

ECOLOGICAL EFFECTS OF EFFLUENT OF FOOD INDUSTRY ON WATER, SEDIMENT AND FISH OF RIVER ONA, IBADAN, NIGERIA

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ABSTRACT

Effects of effluent discharged from food industry at Oluyole Industrial Estate Ibadan on fish, water and sediment of River Ona was investigated. The water, effluent, sediment and fish were sampled monthly (March - December, 2019). Four sampling points (*viz-a- viz* the effluent discharge outlet; point source - where effluent meets with the receiving river; upstream and downstream of the river to the effluents) were chosen. Water physico-chemical parameters and metal concentrations were determined *in-situ* and *ex-situ* using electrometric built-in portable electronic Lamotte tracer pocket tester (Model 1766), portable digital Dissolved Oxygen probes (Model HI9146) and Atomic Absorption Spectrophotometer respectively. Sediment and fish samples were collected at each sampling points by Scoop and cast net respectively. Temperature ranged from 31.93° C - 40.03° C and 31.47° C -34.83⁰C in dry and wet season respectively. Electric Conductivity, pH and Biological Oxygen Demand ranged between 311.51μ Scm⁻¹ and 2267.19μ Scm⁻¹, 7.24 and 9.31 and 14.15mgl⁻¹ and 37.43mgl⁻¹ in dry season and 313.51μ Scm⁻¹ and 1984.70μ Scm⁻¹, 7.19 and 9.01 and 50mgl^{-1} and 35.14mgl^{-1} in wet season respectively. Meanwhile, Dissolved Oxygen level was low in both seasons. Many physico-chemical parameters of River Ona deviated from Standard permissible limit. Generally, Zinc (Zn) > manganese (Mn) > lead (Pb) > iron (Fe) > copper (Cu) in both wet and dry seasons and were higher than standard permissible limit except Zn and Cu. All the metals were concentrated in the effluents > point source > upstream > downstream, while the physico-chemical properties of the sediments were higher than the River water. *Oreochromis niloticus* accumulate least metals at the point source, followed by upstream and then, downstream. Fe $> Mn > Zn > Cu > Pb$ in gills, Fe $> Zn > Mn > Pb > Cu$ in flesh and Fe > Mn > Zn > Pb > Cu in liver in both seasons. The study revealed that the industry discharge effluents with high BOD and COD values amongst others are not in compliance with the standards.

Keywords: Ecology, Effluent, Fish, Metal concentration, Physico-chemical, Pollution ***Correspondence:** oladunjoye.rasheed@gmail.com, +2348058109160

INTRODUCTION

Man, constantly generates wastes. Proper managements of various anthropogenic activities wastes are one of the critical problems of developing countries [1]. In developing countries, many people see aquatic environment as the haven for their waste disposal, not considering its ecological effects. More challenging is the unsafe disposal of these wastes into the ambient environment which water bodies especially freshwater reservoirs are most affected [2], before emptying into ocean.

Influx of unwanted substances into water body cause changes in the physical, chemical and biological characteristics of the aquatic system which has led to ecological imbalance. Industrial effluents contribute a lot to water pollution forming a threat to aquatic plants and animals [3] which are usually pathogens, silt and suspended solid particles such as soils, sewage materials, disposed foods, cosmetics, automobile emissions, construction debris and eroded banks from rivers and other waterways [4].

Aquatic organisms, like fish, accumulate pollutants directly from contaminated water and indirectly through the food chain [5, 6]. Once the toxicant enters the body of the fish, they may affect the organs leading to physiological and pathological disorders [7]. Polluted water bodies are possible source of water-borne diseases like Cholera, Hepatitis and Gastro-enteritis [8]. Water quality is affected by changes in nutrients, sedimentation, temperature, pH, metals, non-metallic toxins, persistent organics, pesticides, and biological factors; among many other factors. The discharge of industrial effluent into water bodies is one of the main causes of environmental pollution in many cities, especially in developing countries. Many of these industries lack liquid and solid waste [including harmful waste] regulations and proper disposal facilities [9] as reported by Chikogu *et al.* [10].

In Nigeria, aquatic environments have suddenly become highly polluted ecosystem in recent times and researches on aquatic pollution has centered on the determination of the various contaminants and the establishment of the effects of these compounds on water quality and aquatic organisms [2, 11]. Presently, open and indiscriminate dumping of solid wastes in drainages and riverbanks without regulations and propel disposal facilities [9] is one of the most critical problems facing the city of Ibadan, Nigeria [12].

Most industries in Oluyole Industrial Estate, Ibadan Nigeria use large volume of water without efficient or nil wastewater treatment plants, thereby, routinely discharge their wastes directly into streams and rivers. The study was aimed to investigate the ecological effects of effluent discharged from a food and beverages industry on water, fish and sediment of River Ona, Ibadan, Nigeria to ascertain the safety of the water and consumption of fish therein.

MATERIALS AND METHODS

Description of the study area

River Ona is a receiving River of effluents from Oluyole food industry (Figure 1) which produces biscuits, candy, and bubble gum among other consumables, situated near the River. The industry is in Oluyole Industrial Estate, Ibadan, Southwest Nigeria ($6^{\circ}.43'$.0" and $3^{\circ}.43'$.60") in degree, minutes, seconds (DMS).

