POLLUTION EFFECT OF STEEL PRODUCTION ON WATER QUALITY OF UDU RIVER (SECTION OF THE WARRI RIVER), DELTA STATE, NIGERIA

Akporido, S. O

Department of Chemistry, Delta State University, Abraka Email: <u>samaccess2006@yahoo.com</u>

ABSTRACT

Waters of Udu River (a section of Warri River) where Delta Steel Factory is Located was studied for the quality characteristics. Water samples were collected twice in a season (dry and rainy seasons) for two years and were analyzed for selected physicochemical parameters (mostly by standard methods) and heavy metals (by flame AAS after digestion). Results obtained are: Temperature ($28.8\pm0.8^{\circ}$ C), pH (6.65 ± 0.12), TS ($21.9\pm1.2 \text{ mgl}^{-1}$), TSS ($0.06\pm0.02 \text{ mgl}^{-1}$), TDS ($21.6\pm0.8 \text{ mgl}^{-1}$), COD ($4.18\pm0.10 \text{ mg} \text{ l}^{-1}$), DO ($5.51\pm0.32 \text{ mgl}^{-1}$), Pb ($32.5\pm4.7 \text{ µgl}^{-1}$), Cd (ND), Cr ($16.6\pm1.8 \text{ µgl}^{-1}$), Fe ($191\pm250 \text{ µgl}^{-1}$), Zn ($66.7\pm9.9 \text{ µgl}^{-1}$), Ni (ND) and Cu ($37.4\pm6.1 \text{ µgl}^{-1}$). The average values of the parameters were generally higher in the study area than in the control area. The average concentration of Pb exceeded guideline values for WHO (2011), SON (2007) and USEPA (2012) which shows that the water is polluted with respect to drinking purpose. Fe correlated strongly with Pb, Cr, Cu, TS, TDS and COD which shows that Fe has the same source as Pb,Cr and Cu and is a component of TS. TDS and COD. This shows that the pollution observed has its source in the steel production activities in the area.

Keywords: Quality characteristics; Udu River; Delta Steel Factory; physicochemical parameters; heavy metals; flame AAS; guideline values; COD; TDS; Pb; Cr; Cu; Zn Ni; Fe.

INTRODUCTION

An important source of heavy metals in the environment is the smelting of metals which most of the time result in atmospheric fallouts when there is rainfall. Related to this is the process of mining, generally mining brings about disposal of tailings, discharge of effluent and emissions which pollutes the atmosphere. Other sources of heavy metal pollution include industrial effluents, domestic effluents, urban storm water runoff, spoil heaps, nonpoint source of heavy metals from cultivated and virgin forest, metal-containing air borne particles, crude oil (Forstner and Whittman, 1983; NRC, 1985; GESAMP, 1993). Heavy metals such as As, Cd, Cr, Cu, Pb, Hg and Mo are known to be toxic at certain concentrations. Effects of some of these metals are well documented (Bryan and Langston 1991; Bryan, 1971; Forstner and Whittman, 1983). The effect of pollution from effluent of a steel processing plant on water, sediments, soil and biota includes depletion of potable water, arable land and fish and other animal resources from the river (Forstner and Whittman, 1983) Studies on the physicochemical characteristics and heavy metals in waters and sediments of rivers in the Niger Delta have been carried out (Adami *et al.*, 2007; Akporido *et al.*, 2000; Akporido and Asagba 2013; Akporido and Ifukor 2009; Ekpo *et al.*, 2012; Kakulu and Osibanjo 1992; Nduka et al., 2011) These workers found appreciable quantities of heavy metals in water with the concentration of some of the metals exceeding national and international guidelines for drinking water and non-drinking water uses. Not much information has been reported on the effect of steel processing around the Warri River where the Delta Steel Company is located.

The Delta Steel Company Ovwian-Aladja was established in the early 1980s to process iron ore and scrap steel into steel rods. The Delta steel company plant is near the Warri River in the southern stretch of the river (it is known locally as the Udu River). The occupation of the people in the area is mainly fishing and crop farming. A moderately high volume of fishing occurs in this stretch of the river. The arable crops include Zea mays (maize), Annas comosus (pineapple), Dioscorea sp. (yam) and Solanum lycoperscium (tomatoes). The tree and fruit crops include

150



Fig 1: Map of study area showing section of Warri River and the sampling stations

Magnifera indica (mango), Elaeis guineensis (oil palm), Cocos nucifera (coconut) and Carica papaya (pawpaw). The effect of the activities in this and other industrial concerns in the region have not been properly monitored. There has been a dearth of information on the pollution status of the environments in this region. The hypothesis of this study is that environments which host this type of industrial concern should increase in heavy metals concentrations in water, sediment, soil and biota. This needs to be tested if this is true for this environment (i.e. environment under study). The present study examined the effect of effluents from a steel processing plant on waters of Udu River (a section of the Warri River) by determining the concentrations of selected heavy metals (Pb, Cd, Cr, Zn, Ni, Fe and Cu) and the determination of some physicochemical parameters of water (temperature, pH, total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO) and chemical oxygen demand (COD).

