovery capacity of the water quality parameters

Parameters	Accumulation Factor [A]	Percentage Recovery Capacity
Pb	6.1	70.0
Mn	2.7	46.4
Ni	2.7	50.0
Cd	2.5	50.0
Cr	7.0	75.0
Cu	18.4	50.0
Cl^-	2.4	53.0
SO_4^{2-}	7.1	42.0
PO_4^{3-}	26.4	90.4
TS	4.2	56.7
Alkalinity	1.8	36.0
EC	2.4	52.0

[A]Ratio of the average level of a given parameter downstream to the average level upstream

DO was not detected in the effluent. This was not surprising considering the high levels of nutrients, organic loads, and total solids contents of the effluent. DO is very crucial for the survival of aquatic organisms and is also used to evaluate the degree of freshness of a river. The water upstream was rich in DO, with DO levels ranged between 5.4 to 8.5 mg/L. These levels could adequately sustain aquatic lives. DO was not detected at any sampling location from the point of effluent discharge and APD6. It was completely depleted until APD7, and the level of DO at APD10 was just 2.5 mg/L. Depletion of the level of DO downstream was due to the enormous amount of organic loads which required high levels of oxygen for chemical oxidation, decomposition or break down.

The levels of alkalinity upstream ranged between 280 and 520 mg $CaCO_3$/L, with an average level of 405 mg $CaCO_3$/L. The average level of alkalinity downstream was accumulated by a factor of 2 compared with the average level of alkalinity upstream. Effluent has an average level of alkalinity of 940 mg $CaCO_3$/L.

Electrical conductivity (EC) is a measure of conducting ionic species in a sample solution. Effluent was of an average level of EC of 22000/Ωcm. High levels of EC of the effluent could be attributed to the high levels of conducting species such as sulphate, chloride, phosphate, and heavy metals present in the effluent. EC levels upstream ranged between 3400 and 7300/Ωcm with an average level of 5775/Ωcm, while the levels of EC downstream was of an average level of 13900/Ωcm.

Sulphate levels upstream ranged from 1.6 to 3.2 mg/L with an average level of 2.3 mg/L. These levels were similar to the natural background sulphate levels of 1-3 mg/L reported in other unpolluted rivers elsewhere (Kudryavtseva, 1999; Offiong and Edet, 1998). The level of sulphate in the effluent was 52 mg/L. Level of sulphate in the effluent could be ascribed to the use of sulphuric acid or sulphate salts, which are commonly used in several industries. Although the average level of sulphate of 16.4 mg/L downstream was accumulated by a factor of 7 compared with the average sulphate level upstream, it was comparatively lower than the sulphate levels of 662 mg/L, 275 mg/L, 168 mg/L and 59 mg/L reported from other pollution studies elsewhere in rivers receiving industrial waste water or effluents of higher sulphate contents (Seleznev and Selezneva, 1999; Stamatis, 1999; Riv'er and Litvinov, 1997).

The average level of phosphate (88.1 mg/L) in the effluent was particularly too high and of great concern. The major sources of phosphate in the effluent were from phosphoric acid, phosphate salts and detergents used for washing in the canteens of most of the industries. A relatively low average phosphate level of 0.175mg/L was found upstream. Discharge of effluent of high phosphate content into the river resulted in increased levels of phosphate downstream with an average phosphate level of 4.62 mg/L. Phosphate was the most accumulated nutrient downstream with an accumulated factor of 26. High levels of phosphate and other nutrients downstream have led to the eutrophication and outbreak of the growth of alga, which could further deplete the DO levels of the river.

The average level of chloride in the effluent was 1279 mg/L. The sources of chloride in the effluent were likely to be from hydrochloric acid, common salt (NaCl) and other chloride containing compounds, which are usually used as raw materials particularly in the food industries. Chloride was of an average level of 474.8 mg/L upstream, and ranged between 279.9 and 629.8 mg/L. The chloride levels downstream were elevated than the chloride level upstream, with an accumulation factor of 2.4. An elevated level of chloride downstream with a corresponding low level upstream of receiving effluent rivers of Upper Volga and Danube has been reported by other researchers in other countries (Chernyavskaya et al., 1993; Riv'er and Litvinov, 1997).

Effluent was of high TS, with an average TS level of 2655 mg/L. TS is the sum total of the suspended solid particulates and dissolved materials in the effluent. The levels of TS upstream were generally lower than the levels downstream with average levels of TS of 328.8 mg/L and 1379.3 mg/L, respectively. Deposition of solid particulates from the effluent through the river course could lead to the reduction in the volume of the water and also impede the free flowing of the river. Long term deposition of materials in the river could also result in flooding, particularly during heavy rain fall which could have both economic and ecological implications.

