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Full Length Research Paper

Concentrations of heavy metals in effluent discharges downstream of Ikpoba river in Benin City, Nigeria

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Various effluent samples were collected from their sources of discharge to the Ikpoba river in Benin City, Edo State between September and October, 2008. Six heavy metals (cadmium, chromium, copper, nickel, lead and zinc) in the effluents and receiving water were analyzed by atomic absorption spectrophotometric technique (AAS) in separate experiments. The concentrations of heavy metals in the effluents were compared with corresponding heavy metal values in the water. The results show that metal concentrations were higher in the effluents than in the water. Total mean metal concentrations (mg/l) recorded in the effluents were as follows: Cd = 0.072; Cr = 0.079; Cu = 0.194; Ni = 0.122; Pb = 0.125 and Zn = 0.174 while corresponding mean values recorded in the water were Cd = 0.043; Cr = 0.072; Cu = 0.152; Ni = 0.091; Pb = 0.110 and Zn = 0.128. Significant differences ($P < 0.05$) were recorded between heavy metal levels in urban run-off effluents and rubber/brewery effluents. No significant differences ($P > 0.05$) were recorded between the concentrations of cadmium in the water procured from the four sampled stations. Significant correlations ($P < 0.05$) were recorded between metals in effluents and water. The concentrations of Cu, Pb and Zn in urban run-off effluents exceeded the limit recommended in effluent discharges to surface waters by the Federal Ministry of Environment (FMENV).

Key words: Heavy metals, effluent discharges, Ikpoba river, Benin City, Nigeria.

INTRODUCTION

Industrial, agricultural and domestic activities have led to the pollution of the Nigerian environment and subsequently increased the problem of waste disposal (Ndiokwere and Ezihe, 1990). The upsurge in urban population and the establishment of industries involved in the manufacture of various agrochemical, petrochemical and house-hold products have resulted to the increase in the production of hazardous substances including heavy metals in developing countries (Ayodele et al., 1991). In Nigeria, effluent discharges from domestic, municipal, trade, industrial and agricultural set-ups which contain various pollutants including heavy metals have been transported in untreated forms through drains, water-ways and soils into inland water-bodies (Oguzie and Okosodo, 2008). The receiving water bodies' loads of pollutants are increased during the rainy season due to flood run-off water and atmospheric precipitation. During the dry season, the action of wind becomes more pronounced in the transport of hazardous substances which bioaccumulate in inland water bodies. The cumulative effects of the pollutants which eventually enter the food chain could cause severe physiological disorders and a host of other problems to aquatic organisms including fish (Odiete, 1999). Studies have shown that long term exposure to low concentrations of some heavy metals resulted in the development of chronic diseases (Lawson, 1989). The forms in which metal pollutants exist in waste water discharges determine their release into the aquatic ecosystem. Some metals become bio-available when soluble airborne solids are dissolved by weak acids such as carbonic acid. Their concentration became augmented by the abundance of metals in road dusts and tyre residues (Lagerweff and Specht, 1970). Run-off flood water from urban industrial, municipal and domestic set-ups transported through impermeable surfaces (streets, asbestos roofs), drains and water-ways have been implicated as sources of heavy metal pollution in urban aquatic environment (Ellis et al., 1986).

In Benin metropolis, large scale wastes are generated by battery recharging workshops, poultry houses, gasoline

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servicing stations, rubber and plastic processing factories, markets and sawmills which use wood preservatives rich in resin acids, dioxins and pentachlorophenol (Corrales and Horton, 1995). Mismanagement of these wastes which are dumped in soils and unsanitary land fills are subjected to weathering and leaching processes by rain and other atmospheric influences resulting in the release of hazardous substances such as cyanides, minerals, heavy metals and organic acids which get to underground water systems and inland water bodies untreated. Their effects render underground and surface waters unsafe for human, recreational and agricultural use. Biotic life is destroyed and natural ecosystems are poisoned. Human life is threatened and the principle of sustainable development is compromised (Rahman et al., 1997). The aim of this study was to determine the concentration levels of heavy metals in effluent discharges to the Ikpoba river and compare same with those of the receiving water.