MATERIALS AND METHODS

Description of Study Area, collection and preservation of samples: The study area is South of Warri town. The Udu River (local name) which is actually a section of the Warri River flows around the East and South part of Warri town. The sampling stations are labeled A, B, C, D, E, F and G. Sampling station A is near to the place where the effluent conduit is suspected to empty into the river. The other six sampling stations of the study area are located on the river downstream from this point separated from each other successively by 1km distance. The study area is shown in Fig. 1 (Map of study area showing section of Warri River and the sampling stations). The two control sampling stations are located on the Ovwuvwe Stream in Abraka area about 120 kilometres from the study area. This area shares the same geological characteristics with the study area but does have any industries of note. They are labeled M and N. Water samples were collected twice in the season (dry and rainy) for two years from July 2007 to February 2009. Samples were collected for the following parameters: Temperature, pH, total solid (TS), total suspended solid (TSS), total

dissolved solids (TDS), chemical oxygen demand (COD), dissolved oxygen (DO), Pb, Cd, Cr, Fe, Zn, Ni and Cu. Grab water samples were collected from the water surface and at mid-depth along the middle axis of the river. Water samples were preserved for each parameter according to standard methods (APHA-AWWA-WEF, 1995).

Analytical Procedures:

Temperature was determined at site by dipping the bulb of a mercury thermometer below the surface of water sample collected in a 100 mL glass beaker (APHA-AWWA-WEF, 1995). The pH of water samples were also determined at site by dipping the glass electrode of a portable pH meter(already standardized by buffer solution (pH 4&7) below the surface of water sample in a 100 ml glass beaker (APHA-AWWA-WEF, 1995). 200ml of water sample was weighed in an evaporating dish and evaporated to dryness and the residue dried to constant weight in an oven at 103° to (APHA-AWWA-WEF, the TS obtain 1995). The TSS was determined by filtering 200ml of water sample through a gooch crucible containing glass-fibre filter disk connected to a suction pump and drying the filtered solid on the glass-fibre disk to constant weight at 103 °C (APHA-AWWA-WEF, 1995). The filtrate from the determination of TSS above was evaporated to dryness and the residue dried to constant weight at 180°C in an oven to obtain the TDS (APHA-AWWA-WEF, 1995). COD was determined by the open reflux method (APHA-AWWA-WEF, 1995).

DO was determined in water samples by the iodometric method with azide modification (samples had earlier been preserved in the field by the addition of 1ml of Mn₂SO4 solution and 1 ml of alkali-iodide-azide reagent to the stage of formation of precipitates of manganese hydroxide flocs) (APHA-AWWA-WEF, 1995).

Heavy metals (Pb, Cd, Cr, Fe, Zn, Ni and Cu) were determined in water samples first by digesting with simultaneous preconcentration of a given volume of water as follow: 5ml of conc. HNO₃ was added to 500ml of water sample in a kjedahl flask, this was dried to almost complete dryness with heat and residue was dissolved with 20 mL of

152

distilled water and transferred to a 50 mL volumetric flask and this was made up to the 50 mL mark. Six heavy metals (Pb, Cd, Cr, Fe, Zn, Ni and Cu) were determined from this digest solution by an AAS spectrophotometer (model: Perkin Elmer AA 200, Waltham, USA) which has already been calibrated with the standard solutions of the metals (APHA-AWWA-WEF, 1995).

Quality Assurance Programme

The quality assurance programme for this study included analysis of blanks, analysis of duplicates and the determination of percentage recoveries of COD and the six heavy metals. Recovery studies were carried out for COD and the six heavy metals. The percentage recovery of COD was determined on a solution of KHP (potassium hydrogen phthalate) by determining COD on standard solutions of potassium hydrogen phthalate (KHP) (i.e. solution which contains 425 mg/L of KHP) and comparing the mean of five determinations to the theoretical value of 500 mgl⁻

Result gave a mean COD of $463 \pm 17 \text{mg/L}$ and percentages recovery of 93.5 ± 4.5 . These fall within the acceptable range for percentage recovery of 90 - 110. The recovery is therefore a good recovery. The results of the determination percentage recovery of the metals are as follows:

94.1±8. 5 %, 91.6±9.3%, 93±10 %, 99±9.5%, 101±8.8%, 91.7±6.8 % and 103±11 % were obtained for Pb, Cd, Cr, Fe, Zn, Ni and Cu respectively. These are also good recoveries.

Statistical Procedure: The means of the values of physicochemical parameters and heavy metals were compared in the four seasons studied (two dry and two rainy seasons) using ANOVA-single factor analysis from Microsoft Excel (Microsoft Corporation LTD) (2007 version). The means of each variable in the seven sampling stations were also compared using ANOVA-single factor analysis from Microsoft Excel (Microsoft corporation LTD) (2007 version). The t-test (two sample, assuming equal variance) was used to compare the means of some of the variables of the study area with those of the control area. The Pearson 2-tailed test was used for the correla-

tion of the values of all variables (with the exception of the pH values) within the Statistic Package for the Social Sciences (SPSS) (version 17) (SPSS, Chicago).