The levels of heavy metals at the sampling points upstream, downstream and in the effluent are presented in Table III. Pb, Mn, and Ni were of average levels of 0.23, 0.93, 0.048 mg/L, respectively, in the effluent, while the average levels of Cd, Cr, and Cu in the effluents were 0.016, 0.09, 0.237 mg/L, respectively. The sources of the heavy metals from the effluent could probably be from the metal work, construction and engineering and agrochemical industries. The average levels of Pb, Mn, Ni, Cd, Cr, and Cu upstream were 0.023, 0.169, 0.011, 0.004, 0.003, and 0.005 mg/L, respectively, while their corresponding average levels downstream were 0.14, 0.456, 0.03, 0.01, 0.021, 0.092mg/L, respectively. Copper was the most accumulated metal downstream with an accumulation factor of 18. Lead and chromium were accumulated by a factor of 6 and 7 than the corresponding average level upstream. Low level of Pb, Mn, Ni, Cd, Cr, and Cu upstream before the point of effluent discharge with the corresponding higher level downstream after the point of effluent discharge in many rivers has also been reported elsewhere (Gasparon and Burgess, 2000; Tsareva et al., 1999; Kashin and Ivanov, 1997). Water downstream is used for irrigation of many vegetables and other food crops along the bank of the river because of its high nutrient contents. Accumulation of heavy metals by crops receiving such contaminated water for irrigation is common and metals could be biomagnified along food chain to a higher tropic level. Consumption of such food crops could expose man to untold heavy metal hazards.

Table III: Levels of heavy metals (mg/L) at the sampling points

Sampling Point	Distance (m)	Pb	Mn	Ni	Cd	Cr	Cu
UPS4	1000	0.01	0.160	0.015	0.003	0.003	0.004
UPS3	750	0.02	0.170	0.011	0.006	0.003	0.006
UPS2	500	0.03	0.180	0.009	0.003	0.002	0.005
UPS1	250	0.03	0.165	0.010	0.003	0.002	0.005
Average Upstream		0.023	0.169	0.011	0.004	0.003	0.005
*STDEV		0.001	0.009	0.003	0.002	0.001	0.001
EFF	0	0.23	0.93	0.048	0.016	0.09	0.237
APD1	250	0.18	0.860	0.032	0.012	0.038	0.128
APD2	500	0.172	0.747	0.030	0.010	0.024	0.122
APD3	750	0.17	0.495	0.029	0.010	0.023	0.117
APD4	1000	0.16	0.388	0.029	0.010	0.020	0.110
APD5	1250	0.16	0.385	0.028	0.010	0.019	0.107
APD6	1500	0.14	0.375	0.027	0.010	0.019	0.105
APD7	1750	0.11	0.344	0.026	0.010	0.018	0.087
APD8	2000	0.11	0.329	0.023	0.010	0.017	0.080
APD9	2250	0.10	0.326	0.022	0.009	0.016	0.067
APD10	2500	0.10	0.308	0.022	0.008	0.012	0.010
Average Downstream		0.14	0.456	0.026	0.010	0.021	0.092
*STDEV		0.03	0.190	0.003	0.001	0.007	0.035

*Standard deviation (±)

Table IV compares the quality of the effluent from this study with the effluent quality guidelines for discharge into surface water in some developing and developed countries. Most of the parameters in the effluent did not meet the minimum requirement to be discharged into the surface water. Parameters such as chloride, total solids, and phosphate in particular were above the recommended limits. The effluent was too acidic and its pH was lower than the effluent quality guideline. However, the levels of sulphate and some metals in the effluent were within the effluent quality standards. Generally, industrial effluents are toxic and discharge of such untreated or poorly treated effluent could have serious consequences on aquatic organisms (Fisher et al., 1998; Moiseenko, 1999).

Unlike in advanced countries where industrial productions are usually done in an environmentally friendly manner through the use of modern and best available technologies or processes, many industries in developing countries still use either outdated or the best practicable technologies due to economic constraints. Treatment of effluents to recommended and safe levels requires additional overhead cost which several industries either cannot afford or are not willing to pay.