Sampling procedure

Four sampling points (Table 1) were mapped using Global Positioning System (GPS) Model IEC 60529 IPX7 (GARMIN eTrex®H) to ensure samples were always taken at the same points on the River between March and December, 2019. Three sampling points: 100meters apart from each point were selected on the river based on location of the effluent point source which was the junction where the effluent emptied into the receiving River, the upstream and downstream respectively. However, the fourth sampling point was the effluent discharge outlet of the industry.

Water sampling

Water samples (effluents and river water) were monthly collected for dry season (November – March, 2019) and wet season (May – October, 2019) for physico-chemical and metal concentration analysis. Grab sampling methods [13 - 16] was employed. Surface water samples were collected using a 500mL

labeled sterile sampling bottle, which were rinsed with distilled water and sample water three times prior to water collection. The bottles were capped, while submerged at 20cm depth in the river, then uncapped for inflow of water into the bottle and later screwed with its cap, while still submerged. The water samples were then stored in an ice chest before transporting to the laboratory.

All the water samples were stored in the Refrigerator at 4°C in the laboratory pending analysis according to standard recommended APHA [17] procedures for water and wastewater examination. Some physico-chemical parameters of the water samples were determined *in-situ* such as pH, E.C, TDS and temperature using electrometric built-in portable electronic Lamotte tracer pocket tester (Model 1766) and DO using portable digital Dissolved Oxygen probes (Model HI9146)while others were determined in the laboratory using various standard procedures.

Sediment sampling

Sediment samples were collected at each sampling points by hand pushing plastic core tubes (7cm diameter) as far as possible into the sediment and transferred into a sterile well labeled black polythene bags which were transported to the laboratory for physico-chemical and metals analysis. The samples were air dried by thinly spreading on a clean laboratory bench surface at room temperature and brought to a relatively homogenous state by thoroughly mixing, and sieving with 2mm mesh before being treated. The pH and the conductivity of the sediment were determined by HACH pH conductivity meter. Total organic carbon was determined by the rapid wet oxidation method based on Walkley and Black [18]. $NO₃²$, $PO₄³$, $SO₄²$ was determined by method outlined in APHA [17]. The metals were determined using Atomic Absorption Spectrophotometer (VGB 210 Bulk Scientific).

Figure 1: Map of Study Area showing the sampling points adapted and modified after Ayodele and Percy [19]

Fish sampling

Fish samples were collected at each sampling point throughout the sampling period. Fish samples were caught with the assistance of local fishermen using cast nets (12-22 mm mesh size). All fishes caught were identified using keys provided by Olaosebikan and Raji [20] text and subsequently confirmed in laboratory by fisheries expert in the Department of Zoology and Environmental Biology of Olabisi Onabanjo University, Ago – Iwoye, Ogun State, Nigeria. *Oreochromis niloticus* was selected for the study based on constant availability in the river during the sampling survey. The samples collected were immediately transferred to the laboratory for metal concentrations analysis.

Concentration determination

The water physico-chemical parameters were determined using standard methods provided by APHA, [17] and Awoyemi *et al*. [21]. Dissolved metals were determined using standard procedure by USEPA [22] as described by Agah *et al.* [23]. Sediment samples were analyzed using standard method outlined by APHA [24]. The fish sample preparation and analysis using Liver, Gills and muscle was carried as described by Taghipour and Aziz [25], Taweel *et al.* [26], Khansari *et al*. [27].

Statistical analysis

Data obtained were subjected to statistical analyses using SPSS version 20.0 [28]. The data were also grouped into dry season (September – December, 2019) and wet season (March – August, 2019). Mean values were compared using Analysis of Variance. Results were presented as Mean ± Standard deviation. Post hoc test was done using the Student-Newman-Keuls (SNK). P value less than 0.05 was considered to be statistically significant. Bioaccumulation factor (BAF) was calculated as the ratio of the concentration of metals in the fish (Conc.Fish) to the concentration of metals in the water (Conc._{Water}).

 $BAF = Conc._Fish}/ Conc._Water$

RESULTS

Physical parameters of the water samples

pH was significantly higher ($p < 0.05$) at the effluent and point source on the receiving water than the upstream and downstream. Also, pH at point source had significantly highest $(p<0.05)$ value during the wet season (Table 2). Meanwhile, temperature was significantly higher at the effluent discharge point. On the other hand, no significant difference in the water temperature at the point source, upstream and downstream. Similarly, electrical conductivity (EC), TDS and turbidity were significantly higher at the effluent than the point source, upstream and downstream. EC in the effluent and point source were higher than World Health Organization [9] standard but lower than FEPA [29], while the upstream and the downstream were however lower than the standard.

Also, levels of pH and TDS at the effluent and point source were higher than the regulated limit [9, 30]. Total dissolved solutes (TDS) and pH values at the upstream and downstream were lower than the regulated limits. On the other hand, water temperatures recorded at the effluent, point source, upstream and downstream were higher than WHO [9] and FEPA [29] standard. No significant difference in the levels of water turbidity recorded at the effluent and the point source which was higher than the upstream and the downstream.

Chemical parameters of the water samples

During dry season, no significant difference $(p > 0.05)$ in dissolved oxygen (DO) from the effluent, point source, upstream and downstream of the River (Table 3). Salinity was significantly higher at the effluent than the point source, upstream and downstream. Also, COD, BOD, sulphate, nitrate, alkalinity and organic matter were significantly higher at the effluent than the point source, upstream and downstream. Meanwhile, phosphate at the effluent and point source were not significantly higher than the upstream and the downstream. While COD, BOD, phosphate and nitrate recorded at the effluent, point source, upstream and downstream were higher than WHO [9] and FEPA [29] standard, DO, sulphate and organic matter were found lower than the standard.