RESULTS AND DISCUSSION

The results of average values obtained for the various parameters in the study area are here given: Temperature (28.8±0.01[°] C), pH $(6.65\pm0.12),$ TS $(21.9\pm1.2 \text{ mgl}^{-1}),$ TSS $(0.06\pm0.02 \text{ mgl}^{-1})$, TDS $(21.6\pm0.8 \text{ mgl}^{-1})$, COD (4.18±0.10 mgl⁻¹), DO (5.51±0.32 mgl⁻¹), Pb (32.5±4.7 µgl⁻¹), Cd (ND), Cr (16.6±1.8 μgl^{-1}), Fe (191±150 μgl^{-1}), Zn (66.7±9.9 μg^{-1} ¹), Ni (ND) and Cu (37.4 \pm 6.1 µgl⁻¹). A close look at the results shows that most values were moderate. The concentration of Pb (32.5±4.7 μ gl⁻¹) and Fe (191±150 μ g⁻¹) are however moderately high. The values of the physicochemical parameters are about the same in all the sampling stations (Table 1). The concentrations of the heavy metals however show some differences in concentration in the different sampling stations e.g. the average concentration of Pb is highest at the B sampling station (i.e. the second sampling station from the factory or effluent discharge point) $(37.5\pm1.9 \ \mu gl^{-1})$ and lowest at G (the seventh and last) sampling station $(28.3\pm5.1 \text{ }\mu\text{gl}^{-1})$. The average concentration of Cr is highest at B (19.0 \pm 1.8 µgl⁻¹) and lowest at D sampling station (15.0 \pm 1.2 µgl⁻¹). The differences in the concentration of Fe is more pronounced, its concentration is highest at F sampling station $(466\pm620 \ \mu gl^{-1})$ and lowest at D sampling station (129 \pm 5.0 µgl⁻¹). The concentration of Zn is highest at D sampling station (83.8±6.9 µgl⁻ ¹) and lowest at G sampling station (55.3 ± 3.1) μ gl⁻¹). The concentration of Cu is highest at C sampling station (43.0 \pm 2.7 µgl⁻¹) and lowest at D sampling station 932.0 \pm 7.7 µgl⁻¹). No explanation could be offered for the observed differences in the concentration of the heavy metals. The variation in the values (or concentrations) of the parameters did not conform to any definite pattern with respect to distance from the factory (or from the point of discharge of effluents) (i.e. it did not increase proportionally to the distance from point of discharge of effluents). The differences in the values of each parameter in the different sampling stations were found not to be statistically

Akporido

significant when compared using analysis of variance (ANOVA-single factor). A comparison of the average values of the physicochemical parameters and heavy metals in the seasons (Table 2) shows that the values were slightly higher in the two dry seasons for example Fe average concentrations for first dry season (240 \pm 360 µgl⁻¹) and second dry season $(244\pm360 \text{ }\mu\text{gl}^{-1})$ while the rainy season values are: first rainy season ($143\pm16 \ \mu gl^{-1}$) and second rainy season $(135\pm15 \text{ }\mu\text{gl}^{-1})$. Another example is Pb. The concentration of Pb in the two dry seasons are: first dry season (36.6±5.4 μ gl⁻¹) and second dry season (33.6±4.8 μ gl⁻¹) while rainy season values are: First rainy season $(31.5\pm4.4 \text{ }\mu\text{gl}^{-1})$ and second rainy season $(30.5\pm4.8 \ \mu gl^{-1})$. These differences in the concentrations between the seasons are however not statistically significant when compared using analysis of variance (ANOVA single factor).

A comparison of values of the physicochemical parameters and heavy metals of study area with those of control area (Table 3) shows that the concentrations of heavy metals are generally higher in the study area water than in the control area water. These differences are statistically significant in the cases of Fe, Pb and Zn respectively when compared using t-test (two samples, with unequal variance). This shows that the study area water is more polluted when compared with the control area water and this is probably as a result of the iron and steel industry located in the area

