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Pollution Indicators in River Kaduna, Kaduna State, Nigeria

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Abstract: The aim of this study is to determine pollutant indicators in River Kaduna, Kaduna State Nigeria. Water and Sediment samples from River Kaduna, Nigeria were collected and analyzed for pH, temperature, total dissolved solid, phosphate, nitrate, sulphate and the organic pollution indicators. These include Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) content of the water samples and Total Organic Carbon (TOC) of the sediment samples. The water and sediment samples were also analyzed for the following metal contents, As, Cd, Cr, Cu, Fe, Mn, Pb and Zn using Atomic Absorption Spectrophotometer (Unicam, Model, SOLAAR 969), while Hg was determined using cold vapour Atomic Absorption Spectrophotometer model AA-670. Organic pollutants were analyst using standard procedure. Correlation coefficients of organo-pollutants with each metal determined were used to establish the relationships between the metals and the organic pollution indicators, notably COD, BOD5 and % TOC. The metal levels correlated highly with BOD, COD and %TOC, which indicate the ability of the organo-pollutants to scavenge the metal ions. The levels of metals found in water samples varied from 0.04-0.29 mg L^{-1} for Mn, 0.05-0.32 mg L^{-1} for Cu, 0.10-3.62 mg L^{-1} for As, 0.08-0.10 mg L^{-1} for Cd, 0.22-1.10 mg L^{-1} for Fe, 0.25-0.70 mg L^{-1} for Zn, 1.72-2.50 mg L^{-1} for Hg and 0.50-0.90 mg L^{-1} for Pb. From the results, the concentration of heavy metals in water and sediment samples, BOD and COD were found to be above the recommended permissible limits set by Federal Environmental Protection Agency (FEPA) Nigeria, World Health Organization (WHO)/European Union (EU). It is inevitable that protective measurement must be started very soon as this may have deleterious effect on aquatic ecosystem and the health of the rural dwellers that use the river water directly for domestic purposes without treatment.

Key words: Pollutant indicators, River Kaduna, Nigeria

INTRODUCTION

A mixture of municipal and industrial wastewater is a major component of water pollution, contributing to oxygen demand and nutrient loading of water bodies, promoting toxic algae bloom and leading to a destabilized aquatic ecosystem (WRC, 2000; DWAF and WRC, 1995; Flessger *et al*., 2003). The mixture of industrial and domestic wastewater contains nitrogen, phosphorus, potassium, total dissolved solids, viruses, trace organic and trace metals specially heavy metals in water bodies to organism and wildlife poses the problem of ultimate disequilibria in the natural ecological balance (Alexander, 2005). Living organisms require trace amounts of some heavy metals including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium and zinc. Excessive levels of essential metals however, can be detrimental to the organism (Konofal *et al*., 2004; Kocak *et al*., 2005). Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium,

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mercury, lead, arsenic and antimony (Konofal *et al*., 2004; Kocak *et al*., 2005) . Heavy metals come from local sources mostly industry (mainly non-ferrous industries, but also power plants and iron, steel and chemical industries), agriculture (irrigation with polluted water) use of mineral fertilizers especially phosphates, contaminated manure, sewage sludge and pesticides containing heavy metals) from waste incineration, burning of fossil fuels and road traffic.

River Kaduna is the main water supply source for Kaduna town and numerous industries. Apart from being a source of water supply, it serves as a sink for industrial and domestic wastes. Some peasant farmers along the course of the river also use water from the river to water their food crops especially vegetables during the dry season. Effluent discharged into receiving waters and the cumulative hazardous effects on the environment have received much attention due to rapid industrialization in modern society (Morrison *et al*., 2001). Therefore assessment of effects of these harmful pollutants in this environment becomes highly important

Kaduna (Lat. 10.52 °N, Long 7.44 °E) is located in Kaduna State, occupies central position in Northern Nigeria (Kaduna, 2004). Industrially, it is one of the most developed cities of Northern Nigeria and textile, brewery and flourmill are some of its dominating industries.