During wet period, there was no significant difference $(p > 0.05)$ in the water salinity level of the effluent, point source, upstream and downstream of the River. Effluent had significant higher BOD, but COD was not significantly different ($p > 0.05$) at the effluent and the point source, likewise at the upstream and downstream of the River. DO was significantly lowest at the effluent and not significantly different (p) > 0.05) at the point source, upstream and the downstream of the River. DO values were found lower than the WHO [9] and FEPA [29] regulated limits.

Levels of metals in the water samples

Iron was not significantly different $(p > 0.05)$ between the effluent and the point source (Table 4), but significantly higher than the upstream and the downstream of the River. On the other hand, manganese, copper, zinc and lead were significantly higher at the effluent, while the metal values reduce from the point source to the upstream and the downstream of the River. Manganese, Fe, Cu and Zn at the upstream and downstream were lower than

WHO [9] limit, but were found higher than the limit in the effluent.

In wet season, Fe was significantly lower at the downstream of the River and not significantly different ($p > 0.05$) in the effluent, point source and the upstream. On the other hand, Mn, Cu, Zn and Pb were significantly higher at the effluent and decrease from the point source, to the upstream and downstream of the River. Manganese at the effluent was above WHO [9] limit, while value at the point source, upstream and the downstream were below the standard. Meanwhile Fe, Cu and Zn at the effluent, point source, upstream and downstream were below WHO [9] limit, Pb were found above the standard limit.

Physico-chemical parameters of the sediment samples

Levels of EC, salinity, organic carbon and organic matter in the sediment of the point source, upstream and downstream of the River showed no significant difference $(p > 0.05)$ in dry season (Table 5). On the other hand, pH, phosphate, sulphate and nitrate were significantly higher in the point source than those of the upstream and the downstream, while alkalinity was significantly higher in the downstream than the point source and the upstream of the River.

In wet season, pH, salinity, organic carbon and organic matter showed no significant difference $(p > 0.05)$ at the point source, upstream and downstream, while EC, phosphate and nitrate were significantly higher at the point source than those of the downstream and the upstream of the River. Sulphate and alkalinity were significantly higher at the upstream and downstream of the River respectively.

Levels of metals in the sediment samples

Manganese was significantly higher in the sediment at the effluent point source of the River than the downstream and upstream during the dry season period (Table 6), while Fe, Cu and Zn were significantly higher at the downstream. Pb was significantly lower at the point source than the upstream and the downstream respectively.

During the wet season, there was no significant difference in Fe, at the point source, upstream and the downstream of the River. On the other hand, Cu and Zn were significantly higher at the downstream, but were not significantly different at the point source and the upstream. Also, Pb was significantly higher in the sediment of the upstream than the downstream and at the point source respectively. Mn was significantly lower at the upstream, but not significantly different between the point source and the downstream of the River.

Levels of metals in the organs of *Oreochromis niloticus*

Oreochromis niloticus was found to be most common and dominant fish species at every catch. Levels of some metals in the gill, flesh and liver of *O. niloticus* during the dry and wet period are shown in Table 7. Manganese, Fe, Cu and Zn in the gills were significantly higher in *O. niloticus* from the downstream to the upstream and the point source respectively. On the other hand, Pb was significantly higher in gills of *O. niloticus* from the point source than those from the upstream and downstream respectively.

Flesh of *O. niloticus* from the point source, upstream and downstream showed no significant difference in the level of Mn. However, Fe and Cu were significantly higher in flesh of *O. niloticus* in the downstream than those from the upstream and point source respectively. The flesh of *O. niloticus* at the point source had the lowest while the downstream and the upstream were higher and not significantly different. Pb in the flesh of *O. niloticus* was highest at the point source and not significantly different from downstream, but lowest at the upstream.

Mn, Fe and Zn in the liver of *O. niloticus* followed similar trend of significantly higher in the upstream than downstream and the point source respectively. On the other hand, liver of *O. niloticus* at the point source had significantly higher levels of Cu in downstream and point source. Mn and Pb in the gill, flesh and liver of the *O. niloticus* collected at the point source, upstream and downstream were above, while

Cu and Zn were below the regulatory USEPA [22] limits. However, except Fe in the flesh of *O. niloticus* at the point source and upstream, Fe in other organs were above the regulatory limits.

Metal bioaccumulation factor in organs of *Oreochromis niloticus*

Bioaccumulation factor of metals in the organs (gill, flesh and liver) of *O. niloticus* at the point source, upstream and downstream of receiving river of effluent discharged from the food industry showed that all the metals were appreciably bio-magnified in the organs of the fish species (Table 8). Of all the metals, Fe has highest biomagnifications and Zn had least in all the organs of the fish from all the three sampling points. Biomagnifications in the fish organs followed the trend: $Fe > Mn > Pb > Cu > Zn$. Similarly, biomagnifications of Pb, Mn and Fe were higher in the liver than the gill and the flesh respectively. Biomagnifications of all the metals were lower at the point source than the upstream and downstream.

During the wet season, there was no bioaccumulation of lead in the organs of *O. niloticus* at the point source, upstream and downstream. On the other hand, all the other metals were biomagnified at the point source than the upstream and downstream.

