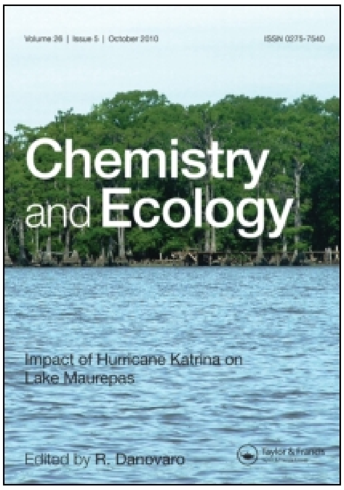

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Impact of brewery effluent on water quality of the Olosun river in Ibadan, Nigeria

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There has been significant pollution of the Olosun river in Ibadan with untreated brewery effluent. The nature and extent of pollution resulting from effluent discharged into this river has not been fully investigated. This study investigated the impact of such effluents on the water quality of the Olosun river. Sampling points of river water included two upstream locations up to 100 m from the discharge point, the effluent discharge point and six points downstream. The Olosun river was sampled up to about 690 m downstream. Sampling of river water was carried out on a monthly basis between March 2001 to March 2002 and January 2004 to December 2004. The physico-chemical impact on the water quality downstream was indicated by reduced pH and dissolved oxygen. The levels of chloride, nitrate, ammonia, dissolved solids, turbidity and BOD were significantly high, arising from the inflow of brewery effluent. The brewery effluent significantly contributed to the levels of Ni, Zn, Cr, Co, Cu, Cd and Pb downstream such that they exceeded the freshwater and drinking water criteria. In addition, the overall concentrations of these heavy metals were well above the background concentration obtained at the upstream location. The levels of these indicator parameters responsible for this brewery effluent quality exceeded the effluent guideline for discharge into surface water. Thus, brewery effluent is among the major sources or factors responsible for river water quality deterioration.

Keywords: brewery effluent; water pollution; Olosun river; water quality; physicochemical impact

1. Introduction

The impact of industrial wastewater on rivers has attracted a lot of attention worldwide because of its overwhelming environmental significance. The physicochemical impact on the water qualities of rivers have been indicated by raised conductivity, by the pollution of water bodies with nitrate, nitrite and soluble reactive phosphorus, by the appearance of tannin and lignin, and by the steady accumulation of inorganic and organic suspended matter along the river [1–6]. Industrial discharges into rivers are one of the causes of irreversible degradation occurring in surface water systems [7–9].

Due to their role in carrying off industrial wastewater, rivers are among the most vulnerable water bodies to pollution. There has been significant impairment of rivers with pollutants, rendering the water unsuitable for beneficial purposes. The use of rivers for beneficial purposes

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such as domestic use, irrigating agricultural lands, recreation, drinking, wildlife propagation and food processing purposes in industries is on the rise, particularly in developing urban areas. With increasing scarcity of treated public water supply, fresh river water has become the alternative source for these purposes [10]. Gadgil [11] indicated that safe drinking water remains inaccessible for about 1.1 billion people in the world, and the hourly toll from chemical contamination of drinking water from various sources is 400 deaths of children (below the age of 5). It is not surprising that there have been outbreaks of epidemics such as cholera and other water-related diseases on several occasions [12–15]. Thus, there is the possibility that rivers are relied on as an alternative for the scarce pipe-borne water for drinking at farther locations downstream, where water supply is chronically insufficient for the inhabitants.

Nowadays the River Olosun is faced with increasing problems of being a receptacle for untreated brewery effluent. Beer production in the brewery industry involves three main steps: malting, brewing and fermentation. The byproducts (e.g. mash, yeast surplus) generated from those steps are responsible for pollution when mixed with effluents. In addition, cleaning of tanks, bottles, machines and floors produces high quantities of polluted water. Brewery effluents, having both chemical (with very high organic contents) and microbial contaminants, results in a rather chaotic layout of utilities such as water supply, irrigation and laundry of the receiving river [16–18]. Most industries in Nigeria lack efficient effluent treatment plants. Therefore they discharge their effluents into water bodies without adequate treatment prior to the discharge. One such industry is the brewery industry in Ibadan, whose effluent is discharged into the Olosun river that flows through the premises of the factory. There has been a gradual decline in utilisation of the Olosun river water for irrigation purposes. The decline in utilisation of the river for such purposes results from vegetation damage and poor soil fertility, as noticed by a few people exploiting the available free land space around the brewery for intensive farming. As a consequence, risk to human health from intake of pollutants through consumption of such crops, and drinking of river water becomes inevitable. Since the River Olosun constitutes an alternative water resource for domestic, drinking and irrigation purposes, it is imperative to have reliable information on the quality of such a river for effective water quality planning and management. There have been several reports on the water quality status of rivers in Ibadan [19–22]. There is still, however, a significant dearth of information about the water qualities of rivers in the country which are constantly used as receptacles for industrial effluent discharges. The information in this study is extremely desirable due to extensive use of the river in receiving untreated industrial effluent, and due to the growing water pollution problems in this part of the country. Therefore, this study presents the impact of brewery effluent as the pollution source on the water quality of the Olosun river. The main objectives of this study were to: (i) evaluate spatial and seasonal trends in water quality at the discharge point and downstream locations; and (ii) compare the water quality of the Olosun river with other water quality standards in a bid to assess the degree of contamination of the river.

2. Materials and methods

2.1. *Description of sampling site and study design*

The brewery industry is located in the Alakia area of Ibadan city. Ibadan is one of the largest cities in Nigeria, with an estimated population of more than 4 million. The Olosun river drains southerly through the more built-up eastern portions of the city (Figure 1). The river flows through an area of factory premises. Effluent from the factory is discharged directly into the river. The point of effluent discharge is fenced in the factory premises. The main activity of this factory is to produce and market different types of beer. The production process involved generates diverse types of effluent of varying composition, but high organic matter characterises all. Some vegetation grows around the effluent discharge point.

This study was designed so that the hydrological profile of the water course of the river, physicochemical quality of the effluent at the discharge point, and the water quality of the river at upstream and downstream locations were investigated. The whole length of the river was divided into two zones based on the location of discharge of effluent into the River Olosun. They are (i) the upstream zone, and (ii) the downstream zone. The point at which effluent discharge entered the watercourse formed the basis for segmentation and was designated as the effluent discharge point. The river was monitored to about 690 m downstream and about 600 m upstream of the effluent. Sampling points were selected along these two extreme locations.

2.2. *Sampling points*

The location of sampling points upstream and downstream of the effluent discharge point was done randomly. Eight sampling points were located along the river course as follows (Figure 1):

(1) Two sampling points located at the upstream location were designated as U-1 (182 m) and U-2 (579 m), i.e. at 182 m and 579 m from the discharge point. Upstream locations were regarded as the control point.
(2) One sampling point was located at the junction where the river flowed out from the factory premises. This sampling point was regarded as the point source of effluent discharge point and was designated as JN (0 m).
(3) Five sampling points were located at varied distances downstream from the discharge point. The points were designated as D-1 (51 m), D-2 (128 m), D-3 (332 m), D-4 (550 m) and D-5 (690 m).