Table IV: Comparison of the effluent quality from this study with effluent standards of some countries

Parameter	Effluent from this study	China[A]	Japan[A]	Caribbean[A]	Kenya[A]	Uganda[A]	Nigeria[B]
pH	5.4	6.0-9.0	6-8.5	6-9	6.9-8.5	6-8	6-9
DO (mg/L)	0.0	-	-	-	-	-	-
Alkalinity(mg $CaCO_3$/L)	940	-	-	-	-	-	-
EC ($\Omega^{-1}cm^{-1}$)	22000	-	-	-	-	-	-
Cl^- (mg/L)	1279.6	-	-		1000	30	600
SO_4^{2-} (mg/L)	52	-	-	-	1000	500	500
PO_4^{3-} (mg/L)	88.1	-	-	-	-	-	5.0
TS (mg/L)	2655	-	-	-	-	-	2000
Pb (mg/L)	0.23	-	0.1	0.1	3	0.1	1
Mn (mg/L)	0.93	10	10	-	-	1.0	5.0
Ni (mg/L)	0.048	1	-	3.0	1.0	1.0	1.0
Cd (mg/L)	0.016	0.03	0.1	2	0.5	0.5	1
Cr (mg/L)	0.09	2.0	0.1	2.0	1.0	1.0	1.0
Cu (mg/L)	0.237	3.0	1.0	3.0	1.0	1.0	1.0

[A] Source: NEMAMNR, 1997; [B] Source: FEPA, 1983

The water of Alaro River is generally used for washing, cooking, fishing, and irrigational purposes. The water is also used for drinking with little or no pretreatment under acute or chronic water shortage. The quality parameters of water from the river were therefore compared with drinking water guidelines. The overall average levels of the water quality upstream and downstream as compared with the drinking water quality standards of some regulatory bodies are shown in Table V. Almost all the parameters determined upstream were within the maximum permissible limit for drinking water, while the levels of parameters such as alkalinity, EC, Cl^-, TS, Pb, Cd, and Cr downstream were significantly above the recommended maximum permissible limit.

Statistical method of analysis was employed to determine the nature and the possibility of other sources of pollutants in the river apart from the effluent. Regression analysis was used to evaluate the correlation between water quality parameter pairs upstream and downstream. There was no significant correlation (at $p < 0.05$) upstream between DO/alkalinity, DO/Cl^-, DO/PO_4^{3-}, DO/TS, alkalinity/EC, alkalinity/Cl^-, SO_4^{2-}/alkalinity, PO_4^{3-}/alkalinity, TS/alkalinity, EC/Cl^-, EC/PO_4^{3-}, Cl^-/SO_4^{2-}, Cl^-/TS, PO_4^{3-}/SO_4^{2-}, PO_4^{3-}/TS, pH/DO, pH/alkalinity, pH/Cl^-, pH/PO_4^{3-}, pH/TS, Pb/Mn, Pb/Cd, Pb/Cu, Mn/Cd, Mn/Cr, Ni/Cd, Ni/Cu, Cd/Cr, and Cr/Cu, whereas they were highly correlated downstream (see Table VI). Non correlation between these parameters upstream was a strong indication of absence of other common source of polluting substances upstream. Slight correlations only occurred between Cl^-/PO_4^{3-}, Mn/Ni and Cd/Cu upstream which could probably be attributed to the intrusion of these parameters from unavoidable or natural phenomena such as leaching of soil nutrients and water run-off. High correlations between all the pair quality parameters downstream confirmed the effluent as the primary and the only common source of the pollutants.

Table V. Comparison of the water quality upstream and downstream with the drinking water guidelines

Parameter	Upstream	Downstream	Maximum permissible limit	Organization/Body
pH	7.8	6.5	6.5-9.2	WHO, 1984; ISI, 1983
DO (mg/L)	7.0	0.63	-	
Alkalinity (mg $CaCO_3$/L)	405	744	500	
EC ($\Omega^{-1}cm^{-1}$)	5775	13900	2500	WHO, 1984
Cl^- (mg/L)	474.8	1126	250	WHO, 1984; USEPA, 1989
SO_4^{2-} (mg/L)	2.3	16.4	400	WHO, 1984
PO_4^{3-} (mg/L)	1.75	4.62	-	
TS (mg/L)	328.8	1379	1000	WHO, 1984
Pb (mg/L)	0.023	0.14	0.01-0.06	WHO, 1984; EC, 1980; CWQG, 1995
Mn (mg/L)	0.169	0.46	-	
Ni (mg/L)	0.011	0.03	1.0	WHO, 1984
Cd (mg/L)	0.004	0.01	0.005	WHO, 1984; CWQG, 1995
Cr (mg/L)	0.003	0.021	0.05	WHO, 1984; USEPA, 1989; CWQG, 1995
Cu (mg/L)	0.005	0.092	1	WHO, 1984; CWQG, 1995