Kaduna river originates from the Kujama hills in Jos Plateau Nigeria and flows for 210 km before reaching Kaduna town and stretches down 100 km into the Shiroro Dam project areas where it finally empties into River Niger (KEPA, 1998).

Industrial and domestic wastes containing high concentration of microbial nutrients would obviously promote an after growth of significantly high coliform bacteria, both in the effluent and the receiving water (Ezeronye and Ubalua, 2005), as a result of these the is a need to determine pollutant levels in this area.

MATERIALS AND METHODS

Sampling Points

Measurement points from the sampling sites have been designated as S_1 to S_4. Point S_1 was located up- stream before the discharge point source into Kaduna river; Point S_2 was the point after the effluent flows in River Kaduna; Point S_3 was the Kakuri, Nassarawa and Makera industrial effluent confluence point while point S_4 was located down- stream after Kudenda area further after S_2.

Sample Collection

Water and sediment samples were monitored through regular weekly grab sample collections for twelve weeks. Samples were collected thrice a week at specified periods between the periods of January to March 2007.

Water samples were collected in plastic containers previously cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% HNO_3 for 72 h and finally rinsed with deionised water prior to usage. Sediments samples were collected into prewashed and dry polyethene bags (Udosen *et al*., 1990). During sampling, sample bottles were rinsed with sampled water three times and then filled to the brim from the four designated sampling points in river Kaduna, while sediments samples were collected using a plastic hand-trowel by scooping the top layer sediments (0.2 cm dept) into a dried polyethene bags. The samples were transported to the laboratory immediately and stored in the refrigerator at about 4°C prior to analysis.

Samples Preparation

Water samples were analyzed as collected without further preparations. Each of the sediment samples was divided in two portions. One half was analyzed for total organic carbon. The other half was prepared for elemental analysis.

Determination of Copper, Cadmium, Chromium, Iron, Zinc, Manganese, Arsenic and Lead in Water and Sediment Samples

The digestion procedure of dried 2 g of the pulverized samples basically involved the use of 20.0 cm^3 of aqua regia and 10.0 cm^3 of 50% v/v H_2O_2. The water samples were digested as follows. One hundard cubic cetimeter of the sample were transferred into a beaker and 5 mL concentrated HNO_3 were added. The beaker with the content was placed on a hot plate and evaporated down to about 20 mL. The beaker was cooled and another 5 mL concentrated HNO_3 was also added. The beaker was covered with watch glass and returned to the hot plate. The heating was continued and then small portion of HNO_3 was added until the solution appeared light coloured and clear. The beaker wall and watch glass were washed with distilled water and the sample was filtered to remove some insoluble materials that could clog the atomizer. The volume was adjusted to 100 cm^3 with distilled water (Radojevic and Bashkin, 1999). Heavy metals (copper, cadmium, chromium, iron, zinc, manganese and lead) in sediment and water samples were determined using Atomic Absorption Spectrophotometer (AAS, Unicom model SOLAAR 969).

Determination of Mercury in the Water Samples

Mercury in the water sample was extracted using standard procedure (Standard Methods, 1976). Cold vapour Atomic Absorption Spectrophotometer model AA-670 was used for the estimation of mercury. The method involves reduction of mercury compounds by Sn^{2+} to metallic Hg, which is then vaporized in a steam of air and swept through an absorption cell placed in the path of the hollow cathode lamp beam. Standard calibration curve method was used for the determinations as described in the manufacturers instruction manual.

Determination of Total Organic Carbon (TOC)

Walkley-Black titration method as reported by (Gadde and Laitnen, 1974) was used for TOC determination. The method basically involves the oxidation of the organic material in sediment with $K_2Cr_2O_7$ and H_2SO_4. Then $K_2Cr_2O_7$ is back titrated with Ferrous Ammonium Sulphate solution using fifteen drops of Sodium diphenylamine Sulphate solution as indicated.