			Dry Season			
Parameters	Effluent	Point Source	Upstream	Downstream	FEPA [29]	WHO [9]
pH	8.89 ± 0.92 ^a	9.31 ± 0.38 ^a	7.55 ± 0.26^b	7.24 ± 0.33^b	$7 - 8.5$	$6.5 - 8.5$
EC [μ Scm ⁻¹]	2267.19 ± 195.42^a	1590.24 ± 216.93^b	311.51 ± 8.18 ^c	321.21 ± 3.70 ^c	10,000	${}_{\leq 1000}$
Temp.[⁰ C]	40.03 ± 3.57 ^a	33.00 ± 1.73^b	31.93 ± 1.46^b	34.13 ± 2.15^b	$24 -$ 28	
$TDS [mgl-1]$	1169.23 ± 773.46^a	$744.85 + 538.12^b$	$207.80 + 4.52$	214.03 ± 3.14 °	500	≤ 500
Turbidity [NTU]	$18.86{\pm}4.38^{\mathrm{a}}$	14.95 ± 2.98 ^b	10.57 ± 2.50 ^c	7.19 ± 2.23 ^d		
			Wet Season			
pH	8.19 ± 0.20^b	9.01 ± 0.33 ^a	7.19 ± 0.14 ^c	7.26 ± 0.23 ^c	$7 - 8.5$	$6.5 - 8.5$
EC [μ Scm ⁻¹]	$1984.70 + 31.10a$	$1531.07 \pm 95.68^{\circ}$	313.51 ± 10.51 ^c	323.30 ± 10.42 ^c	10,000	${}_{\leq 1000}$
Temp.[⁰ C]	34.83 ± 0.29^a	32.27 ± 0.23 °	31.47 ± 0.49 ^d	33.33 ± 0.58^b	$24 -$ 28	
$TDS [mgl-1]$	1716.28 ± 97.93 ^a	1187.97 ± 11.38^b	216.13 ± 1.91 ^c	224.30 ± 9.22 ^c	500	≤ 500
Turbidity [NTU]	$11.57 \pm 1.25^{\text{a}}$	10.39 ± 0.47 ^a	7.61 ± 0.70^b	$4.72 + 0.52$ ^c		

Table 2: Physical parameters of effluents discharge from the food industry and water samples from River Ona throughout the sampling periods

 $a_{bcd}Mean$ [\pm Standard deviation] in the same row having similar superscripts are not significantly different at $p >$ 0.05

Keys: EC- Electrical Conductivity, TDS- Total Dissolved Solids, FEPA- Federal Environmental Protection Agency, WHO-World Health Organization.

Dry Season							
Parameters	Effluent	Point Source	Upstream	Downstream FEPA [29]		WHO [9]	
Salinity [ppt]	1.14 ± 0.10^a	0.80 ± 0.11 ^b	0.15 ± 0.01 ^c	0.15 ± 0.01 ^c			
COD [mgl ⁻¹]	78.93 ± 1.30^a	67.90 ± 5.10^b	25.74 ± 2.36 ^d	41.02 ± 2.82 ^c	≤ 5.0		
$BOD [mgl-1]$	37.43 ± 1.07 ^a	30.28 ± 1.19^b	14.15 ± 1.41 ^d	20.23 ± 1.30 ^c	10		
$DO [mgl-1]$	$3.77 \pm 2.65^{\text{a}}$	4.01 ± 2.50 ^a	5.22 ± 0.91 ^a	4.62 ± 1.43^a	10	7.5	
$PO_4[mgl^{-1}]$	6.34 ± 7.32 ^a	6.38 ± 6.21 ^a	0.67 ± 0.84^b	1.15 ± 0.93^b	$0 - 0.05$	$0 - 0.05$	
$SO_4[mgl^{-1}]$	55.25±51.14 ^a	$34.05 \pm 32.75^{\rm b}$	0.49 ± 0.69 ^c	0.46 ± 0.71 c	500	≤ 100	
$NO3[mgl-1]$	113.82 ± 7.26^a	97.92 ± 8.52^b	78.50 ± 3.81 ^d	86.04 ± 8.37 ^c	$0 - 0.05$	≤ 45	
Alkalinity $[mgl-1]$	293.19 ± 34.80^a	190.41 ± 71.87 ^b	129.34 ± 25.39 °	94.39 \pm 18.76 ^d			
$OM [mgl-1]$	1.31 ± 0.32 ^a	0.30 ± 0.09^b	0.13 ± 0.06^b	0.10 ± 0.04^b		≤ 3.0	
			Wet Season				
Salinity [ppt]	0.34 ± 0.50 ^a	0.44 ± 0.35 ^a	0.11 ± 0.03 ^a	0.10 ± 0.07 ^a			
COD [mgl ⁻¹]	76.75 ± 7.56^a	62.12 ± 11.25^a	24.04 ± 7.78 ^b	37.49 ± 5.69^b	≤ 5.0		
$BOD [mgl-1]$	35.14 ± 4.23 ^a	27.41 ± 5.07^b	11.50 ± 3.51 ^c	15.98 ± 1.69 ^c	10		
$DO [mgl-1]$	5.67 ± 2.00^b	7.60 ± 3.08 ^a	7.64 ± 1.51 ^a	6.94 ± 0.91 ^a	10	7.5	
$PO4[mgl-1]$	4.09 ± 6.83 ^a	4.15 ± 3.63^a	0.62 ± 0.98 ^b	0.59 ± 0.89^b	$0 - 0.05$	$0 - 0.05$	
SO_4 [mgl ⁻¹]	49.48±85.66 ^a	28.89 ± 38.21^b	0.54 ± 0.94 c	0.68 ± 1.18 ^c	500	≤ 100	
$NO3[mgl-1]$	100.30 ± 2.80 ^a	77.73 ± 6.50^b	76.07 ± 7.40^b	70.96 ± 2.19^b	$0 - 0.05 \leq 45$		
Alkalinity $[mgl-1]$	252.12 ± 11.70 ^a	123.41 ± 5.14^b	114.37 ± 10.43^b	80.14 ± 15.06 c			
$OM [mgl-1]$	1.01 ± 0.01 ^a	0.18 ± 0.01 ^b	0.05 ± 0.01 c	0.04 ± 0.01 c		≤ 3.0	