2.3. *Sampling and chemical analysis*

Water samples were collected each month at eight points along the river, with a view to monitoring changes caused by the seasonal hydrological cycle during the study period (January 2001 to December 2002 and January 2004 to December 2004). January to April and November to December of each sampling period were selected as the dry season, while May to October was the rainy season. The sampling was undertaken by first rinsing the clean plastic bottles with the river water before collecting the samples. The samples were then stored in an ice chest. Separate samples collected for heavy metal analysis were fixed in the field with 3 ml analar grade nitric acid per litre sample.

All laboratory analyses were carried out following the standard protocols [23,24]. The water velocity of the river was measured at each of the eight sampling points using a calibrated water current meter (Valepost BFM002) following the area–velocity method [25]. Water temperature was measured on site using a mercury thermometer. The samples were analysed for the following parameters, using specific standard methods: turbidity (turbidimetry), alkalinity (acid-base titrimetry), total solids (TS), total suspended solids (TSS) (gravimetry), chloride (Cl^-) (mercurimetric titration), nitrate (NO_3^-) (phenodisulphonic acid colorimetric method), sulphate (SO_4^{2-}) (turbidimetry), phosphate (PO_4^{3-}) (molybdenum blue colorimetric method), ammonia (NH_4) (nesslerisation colorimetric method), dissolved oxygen (DO) (Winkler's titration), biochemical oxygen demand (BOD) (dilution method with Winkler's titration) and chemical oxygen demand (COD) (potassium dichromate oxidation and titrimetry). Apparent colour of samples was determined by measuring the absorbance at suitable wavelength by using Cecil UV-Visible spectrophotometer (model CE 2501, 2000 series). Nickel (Ni), Zinc (Zn), Chromium (Cr), Cobalt (Co), Copper (Cu), Cadmium (Cd), Calcium (Ca) and Lead (Pb) were determined by atomic absorption

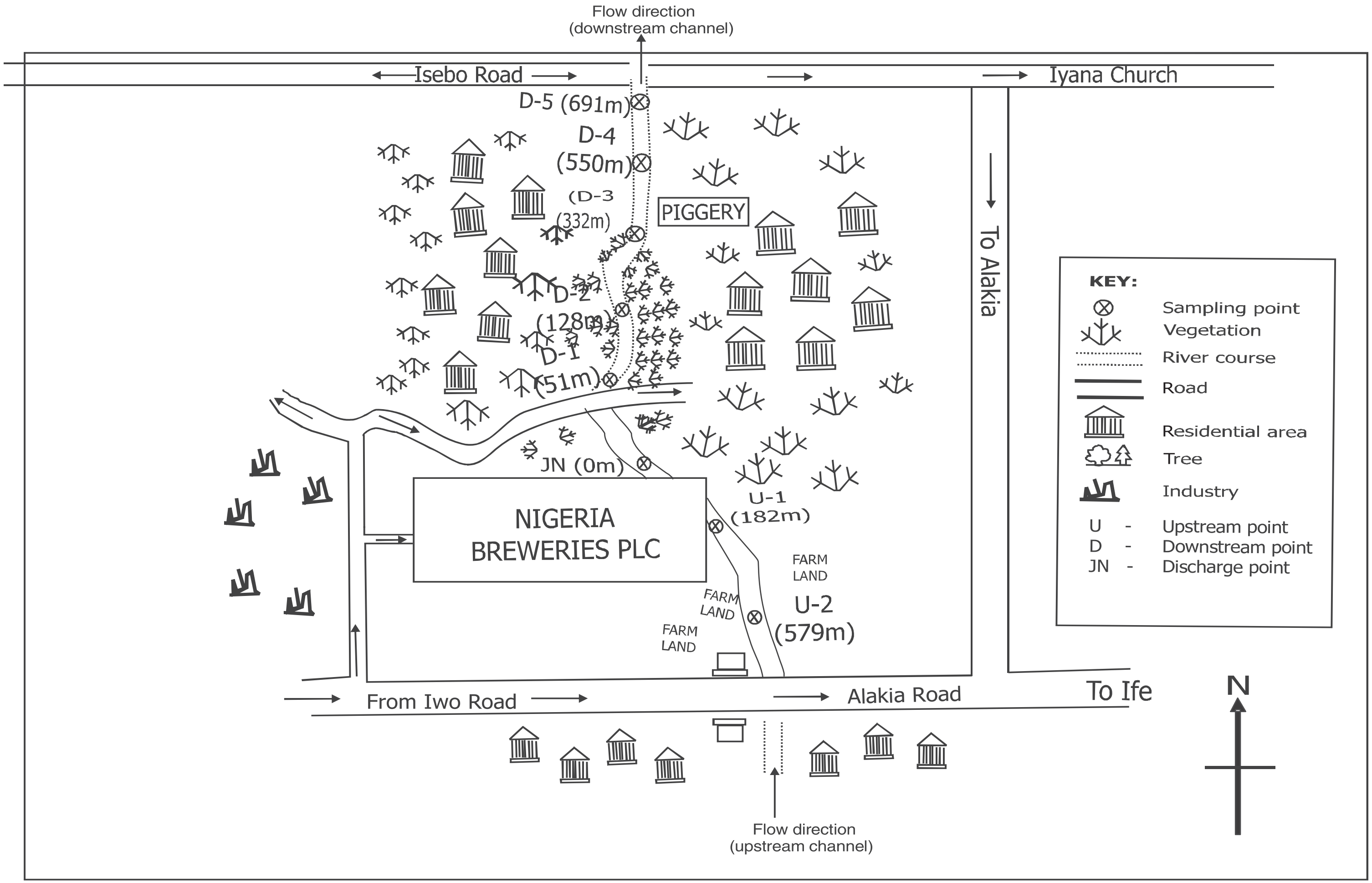

Figure 1. Selected portion of the River Olosun at Alakia of Ibadan showing sampling points.

spectrophotometry (Perkin Elmer model 2380). Quality control of metal measurements in water was verified by including process blanks and carrying out recovery study. The mean percent of spiked samples was between 99.3% and 100%. Standards for the atomic absorption analysis were obtained as the commercial BDH stock metal standards from which working standards were prepared by appropriate dilution. Triplicate determination of each sample was carried out.

2.4. *Statistical analysis of analytical data*

The Kruskal–Wallis non-parametric analysis of variance on ranks (alpha = 0.05) was used to assess the correlation between water quality upstream and downstream. Duncan multiple range test of variable at $p < 0.05$ was used to confirm that the differences observed between the levels of water quality parameters at upstream and downstream locations were significant [26,27]. Data shown in Tables 1–3 are means of 15 and 18 values for rainy and dry seasons respectively, i.e. three measurements of each parameter for five (rainy season) and six (dry season) months respectively.