Analysis of Water Samples for Organic and Physical Pollutants

Chemical oxygen demand was determined following the $K_2Cr_2O_7$ titration method by using Ferroin indicator as reported by (Radojevic and Bashkin, 1999). Biological oxygen demand and dissolved oxygen was determined by dilution method as reported by (Radojevic and Bashkin, 1999). pH and temperature (°C) were measured using WTW pH Electrode SenTix 41, while TDS was determined by using a C0150 conductivity meter.

Determination of Sulphate, Nitrate and Phosphate in Water Samples

Sulphate, nitrate and phosphate were determined using standard procedure (Standard methods, 1976; DWAF, 1992). Nitrate as N was determined by the cadmium reduction metal method, while the concentration of phosphate in the samples were determined using the ascorbic acid method by reacting it with added reagent containing molybdate and an acid to give a blue coloured complex.

RESULTS AND DISCUSSION

The pH of most natural and surface water ranged between 6.5-8.5 (Table 1). The results depicted in Table 1, show that only values obtained for up-stream (S_1) of River Kaduna, were within the acceptable levels. Other sampling areas of the river, S_2, S_3 and S_4 had values far above the recommended pH levels provided by Federal Environmental Protection Agency (FEPA) Nigeria. Out of the four sampling locations; S_3 showed the highest pH values. This indicates that the industrial effluent discharged into the river is alkaline with average pH value of 12.2±0.23 mg L^{-1}, while point S_2 and S_4 showed noticeable increases in pH values compared to point S_1, this increase could be the lingering impact of the industrial effluent discharged into the rive body.

Temperature of water samples at different locations ranged from 26.4±1.10 to 30.1±0.88°C (Table 1). With exception of S_1, all the three locations showed similar values, this difference could be attributed to the influence of S_3 effluent confluence point flowing into points S_2 to S_4. All the values were above the permissible limits of US-EPA and WHO of 12°C for drinking water standard.

The concentrations of sulphate, nitrate and phosphate in water samples of River Kaduna at various sampling points are shown in Table 2, with values ranging from 5.5±0.80 to 44.7±3.60 mg L^{-1}. Point S_1 had the lowest phosphate values (7.4±0.20 mg L^{-1}), however point S_3 with an average phosphate values of 44.7±3.60 mg L^{-1} had the highest. This value is about six time what was obtained for S_1 and ten times what is allowable for a clean water environment. Going by EU and WHO standards, point S_3 therefore exhibited pollution tendency and could proliferate phosphate-feeding bacteria (Santschi, 2001).

High concentration of phosphate was also observed in point S_2 and S_4. The high concentration values could be as a result of the discharge of effluents from S_3, which flow into the river. The overall mean phosphate levels from all the sampling points were higher than limits set by WHO and FEPA for drinking water.

Levels of nitrate in the sampling points ranged from 22.4±1.90 to 41.2±1.60 mg L^{-1} (Table 1), the result showed that point S_3 had the lowest values while point S_1 and S_4 showed the highest values. This high value of nitrate in point S_1 and S_4 might be attributed to a natural process of correcting the deficiency of nitrate as a result of human and animal waste or fertilizer runoffs into the river due to farming activities carried out along the river banks near this area. Although nitrate values obtained in this study were below the WHO and FEPA tolerance limit (45 mg L^{-1}) for drinking water.

Concentration of sulphate in all the sampling points varies between 5.5±0.80 to 22.7±1.54 mg L^{-1} (Table 1). Point S_1 and S_4 revealed the presence of high sulphate concentration, point S_2 and S_3 showed a depletion of this ion. The low concentration of sulphate (point S_2 and S_3)

Table 1: Average Concentrations of (pH, T°C, SO_4^{2-}, NO_3^-, PO_4^{3-}) in River Kaduna at various sampling points (January to March 2004)

	Concentrations (mg L^{-1})				
Sampling points	pH	T°C	SO_4^{2-}	NO_3^-	PO_4^{3-}
S_1	7.6±0.36	26.4±1.10	18.1±2.20	41.2±1.60	7.4±0.20
S_2	10.9±0.34	28.3±0.95	7.5±0.37	30.3±0.80	19.3±0.15
S_3	12.2±0.23	30.1±0.88	22.7±1.54	22.4±1.90	44.7±3.60
S_4	9.4±0.27	29.8±0.63	5.5±0.80	40.4±3.00	22.7±1.00