Table1: Average values of parameters in each of the sampling stations in the

parame te rs	SS/A	SS/B	SS/C	SS/D	SS/E	SS/F	SS/G
Temperature (⁰ C)	29.3±0.8	28.9±0.5	28.9±0.7	28.8±0.8	28.8±0.8	28.4±1.0	28.5±1.0
pH	6.65±0.21	6.54 ± 0.08	6.80±0.06	6.71±0.09	6.61 ± 0.06	6.61 ± 0.08	6.61±0.06
TS (mgl-1)	22.7±0.9	23.2±1.9	22.0±1.0	21.1±0.5	21.9±0.8	20.9±0.9	21.9±0.7
TSS (mgl-1)	0.07 ± 0.02	0.05 ± 0.01	0.05 ± 0.01	0.06 ± 0.02	0.06 ± 0.02	0.06 ± 0.01	0.07 ± 0.02
TDS (mgl-1)	21.9±0.3	22.8±0.4	22.1±1.0	20.6±0.3	21.7±0.7	21.4±0.27	21.1±0.4
COD (mgl ⁻¹)	4.23±0.09	4.16±0.06	4.21 ± 0.08	4.17±0.17	4.18±0.66	4.17±0.10	4.17±0.11
DO (mgl ⁻¹)	5.39±0.28	5.47±0.34	5.45±0.33	5.53±0.31	5.59±0.35	5.55±0.38	5.63±0.31
Pb (µgŀ¹)	36.5±1.9	37.5±1.9	33.3±3.7	31.0±4.8	31.2±4.5	30.0±2.4	28.3±5.1
Cd (µgl-1)	0	0	0	0	0	0	0
Cr (µgŀ¹)	16.0±1.3	19.0±1.8	15.5±1.2	15.0±0.8	16.8±1.6	16.8±0.9	17.3±1.6
Fe (µgl ⁻¹)	159±35	160 ± 5.4	140±5.0	129±5.0	152±3.9	466±620	134±6.2
Zn (µgŀ¹)	71.5±3.9	70.3±5.4	66.3±5.3	83.8±6.9	60.8±3.2	59.3±3.2	55.3±3.1
Ni (µgŀ¹)	0	0	0	0	0	0	0
Cu (µgl-1)	35.8±6.8	36.8±3.2	43.0±2.7	32.0±7.7	42.3±6.6	36.5±4.4	35.8±2.4

TABLE 2: Average values of physicochemical characteristics in each of the seasons

Parameters	First Rainy sea- son	First dry season	Second Rainy season	Second dry season
Temperature(°C)	28.8±0.6	28.8±0.9	28.8±1.1	28.8±0.7
pH at 25°C	6.65±0.10	6.65±0.90	6.66±0.11	6.64±0.17
$TS(mgl^{-1})$	21.6±0.8	22.0±1.0	22.0±1.1	22.0±1.9
TSS (mgl^{-1})	0.05±0.01	0.06±0.02	0.05 ± 0.01	0.07±0.02
TDS (mgl^{-1})	21.5±0.8	21.6±0.9	21.5±0.8	21.6±0.9
$COD (mgl^{-1})$	4.13±0.07	4.22±0.11	4.13±0.07	4.23±0.10
$DO (mgl^{-1})$	5.48±0.3	5.85±	5.48±0.3	5.55±0.35
Pb (µgl ⁻¹)	31.5±4.4	36.6±5.4	30.5±4.8	33.6±4.8
$Cd (\mu g l^{-1})$	0.00	0.00	0.00	0.00
$Cr (\mu g l^{-1})$	16.0±1.5	17.2±1.9	16.0±1.5	17.2±1.9
$Fe(\mu gl^{-1})$	143±16	240±360	135±15	244±360
$Zn \ (\mu g l^{-1})$	66.6±9.2	67±11	66.6±9.2	67±11
Ni (µgl ⁻¹)	0.00	0.00	0.00	0.00
Cu $(\mu g l^{-1})$	36.6±5.4	38.2±7.0	36.6±5.4	38.2±9.0

(154)

 Table 3: comparison of values of physicochemical characteristics of water of study area with that of

Parameters	Study Area	Control Area
Temperature	28.8±0.8	28.1±0.8
pH at 25°c	6.65±0.12	6.99±0.14
$TS (mgl^{-1})$	21.9±1.2	27.7±1.0
TSS (mgl ⁻¹)	0.06 ± 0.02	0.05 ± 0.01
TDS (mgl ⁻¹)	21.6±0.8	17.1±1.3
$COD (mgl^{-1})$	4.18±0.10	4.02±0.03
$DO(mgl^{-1})$	5.51±0.32	5.39±0.18
Pb (µgl ⁻¹)	32.5±4.7	25.5±2.4
$Cd (\mu gl^{-1})$	0.00	0.00
Cr (µgl ⁻¹)	16.6±1.8	16.4±1.4
Fe (µgl ⁻¹)	191±150	125±6.8
$Zn (\mu gl^{-1})$	66.7±9.9	49.4±5.2
Ni (µgl ⁻¹)	0.00	0.00
Cu (µgl ⁻¹)	37.4±6.1	34.9±4.0

since the two areas can be said to be located in the same geographical and geological region.

A comparison of values of physicochemical parameters and heavy metals of study area with national and international guidelines for drinking water (Table 4) shows that the mean concentration of Pb in study area $(32.5\pm4.7\mu gl^{-1})$ is higher than SON guideline value (10.0 µgl⁻¹), WHO's 2011 guideline value (10.0 µgl⁻¹) and USEPA maximum contaminant level (MCL) (15.0 µgl⁻¹), Canadian Drinking water Quality guidelines maximum acceptable concentration (10 μ gl⁻¹). The high concentration of Pb in the study area water is a consequence of the iron and steel industry in the area since concentration of Fe correlated very strongly with concentration of Pb (Table 5) (correlation coefficient is significant at 0.01 confidence level). This shows that Fe and Pb has identical source. The mean concentration of Fe is also fairly high $(191\pm250 \text{ mgl}^{-1})$ although it does not exceed any of the guidelines values (Table 4).