3. Results and discussion

3.1. *Characteristics of the Olosun river at the discharge point*

The average levels of water quality parameters at the discharge point, upstream and downstream locations of the river are presented in Tables 1–3. Pollution levels were observed to be higher in the effluent at the discharge point than that of the upstream and downstream of the river. This is deduced from the average levels of water quality parameters at the discharge point being higher than the corresponding levels at upstream and downstream locations (Tables 1–3). The effluent was characterised by considerable pollutant of suspended matter, dissolved matters and high values of turbidity and COD. The overall average levels of these parameters at the discharge point were much higher than the available discharge standards stated ([28] WHO, European Discharge Standards and Proposed Discharge Standards 2006 for India) in Table 4.

Table 1. Average levels of water quality parameters at upstream, discharge point and downstream of the Olosun river during rainy and dry seasons 2001.

	Rainy season 2001			Dry season 2001		
Parameter	Upstream	Discharge point	Downstream	Upstream	Discharge point	Downstream
pH	7.8 ± 0.2^{b}	6.1 ± 0.6^{a}	6.6 ± 0.2^{a}	6.9 ± 0.2^{a}	5.8 ± 0.3^{c}	6.7 ± 0.4^{a}
Temperature (°C)	26.5 ± 0.7^{a}	27.5 ± 0.7^{a}	27.5 ± 0.6^{a}	27.8 ± 0.4^{a}	27.8 ± 0.8^{a}	28.5 ± 0.9^{a}
Total solids (mg/l)	215 ± 24^{b}	1880 ± 110^{c}	1710 ± 150^{ac}	227 ± 36^{b}	2600 ± 690^{d}	2310 ± 600^{e}
TDS (mg/l)	161 ± 19^{b}	1450 ± 180^{a}	1400 ± 200^{a}	160 ± 35^{b}	1770 ± 390^{c}	1830 ± 620^{d}
TSS (mg/l)	53.8 ± 20.2c	429 ± 78^{b}	301 ± 46^{a}	70.8 ± 28.8^{c}	832 ± 330^{d}	482 ± 160^{b}
Turbidity (FTU)	2.8 ± 1.1^{b}	16.5 ± 3.5^{a}	11.1 ± 3.3^{a}	8.3 ± 5.1^{d}	35.4 ± 5.0^{c}	29.4 ± 4.0^{e}
Cl^- (mg/l)	119 ± 5^{b}	372 ± 32^{a}	293 ± 19^{c}	115 ± 4^{b}	418 ± 13^{d}	331 ± 25^{a}
NO_3^- (mg/l)	11.1 ± 0.9^{b}	30.7 ± 1.8^{a}	27.3 ± 2.6^{c}	11.8 ± 0.9^{b}	47.5 ± 9.1^{d}	39.1 ± 9.4^{a}
NH_3 (mg/l)	2.64 ± 0.40^{b}	17.5 ± 1.2^{a}	12.0 ± 1.1^{c}	2.61 ± 0.86^{b}	13.1 ± 3.1^{c}	10.1 ± 0.7^{c}
SO_4^{2-} (mg/l)	6.8 ± 1.2^{c}	24.2 ± 0.9^{a}	17.8 ± 2.2^{b}	6.9 ± 3.6^{c}	26.1 ± 4.5^{a}	23.3 ± 5.1^{a}
PO_4^{3-} (mg/l)	0.02 ± 0.01^{b}	0.19 ± 0.01^{a}	0.13 ± 0.01^{c}	0.03 ± 0.01^{b}	0.27 ± 0.07^{a}	0.19 ± 0.08^{a}
DO (mg/l)	4.3 ± 1.6^{b}	0.85 ± 0.40^{a}	1.9 ± 1.1^{c}	3.3 ± 0.4^{b}	1.05 ± 0.32^{ac}	ND
BOD (mg/l)	2.81 ± 0.25^{bc}	11.6 ± 1.5^{a}	9.3 ± 1.4^{a}	2.9 ± 1.9^{c}	20.4 ± 5.2^{d}	14.1 ± 5.0^{a}
COD (mg/l)	62 ± 14^{b}	947 ± 130^{a}	680 ± 41^{c}	94 ± 17^{b}	1300 ± 42^{d}	1110 ± 72^{e}
Depth (m)	0.11 ± 0.01^{a}	0.12 ± 0.01^{a}	0.14 ± 0.01^{a}	0.10 ± 0.02^{a}	0.12 ± 0.02^{a}	0.13 ± 0.03^{a}
Velocity (m/s)	0.16 ± 0.01^{b}	0.43 ± 0.01^{a}	0.35 ± 0.01^{a}	0.13 ± 0.01^{b}	0.42 ± 0.01^{a}	0.30 ± 0.02^{a}

Note: ND = Not detected; means within rows with different superscripts (a,b,c,d,e) are significantly different ($p < 0.05$).

Table 2. Average levels of water quality parameters at upstream, discharge point and downstream of the Olosun river during rainy and dry season 2002.

	Rainy season 2002			Dry season 2002		
Parameter	Upstream	Discharge point	Downstream	Upstream	Discharge point	Downstream
pH	7.9 ± 0.3^{b}	6.4 ± 0.4^{a}	7.0 ± 0.3^{b}	7.2 ± 0.2^{b}	4.7 ± 0.3^{c}	6.2 ± 0.3^{a}
Temperature (°C)	26.3 ± 0.9^{a}	26.6 ± 0.8^{a}	26.6 ± 0.9^{a}	26.1 ± 0.2^{a}	26.8 ± 0.4^{a}	26.6 ± 0.5^{a}
Total solids (mg/l)	258 ± 81^{b}	2090 ± 400^{a}	1750 ± 330^{c}	223 ± 39^{b}	2070 ± 260^{a}	1830 ± 230^{c}
TDS (mg/l)	193 ± 98^{b}	1620 ± 380^{a}	1480 ± 340^{c}	162 ± 28^{b}	1530 ± 170^{ac}	1440 ± 210^{ac}
TSS (mg/l)	64.8 ± 36.4^{b}	462 ± 160^{a}	271 ± 100^{c}	62.0 ± 13.2^{b}	542 ± 110^{a}	388 ± 84^{d}
Turbidity (FTU)	7.3 ± 5.4^{b}	34 ± 23^{a}	22 ± 15^{ac}	4.7 ± 2.3^{b}	33 ± 11^{a}	24.2 ± 9.4^{ac}
Cl^{-} (mg/l)	110 ± 3^{b}	371 ± 35^{a}	296 ± 43^{c}	112 ± 3^{b}	393 ± 19^{a}	331 ± 28^{a}
NO_3^{-} (mg/l)	16.6 ± 5.2^{b}	47 ± 14^{a}	40 ± 12^{a}	15.6 ± 3.5^{b}	41.3 ± 4.7^{a}	34.8 ± 5.2^{a}
NH_3 (mg/l)	2.80 ± 0.44^{b}	11.7 ± 2.1^{a}	9.3 ± 3.2^{ac}	2.23 ± 0.78^{a}	11.1 ± 2.6^{a}	9.1 ± 1.5^{ac}
SO_4^{2-} (mg/l)	7.7 ± 2.5^{b}	22.4 ± 7.7^{a}	17.7 ± 4.7^{c}	6.8 ± 2.1^{b}	36.0 ± 6.9^{d}	27.2 ± 4.0^{a}
PO_4^{3-} (mg/l)	0.03 ± 0.01^{b}	0.17 ± 0.05^{a}	0.12 ± 0.02^{a}	0.03 ± 0.01^{b}	0.15 ± 0.04^{a}	0.13 ± 0.02^{a}
DO (mg/l)	5.7 ± 1.2^{b}	1.51 ± 0.66^{a}	2.3 ± 1.0^{a}	3.2 ± 1.0^{c}	1.13 ± 0.24^{a}	0.36 ± 0.59^{d}
BOD (mg/l)	1.99 ± 0.58^{b}	14.8 ± 4.8^{a}	9.7 ± 3.7^{c}	1.90 ± 0.42^{b}	14.3 ± 3.8^{a}	11.8 ± 3.3^{ac}
COD (mg/l)	119 ± 83^{b}	855 ± 230^{a}	649 ± 250^{c}	78 ± 23^{d}	960 ± 17^{e}	852 ± 72^{a}
Depth (m)	0.15 ± 0.04^{a}	0.15 ± 0.03^{a}	0.18 ± 0.04^{a}	0.12 ± 0.03^{a}	0.14 ± 0.03^{a}	0.12 ± 0.02^{a}
Velocity (m/s)	0.17 ± 0.03^{a}	0.43 ± 0.01^{a}	0.38 ± 0.06^{a}	0.16 ± 0.03^{b}	0.41 ± 0.01^{a}	0.37 ± 0.03^{a}