The values given in the table above are means of replicate values (n = 24), S_1 = Up-Stream before the discharge point source, S_2 = Point after the effluent flows into River Kaduna, S_3 = Kakuri, Nassarawa and Makera industrial effluent confluence point, S_4 = Down-Stream (after Kudenda Area) further after S_2

Table 2: Mean Concentrations of DO, COD, BOD, TDS (mg L^{-1}) and %TOC determination in River Kaduna at various sampling points (January to March 2004)

Sampling points	DO	COD	BOD	TDS	TOC (%)
S_1	8.6±0.20	170.0±8.00	7.8±0.20	140.0±25.00	1.1±0.50
S_2	5.4±0.10	770.0±7.00	9.4±0.30	490.0±47.00	2.4±0.40
S_3	5.8±0.10	1190.0±1.10	17.0±0.30	760.0±42.00	3.6±0.40
S_4	6.2±0.40	630.0±10.0	14.5±0.20	760.0±42.00	3.3±0.60

The values given in the table above are means of replicate values (n = 24), S_1 = Up-Stream before the discharge point source, S_2 = Point after the effluent flows into River Kaduna, S_3 = Kakuri, Nassarawa and Makera industrial effluent confluence point, S_4 = Down-Stream (after Kudenda Area) further after S_2, DO = Dissolved Oxygen, COD = Chemical Oxygen Demand, BOD = Biological Oxygen Demand, TDS = Total Dissolved Solid, TOC = Total Organic Carbon could be as a result of precipitation of the ion, thereby rendering it unavailable in the water sample (Ademoroti, 1996). Another possibility could also be as a result of sulphate discharged in the effluent sample, which might have been used up as a source of oxygen by bacteria or converted into H_2S under anaerobic condition (Ademoroti, 1996).

The result of DO at various sampling points showed that point S_1 had an average DO value of 8.6±0.20 mg L^{-1}, S_2 and S_3 each with similar DO values of 5.4±0.10 and 5.8±0.10 mg L^{-1}, respectively, while point S_4 had value of (6.2±0.40 mg L^{-1}) (Table 2). Dissolved Oxygen (DO) levels in freshwater range from 8 mg L^{-1} at 25°C to 15 mg L^{-1} at 0°C (WHO, 1993). The decrease in values at point S_2 and S_3 when compared to S_1 as in Table 1, might be attributed to the fact that the waste effluent discharge from the textile industries within this area contains high concentration of organic matter and nutrients which could lead to decrease in DO values as a result of increased microbial activity occurring during the degradation of organic matter (Chapman, 1996). The rise in the level of DO as obtained further downstream (S_4) might be due to a possible replenishment of the dissolved oxygen content of the river.

Levels of Dissolved Oxygen (DO) affect the BOD_5 and COD values of a water body (Table 2). BOD_5 of a system is usually increased by the addition of both organic and inorganic substances to the environment. Point S_3, the effluent discharge point had the highest values (1190.0±1.10 and 17.0±0.30 mg L^{-1}), while S_1 showed the lowest values (170.0±8.00 to 7.8±0.20 mg L^{-1}) for COD and BOD_5, respectively. It could therefore be noted that point S_3 had comparatively more organic pollutant as BOD_5 and COD are used as organic pollutant indicators. The levels of COD and BOD_5 in the sampling point exceeded the 10 mg L^{-1} COD and 6 mg L^{-1} BOD WHO and EU maximum permissible level for drinking water and aquatic life (Chapman, 1996). It is of remark that the WHO, (2003) and USEPA, (1991) gave acceptable limits of TDS in any quality water at 1000 mg L^{-1} and 500 mg L^{-1}, respectively. From Table 2, point S_1, S_2 and S_4 gave average TDS values of 140.0±25.00, 490.0±47.00 and 760.0±42.00 mg L^{-1}, respectively. These values were less than the maximum allowable limits set by WHO and US-EPA. Point S_3 with average TDS value of 1850.0±30.00 mg L^{-1} was highest; this point is the Kakuri, Makera and Nasara industrial effluents confluence point, which subsequently flows into River Kaduna contributing to an increased TDS in points S_2 and S_4. Similar trend was obtained for %TOC (Total organic Carbon). Total organic carbon content of sediments are usually recycled or fixed by the biological and chemical agents both within the sedimentary compartment and in the water column (Sadasivan and Baskin, 2000).