MATERIALS AND METHODS

Study area

The study was conducted downstream of the Ikpoba reservoir in Benin City which lies between latitude 06.5^{l} North and longitude 05.8^{l} East. The river receives effluent discharges from rubber processing factories, breweries and various mini-factories whose effluents are discharged into the river through drains and waterways during the rainy season. Details of the study area including the sampled stations had earlier been described by Okhagbuzo (2008) and are shown in Figure 1.

Four sites were chosen for the study based on effluent characteristics. Station 1 (Okhoro) served as the control site and is before the reservoir. The station is assumed to be relatively free from effluent discharges. Station 2, (Temboga) receives effluent discharge from a rubber processing factory (Ordia rubber). Station 3 (Bridge) receives effluent discharges through flood run-off water from the City's industrial areas while station 4 (Brewery) receives brewery effluent from Guinness Nigeria Plc.

Sample collection and preparation

Duplicate water samples (2 l) were collected randomly from the four (4) sampled stations between September and October, 2008. The water samples were acidified to pH 1.5 with nitric acid after collection (Apha, 1992). They were sealed and stored in plastic containers which were previously washed with dilute nitric acid and rinsed with distilled water.

Duplicate effluent samples (2 l) were also collected on same date and time at point sources prior to their discharge into the receiving water and given the same acid treatment as per water. All samples were transported to the laboratory preserved in ice packs.

Digestion and analysis

In the laboratory, water samples were digested using standard procedures with pre-concentrated nitric acid (Parker; 1972). Effluent samples were digested as per water but with modifications as described by Allen (1989). 50 ml aliquot from a well mixed acid preserved effluent sample was transferred to a 250 ml beaker.

Concentrated nitric acid (10 ml) and hydrochloric acid (5 ml) were added to contents of the beaker and heated on a hot plate at 85°C under a hood until the volume of the content of the beaker was reduced to approximately 10 ml. The beaker was covered with a watch glass, refluxed for 30 min and subsequently allowed to cool and stand overnight to allow precipitates settle. Thereafter, the clear supernatant was transferred to a 25 ml volumetric flask, diluted to volume with distilled water, mixed thoroughly and stored in a sterile reagent bottle with a glass stopper prior to analysis. In all cases, blanks were prepared using the same quantity of mixed acids.

The concentrations of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in water and effluent digests were analyzed using an atomic absorption spectrophotometer (UNICAM 929) fitted with solar software. Each digest was analysed 3 times. The standard solution for instrument calibration was prepared by dissolving 1000 mg analar grade metal salt using 1l distilled water. Standard and blank samples were run with each set of experiment. Accuracy of the method used was assessed by the analysis of three replicate samples which yielded standard deviations less than 5% for Cu, Pb and Zn and 1% for Cd, Cr and Ni: Percent recovery experiments on metal samples spiked with authentic releasing agents were carried out as part of the analytical data quality assurance. Values obtained were in excess of 92%. The limits of detection were as follows: Cd, 0.01 µg/g; Cr, 0.05 µg/g; Cu, 0.05 µg/g; Ni, 0.02 µg/g; Pb, 0.05 µg/g and Zn, 0.02 µg/g. One-way analysis of variance (ANOVA) and Pearson's correlation coefficient were used in all cases for mean metal level comparisons at 5% level of significance.

RESULTS

Heavy metal concentrations in the effluents

The metals detected in the effluents include cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn).

Table 1 shows the mean concentration values (mg/l) of the various metals in the effluents at the four sampled stations. The range of Cd in the effluents varied from not detected value (Nd) at station 1 through 0.002 mg/l at station 4, 0.015 mg/l at station 2 to 0.055 mg/l at station 3 were the highest value for Cd was recorded. Cr in effluents varied from 0.001 mg/l at stations 1 and 4, respectively, through 0.002 mg/l at station 2 to 0.075 mg/l at station 3. Cu concentrations ranged from 0.010 mg/l at station 4, through 0.003 mg/l at station 1, 0.01 mg/l at station 2 to 0.150 mg/l at station 3 which recorded the highest Cu value.

