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Effect of Steel Production on the Quality of Soil Around Udu Section of Warri River in the Vicinity of a Steel Plant, Nigeria

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ABSTRACT
Street production is a major contributor of heavy metals to the environment. Soil samples were collected from seven sampling stations around Udu River in the vicinity of a steel plant and two sampling stations as control from around Ovwuvwe stream for two years (two dry and two rainy seasons). Heavy metals were determined by flame atomic absorption spectroscopy after digestion with 2M HNO_3 and physicochemical parameters determined by various standard methods. Important results are pH (5.85±0.32), Fe (3110±1500 mg kg^{-1}), Pb (126±40 mg kg^{-1}), Cd (9.2±6.4 mg kg^{-1}), Zn (112±41 mg kg^{-1}), Ni (44±50 mg kg^{-1}) and Cu (18.3±8.2 mg kg^{-1}). The average concentrations of all the metals with the exception of Cu exceeded different soil guideline values with which they were compared. Most sampling stations are polluted with heavy metals, the contamination factor of the heavy metals exceeded unity in most sampling sites. The Pollution Load Index (PLI) of stations A and C are 4.03 for each, respectively, they were ranked as moderately polluted to highly polluted and they are the most polluted sampling stations. It was also observed that sampling stations nearer the steel plant are more polluted than others.

Key words: Heavy metals, physicochemical parameters, steel plant, atomic absorption spectroscopy, pollution load index, Udu River, soil guideline values, contamination factor

INTRODUCTION
Heavy metals generally enter into the environment (e.g., soil water, sediment and biota) through different sources among which are mining and smelting of metals and other metal processes (including steel production and electroplating), Atmospheric fallouts (release from exhaust of motor vehicles and other machines where, there is combustion of fossil fuels), from agricultural (or agronomic) effluents and oil spillages (Forstner and Wittmann, 1983). Steel production industries and associated industries such as coking industries contribute by far the largest proportion of heavy metals to the environment globally (Upadhyay *et al.*, 2006; Yang *et al.*, 2007, 2009, 2012; Hoodaji *et al.*, 2010; Jia *et al.*, 2010; Annicchiarico *et al.*, 2011; Bai *et al.*, 2012; Burniston *et al.*, 2011; Mariet *et al.*, 2011; Wang *et al.*, 2011; Haapala *et al.*, 2012; Zhang *et al.*, 2012; Giri *et al.*, 2013; Qu *et al.*, 2013). The production of steel and steel products consumes materials and energy resources and creates waste and emissions (Haapala *et al.*, 2012).

Quantification of heavy metal in soil, water, sediment and biota has also been taking place in the Niger Delta and Nigeria. Most of such studies have been carried out in oil prospecting and processing area especially in areas where oil spillages have taken place (Ekundayo and Obuekwe, 2000; Osuji and Onojake, 2004; Osuji and Adesiyan, 2005; Nduka and Orisakwe, 2009; Umoren and Udousoro, 2009; Williams and Benson, 2010; Adeniyi and Owoade, 2010; Ossai *et al.*, 2010; Nduka and Orisakwe, 2011). Some studies have, however, been carried out on the effect of effluents from manufacturing industries (Otokunefor and Obiukwu, 2005; Nduka and Orisakwe, 2009; Ipeaiyeda and Onianwa, 2009; Akporido, 2013; Akporido and Ipeaiyeda, 2013; Akporido and Asagba, 2013). Effects of individual heavy metals to man, animals and plants have been well documented (Nriagu and Pacyna, 1988; Langston, 1990; Bryan and Langston, 1992; Forstner and Wittmann, 1983; Sharma and Agrawal, 2005).

The use of pollution indexes for the determination of pollution status of an area has proved useful. These indexes have an averaging nature capable of aggregating all contaminants into one value (Lee *et al.*, 2009). Among the indexes that has commonly been used in literature are the Muller geoaccumulation index (I_{geo}), pollution load index, enrichment factor, integrated pollution index, combined pollution index and ecological risk index (Muller, 1979; Long and Macdonald, 1998; Upadhyay *et al.*, 2006; Zhou *et al.*, 2007; Lee *et al.*, 2009; Giri *et al.*, 2013).

Delta steel company limited was established in the 1980s by the Federal government of Nigeria to boost the industrial sector. The steel plant which is designated to produce steel rods has been in full operation up to the middle of the1990s, when it was privatized. It is still in operation but not operating at full capacity, the adjoining areas are mainly used for crop farming. The arable crops include *Dioscorea* sp. (yam), *Solanum lycoperscium* (tomatoes), *Manihot esculanta* (cassava), *Zea mays* (maize), *Annas comosus* (pineapple), vegetables such as *Telfera occidentalis* (fluted pumpkin). *Magnifera indica* (mango), *Elaeis guineensis* (oilpalm), *Cocus nucifera* (coconut) and *Carica papaya* (pawpaw) are some of the tree fruit crops grown in the area.