Table 3: Chemical parameters of the effluents discharge from the food industry and water samples from River Ona

 a_{abcd} Mean [\pm Standard deviation] in the same row having similar superscripts are not significantly different at p > 0.05

Keys: COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, DO- Dissolved Oxygen, NO3- Nitrate, SO4- Sulphate, PO4- Phosphate, OM- Organic Matter, FEPA- Federal Environmental Protection Agency, WHO-World Health Organization.

Table 4: Levels of metals [mg/l] in the effluent discharge from the food industry and water samples from River Ona

Dry season						
Sample	Mn (mgl ⁻¹)	Fe $(mgl-1)$	Cu (mgl ⁻¹)	\mathbf{Zn} (mgl ⁻¹)	Pb (mgl ⁻¹)	
Effluent	0.85 ± 0.10^a	0.47 ± 0.12^a	0.32 ± 0.06^a	$4.77 \pm 0.95^{\text{a}}$	0.66 ± 0.12^a	
Point Source	0.48 ± 0.16^b	0.36 ± 0.10^a	0.17 ± 0.08^b	2.58 ± 0.62^b	0.29 ± 0.09^b	
Upstream	0.21 ± 0.04 ^c	0.22 ± 0.05^b	0.12 ± 0.06^b	1.19 ± 0.52 ^c	0.18 ± 0.04^b	
Downstream	0.12 ± 0.04 ^c	0.14 ± 0.06^b	$0.10 \pm 0.05^{\rm b}$	0.82 ± 0.29 ^c	0.11 ± 0.03^b	
WHO [9]	0.5	0.3	2	3	0.01	
USEPA [22]	0.05	0.3	\mathbf{I}	5	0.005	
		Wet season				
Effluent	0.65 ± 0.11 ^a	$0.24 \pm 0.05^{\text{a}}$	$0.21 \pm 0.07^{\text{a}}$	2.81 ± 0.62^a	0.37 ± 0.14 ^a	
Point Source	0.28 ± 0.02^b	0.20 ± 0.02^a	0.07 ± 0.02^b	$1.98 \pm 0.03^{\text{a}}$	0.19 ± 0.01^b	
Upstream	0.14 ± 0.02 ^c	0.14 ± 0.02^a	$0.04 \pm 0.01^{\rm b}$	$0.59+0.13b$	0.11 ± 0.02^b	
Downstream	0.06 ± 0.01 ^c	0.04 ± 0.02^b	0.03 ± 0.01^b	0.51 ± 0.08^b	0.05 ± 0.02^b	
WHO [9]	0.5	0.3	2	3	0.01	
USEPA [22]	0.05	0.3		5	0.005	

abcd_{Mean [±Standard deviation]} in the same column having similar superscripts are not significantly different at p > 0.05. **Keys:** Mn-Manganese, Fe-Iron, Cu-Copper, Zn-Zinc, Pb-Lead, FEPA- Federal Environmental Protection Agency, WHO - World Health Organization.

 $a^{abc}Mean$ [\pm Standard deviation] in the same row having similar superscripts are not significantly different at p > 0.05

Keys: pH - Hydrogen ion Concentration, E.C - Electrical Conductivity, PO₄ - Phosphate, SO₄ - Sulphate, NO₃ -Nitrate, O.C. - Organic Carbon, O.M. - Organic Matter

 a^{abc} Mean [\pm Standard deviation] in the same row having similar superscripts are not significantly different at p > 0.05