The highest concentration of Ni (0.103 mg/l) was recorded at station 3 while the lowest value (0.001 mg/l) was recorded at station 1 (control site). The highest concentration of Pb (0.107 mg/l) was recorded at station 3 while the lowest value (0.008 mg/l) was recorded at station 4. Pb was not detected (Nd) at station 1. Zn concentration in effluents ranged from 0.00 mg/l at station 1 through 0.016 mg/l at station 4, 0.036 mg/l at station 2, to 0.120 mg/l at station 3. The rank profile of the heavy metals in the effluents was Cu > Zn > Pb > Ni > Cr > Cd. One way analysis of variance (ANOVA) performed on effluent data among metal concentrations show significant

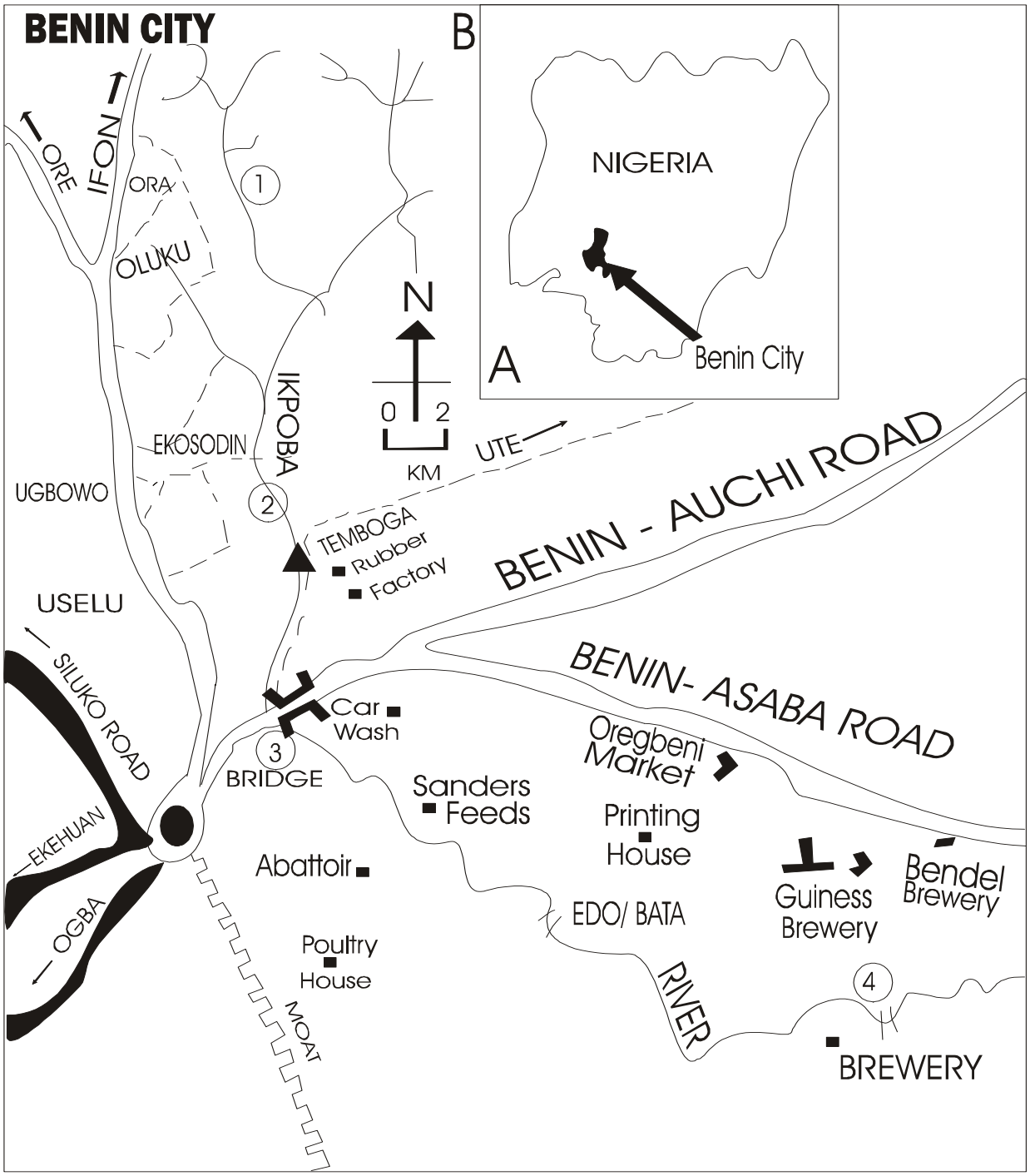

Figure 1. The study area. **A)** Nigeria showing Benin City; **B)** The river studied showing four sampling stations. Source: Federal Survey Nigeria 1964.

differences ($P < 0.05$) between metal values sampled in urban run-off effluent (Station 3) and those of effluents procured from Stations 1, 2 and 4 (Table 1). No significant differences ($P > 0.05$) were recorded in the concentrations of metals sampled at stations 1, 2 and 4 despite the seemingly high variations in their metal concentrations.

Heavy metal concentrations in the water

Presented in Table 2 are mean concentration values (mg/l) of heavy metals in the water.

The range of Cd in the water varied from 0.001 mg/l at station 1 through 0.003 mg/l at station 2, 0.11 mg/l at station 4 to 0.028 mg/l at station 3 where the highest Cd

Table 1. Mean concentration values mg/l (SD in parenthesis) of heavy metals in three replicate samples of effluents downstream of the Ikpoba river.

Heavy metal	Station 1 (Okhoro)	Station 2 (Temboga)	Station 3 (Bridge)	Station 4 (Brewery)
Cd	Nd	0.015^{b} (+ 0.001)	0.055^{a} (+ 0.002)	0.002^{ab} (+ 0.001)