As, it has been mention earlier not much attention has been given to other industrial areas in the study of the environment in the Niger delta except for areas in which oil prospecting and processing are taking place. Report on study of the environment containing the steel plant or the effect of production of steel in the area is scanty. The hypothesis of the study is that an area with active production of steel should have elevated concentrations of heavy metals. This can be tested by determining the concentrations of selected common toxic heavy metals.

This study examined the pollution status of the soil by heavy metals by determining the concentrations of of six heavy metals (Cu, Ni, Cd, Pb, Zn, Fe) in soils of area around the steel plant and determining the levels of selected soil physicochemical parameters such as pH, Total Organic Carbon (TOC), Total Organic Matter (TOM), particle size analysis (soil texture: Clay, silt and sand). The pollution status of each of the sampling stations will also be determined using Contamination Factor (CF) and the Pollution Load Index (PLI).

MATERIALS AND METHODS

Description of study area: The Delta Steel Company, Ovwian Aladja is located between the two towns i.e., Ovwian and Aladja. The Udu River (a section of Warri River) separates the areas containing the two towns from Warri main town as shown in Fig. 1 (Map of Study Area). The co-ordinates of the sampling station as taking with the Global (or Geographical) Positioning System

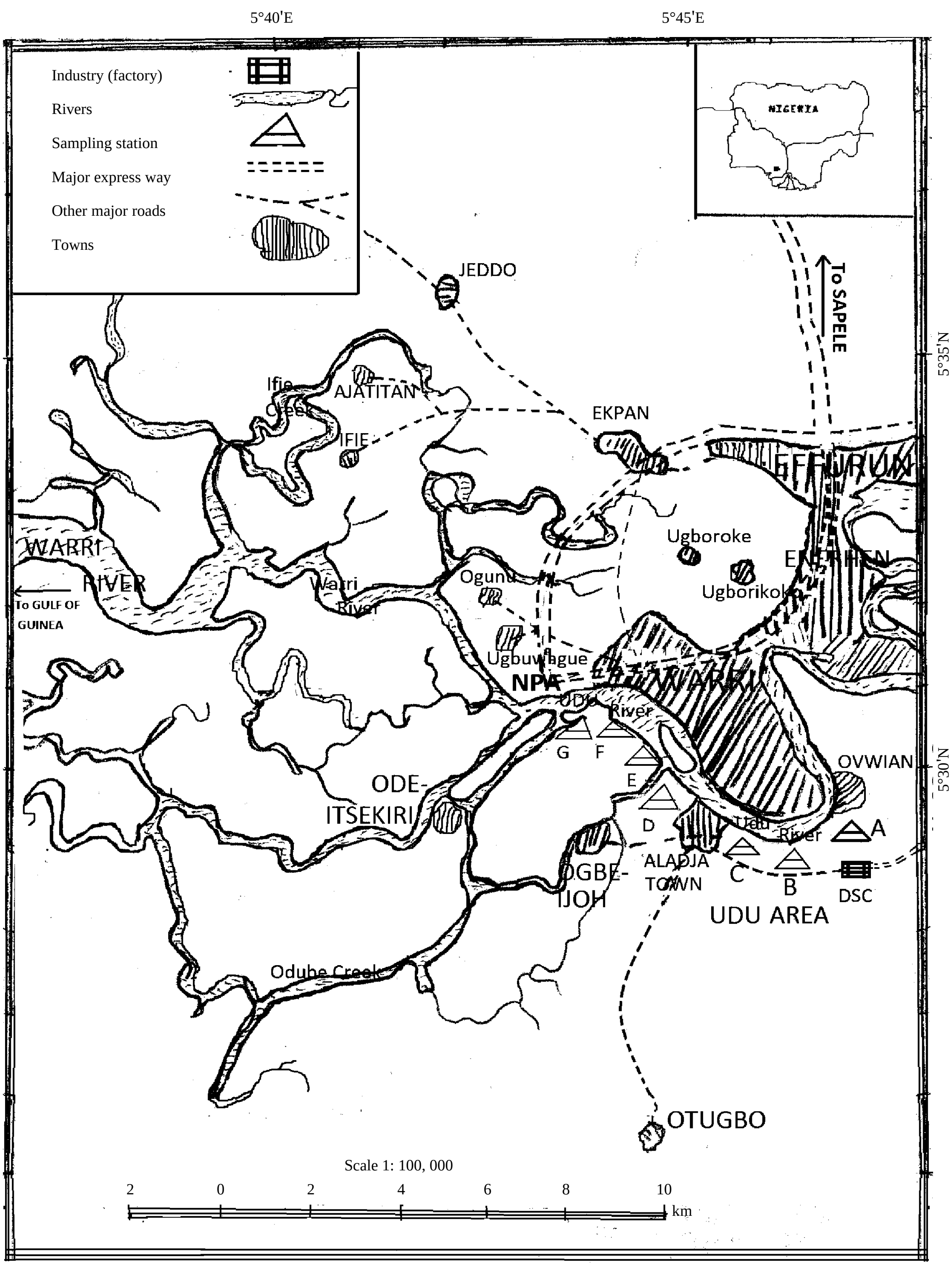

Fig. 1: Map of study area showing a section of Warri River and sampling stations

(GPS) are: Point A (N 05°29.10' and E005°46.65') is point at which effluents from DSC enters into the river from underground conduit. The next sampling stations in successive order are B(N 05°29.30' and E 005°46.00'), C (N 05°29.75' and E 005°45.10'), D (N 05°30.21' and E 005°44.65'), E (N 05°30.65' and E 005°44.20'), F (N 05°30.55' and E 005°43.70') and G (N 05°29.97' and E 005°43.50'). Successive sampling stations are separated from each other by a distance of 1 km. Control samples were taken near the Bank of Ovwuvwe stream about 100 km from the study area a relatively cleaner environment. This is a rural area devoid of industries that can bring about pollution especially pollution from heavy metals. Since, it is a rural area, factors which promotes urbanization are also absent. Two sampling stations were established here.

Design of study/location and preservation of samples: Samples of soil were collected twice every season (i.e., once in each quarter of the year). Samples were collected in dry and rainy seasons for two years (2007-2009). The sampling design consisted of delimiting in every sampling station a sampling area of 70×70 m. This sampling area was then divided into 100 grid plots of 7×7 m area. Thus, thirty three grid plots were randomly selected. From these plots, three replicates of pre-determined quadrates were established and soil samples were taken from each. Samples were manually taken at 0-15 cm (surface) and 15-30 cm (subsurface). Grab samples collected at the surface and subsurface separately from the 33 grid plots were mixed together in well labeled plastic (polyethylene) bags to obtain one surface and subsurface composite samples, respectively. Soil samples were collected 10 m from the bank of the river (Udu River). Samples were transferred to the laboratory in an ice chest. In the laboratory, the samples were air-dried.