The knowledge of the overall concentration of pollutants in the effluent receiving rivers or streams is critical, but is not enough to determine the spatial and temporal changes of the river water quality from pollution stress. River or stream has natural recovery capacity or self-purification ability in which the pollutants are removed, redistributed, decomposed or transformed to harmless substances. Self-purification capacity of water is a good indicator to evaluate the ecological status of a water body (Ernestova and Semenova, 1994). Self-purification of rivers primarily involves chemical oxidation, biodegradation of organic material, volatilization of volatile organic compounds, and deposition of solid or particulate materials into the sediment and dilution of the contaminants by water. Self-purification of river involves complex mechanism and depends on several factors such as the flow rate, time, temperature, presence of micro organisms, pH, and dissolved oxygen content of the water. The nature of the contaminants also plays significant roles on the river recovery capacity. Hence, some rivers quickly recover from pollution stress than others depending on the prevailing factors. The degree of river's recovery capacity (RRC) expressed in percentage of the Alaro River over the stretch of the investigated river section from the effluent pollutional loads was calculated using the formula adapted from Ernestova and Semenova (1994):

$$RRC = \frac{(S_0 - S_1)}{S_0} * 100$$

where, S_0 is the level of the parameter at the furthest-downstream sampling point (APD10) and S_1 is the corresponding average level upstream where there was no pollution. The percentage recovery capacities of the river for Mn, Ni and Cd were 46.4 %, 50.0 %, 50.0 %, while the percentage recovery capacities for Pb and Cr were 70 and 75 %, respectively. The natural heavy metal removal mechanisms from river are through redistribution and partitioning of the metals between water and sediment and bioaccumulation by plants or aquatic organisms. Chloride, sulphate, TS and alkalinity have percentage recovery capacities of 53 %, 42 %, 56.7 % and 36.0

%, while phosphate has the highest percentage recovery capacity of 90 %. Although deposition of these materials into sediment plays prominent role in their natural removal from water, phosphate could particularly also be utilized as nutrient by alga and other aquatic plants. This might explain the high percentage recovery capacity of the river for phosphate. Sedimentation is a mechanism of removing pollutants from the river, but it could also serve as a secondary source of pollution through the redistribution of the deposited pollutants back into the water under certain conditions.

Table VI. Correlation coefficient between water quality parameter pairs upstream and downstream

	Correlation coefficient (r^2)	
Quality parameter pairs	upstream	downstream
DO/alkalinity	0.45	0.68
DO/Cl^-	0.07	0.68
DO/PO_4^{3-}	0.13	0.63
DO/TS	0.03	0.75
Alkalinity/EC	0.37	0.78
Alkalinity/Cl^-	0.15	0.98
SO_4^{2-}/alkalinity	0.02	0.89
PO_4^{3-}/alkalinity	0.00	0.98
TS/ alkalinity	0.14	0.95
EC/Cl^-	0.42	0.80
EC/PO_4^{3-}	0.01	0.80
Cl^-/SO_4^{2-}	0.28	0.88
Cl^-/TS	0.06	0.94
PO_4^{3-}/SO_4^{2-}	0.01	0.90
PO_4^{3-}/TS	0.10	0.94
Pb/Mn	0.44	0.57
Pb/Cd	0.03	0.50
Pb/Cu	0.18	0.90
Mn/Cd	0.01	0.51
Mn/Cr	0.26	0.83
Ni/Cd	0.00	0.63
Ni/Cu	0.40	0.76
Cd/Cr	0.33	0.82
Cr/Cu	0.01	0.53
pH/DO	0.01	0.50
pH/alkalinity	0.02	0.89
pH/Cl^-	0.44	0.87
pH/PO_4^{3-}	0.47	0.89
pH/TS	0.35	0.86
Cl^-/PO_4^{3-}	0.65	0.98
Mn/Ni	0.60	0.62
Cd/Cu	0.67	0.70

4. CONCLUSION

The results of the study revealed that the water qualities of Alaro River were adversely affected and impaired by the discharge of industrial effluent. The levels of parameters downstream were significantly elevated than the corresponding levels upstream. The quality of the industrial effluent was poor and did not meet the minimum requirement to be discharged into surface water. The river's recovery capacities over the stretch of the studied section were fairly good but vary among the water quality parameters.

5. RECOMMENDATIONS

Effluents should be treated to safe levels by the industries before discharging to the rivers or streams. Nigerian Environmental Protection Agency and other environmental regulatory bodies should be more aggressive and effective in environmental monitoring, assessment and enforcement of environmental laws and regulations. People should desist from the use of effluents or contaminated water for irrigation of any kind. Finally, simple water treatments such as filtration, addition of alum and boiling are recommended before water is used for washing, cooking or drinking to prevent the outbreak of epidemics in this fast growing developing and highly populated country.

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