Cr	0.001^{ab} (± 0.001)	0.002^{ab} (± 0.001)	0.075^{a} (± 0.003)	0.001^{ab} (± 0.001)
Cu	0.003^{ab} (± 0.002)	0.031^{b} (± 0.002)	0.150^{a} (± 0.002)	0.010^{b} (± 0.001)
Ni	0.001^{ab} (± 0.001)	0.013^{b} (± 0.001)	0.103^{a} (± 0.002)	0.005^{ab} (± 0.001)
Pb	Nd	0.010^{b} (± 0.002)	0.107^{a} (± 0.002)	0.008^{ab} (± 0.003)
Zn	0.002^{ab} (± 0.001)	0.036^{b} (± 0.005)	0.120^{a} (± 0.001)	0.016^{b} (± 0.001)

Data are presented as means ± SD of three (3) determinations.
Means followed by the same superscript are not significantly different at 5% probability level.
Nd = Not detected; SD= standard deviation.

Table 2. Mean concentration values mg/l (SD in parenthesis) of heavy metals in three replicate samples of water downstream of the Ikpoba river.

Heavy metal	Station 1 (Okhoro)	Station 2 (Temboga)	Station 3 (Bridge)	Station 4 (Brewery)
Cd	0.001^{ab} (± 0.001)	0.003^{ab} (± 0.001)	0.028^{b} (± 0.002)	0.011^{b} (± 0.002)
Cr	0.002^{ab} (± 0.001)	0.005^{ab} (± 0.001)	0.050^{a} (± 0.002)	0.015^{b} (± 0.002)
Cu	0.018^{b} (± 0.001)	0.013^{b} (± 0.002)	0.101^{a} (± 0.002)	0.020^{b} (± 0.001)
Ni	0.003^{ab} (± 0.001)	0.010^{b} (± 0.002)	0.065^{a} (± 0.003)	0.013^{b} (± 0.001)
Pb	0.002^{ab} (± 0.001)	0.016^{b} (± 0.001)	0.080^{a} (± 0.002)	0.012^{b} (± 0.001)
Zn	0.012^{b} (± 0.002)	0.005^{ab} (± 0.001)	0.095^{a} (± 0.002)	0.016^{b} (± 0.002)

Data are presented as means ± SD of three (3) determinations.
Means followed by the same superscript are not significantly different at 5% probability level.
SD= Standard deviation.

value was recorded. A similar pattern was observed in respect of Cr in water which varied from 0.002 mg/l at station 1, 0.005 mg/l at station 2, 0.015 mg/l at station 4 to 0.050 mg/l at station 3 where the highest Cr value was recorded.