A comparison of the water characteristics of study area with national and international guidelines for non-drinking water uses (Table 6) revealed that the pH of study area water (6.65 ± 0.12) fell outside the range for pH for iron and steel water guideline (6.8 -7.0), guidelines for power generating water (8.8 - 9.4) and guidelines for irrigation water (7.0 - 8.5) (by the California state water quality control Board) (Van der Leeden et al., 1990). The concentration of TDS of study area ($21.6\pm0.8 \text{ mgl}^{-1}$) exceeded guideline for power generating water (boiler feed water) $(<0.5 \text{ mgl}^{-1})$. The average concentration of COD of study area water $(4.18\pm0.10 \text{ mgl}^{-1})$ exceeded guideline for power generating water (Boiler feed water) (<1.00 mgl⁻¹). The average concentration of Fe in the study area water $(191\pm250 \text{ }\mu\text{gl}^{-1})$ exceeded guidelines for pulp and paper (fine paper) water (100 µgl⁻¹) and power generating water (10.0 μ gl⁻¹). The average concentration of Zn (66.7±9.9 µgl⁻¹) exceeded guideline value for power generating water ($<10.0 \ \mu gl^{-1}$). The average concentration Cu $(37.4\pm6.1 \,\mu gl^{-1})$ exceeded guidelines value for power generating water (boiler feed water) $(<10.0 \text{ }\mu\text{gl}^{-1})$ and aquatic life rearing water $(20.0 \text{ }\mu\text{gl}^{-1})$. The water of study area is therefore not suitable for iron and steel, power generating, irrigation, aquatic life rearing, livestock rearing and pulp and paper industries.

A Pearson (2-tailed) correlation of values of all the physicochemical parameters (with the exception of the pH) and heavy metals obtained for the study area (Table 5) shows that the average concentration of iron correlates strongly with the average concentration of TS, TDS, COD, Pb, Cr and Cu (coefficient of correlation significant at 0.01 confidence level). This shows that Fe is an important component of TS, TDS and COD in the environment of the study area. Fe, Pb, Cr and Cu have identical source which is probably the iron and steel industry located in the area. The average concentration of Zn correlates strongly with that of Pb (correlation coefficient significant at 0.05). This also shows that both have identical source.

Results from this study were also compared with results for rivers in other places. Most of the results were comparable with results obtained for the other rivers (Table 7). Some of the results were however lower and some higher in other cases (Table 7) The average temperature of the study area 28.8±0.8 °C $(27 - 30.5 \ ^{\circ}C)$ is comparable with results obtained for Benin River (27.6±1.6 °C). Elechi Creek $(28 - 32 \ ^{0}C)$ and Ogunpa/Ona rivers (26 -32 ⁰C). The average pH of study area water 6.65 ± 0.12 (6.2 - 6.9) is comparable with those for Benin River (5.9±1.1), Elechi Creek (6.4 – 7.7), Ogunpa/Ona (6.6 - 8.1), Ndokwa rivers (6.90±0.18), and Crooked Creek (6.68±0.67).. The average value of DO 5.51±0.32 mg/L

(155)

Parameters	Results from present study (udu river)	Nation drinking water standards (SON, 2007)	WHO'S Drinking water standards (WHO, 2011)	USEPA (MCL) (USEPA, 2012)	Canadian Standards (MAC)(Health Canada, 2012)	FMEHUD permissible limit standards (FMEHUD, 1991)
pH at 25°c	6.65±0.12	No guideline	No guideline	6.5-8.5*	6.5 – 8.5 (AO)	6.5-8.5
TDS (mgl ⁻¹)	21.6±0.8	No guideline	No guideline	500^*	NS	500
$COD (mgl^{-1})$	4.18±0.10	-	-	-	NS	-
$DO (mgl^{-1})$	5.51±0.32	No guideline	No guideline	No guideline	NS	7.50
Pb (µgl ⁻¹)	32.5±4.7	10.0	10.0	15.0	10.0	50.0
$Cd (\mu gl^{-1})$	0.00	3.00	3.00	500	5.00	10.0
Cr (µgl ⁻¹ 1	16.6±1.8	50.0	50.0	100	50.0	50.0
Fe (μ gl ⁻¹)	191±250	300	No guideline	No guideline	<u><</u> 300 (AO)	1000
$Zn (\mu gl^{-1})$	66.7±9.9	3000	No guideline	50	5000	5000
Ni (μ gl ⁻¹)	0.00	No guideline	70.0	No guideline	NS	50.0
Cu (µgl ⁻¹)	37.4±6.1	1000	2000	1300	1000	100

 Table 4: Comparison of water characteristics of study area water with national and international guidelines for drinking water