Keys: Mn - Manganese, Fe - Iron, Cu - Copper, Zn - Zinc, Pb - Lead

Dry Season							
Organ	Sample	Manganese	Iron	Copper	Zinc	Lead	
Gill	Point Source	22.75 ± 1.27 ^c	183.73 ± 40.56 ^c	1.84 ± 0.30^b	19.33 ± 7.35^b	8.82 ± 1.96^a	
	Upstream	28.40 ± 0.58 ^b	222.33 ± 51.34^b	2.10 ± 0.95^b	21.52 ± 2.06^b	5.67 ± 0.66^b	
	Downstream	33.98±15.81 ^a	396.99±42.49 ^a	9.81 ± 2.61 ^a	30.38 ± 2.38 ^a	3.26 ± 0.49 ^c	
Flesh	Point Source	9.27 ± 1.06^a	48.37 ± 5.87 ^c	2.15 ± 1.69^b	24.69 ± 2.82^b	$9.56 \pm 0.60^{\text{a}}$	
	Upstream	11.11 ± 2.46^a	87.06 ± 8.76 ^b	2.81 ± 1.67^b	$30.03 \pm 6.05^{\text{a}}$	3.32 ± 0.60^b	
	Downstream	$9.00 \pm 2.05^{\text{a}}$	205.35 ± 16.16^a	7.30 ± 0.81 ^a	27.37 ± 11.78 ^a	8.22 ± 0.66^a	
Liver	Point Source	18.09 ± 5.78 ^c	148.99 ± 22.56 ^c	17.58 ± 2.53 ^a	15.48 ± 2.06 ^c	40.51 ± 5.59 ^a	
	Upstream	366.43 ± 10.69 ^a	$627.56 + 36.23a$	7.17 ± 1.12 ^c	51.88 ± 8.00^a	13.93 ± 4.97 ^c	
	Downstream	52.10 ± 8.64^b	243.14 ± 5.43^b	11.49 ± 1.07^b	29.39 ± 9.98 ^b	23.88 ± 2.13^b	
			Wet Season				
Gill	Point Source	22.28 ± 4.68 ^b	137.05 ± 4.03 ^c	$0.55 \pm 0.05^{\rm b}$	16.10 ± 1.13 ^a	0.00 ± 0.00	
	Upstream	25.28 ± 1.90^b	159.52 ± 2.82^b	1.04 ± 0.07 ^b	17.76 ± 8.34 ^a	0.00 ± 0.00	
	Downstream	6.41 ± 3.80^a	214.75 ± 27.09^a	7.02 ± 1.04 ^a	$18.67 \pm 2.05^{\mathrm{a}}$	0.00 ± 0.00	
Flesh	Point Source	9.49 ± 0.64^b	47.13 ± 12.54 ^c	0.49 ± 0.02^b	21.36 ± 3.03^a	0.00 ± 0.00	
	Upstream	12.59 ± 1.69^a	98.11 ± 5.06^b	0.74 ± 0.07^b	19.65 ± 1.13^a	0.00 ± 0.00	
	Downstream	6.77 ± 1.22 ^c	117.22 ± 17.45^a	$5.29 \pm 1.05^{\text{a}}$	16.69 ± 1.97 ^a	0.00 ± 0.00	
Liver	Point Source	2.64 ± 0.63 c	7.63 ± 1.57 ^c	0.39 ± 0.05^b	13.30 ± 0.43 ^c	0.00 ± 0.00	
	Upstream	339.28±21.23 ^a	69.76 ± 1.89^b	1.34 ± 0.10^b	40.28 ± 1.97 ^a	0.00 ± 0.00	
	Downstream	39.19 ± 2.17 ^b	182.41 ± 8.35 ^a	5.79 ± 0.75 ^a	23.05 ± 2.18^b	0.00 ± 0.00	
USEPA [22]		1	100	30	100	0.05	

Table 7: Levels of metals [mg/kg] in the organs of *Oreochromis niloticus* of River Ona

abcMean [±Standard deviation] in the same column for each of the fish organ having similar superscripts are not significantly different at p > 0.05. **Keys**: USEPA - Unites States Environmental Protection Agency

	Dry Season				
Sample	Manganese	Iron	Copper	Zinc	Lead
Point Source	47	510	11	$\overline{7}$	30
Upstream	135	1011	18	18	32
Downstream	283	2836	98	37	30
Point Source	19	134	13	10	33
Upstream	53	396	23	25	18
Downstream	87	1467	80	45	36
Point Source	38	610	154	$\overline{4}$	210
Upstream	2578	2853	84	47	116
Downstream	434	1737	115	36	217
	Wet Season				
Point Source	79	685	8	8	$\mathbf{0}$
Upstream	181	1139	26	30	$\boldsymbol{0}$
Downstream	575	5851	234	37	$\boldsymbol{0}$
Point Source	33	236	$\overline{7}$	11	$\mathbf{0}$
Upstream	90	701	19	33	$\mathbf{0}$
Downstream	107	3194	176	33	$\boldsymbol{0}$
Point Source	9	38	5	$\overline{7}$	$\boldsymbol{0}$
Upstream	2423	498	34	68	$\boldsymbol{0}$
Downstream	619	4970	193	45	$\boldsymbol{0}$

Table 8: Metal Bioaccumulation factor in the organs of *Oreochromis niloticus* of River Ona

DISCUSSION

Physical parameters of the water

Temperatures recorded at the upstream and downstream of the river were far above temperature recorded for tropical aquatic environments by various researchers such as Eniade and Bello-Olusoji [30], Uzoekwe and Oghosanine [31], Dimowo [32] which might be due to the effluents, but in agreement with Jaji *et al.* [33] findings. Significant higher water temperature observed in dry season might be due to high sunshine rate and low water volume which make the river water temperature to increases. Meanwhile, water temperature recorded in wet season was lower to dry season values which might be due to increase in rain drops which will have reduced atmospheric temperature and increase the river water volume.

Conductivity of water is a function of the concentration of soluble ionic salt present in the wastewater. Thus, the increase in the salinity of the receiving water body is as a result of high concentration of ionic salts present in the wastewater [34]. At high temperature, rate of atmospheric oxygen dissolution in water is usually low and this affects the sustainability of the aquatic habitats. Also, alteration of the pH level of the receiving water could affect the solubility of essential elements such as Aluminiun (Al), Fe, Boron (B), Cu and Mn [35].

Values of pH at upstream and downstream of the rivers were identical and ranged between 7.24 \pm 0.33 and 7.55 \pm 0.26 which was within FEPA [29] and WHO [9] standards. These values were not significantly difference both in wet and dry seasons which were in line with Ogunlaja and Ogunlaja [36], Uzoekwe and Oghosanine [31] and Osibanjo *et al.* [37] findings. Higher pH value in the effluents and at the river point source both seasons indicates the basic nature of the effluents entering into the River.