Note: Means within rows with different superscripts (a,b,c,d,e) are significantly different ($p < 0.05$).

Table 3. Average levels of water quality parameters at upstream, discharge point and downstream of the Olosun river during rainy and dry season 2004.

	Rainy season 2004			Dry season 2004		
Parameter	Upstream	Discharge point	Downstream	Upstream	Discharge point	Downstream
pH	8.2 ± 0.2^{b}	6.9 ± 0.3^{a}	7.1 ± 0.4^{a}	7.3 ± 0.1^{a}	4.6 ± 0.2^{c}	6.3 ± 0.3^{a}
Temperature (°C)	26.7 ± 0.6^{a}	27.0 ± 0.1^{a}	27.1 ± 0.2^{a}	26.7 ± 0.6^{a}	26.7 ± 0.5^{a}	27.0 ± 0.2^{a}
Total solids (mg/l)	200 ± 16^{a}	1960 ± 160^{b}	1440 ± 120^{c}	303 ± 15^{a}	2430 ± 110^{d}	1880 ± 83^{b}
TDS (mg/l)	147 ± 32^{b}	1490 ± 71^{a}	1160 ± 67^{d}	204 ± 15^{b}	1490 ± 87^{a}	1220 ± 140^{e}
TSS (mg/l)	85.7 ± 29.0^{b}	476 ± 92^{a}	284 ± 87^{c}	99.3 ± 27.3^{b}	940 ± 60^{d}	674 ± 160^{e}
Turbidity (FTU)	8.3 ± 4.1^{b}	38 ± 16^{a}	20.7 ± 8.0^{c}	8.0 ± 4.9^{b}	32.3 ± 6.8^{a}	20.9 ± 5.6^{ac}
Total hardness (mg/l)	107 ± 9^{b}	298 ± 79^{a}	214 ± 51^{c}	175 ± 52^{e}	725 ± 380^{d}	562 ± 260^{f}
Alkalinity (mg/l)	77 ± 13^{b}	173 ± 39^{a}	126 ± 16^{a}	120 ± 6^{a}	298 ± 61^{c}	224 ± 41^{c}
Cl^{-} (mg/l)	108 ± 1^{b}	330 ± 42^{a}	276 ± 32^{c}	120 ± 2^{b}	403 ± 28^{d}	333 ± 23^{a}
NO_3^{-} (mg/l)	12.0 ± 5.0^{b}	50 ± 19^{a}	33 ± 12^{c}	12.9 ± 1.8^{b}	53 ± 11^{a}	37.3 ± 9.1^{c}
NH_3 (mg/l)	2.81 ± 0.53^{b}	16.8 ± 7.5^{a}	9.9 ± 4.8^{c}	3.08 ± 0.83^{b}	15.4 ± 4.3^{a}	10.4 ± 1.8^{c}
SO_4^{2-} (mg/l)	9.7 ± 2.9^{b}	40.2 ± 5.3^{a}	25.4 ± 4.4^{c}	14.6 ± 3.8^{b}	40.6 ± 1.8^{a}	27.8 ± 4.5^{c}
PO_4^{3-} (mg/l)	0.07 ± 0.02^{b}	0.57 ± 0.06^{a}	0.34 ± 0.05^{c}	0.15 ± 0.03^{d}	0.55 ± 0.12^{a}	0.37 ± 0.08^{c}
DO (mg/l)	6.2 ± 0.4^{b}	1.71 ± 0.55^{a}	2.91 ± 0.15^{c}	3.3 ± 0.8^{c}	1.36 ± 0.28^{a}	2.2 ± 1.0^{c}
BOD (mg/l)	2.40 ± 0.46^{b}	14.6 ± 1.9^{a}	8.7 ± 2.2^{c}	2.60 ± 0.47^{b}	13.5 ± 0.95^{a}	9.0 ± 0.5^{c}
COD (mg/l)	133 ± 35^{b}	800 ± 45^{a}	528 ± 110^{c}	170 ± 23^{b}	1240 ± 100^{d}	883 ± 90^{a}
Ca (mg/l)	87.9 ± 5.5^{b}	272 ± 76^{a}	184 ± 45^{c}	119 ± 10^{b}	497 ± 150^{d}	377 ± 130^{a}
Ni (mg/l)	0.08 ± 0.02^{b}	0.15 ± 0.02^{a}	0.11 ± 0.02^{a}	1.18 ± 0.16^{c}	1.97 ± 0.45^{d}	1.33 ± 0.19^{c}
Zn (mg/l)	0.37 ± 0.27^{b}	2.03 ± 0.93^{a}	1.24 ± 0.61^{c}	1.12 ± 0.45^{c}	6.81 ± 2.9^{d}	5.3 ± 3.1^{d}
Cr (mg/l)	<0.02	<0.02	<0.02	<0.002	0.14 ± 0.13^{a}	0.06 ± 0.04^{b}
Co (mg/l)	<0.01	<0.01	<0.01	0.27 ± 0.05^{b}	0.49 ± 0.17^{a}	0.31 ± 0.08^{b}
Cu (mg/l)	0.20 ± 0.13^{b}	0.31 ± 0.15^{a}	0.23 ± 0.13^{b}	0.33 ± 0.09^{a}	0.42 ± 0.14^{ac}	0.36 ± 0.07^{a}
Cd (mg/l)	<0.002	0.03 ± 0.01^{a}	<0.002	0.04 ± 0.01^{a}	0.14 ± 0.09^{b}	0.06 ± 0.03^{a}
Pb (mg/l)	<0.05	0.07 ± 0.05^{a}	0.02 ± 0.01^{b}	0.06 ± 0.05^{a}	0.24 ± 0.07^{c}	0.12 ± 0.02^{d}
Depth (m)	0.33 ± 0.14^{a}	0.35 ± 0.16^{a}	0.25 ± 0.06^{b}	0.26 ± 0.09^{b}	0.28 ± 0.09^{b}	0.19 ± 0.04^{d}
Velocity (m/s)	0.19 ± 0.01^{b}	0.42 ± 0.02^{a}	0.37 ± 0.02^{c}	0.15 ± 0.01^{b}	0.41 ± 0.01^{a}	0.33 ± 0.03^{c}