*Secondary maximum contaminant level (USEPA secondary drinking water stan-

dard)

WHO = World Health Organization

USEPA = United States Environmental Protection Agency

SON = Standard Organization of Nigeria

MCL = *maximum* contamination level

MAC = maximum acceptable concentration

FMEHUD= Federal Ministry of Environment, Housing and Urban development

(Nigeria)

AO = aesthetic objective

Table 5: Pearson (Z-tailed) correlation of values of some physiochemical parameter of study area water (N=56)

	TS	TSS	TDS	DO	Pb	Cd	Cr	Fe	Zn	Ni	Cu	COD
TS												
TSS	0.110											
TDS	0.553**	-0.222										
DO	-0.119	0.335*										
Pb	0.238	0.088										
Cd	а		а	а	а							
Cr	0.433	-0.089	0.608**	-0.029	0.210	а						
Fe	0.325	-0.231	0.387**	- 0.454**	0.492**	а	0.380					
Zn	-0.126	0.110	0.033	0.003	0.333	а	0.220	0.061				
Ni	а	а	а	а	а	а	а	а				
Cu	0.102	-0.142	0.239	0.007	-0.218	а	0.134	0.380**	-0.411**	а		
COD	0.038	0.195	0.275	0.144	0.017	а	0.181	0.087	0.044	а	0.368**	

** correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2tailed)

a. Cannot be computed because at least one of the variable is constant

 Table 6: Comparison of water characteristics of study are with national and international guidelines for non-drinking water uses

Parameters	Results from present study (Udu river)	Guidelines for pulp and paper (fine paper(CCRE M, 1987)	Guidelines for Iron and steel industry water (CCREM, 1987)	Guideline for petroleum industry water (CCREM, 1987)	Guidelines for power generating industry water feed water (CCREM, 1987)	FAO 1985 Guidelines for irrigation water (threshold concn.) (Van der Leeden et al.,1990)	Guidelines for aquatic life rearing (fresh water by CSWQCB (Van der Leeden et al.,1990)	Guidelines for recreation drinking water by CSWQCB (Van der Leeden et al, 1990)	Guidelines for beverages industry water food (caning freezing) (CCREM, 1987)	Textile industry water (FMEHUD, 1991).	Guidelines for livestock rearing water (LT)by OME (Van der Leeden et al., 1990)
Temperature	28.8±0.8	No guideline	<38				34.0	50.0		35-40	
pH at 25°c	6.65±0.12	No guideline	6.8 - 7.0	6.0 - 9.0	8.8 - 9.4	7.0-8.5	6.5 - 8.5	6.0 - 10.0	6.5 - 8.5	6.0 – 9.0	5.6 - 9.0
TSS (mgl ⁻¹)	0.06 ± 0.02	<10.0	<25	<10	< 0.05		100		<10.0	30.0	
TDS (mgl ⁻¹)	21.6±0.8	<200	<1000	<750	<0.5	500	2000		<500	200	
COD (mgl ⁻¹)	4.18 ± 0.10	-	-	-	<1.00	-	-	-	-	-	-
DO (mgl ⁻¹)	5.51±0.32	-			< 0.007						
Pb (µgl ⁻¹)	32.5±4.7	-	-	-	-	-	500	-	-	-	-
Cd (µgl ⁻¹)	0.00	-				10.0	10.0				
Cr (µgl ⁻¹)	16.6±1.8	-	-	-	-	-	-	-	-	-	-
Fe (µgl ⁻¹)	191±250	100	-	<1000	<10.0	5000	No guideline	-	< 200	<1000	
$Zn (\mu gl^{-1})$	66.7±9.9				<10.0	5000	100			<10000	25000
Ni (µgl ⁻¹)	0.00	-	-	-	-	200	50.0	-	-	-	1000
Cu (µgl ⁻¹)	37.4±6.1	-	-	-	<10.0	200	200	-	No	<1000	-
									guideline		

CSWQCB	= California State Water Quality Control Board (standards for irrigation)
LT	= Limiting Threshold
CCREM	= Canadia Council of Resources and Environment Ministers
FMEHUD	= Federal Ministry of Environment Housing and Urban Development
FAO	= Food and agriculture organization
OME	= Ontario ministry of Environment

Table 7: Comparison of results obtained for study area with results obtained for rivers elsewhere