Cu values took the same pattern but with the lowest value (0.013 mg/l) at station 2. Cu value of 0.018 mg/l was recorded at station 1, 0.020 mg/l at Station 4 and the highest value (0.101 mg/l) at Station 3. The highest concentration of Ni (0.065 mg/l) was recorded at station 3 while the lowest value (0.003 mg/l) was recorded at station 1. The highest concentration of Pb (0.080 mg/l) was recorded at station 3 while the lowest value (0.002 mg/l) was recorded at station 1. The highest value (0.095 mg/l) in respect of Zn was recorded at Station 3 while the lowest value (0.012 mg/l) was recorded at Station 1.

The rank profile of heavy metals in the water was Cu > Zn > Pb > Ni > Cr > Cd. One-way analysis of variance (ANOVA) performed on water data among metal concentrations showed that at three of the four stations, no significant differences ($P > 0.05$) were recorded between the concentrations of Cd in the water sampled from the four stations (Table 2). Significant differences ($P < 0.05$) were however, recorded between the concentrations of Cr, Cu, Ni, Pb and Zn at Station 3 and same metal values at stations 1, 2 and 4 where no significant differences ($P > 0.05$) were recorded (Table 2). Among the metals studied, significant correlations were observed between Cu levels in effluent and Cd levels in the water ($r = 512$, $P < 0.05$) and between Ni, Pb and Zn in effluents and Cu, Ni and Cd in the water ($r = 0.556$, 0.615 and 0.524, respectively; $P < 0.05$). There were also significant correlations between many other metals in the effluents and water at the four sampled stations. These correlations are shown in Table 3.

DISCUSSION

Water samples downstream of the Ikpoba river and corresponding effluents discharged into it from municipal, industrial, agricultural and domestic sources were analysed to ascertain the heavy metal concentrations in the effluents and the receiving water. The river provides water for domestic, recreation and fishing activities for inhabitants of Benin metropolis and beyond.

In the present study, the levels of heavy metals are higher in the effluents than in the water. The concentrations of metals are highest in water and effluent samples procured at station 3 than those from other stations (1, 2 and 4).

Station 3 (Bridge) being the largest source of wastes from the city centre contains relatively high concentrations of the metals. This station and adjourning areas are

Table 3. Correlation matrices for heavy metals concentrations in the effluents at the sampled stations.

	CDW	CRW	CUW	NIW	PBW	ZNW
Station 1 (Okoro)						
CDE	1					
CRE	- 0.320	1				
CUE	0.512*	0.520*	1			
NIE	0.330	- 0.380	0.556*	1		
PBE	- 0.315	- 0.428	- 0.317	0.615*	1	
ZNE	0.524*	0.321	0.481	0.328	0.565*	1
Station 2 (Temboga)						
CDE	1					
CRE	0.420	1				
CUE	- 0.310	0.520*	1			
NIE	- 0.325	- 0.350	- 0.322	1		
PBE	0.516*	0.311	0.413	0.325	1	
ZNE	- 0.382	0.568*	0.613*	- 0.228	- 0.380	1
Station 3 (Bridge)						
CDE	1					
CRE	0.526*	1				
CUE	0.330	- 0.286	1			
NIE	- 0.218	0.500	- 0.348	1		
PBE	- 0.310	- 0.421	0.560*	0.370	1	
ZNE	0.513	0.326	0.615*	0.256	0.227	1
Station 4 (Brewery)						
CDE	1					
CRE	- 0.310	1				
CUE	0.420	0.338	1			
NIE	0.381	- 0.246	0.536*	1		
PBE	- 0.268	0.421	- 0.219	0.438	1	
ZNE	0.546*	- 0.333	0.427	- 0.373	0.503*	1