Table 3 provides the values of the sediment samples while the values for the water are shown in Table 4. It is evident that the sediment elemental levels were generally high. Fe showed the highest-level at all sampling points ranging from 320 K±78 K (S_1) to 484K±1200 (S_4) (K= X 1000). Of concern are the high concentrations of Pb (4630 ±38K µg g^{-1}) and Cd (66±13 to 132±13 µg g^{-1}) in this area (Table 3). Both elements are implicated as toxic elements to biosystems and therefore of environmental concern. River sediments usually serve as repository of elements in aqueous environments. This conform with report by Stephens *et al.* (2001), that sediment could act as sink for a wide range of contamination including heavy metals from various sources (Agricultural and wastewater discharged). Upon any from of disturbance the elements are resoolubilized into the

Table 3: Mean concentration of heavy trace elements (µg g^{-1}) in sediment samples from River Kaduna at various sampling points (January to March 2004)

Sampling points	Pb	Fe	Zn	Cd	Cr	Cu	Mn
S_1	8050±104.00	320K±78K	5810±198	110±10	960±440	1820±140	9200±990
S_2	20K±33K	155K±16K	12K±2540	66±13	990±400	3100±270	6570±690
S_3	20K±38K	380K±33K	21K±1190	99±10	730±330	7260±254	4130±560
S_4	4620±55.00	484K±1200	25K±2240	132±13	1160±300	1400±330	8050±1980

The values given in the table above are means of replicate values (n = 24), S_1 = Up-Stream before the discharge point source, S_2 = Point after the effluent flows into River Kaduna, S_3 = Kakuri, Nassarawa and Makera industrial effluent confluence point, S_4 = Down-Stream (after Kudenda Area) further after S_2, K = X 1000)

Table 4: Mean concentration of heavy trace elements (mg L^{-1}) in water samples from River Kaduna at various sampling points (January to March 2004)

Sampling points	Pb	Fe	Zn	Cd	Hg	Cu	Mn	As
S_1	0.50±0.20	0.22±0.08	0.70±0.90	0.08±0.03	1.72±0.50	0.05±0.02	9200±990	0.10±0.01
S_2	0.60±0.24	0.50±0.15	0.60±0.77	0.09±0.04	2.10±0.44	0.08±0.12	6570±690	0.22±0.01
S_3	0.62±0.11	1.88±0.70	0.25±0.36	0.10±0.03	2.50±0.50	0.32±0.54	4130±560	3.62±0.41
S_4	0.60±0.06	1.10±0.23	0.40±0.01	0.09±0.03	2.20±0.60	0.06±0.01	8050±198	0.27±0.02

The values given in the table above are means of replicate values (n = 24), S_1 = Up-Stream before the discharge point source

S_2 = Point after the effluent flows into River Kaduna, S_3 = Kakuri, Nassarawa and Makera industrial effluent confluence point

S_4 = Down-Stream (after Kudenda Area) further after S_2

surrounding water (Gonzalez *et al,* 2000). As evident the levels of these metals in the water samples were much less, notable. Table 4 for instance the values for As, Pb and Hg in the water samples were higher than limits set by WHO and FEPA. Levels of Pb, Cd and Zn could have come from emissions from use of gasoline engines in cars and generating plants (Boruvka *et al.*, 1996).

Reported chromium values in the sediments may have occurred from discharges from the textile industries in this area. Other possible sources of these elements may include refuse incineration and bush burning for farming purposes, which is prevalent in this part of Kaduna state. It could be remarked that some of these elements exceeded the levels stipulated by WHO/UNEP for water sources utilized for various purposes.