Country	River	Temp	pН	TS	TSS	TDS	COD	DO	Pb	Cd	Cr	Fe	Zn	Ni	Cu	References
		⁰ C		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	$(\mu g/L)$	(µg/L)	(µg/L)					
Nigeria	Benin	27.6±	5.9±	-	80.4	$3300\pm$	-	4.7±1.0	-	-	-	-	-	-	-	Courant et al.,
	River	1.6	1.1		±130	7700										1987
Nigeria	Elechi	28 -	6.4 –	-	-	1240-	-	4.16 -	1.00 -	7.00 -	-	-	2.00 -	27 -	1.00 -	Obire et al.,
	Creek	32	7.7			19800		6.62	160	25.4			822	945	58100	2003
Nigeria	Ogunpa	26 -	6.6 -	160 -	10 -	0.1 –	-	0.2 –	<10.0-	<1.00-	2.00 -	-	1.00 -	<1.00-	<1.00-	Onianwa et al.,
	/Ona	32	8.1	1480	270	5.9		8.3	8600	23.0	19.0		35.0	27.0	39.0	2001
Nigeria	Niger	-	6.3	-	-	30.0	-	-	ND	ND	100	-	1010	-	ND	Asonye et al.,
	River															2007
Ngeria	Ndokwa	-	6.90±	-	34.9±	45±	67±	7.7±	12±	-	-	$640\pm$	18±21	132±	-	Akporido and
	river		0.18		9.3	32	40	2.7	10			330		89		Ifukor, 2007
USA	Crook	-	$6.68\pm$	-	7.1±	$200\pm$	-	-	310±	730±	-	-	$2770\pm$	-	24±19	Jennett and
	Creek		0.65		7.7	200			360	350			590			Foil, 1979
Nigeria	New	-	-	-	-	-	-	-	850	560	50.0		65.9	-	2080	Wegwu and
	Calabar															Akininwor,
	River															2006
Nigeria	Udu	$28.8\pm$	6.65±	21.9±	0.06±	21.6±	4.18±	5.51±	32.5±	ND	16.6±	191±	66.7±	ND	37.4±	Present study
	River	0.8	0.12	1.2	0.02	0.8	0.10	0.32	4.7		1.8	150	9.9		6.1	
Nigeria	Udu	27 –	6.2 -	19.5 -	0.03 -	20.1 -	3.95 -	5.11 -	23 -	ND	14 -	119 -	52 -	ND	23 -	Present study
-	River	30.5	6.9	26.8	0.09	23.3	4.40	6.00	40		20	1476	92		50	-

(5.11 - 6.00 mg/L) is comparable with values obtained for Benin River (4.7±1.0 mg/L), Elechi Creek (4.16 - 6.62 mg/L), Ogunpa/Ona (0.2 - 8.3 mg/L) and Ndokwa rivers (7.2 ± 2.7) mg/L). The average concentration of Pb in study area water $(32.5 \pm 4.7 \ \mu g/L)$ or the range $(23 - 40 \,\mu\text{g/L})$ is comparable with those obtained New Calabar River (12±10 µg/L) and Elechi Creek $(1.00 - 160 \mu g/L)$. It is however lower than those obtained for Ogunpa/ Ona rivers ($<10.0 - 8600 \mu g/L$) and Crooked Creek (310±360 µg/L) The average concentration of Cr in the study area (16.6 \pm 1.8 µg/L) or the range $(14 - 20 \ \mu g/L)$ is comparable with concentrations obtained for New Calabar River (50.0 µg/L) and Ogunpa/Ona (2.0 -19.0 μ g/L). It is lower than value for Niger River (at Patani) (100 µg/L). The average concentration of Fe in study area (191 \pm 150 µg/L) or the range $(119 - 1476 \ \mu g/L)$ is comparable with that obtained for Ndokwa rivers $(640\pm330 \ \mu g/L)$. All other parameters showed this trend i.e most result were comparable while some were higher and others lower in some cases (Table 7)

CONCLUSION

Water samples collected from seven sampling stations on the Udu river (section of Warri river) were analyzed for different physicochemical parameters and six heavy metals. The concentrations of heavy metals are generally higher in the study area than in the control area and these differences are actually significant in cases of Pb, Zn and Fe which indicate that the quality of water of study area is less than those of control area. The quality of water from the area studied is low, the mean concentration of Pb is higher than guideline values for drinking water (WHO, SON and USEPA) and also the mean concentration of some of the physicochemical parameters and heavy metals also exceed guideline values for non-drinking uses of water. The water of the study area can be adjudged to be polluted and require very rigorous treatment before it can be used for drinking. The National Environmental Standards and Regulatory Enforcement Agency (NESREA) (i.e. of Nigeria) should ensure that the relevant National protection regulations in the NESREA Act 2007 : The Effluent Limitation Regulation; Pollution Abatement in Industries and Facilities Generating Waste regulation and Management of solid and Hazardous Waste regulation are strictly enforced especially as it pertains to the steel industry in Nigeria. This will help to reduce the deteriorating tendency of the environment in this area.