TDS at the river upstream and downstream corresponded with values recorded by Osibanjo *et al.* [37] at River Alaro, Nigeria. The insignificant difference in the TDS at the upstream and downstream indicates turbulence, while higher values at point source were indicative of industrial pollution. Values at the upstream and downstream showed a drastic reduction compared to the effluents and the river point source value.

This reduction might be due to several physico-chemical reactions such as sedimentation, coagulation, fixation, amongst other factors like oxidation and precipitation [38] of the river water. Also, decrease in the TDS at the upstream and downstream may be attributed to the prolonged deposition of solids of the effluents along the river course which may have been retarded in the river flow with consequent rapid deposition of the solids [2].

Similar to TDS, the electrical conductivity (E.C) of the effluents and the river point source were higher and significant compared to the river upstream and downstream in both seasons. This correlates with higher values of exchangeable ions estimated in the effluents and dissolved ions are responsible for electrical conductivity. Significantly higher EC in dry season than the wet might be due to dry and wet seasonal fluctuation respectively. Conductivity values observed were higher than the observation of Ushurine [39] in River Ethiope (77.52s/cm), River Ase (32.45s/cm) and Warri River (318.72s/cm) reported values.

Higher turbidity in the effluents, river point source, upstream and downstream in both seasons can be attributed to decomposing organic matter in the effluents. Excessive turbidity in water can cause problems for water purification processes such as flocculation and filtration which may increase treatment cost [31]. Muwanga and Barifaijo [40] also recorded high turbidity in effluents from food industries. Also, turbidity causes decrease in photosynthesis process since turbidity precludes deep penetration of light in water [41].

Chemical parameters of the water

pH of the effluents is basic in nature which are not capable of stemming the pH of their respective receiving water bodies. Thereby, stabilize the fundamental properties such as alkalinity, metal solubility and water hardness. Also, there might be pH influence on the river similar to previous studies [40, 42]. pH has profound effects on water quality affecting the solubility of metals, alkalinity and hardness of water [37].

Alkalinity in the river point source, upstream and downstream in both seasons were not significantly different to each other, while the alkalinity value of the effluents was significantly higher in both seasons was in conformity with the findings of Osinbanjo *et al.* [37] on River Ona and River Alaro.

Sulphates (SO₄) in Rivers Ona at both seasons were higher than the natural background sulphate levels of 1.0 – 3.0 mg/l reported for unpolluted rivers [43-44]. The elevated levels of sulphate at the point source may be attributed to increase in influx of elevated sulphate level of the effluents to the river. The mean sulphate levels obtained in the effluents and the river pollution point source suggest the possibility of non-removal of sulphur from sub-aqueous bio-geochemical cycle. However, sulphate levels found in this study were considered relatively low when compared with other studies of Selezneva and Selezneva [45] and Stamatis [46].

Phosphate in effluents and the river point source at both seasons were extremely higher than the standard limits which similar to some findings in the pollution status of some Nigerian rivers [31, 37]. Phosphorus is the second most accumulated nutrient in rivers among other nutrients which had been reportedly encourage eutrophication and could further deplete dissolved oxygen of rivers [2, 47]. However, they are essential nutrients to plants, but when found in excess quantities, stimulates excessive plant growth such as algae bloom [48].

In addition, extensive use of phosphate salts as industrial raw materials, detergents for washing purposes in industries, and land application of phosphorus-containing fertilizers can be other possible sources. Unpolluted water usually contains only minute amount of nitrate [33]. Higher nitrate content may cause by the effluent discharge into the river which were not significantly different except at the wet season period which indicates that the effluent discharged might not be the only source of nitrate in the water body. This corroborates Alao *et al.* [49], Sandhya and Sonawane [50] findings that nitrogenbased fertilizers as well as poultry and other agricultural wastes from farms have significantly contribution to the elevated nitrate levels in rivers.

Dissolved oxygen (DO) in the effluent, river point source, upstream and downstream in both seasons were not particularly significant except in the effluent during wet season. This might be due to high volume of the effluent water that greatly makes significant impacts in the river dissolved oxygen. However, Osibanjo et al. [37] observed a reduction in DO value (5.47 mgl^{-1}) in the industrial zone of River Alaro which indicates that enormous amounts of organic loads require high oxygen level for chemical oxidation and decomposition.

Also, a similar trend was observed towards the downstream with a drastic decrease in DO level. DO is crucial to the survival of aquatic organisms and ultimately in establishing the degree of freshness of a river [2]. Moreso, decrease in DO concentrations could be attributed to breakdown of organic matter by aerobic microbes. Odukuma and Okpokwasili [51] reported that this may be partly due to the displacement of dissolved oxygen by dissolved solids within the effluent.

The river had appreciable increase in chemical oxygen demand (COD) at the point source and downstream, confirming the impact of industrial discharges on water quality of the rivers. COD is the amount of oxygen used up from a water sample by organic and inorganic chemicals as they break down which suggests that the industries probably have inefficient wastewater treatment plants as opined by various researchers [37, 40, 49, 50].

The COD values revealed that the river was polluted particularly in the industrial areas and higher COD values at the downstream suggests that other sources might be responsible for the gross organic pollution which may include escape of leachate from dumpsites, agricultural and urban runoffs, etc. Based on the classification of surface waters, the river with a COD value range between 24.04±7.78 (wet season) and 67.90±5.10 (dry season) may be categorized as being polluted which was also in agreement with Oladele *et al*. [42] and Osibanjo *et al.* [37] findings.