Note: Means within rows with different superscripts (a,b,c,d,e,f) are significantly different ($p < 0.05$).

Table 4. Comparison of the quality of effluent discharged into and Olosun river and brewery effluent qualities of some countries with some effluent quality standards.

Parameters	Effluent discharge into Olosun river		Effluent qualities of some countries		Effluent quality standards		
	*Overall average	Range	[a]Brewery effluent in Yaounde, Cameroun	[b]Brewery effluent in Benin, Nigeria	[c]WHO Discharge limits	[d]European Discharge standards (after Rijs, 1994)	[e]Proposed discharge standards 2006 for India
pH	5.9 ± 0.4	4.3–7.1	4.9–4.2	6.41	6.5–9.5	–	6.0–8.5
Temperature (°C)	27.0 ± 0.8	26–28	–	–	–	–	–
TS (mg/l)	2160 ± 320	1580–3800	–	280	–	–	–
TDS (mg/l)	1590 ± 280	1210–2380	480 ± 92	92.5	1000	–	–
TSS (mg/l)	608 ± 250	318–992	740 ± 115	187	30	30	20
Turbidity (FTU)	33 ± 14	12–66	245 ± 98	150	5	–	–
Total hardness (mg/l)	512 ± 340	228–1140	–	–	–	–	–
Alkalinity (mg/l)	236 ± 82	130–340	–	–	–	–	–
Cl^- (mg/l)	384 ± 37	290–435	–	–	–	–	–
NO_3^- (mg/l)	46 ± 12	27.2–71.3	–	3.2	–	15	–
NH_3 (mg/l)	13.4 ± 3.9	8.84–25.4	–	11.4	–	–	15
SO_4^{2-} (mg/l)	30.3 ± 9.3	19.0–45.8	–	–	–	–	–
PO_4^{3-} (mg/l)	0.28 ± 0.17	0.10–0.65	–	–	–	2	3
DO (mg/l)	1.38 ± 0.58	<0.46–2.46	–	0.81	–	–	–
BOD_5 (mg/l)	15.4 ± 4.5	10.2–28.4	925 ± 82	360	50	20	–
COD (mg/l)	1010 ± 230	560–1340	1195 ± 170	729	150	125	125
Ca (mg/l)	385 ± 160	200–595	–	–	–	–	–
Ni (mg/l)	1.06 ± 0.90	0.13–2.40	–	–	–	–	1.0
Zn (mg/l)	4.4 ± 3.3	2.3–9.45	–	–	–	–	5.0
Cr (mg/l)	0.21 ± 0.08	<0.02–0.27	–	–	–	–	2
Co (mg/l)	0.49 ± 0.17	<0.01–0.60	–	–	–	–	
Cu (mg/l)	0.36 ± 0.14	0.17–0.56	–	–	–	–	1.0
Cd (mg/l)	0.11 ± 0.09	<0.01–0.24	–	–	–	–	
Pb (mg/l)	0.19 ± 0.09	<0.05–0.31	–	–	–	–	0.1

Note: [a]Source = [17]; [b]Source = [29]; [c]Source = [44]; [d]Source = [45]; [e]Source = [46]; *Overall average = pooled mean ± pooled standard deviation.

The overall average pH value was 5.9 ± 0.4 with a range of 4.3–7.1 (Table 4). Most of the pH values of the effluent during the dry season were below the industrial effluent discharge limits. The low pH value is due to acidic discharges (i.e. beer and by-products) resulting from beer production. Thus, the effluent is acidic and has the potential to acidify the river water. The average level of ammonia in the effluent at the discharge point during both dry and rainy seasons ranged from 11.1 ± 0.6 mg/l to 17.5 ± 0.2 mg/l (Tables 1–3). The overall turbidity of the effluent ranging from 12–66 FTU indicates the quantity of TSS in it, particularly at such high solid concentration (Table 4). Turbidity does not directly correlate with suspended concentration because colour can sometimes interfere with its measurement; nonetheless it affords a relative indication of solid levels [29]. The presence of ammonia concentrations in the effluent has its origin from the proteins and chitins load contained in the brewing waste. Apart from high organic content of brewery effluent, spent wash generated from the fermentation step also contains nutrients in the form of nitrogen. Spent wash is the dark brown distillery wastewater generated during the fermentation step of beer production [6]. The total nitrogen concentration of the waste load can be seen as the sum of organic and ammonium nitrogen. Ouboter et al. [30] explained that almost all of the proteins in brewery effluent is mineralised and nitrified in the river. Mineralisation occurs through the activity of proteolytic and deaminative bacteria, initially hydrolysing protein to peptides and amino acids and finally by deamination to ammonium (NH_4^+). This explains the major source of ammonia in the brewery effluent and river water. The nitrification reaction produces nitrates. Nitrification is the process resulting in the conversion of ammonium to nitrite and then to nitrate. These two biochemical reactions are mediated by nitrosomonas and nitrobacter bacteria [1]. The range of phosphate in the effluent was from 0.15 ± 0.04 mg/l to 0.57 ± 0.06 mg/l (Tables 1–3). The discharge of phosphate salts and detergents used for washing in the factory is a regular source of phosphate at the discharge point. At this sampling point, dissolved oxygen levels were much lower than corresponding levels for either upstream or downstream sampling points. The mean DO levels at the discharge point during the sampling periods were from 0.85 ± 0.40 mg/l to 1.71 ± 0.55 mg/l (Tables 1–3). The effect of effluent upon the available dissolved oxygen in the river was noticed by depression in level at the discharge point. The effluent probably contained a high organic load of matter than could have consumed the available dissolved oxygen content of the river.