REFERENCES

- Adami, G., Cabras, I., Predozani, S., Barbiei, P. and Reisenhofer, E. (2007).
 Metal pollution assessment of surface sediments along a new gas pipeline in the Niger Delta (Nigeria). Environmental Monitoring and Assessment 125 (1 3): 291 299
- Akporido, S.O and Asagba, S.O. (2013). Quality Characteristics of soil close to the Benin River in the vicinity of a lubricating oil producing factory, Koko, Nigeria. *International Journal of Soil Science* 8 (1): 1 – 16.
- Akporido, S.O. and Ifukor, D.I. (2009). Effects of oil prospecting on surface and underground waters in Ndokwa West and Ndokwa East Local Government Areas of Delta State, Nigeria. *Journal of Engineering Science and Technology* 4 (3): 79 87.
- Akporido, S.O., Emuobonuvie, J. and Akporido, C.E. (2000). Study of the quality characteristics of surface and underground water in Sapele and Ogharefe Oil Producing areas of Delta State, Nigeria. Nigerian Journal of Science and Environment 2: 17 22.
- APHA AWWA WEF, (1995). Standard methods for the examination of Water and Wastewater. American Public Health Association – American Water Works Association – Water Environment Federation. New York.
- Asonye, C.C., Okolie, N.P., Okenwa, E.E. and Iwuayanwu, U.G. (2007). Some physical characteristics and heavy metal profiles of Nigerian rivers, streams and water ways. *African Journal of Biotechnology* 6 (5): 617 – 624.
- Bryan, G. W. (1971). The effects of heavy metals (other than mercury) on marine and estuarine organisms. *Proceeding of the Royal Society London B*177: 389-410.

(158)

- Bryan, G.W. and Langston, W.J. 1992. Bioavailability, accumulation and effect of heavy metals in sediments with special references to United Kingdom estuaries review. *Environmental Pollution* 76: 89-137.
- **CCREM (1987).** Canadian Water Quality Guidelines. Canadian Council of Resources and Environment Ministers. Winnipes.
- Courant, R., Powel, B. and Micheal, J. (1987). Water – type classification for Niger Delta. In proceedings of 1985 Seminar on the Petroleum Industry and the Nigerian Environment. The Petroleum inspectorate, NNPC and Environment Planning Division Federal Ministry of Works and Housing, Lagos. 387p.
- Ekpo, B. O., Oyo-Ita, O. E., Oros, D. R. and Simoneil, B. R. T. (2012). Distribution and sources of Polycyclic aromatic hydrocarbons in surface sediments from Cross River Estuary S. E. Niger Delta. Environmental Monitoring and Assessment 184 (2): 1037 – 1047
- **FMEHUD (1991).** Standards for water quality: drinking water. FMEHUD P.M.B. 265 Garki Abuja.
- Forstner, U. and Whittman, G.T.W. (1983). Metals in the aquatic environment. Springer-Verlag Berlin Heidelberg, New York, Tokyo.
- Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP). (1993). Impacts of Oil and related Chemicals and Wastes in the Marine environment. GESAMP Reports and Studies: No 50 International Marine Organization, London.
- Health Canada. (2012) Guidelines for Canadian drinking water quality- summary Table Water, Air and Climate Change Bueau, Healthy environment and Safety Branch, Health Canada; Retrieved 22/08/2013 from: http://www.hcsc.gc.ca/ewh-semt/alt_formats/pdf/pubs/ w a t e r - e a u / 2 0 1 2 - s u m _ g u i d e res recom/2012-sum guide-
- Jennett, J.C. and Foil, S.L. (1979). Trace metal transport from mining, milling and

smelting water shed. *Journal of Water Pollution Control Federation* **51 (2):** 378 – 403.

- Kakulu, S.E. and Osibanjo, O. (1992). Pollution of studies of Nigeria rivers: trace metal levels of surface waters in the Niger Delta area. *International Journal of Environmental studies* 41 (3 & 4): 287 – 292.
- Nduka, J.K. and Orisakwe, O. E. (2011). Water-quality issues in the Niger Delta of Nigeria: A look at heavy metal levels and some physicochemical properties. Environmental Science and Pollution Research 18 (2): 237 – 246
- NRC (1985). Oil in the sea: inputs, fates and effects. National Academy Press, Washington D.C., 607p.
- Obire, O., Tamuno, D.C. and Wemedo, S.A. (2003). Physico-chemical quality of Elechi creek in Port Harcourt. Journal of Applied Science and Environmental Management 7 (1): 43 – 49.
- Onianwa, P.C., Ipeayeda, A. and Emurotu, J.E. (2001). Water quality of the urban rivers and streams of Ibadan Nigeria. *Environmental Education and Information* 20 (2): 107 – 120.
- SON (2007). Nigeria Standard for drinking water quality retrieved 09/08/2008 from http://www.unicef/ng/nigeria-publications-Nigeria.
- USEPA (2012). 2012 edition of drinking water standards and health advisories. Retrieved 22/08/2013 from http:// www.epa.gov/waterscience/
- Van der Leeden, F., Troise, F.L. and Todd, D.K. (1990). The water Encyclopaedia. Second Edition. Lewis Publishers, Chelsea.
- Wegwu, M.O. and Akiniwor, J.O. (2006). Assessment of heavy metal profile of the New Calabar River and its impact on juvenile *Clarias gariepinu*. *Chemistry and Biodiversity* 3 (1): 79 – 87.
- WHO (2011). WHO's drinking water standards 2011. Retrieved 22/08/2013 from http://www.who.int/publications/ guidelines/environmental_health/en/ index.html

(159