Biochemical Oxygen Demand (BOD)in the effluents, point source, upstream and downstream in both seasons were significantly different and higher than the normal background level of 2–3mg/l BOD values from food industries [52]. This is due to

discharge of organic matter (e.g. fish flesh, blood, flour, food fragments) from processing line into wastewaters from the food industries. Lower BOD can be attributed to dilution effects and natural purification mechanisms such as respiratory breakdown, biological and physical uptakes in the aquatic ecosystem.

Salinity of the receiving river at the point source, upstream and downstream ranged between 0.10 ± 0.07 (wet season) and 0.80 ± 0.11 (dry season) in both seasons indicate that the river is a typical freshwater ecosystem. However, the salinity may increase with increase in tidal seawater incursion, coupled with reduced flood, water inflow from associated rivers, creeks and freshwater with high salinity.

Metals in the water

Generally, higher $Zn > Mn > Pb > Fe > Cu$ observed in both wet and dry seasons were concentrated in the effluents > receiving river point source > upstream > downstream. This showed that the receiving water body is being polluted by other sources and metals which could be traceable to other industrials activities especially agro-allied industries and waste dump [53]. Higher metals concentrations were recorded in dry season which concur with the findings of Lawson [54], Nhapi *et al.* [14], Badr *et al*. [55] and Fafioye *et al*. [56] which might be due to dry seasonal encroachment and intense anthropogenic activities with continuous increase in the amount of metals in the water body.

As observed by Muwanga and Barifaijo [40], low levels of Cu along the river downstream are attributed to the natural purification processes within the river. Aquatic organisms consumed by people as food are known to accumulate heavy metals by up taking it to a level that present risks to consumers [57- 58] and sometimes the organism itself [57].

Significant difference $(p < 0.05)$ in all the metals at the point source, upstream and downstream, while the effluents were not significantly different in both seasons were not in conformity with Bolawa and Gbenle [59] and Awoyemi *et al.* [21] findings. However, this study was in agreement with Bala *et al.* [60] and Badr *et al*. [57] findings on the determination of some metals collected from two pollution-prone irrigation areas around Kano metropolis which showed that mean values of all metals (except Zn)were significantly high ($p < 0.05$) with mean values exceed the acceptable limits.

Physico-chemical parameters of the sediments

Physico-chemical properties of the sediments showed pH values not in line with Swingle [61] findings who reported that organic waste reduces the pH of water and sediments to acidic level. Meanwhile, sulphate and phosphate at each point (point source, upstream and downstream) in both seasons were higher than the effluents discharge values. There is a significant difference in sulphate and phosphate between the effluent discharge (P<0.05 and the sulphate and phosphate level in the sediment. Therefore, it is obvious that high phosphate and sulphate in the sediments does not emanate from effluent discharge but probably as a result of poor sanitations and leaches from nearby pit latrines [62] and other industrial wastes such agro-allied industries.

Metals in the sediments

Mean concentration were found to be higher in Fe > $Mn > Zn > Pb > Cu$ in the sediment at each point (point) source, upstream and downstream) in both seasons than in the effluent's discharges. This indicates the accumulation ability of these metals and the ability of the water sediment to store metals in manifolds. Also, the metals might not only be from the effluent's discharges, rather, an introduction and accumulation from nearby industrial wastes.

High metals in sediments may also be attributed to occupational fields such as automobile mechanics, steel making, welding, cutting, glass and ceramic production [63]. Meanwhile, low level can be due to washing of soil into surface water by flood and infiltration into underground water. Lead exposure has been associated with hypochromic anaemia with basophilic stifling of erythrocytes [64].

Metals in *Oreochromis niloticus*

O. niloticus at the point source accumulate least metals concentrations, followed by upstream and then, downstream. The metals were accumulated in ascending order of $Fe > Mn > Zn > Cu > Pb$ for gill, $Fe > Zn > Mn > Pb > Cu$ for flesh and $Fe > Mn > Zn$ $> Pb > Cu$ for liver in both seasons. This conforms to the findings of George *et al.*[65], Sunday *et al.*[66] and Fafioye *et al.*[56] researches on different Nigerian water fish species. The variability and significant differences in all the metals across the organs/tissue of *O. niloticus* could be as a result of their diet and habitat as opined by Kim *et al.* [67-68].

Kamaruzzaman *et al.* [69] indicated that there was relationship among metal concentrations and several other intrinsic factors in fish such as size, genetic composition and age. Moreso, *O. niloticus* accumulates metals in liver $>$ gill $>$ flesh in the fish species in both seasons was in agreement with Christopher *et al.* [70] who studied the distribution of Pb, Zn, Fe, Cd, As and Hg in bones, gills, livers and muscles of *O. niloticus* from Henshaw town beach market in Calabar Nigeria.

CONCLUSION

The river is a recipient of effluents from food and beverages industry with some identified pollutants in the form of organic load, suspended solids, phosphate, nitrate and sulphate which led to significant pollution of the river water. Also, the study shows that the industries discharge effluents with high degree of BOD and COD values which are not in compliance with FEPA and WHO set standards.

Should these companies continue to discharge untreated wastes into the environment there will be building up in the metal concentrations in the water bodies and may pose serious threat to both aquatic habitat and human beings that consume this aquatic biota. The study establishes that the surface water quality was significantly affected by the industrial discharges as indicated by the accumulation factors of metals in water and fish examined.

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