3.2. *Characteristics of the upstream and downstream river water*

As a response to increased rainfall, water depths increased during the rainy season beyond the average depths of water in the dry season (Tables 1–3). The water velocities downstream were much higher than what seemed to be normal water velocities of the river at upstream locations. The flow of effluent from the factory premises was usually high, which caused high water velocity at the discharge point on the river. The velocity of the river was expected to increase with increased flow of discharges and to enhance the dispersion of effluent pollutants downstream. The average velocity upstream of the river during the rainy season ranged from 0.16 ± 0.01 m/s to 0.19 ± 0.01 m/s and 0.13 ± 0.01 m/s to 0.16 ± 0.03 m/s during the dry season. These average water velocities decreased as effluent flowed downstream, since the depths of water seemed to be about the same values along the river course.

The average pH values upstream were much higher than the corresponding values downstream. The pH fall is traceable to acidic discharge of effluent into the river, whose pH was low compared to the pH of water upstream. The average pH values of upstream and downstream of the river during the rainy season 2002 and 2004 were higher than the corresponding values during the dry season (Tables 2 and 3). The average alkalinity levels of the river at the upstream locations during the rainy and dry seasons were 77 ± 13 mg/l and 120 ± 6 mg/l, respectively (Table 3). These alkalinity levels were raised to 126 ± 16 mg/l and 224 ± 41 mg/l at the downstream location during both seasons respectively (Table 3). The increase was due to the inflow of effluent discharges characterised with high alkalinity levels at all occasions.

River water is made ‘hard’ by the calcium dissolved in it. Hard water is that which contains dissolved calcium and usually some magnesium. The maximum permissible hardness of 500 mg/l is required by WHO for water above which it is described as hard water. Water of hardness level 50–100 mg/l is classified as moderately soft, while 100–150 mg/l is slightly hard [31]. The levels of total hardness and calcium in downstream water of the river were much higher than the upstream total hardness and calcium levels (Table 3). The average total hardness levels downstream of the river were 214 ± 51 mg/l and 562 ± 260 mg/l during the rainy and dry seasons (Table 3). Therefore, the river presumably has had much more deposit of dissolved calcium and magnesium ions that caused hardness, which constitute the major problem to people who rely on the river water downstream for laundry purposes.

There was a rise in average levels of TS and TSS throughout the study period at downstream location compared to that of upstream location. This is attributable to draining of effluent discharges with high TS and TSS levels into the river. The levels of TS during the rainy season were generally lower than the corresponding levels during the dry season at downstream location. Tables 1 to 3 reveal such comparison in average TS levels between the rainy and dry periods as follows: 1710 ± 150 mg/l $<$ 2310 ± 600 (year 2001); 1750 ± 230 mg/l $<$ 1830 ± 30 mg/l (year 2002); 1440 ± 120 mg/l $<$ 1880 ± 83 mg/l (year 2004). Actually the solubilisation of solid discharges during the rainy season is mostly responsible for less TS level in the river. The World Water Council stated in their year 2000 report [32] that there is a water crisis today, which is not concerned with having little water to satisfy the needs, but it is a crisis of managing water so poorly that billions of people and the environment suffer badly. On the top of the agenda is pollution, especially in Nigeria, where there is too much river water available as an alternative source for drinking, irrigation and recreational purposes with little or no pretreatment under acute water shortage. Therefore, the quality parameters of the river water downstream were compared with drinking water standards and water quality characteristics in relation to various beneficial purposes (Tables 5 and 6). Deposition of solid particulates from the effluent through the river course could be responsible for the average downstream TDS levels that were much higher than the limit of 1200 mg/l by WHO (Table 5). From upstream to downstream, the turbidity, Cl^-, NH_3, Ni, Zn, Cr, Co, Cu, Cd and Pb levels of samples increased considerably and were significantly above the recommended water quality standards (Table 5). Virtually all the TSS values at downstream locations were found to be much higher than the allowable TSS threshold limit of 100 mg/l for recreational water quality, above which the river is seriously impaired for recreational purposes [33].

Analysis of variance was used to assess the correlation between water quality upstream and downstream. This statistical comparison of water quality parameter for turbidity, Cl^-, NO_3^-, NH_3, SO_4^{2-} are significantly differently at $p = 0.05$ (Table 7). The average chloride level downstream was above the acceptable chloride limit of 250 mg/l for aquatic life (Table 5). An elevated level of chloride downstream with a corresponding low chloride level upstream of receiving effluent rivers of upper Volga and Danube had been reported in the literature [34,35]. The average nitrate level downstream of the river ranged from 27.3 ± 2.6 mg/l to 40 ± 12 mg/l (Tables 1–3). These high nitrate levels as obtained during the study period were far above the nitrate level of 3.2 mg/l reported in the literature for brewery effluent in Benin (Table 4) discharged into surface water. The conversion of organic forms of nitrogen in protein and chitin containing materials in the effluent to ammonium nitrogen is a possibility as the river flows downstream. This fact in a way could account for the high mean ammonia levels ranging from 9.1 ± 1.5 mg/l to 12.0 ± 1.1 mg/l for downstream locations compared to upstream ones. Such conversion could have been mediated by a number of heterotrophic microorganisms, such as bacteria, fungi, and antinomycetes probably present in the river water and effluent. The microorganisms produce a wide variety of

Table 5. Comparison of overall average water quality of Olosun river with some water quality standards.

Parameters	Olosun river		Water quality standards			
	Upstream	Downstream	[a]WHO	[b]CQC	[c]FQC	[d]USEPA
pH	7.5 ± 0.1	6.6 ± 0.1	6.5–9.5	6.5–9.0	6.5–8.0	6.5–8.0
Temperature (°C)	26.7 ± 0.1	27.2 ± 0.1	–	–	–	–
TS (mg/l)	240 ± 4	1810 ± 200	–	–	–	–
TDS (mg/l)	173 ± 4	1470 ± 70	<1200	500	–	500
TSS (mg/l)	71.2 ± 5.6	389 ± 130	–	–	–	–
Turbidity (FTU)	6.8 ± 0.3	24.5 ± 5.8	5	–	–	–
Ca^{2+} (mg/l)	103 ± 4	281 ± 58	–	–	–	–
Total hardness (mg/l)	141 ± 3	388 ± 73	500	–	–	–
Alkalinity (mg/l)	98.7 ± 3.1	175 ± 35	–	–	–	–
Cl^- (mg/l)	113	312 ± 43	250	250	200	250
NO_3^- (mg/l)	14.0 ± 0.5	36.6 ± 5.9	50.0	–	10.0 ($NO_3^- + NO_2^- - N$)	10.0
NH_3 (mg/l)	2.67 ± 0.07	9.8 ± 2.1	<1.5	–	1.0	–
SO_4^{2-} (mg/l)	8.40 ± 0.39	22.9 ± 5.0	500	500	250	–
PO_4^{3-} (mg/l)	0.05	0.19 ± 0.05	–	–	0.30	–
DO (mg/l)	4.42 ± 0.04	2.13 ± 0.48	–	5.5–9.5	≥5.0	–
BOD (mg/l)	2.34 ± 0.09	10.8 ± 3.1	–	–	≤6.0	–
COD (mg/l)	109 ± 5	798 ± 135	–	–	–	–
Ni (mg/l)	0.64 ± 0.01	0.72 ± 0.19	0.02	0.025	0.03	0.05
Zn (mg/l)	0.75 ± 0.06	3.24 ± 0.73	0.01	0.03	0.20	0.12
Cr (mg/l)	<0.002	0.09 ± 0.06	–	0.05	0.05	0.10
Co (mg/l)	0.28 ± 0.01	0.31 ± 0.09	–	0.05	–	–
Cu (mg/l)	0.27 ± 0.01	0.30 ± 0.03	–	0.024	0.05	0.009
Cd (mg/l)	0.04	0.06 ± 0.03	0.003	–	0.001	0.002
Pb (mg/l)	0.09 ± 0.01	0.11 ± 0.05	0.01	0.017	0.05	0.003