Notable among these are Mercury and Lead with recommended values for drinking water, fisheries and aquatic life given as 0.0001-0.001 mg L^{-1}, (Hg) and 0.01-0.007 mg L^{-1}, (Pb) respectively (Committee for fisheries, 1993).

Mercury has a range of 1.72 to 2.50 mg L^{-1} and Lead with a range of 0.09-0.62 mg L^{-1}. Each element had values comparably higher than the acceptable limits set by WHO/UNEP. These organizations have recommended the amount of these metals present in water bodies not to exceed the above-mentioned values. Cadmium whose maximum allowable levels for both drinking and fisheries water are recommended by WHO/EU as 0.03 mg L^{-1} and 0.0002 mg L^{-1}, respectively (WHO, 2003). Cd values obtained here ranged from 0.08-0.10 mg L^{-1}, which were comparably high compared to the river standards mentioned.

It is of remark that, the reported levels of Cd in River Kaduna water and sediment samples are about fifty times higher than the World Health Organization Standard. The amounts of these toxic metals namely As, Pb, Cd and Hg in water samples from the four sampling points were observed to vary in an increasing order from point S_1 to S_4 with points S_3 and S_4 comparably showing the highest levels.

The scavenging ability of the organo-pollution indicators, BOD_5, COD and %TOC were examined by determining their correlation coefficients with the metals (Table 5). Elements with high correlation values indicate the ability of the organo-pollutants to scavenge the particular metal ions. The results of the correlation coefficient values indicated that, Zn, Cu, Fe and Mn showed relatively high positive values. This suggests that, the higher the values of the organo-pollution indicators in the aqueous samples, the more the metal ions present. Chromium showed a high negative correlation values with the organo-pollutants.

The high levels of BOD_5 and COD might be ascribe to organic contaminations entering the systems from municipal waste and industrial effluent which are some of the major sources of organic wastes entering the waterways (Ademoroti, 1996). These organic materials eventually are broken down by bacteria, which require oxygen for decomposition process. Since there is a large amount of organic matter to be broken down, the bacteria remove large quantities of dissolved oxygen from the system, thereby increasing the levels of BOD_5 and COD (Black, 1977). This conforms with reports by Quinby-Hunt *et al.* (1986) that a low DO indicates a high COD and BOD_5 values.

Table 5: Correlation coefficient values for BOD_5, COD and TOC (%) with each of the heavy trace elements of sediment samples in River Kaduna

	Correlation coefficient (r)		
Trace element	BOD	COD	TOC (%)
Mn	0.64	0.05	0.80
Cr	-0.60	-0.40	-0.80
Pb	0.09	0.22	0.50
Zn	0.62	0.80	0.74
Cd	0.34	0.60	0.64
Cu	0.70	0.74	0.63
Fe	0.72	0.80	0.80

COD = Chemical Oxygen Demand; BOD = Biological Oxygen Demand; TOC = Total Organic Carbon

High levels of heavy metals and temperature in River Kaduna could be traced to urban and industrial wastes (Arah, 1985). Inflow wastewaters to River Kaduna have been found polluted with untreated industrial wastes, which are carelessly discharged, directly or indirectly into the river.

Thus the cumulative impact is that heavy metals, temperature, BOD5 and COD levels are kept high, which might be due to high influxes from industrial wastes, including the immense urban run-off, while pH, nitrate, phosphate, sulphate, TDS, DO, are kept low.

CONCLUSION

The results of these study revealed that most of the parameters; heavy metal in water and sediment samples, BOD_5 and COD were found to be above the recommended permissible limits stipulated by FEPA, WHO and EU. Only few parameters were within the allowable limits. The distribution of metals in the different samples showed that concentrations of the metals depend on the types and sources of the samples. It is inevitable that protective measurement must be started now as this may have deleterious effect on aquatic ecosystem and the health of the rural dwellers that use the river water directly for domestic purposes without treatment.

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