CDW - Cd in water, CRW - Cr in water, CUW - Cu in water.
NIW - Ni in water, PBW - Pb in water, ZNW - Zn in water.
CDE - Cd in effluent, CRE - Cr in effluent, CUE - Cu in effluent.
NIE - Ni in effluent, PBE - Pb in effluent, ZNE - Zn in effluent.
*Asterisks indicate significant correlation ($P < 0.05$).

the leading centre from where municipal, industrial and domestic wastes are generated and dumped indiscriminately by the inhabitants. The area is the leading centre for trade and mini-factory activities that generate wastes rich in heavy metals from duplicating and printing houses, gasoline servicing stations, poultry houses, market wastes, paints and dyes for clothing items and fumes from high vehicular traffic. According to Yong et al. (1992), heterogenous masses from municipal, industrial and domestic throwaways were implicated as sources of metal pollutants in the aquatic environment. Oguzie (1999) reported relatively high levels of cadmium, lead and copper in effluents discharged into Ikpoba river during the rainy season. Similar reports on these metals were documented for the same river by Obasohan and Oronsaye (2000). The effects of flood water in Benin metropolis after heavy rains is often devastating, as run-off water often transports loads of soil containing wastes through open drains and road surfaces from the City to Ikpoba river. Leachates from garbage and solid wastes often find their way into the river through underground drainage and surface flood run-off during the rainy season.

The concentration of cadmium in water and effluents were relatively high in urban flood run-off effluents attributable to inputs from car wash and other domestic uses. According to Lagerweff and Specht (1970), cadmium and its compounds are associated with vehicle tyres which produce wastes as a result of wear and tears associated with high vehicular traffic. Certain industries involved in electroplating, pigments production, chemicals and alloy processing are sources of cadmium to the urban environ-

ment. The total mean concentrations of cadmium recorded in the water (0.043 mg/l) and effluent (0.072 mg/l) are higher than the value (0.040 mg/l) reported by Obasohan and Oronsaye (2000) and the value (0.010 mg/l) reported by Obasohan et al. (2006) for Ogba river water. The value for effluent was higher than the value (0.046 mg/l) reported for Ikpoba river by Oguzie (1999). The mean concentration of cadmium in the water is below the limit (< 1 mg/l) recommended by the World Health Organization (WHO) (1989) in drinking water. Cadmium level in effluent discharges recorded in the present study are below the value (1 mg/l) recommended by the Federal Ministry of Environment (FMENV, 1991) in industrial effluents.

Chromium (Cr) levels in the water and effluents were relatively high in urban run-off water than in rubber and brewery wastewater. The relatively high chromium level in water may not be unconnected with inputs from anthropogenic sources such as wastewater derived from the production of leather, wood preservatives and pigments derived from printing and dying mini-factories. This observation corroborated previous findings by Obasohan and Oronsaye (2000). The total mean concentrations of chromium recorded in the water (0.072 mg/l) and effluents (0.079 mg/l) are lower than total mean chromium value (0.534 mg/l) reported by Egborge (1991) for Warri river. The mean concentration of chromium in the water is higher than the limit (0.05mg/l) recommended by the World Health Organization (WHO) (1989) in drinking water. The levels of chromium in effluents are below the 1 mg/l value recommended by the Federal Ministry of Environment (FMENV, 1991) in industrial effluents. Copper concentrations in the water and effluents were relatively higher than those of all other metals especially in urban run-off effluents where a mean concentration level of 0.150 mg/l was recorded. This value was slightly higher than mean copper value (0.101 mg/l) recorded in the water. However, no significant differences ($P > 0.050$ were recorded between copper concentrations at stations 1, 2 and 4. The total mean concentrations of copper in the water (0.152 mg/l) and effluent (0.194 mg/l) are higher than total mean copper value (0.055 mg/l) recorded in Ogba river (Oguzie and Igwegbe, 2007) and mean copper value (0.049 mg/l) reported by Obasohan et al. (2006) in Ogba river in Benin City, respectively. Copper value in effluent is higher than Cu value (0.22 mg/l) reported for Ikpoba river by Oguzie (1999). The mean concentration of copper in the water is comparable to the limit (1.5 mg/l) recommended by the World Health Organization (WHO) (1989) in drinking water. Copper levels in effluents are higher than the value (1 mg/l) recommended by the Federal Ministry of Environment (FMENV, 1991) in industrial effluents. Nickel was reported to be a vital commodity in every area of industrial activity and has found wide application in the manufacture of batteries, fertilizer, welding products, electroplating and household appliances (Sreedevi et al., 1992). Relatively high concentrations of nickel were recorded in water and effluents especially in urban run-off water where nickel has a mean value of 0.103 mg/l. The total mean concentration of nickel in water (0.091 mg/l) and effluent (0.122 mg/l) are lower than mean nickel value (0.183 mg/l) reported by Fufeyin (1994) for Ikpoba reservoir water and the value (44.5 mg/l) reported for Warri river by Egborge (1991). The concentrations of nickel in effluents are higher than the < 1 mg/l value recommended by the Federal Ministry of Environment (FMENV, 1991) in industrial effluents.