Notes: WHO = WHO drinking water guidelines, CQC = Canadian water quality criteria for aquatic freshwater life, FQC = Flemish quality criteria for aquatic freshwater, USEPA = US Environmental Protection Agency. [a]Source = [28]; [b]Source = [47]; [c]Source = [48]; [d]Source = [49].

extracellular enzymes capable of degrading protein containing material (profeinases, peptidases) and non-protein components (chitanases, kinases) into ammonium nitrogen.

The phosphate level was noticed to be generally low at upstream locations where anthropogenic pollution was minimal. This is in conformity with [36] findings which indicated that inflow streams are low in phosphate when they are not influenced by human activities. The mean phosphate level ranging from 0.12 ± 0.02 mg/l to 0.37 ± 0.08 mg/l was obtained at downstream location (Tables 1–3). This indicates that the average phosphate levels obtained during the study period are rather on the high side judging from the fact that total phosphate concentrations greater than 0.1 mg/l are regarded as unacceptably high in most freshwater system [37]. Environmental concerns associated with phosphate centre on its stimulation of algae growth in the river to ecologically undesirable levels that can further deplete the DO level of the river. The mean DO levels for downstream location ranged from 0.36 ± 0.59 mg/l to 2.91 ± 0.15 mg/l (Tables 1–3). The overall DO levels were much lower than the permissible DO limit for aquatic freshwater life (5.5–9.5 mg/l), despite the dilution of effluent that occurred as the river flowed downstream (Table 5). The average BOD values of upstream water were lower than the corresponding values of the downstream. This increase in BOD of the downstream represents an organic loading of the river by brewery discharges. This is in accordance with the fact that high organic load is found in wastewaters from rising of bottles and mixing tanks, which consequently affect high bacterial population and very low oxygen level in the river [10,38]. The average COD values of the river water showed similar pattern of being high at downstream location compared to upstream location. The average COD values of downstream river water varied from 528 ± 110 mg/l to 1110 ± 72 mg/l (Tables 1–3). These COD values were far above the European effluent discharge limit of 125 mg/l.

Table 6. Comparison of average water quality of Olosun river with optimum values of water quality characteristics in relation to type of beneficial use.

	Olosun river						
Parameters	Upstream	Downstream	[a]Domestic water supply	[a]Recreation (bathing and swimming)	[a]Wildlife propagation (fish)	Irrigation	[a]Industrial (food processing)
pH	7.5 ± 0.1	6.6 ± 0.1	6.8–7.2	6.8–7.2	6.5–8.5	6.5–8.5	6.5–8.5
Temperature (°C)	26.7 ± 0.1	27.2 ± 0.1	–	–	–	–	–
TS (mg/l)	240 ± 4	1810 ± 200	500	–	1000	500	500
TDS (mg/l)	173 ± 4	1470 ± 70	–	–	–	–	–
TSS (mg/l)	71.2 ± 5.6	389 ± 130	–	100	–	–	–
Turbidity (FTU)	6.8 ± 0.3	24.5 ± 5.8	5.0	5.0	5.0	–	5.0
Ca^{2+} (mg/l)	103 ± 4	281 ± 58	–	–	–	–	–
Total hardness (mg/l)	141 ± 3	388 ± 73	100	–	–	–	–
Alkalinity (mg/l)	98.7 ± 3.1	175 ± 35	–	–	–	–	–
Cl^- (mg/l)	113	312 ± 43	750	–	2500	750	1000
NO_3^- (mg/l)	14.0 ± 0.5	36.6 ± 5.9	–	–	–	–	–
NH_3 (mg/l)	2.67 ± 0.07	9.8 ± 2.1	–	–	–	–	–
SO_4^{2-} (mg/l)	8.40 ± 0.39	22.9 ± 5.0	–	–	–	–	–
PO_4^{3-} (mg/l)	0.05	0.19 ± 0.05	–	–	–	–	–
DO (mg/l)	4.42 ± 0.04	2.13 ± 0.48	5.0	5.0	5.0	–	5.0
BOD (mg/l)	2.34 ± 0.09	10.8 ± 3.1	–	5.0	10.0	–	–
COD (mg/l)	109 ± 5	798 ± 135	–	–	–	–	–

Note: [a]Source = Van der Leeden (1990) [33].

Table 7. Correlation coefficients (r) for the pairs of water quality characteristics of Olosun river.

	pH	TS	TDS	TSS	Turbidity	Alkalinity	Total hardness	Cl^-	NO_3^-	NH_3	SO_4^{2-}	PO_4^{3-}	DO	BOD
TS	0.634													
TDS	0.583	0.990												
TSS	0.651	0.996	0.974											
Turbidity	0.514	0.836	0.864	0.836										
Alkalinity	0.641	0.992	0.983	0.998	0.850									
Total hardness	0.674	0.994	0.997	0.997	0.833	0.997								
Cl^-	0.657	0.993	0.971	0.998	0.826	0.999	0.999							
NO_3^-	0.651	0.994	0.979	0.993	0.795	0.990	0.996	0.995						
NH_3	0.628	0.997	0.981	0.999	0.852	0.998	0.996	0.997	0.992					
SO_4^{2-}	0.639	0.990	0.976	0.974	0.772	0.983	0.991	0.990	0.990	0.987				
PO_4^{3-}	0.629	0.998	0.982	0.998	0.825	0.994	0.996	0.996	0.996	0.998	0.994			
DO	−0.506	−0.981	−0.968	−0.978	−0.791	−0.970	−0.980	−0.971	−0.974	−0.980	−0.975	−0.985		
BOD	0.667	0.989	0.970	0.990	0.769	0.984	0.993	0.992	0.999	0.987	0.999	0.993	−0.972	
COD	0.650	0.993	0.987	0.983	0.796	0.978	0.989	0.984	0.996	0.985	0.996	0.991	−0.971	0.995

	Pb	Ni	Cu	Cr	Co	Cd
Zn	0.854	0.846	0.868	−0.933	0.993	−0.155
Pb		0.846	0.956	0.661	0.832	0.990
Ni			0.671	0.623	0.786	0.862
Cu				0.919	0.894	0.849
Cr					0.970	0.921
Co						0.988

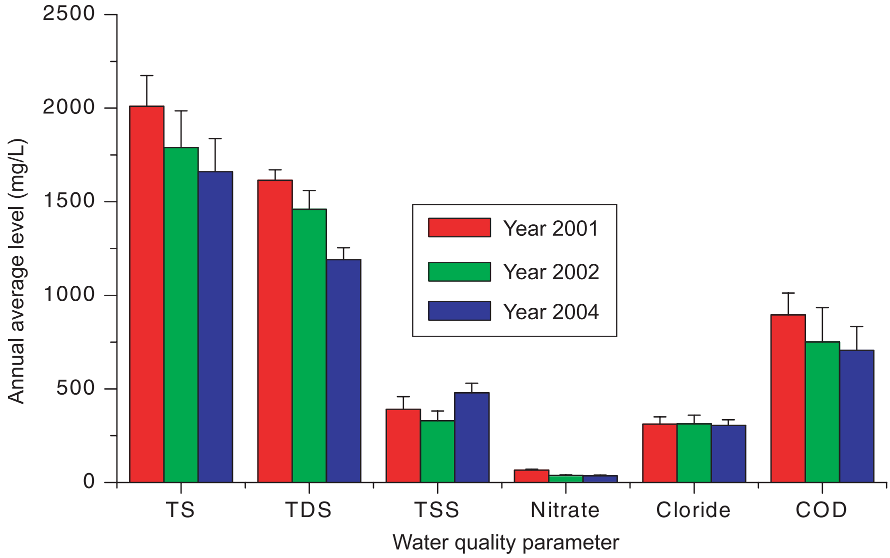

Figure 2. Temporal variations of total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), nitrate, chloride and COD levels at downstream location between sampling periods 2001 and 2004.

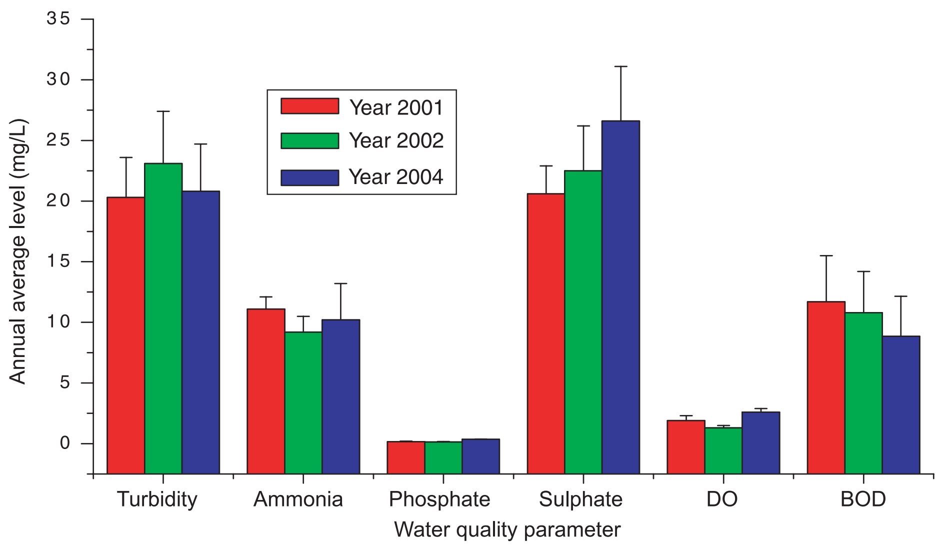

Figure 3. Temporal variations of turbidity, ammonia, phosphate, sulphate, DO and BOD levels at downstream location between sampling periods 2001 and 2004.

Table 3 shows elevated contents of Ni, Zn, Cu and Pb in downstream river water compared to the corresponding levels in upstream water. The levels of Ni, Zn, Co, Cu, Cd, and Pb in upstream and downstream river water were much higher than the WHO and other quality standards for aquatic freshwater life (Table 5). High levels of these metals in downstream river water are traceable to brewery discharges in the river. The river is a potential source of irrigation water for various vegetables along the bank of the river, possibly because of its high plant nutrient contents. Build-up of heavy metals, particularly Ni, Zn, Cu and Pb by crops in intensively cultivated wastewater-irrigated soil is a possibility. There is potential that they could become bioavailable for crops. As such, consumption of such crops or vegetables could induce heavy metal hazards in humans.

Some microbial activities in the soil are inhibited by increases in heavy metal concentrations. For instance, Pb might decrease the amount of substrate available for bacterial and fungal respiration through the formation of complexes. Increased Zn concentration is known to inhibit the nitrification rate in soil, which subsequently affects the biological functioning of that soil. Three studies [39–41] observed that fibre crops such as flax and cotton did take up heavy metals when grown in heavily contamination soils. Fazeli et al. [42] examined the uptake of heavy metals by rice grown in paddies irrigated with untreated effluent from an industry.

3.3. *Spatial and seasonal trends in water quality at discharge and downstream locations*

The levels of some water quality parameters at downstream locations in the dry season are generally higher than the corresponding levels in the rainy season. These parameters include TS, TDS, TSS, total hardness, SO_4^{2-}, PO_4^{3-}, BOD, COD, Ni, Zn, Cr, Co, Cu, Cd and Pb (Tables 1–3). This implies that the Olosun river is subject to climatic variation. This is in addition to anthropogenic input into the Olosun river of brewery effluent, which is subject to variation in character or quality determined by treatment it receives prior to discharge into the river.

There was an indication of decreased contamination of the Olosun river between the years 2001 and 2004. Figures 2 and 3 show that the relative contribution of organic load at downstream locations as evidenced from BOD and COD levels has decreased with time. This decrease represents an organic loading abatement in connection with the occurrence of the natural self purification capacity of the Olosun river. The aquatic organisms, e.g. *Zoothanium* sp. possibly present in the Olosun river have the ability to breakdown organic components of the effluent. The capability of the river to undergo this is known as self purification [43]. Similarly the TS, TDS, Cl^- and NO_3^- levels in downstream water decreased with the sampling periods (Figure 2). Between 2001 and 2004, there were many differences in the levels of water quality parameters obtained for the four downstream sampling locations. These levels of water quality parameters generally decreased downstream, suggesting the dilution of pollutant concentrations.

4. Conclusions

This study revealed that the Olosun river was among the most vulnerable of water bodies to pollution. The River Olosun is a recipient of brewery effluent of poor quality that does not meet the stipulated minimum requirement for discharge into surface water. Effluent from this brewery has a high organic load of matter which inevitably leads to the deterioration of the receiving Olosun river. This constitutes a considerable factor of pollution that has an impact on the physicochemical characteristics of the Olosun river. The levels of parameters responsible for water quality downstream were significantly higher than the corresponding levels upstream. Therefore, the elevation in levels of indicator parameters downstream subsequently render the river water unwholesome for intended beneficial purposes, such as cooking, drinking, irrigation and aquatic life support.

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