Relatively higher mean concentration of lead than nickel was recorded in the water and effluents in the present study especially in the water and effluents sampled at Station 3 (Bridge). Like cadmium, lead and its compounds are present in municipal and industrial wastes and are transported into urban rivers through flood run-off water. Gasoline servicing stations and high vehicular traffic are also sources of lead which get into inland water bodies through atmospheric precipitation. Apart from metal values recorded at station 3, no significant differences ($P > 0.05$) were recorded between the concentrations of lead at stations 1, 2 and 4 though lead concentrations vary among the stations. The total mean concentration of lead in the water (0.110 mg/l) and effluents (0.125 mg/l) are higher than mean lead value (0.025 mg/l) reported for lead in Ogba river by Oguzie and Igwegbe (2007) and lead value (0.021 mg/l) reported for the same river by Obasohan et al. (2006). Lead value in effluents is higher than lead value (0.034mg/l) reported for Ikpoba river by Oguzie (1999). Lead concentration in water is higher than the value (0.05 mg/l) recommended by the World Health Organization (WHO) (1989) in drinking water. The value in effluent is higher than the value (< 1 mg/l) recommended by the Federal Ministry of Environment (FMENV, 1991) in industrial effluents. Zinc levels in water and effluents are relatively higher than corresponding zinc levels in rubber and brewery wastewater. Except copper, the concentrations of zinc in urban run-off water are higher than those of other metals. However, no significant differences ($P > 0.05$) were recorded between the concentration of zinc at stations 1, 2 and 4 despite the variations in zinc concentrations at the three stations. Zinc is sourced from industries involved in smelting, electro-galvanizing, mining and metallurgy and in the production of pesticides, rubber and plastics and various alloys. Zinc is also present in mixed effluents (dungs, poultry droppings and fertilizer) including human and animal food where it is concentrated in excretions which get flushed into inland water bodies through flood run-off water. The total mean concentration of zinc in the water (0.120 mg/l) is comparable to Zn value (0.121 mg/l) recorded in water of the lower Ikpoba river (Oguzie, 1999). The level in effluent (0.174 mg/l) is higher than Zn value (0.085) reported for Ikpoba river by Oguzie (1999). Zinc concentration in water is lower than the value (15 mg/l) recommended by the World Health Organization

(WHO) (1989) in drinking water. Zinc value in effluent is higher than the value (< 0.1 mg/l) recommended by the Federal Ministry of Environment (FMENV, 1991) in Industrial effluents.

The present study shows that Ikpoba river water is polluted with chromium and lead and is therefore unfit for human consumption. Effluents on the other hand have high concentrations of copper, nickel, lead and zinc which exceeded the limits recommended by the Federal Ministry of Environment for discharge into surface waters in Nigeria. From the foregoing, it has become very necessary to implement existing policies to check unwarranted dumping of refuse and the discharge of harmful substances into inland water bodies to avert possible hazards. The need for regular monitoring of inland water bodies should be intensified and culprits apprehended and disciplined.

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