Analytical procedures: pH of soil was determined by dipping the electrode of pH-meter in the supernatant solution of a mixture of air-dried soil and distilled water in a ratio 1:1 (Black, 1965). Metals were determined by adding 50 mL of 2 M HNO_3 to 5 g of air-dried soil already sieved through 2 mm capacity sieve in a 100 mL glass beaker. This was placed on a boiling water bath for 2 h stirring at 15 min interval. The digest was filtered and subsequently analyzed using atomic absorption spectrophotometer (Perkin Elmer AA200, Waltham, USA) (Anderson and Morel, 1978; Allen *et al.*, 1989). Total Organic Carbon (TOC) was determined (Walkley and Black, 1934). Total Organic Matter (TOM) was obtained from the TOC value determined by multiplying the value of TOC by a factor 1.724 (Klute, 1986). Particle size analysis was carried out by the hydrometer method as described in manual by Allen *et al.* (1989) to obtain the texture of soil (sand, silt and clay):

$$\text{Contamination Factor (CF)} = \frac{\text{Concentration of heavy metal}}{\text{Background value}}$$

$$\text{Pollution Load Index (PLI)} = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}$$

Quality assurance programme: Blanks and duplicates were determined for every sample as part of quality control. Percentage recoveries were determined for all the metals. The following average percentage recoveries for five determinations of each metal were obtained: Cu (95.1±3.8%), Zn (101±7.7%), Pb (95.6±2.8%), Cd (95.5±1.9%), Ni (92.5±2.2%) and Fe (99.3±6.5%).

Statistical procedures and packages employed: The statistical procedures and packages employed included the following, the comparison of mean of concentrations of each parameters in the four seasons studied and the mean of concentrations in the seven sampling stations was carried out by using analysis of variance (ANOVA-single factor) with Microsoft excel (2007 version) at 0.05 confidence level. The comparison of the mean of the concentration of a parameter in the study area with the mean of the corresponding parameter in the control area was carried out using t-test (two sample, assuming equal variance) with Microsoft excel (2007). The comparison of the mean of a set of values for two areas i.e. study area with control area was carried out using student t-test at 0.05 confidence level. Bivarate correlation of pollutant parameters (heavy metals) in matrix by Pearson (2-tail tailed) correlation was employed from the Statistical Package of the Social Sciences (SPSS, 2002) (version 17) (SPSS, Chicago).

RESULTS AND DISCUSSION

The average concentrations of the pollutant parameters (i.e., the heavy metals) were higher at the first three sampling stations from the point of entry of effluents from the Delta Steel Company (DSC) into the Udu River and/or from the company itself (Table 1). The average concentration of Pb is highest at sampling station A (176±6.6 mg kg^{-1}). Ni has its highest average concentration at sampling station B (132±14 mg kg^{-1}) and its second highest concentration at sampling station A (69±57 mg kg^{-1}). Fe has its highest concentration at point C (5600±470 mg kg^{-1}) and its second highest concentration at sampling station A (4740±720 mg kg^{-1}) (Table 1). The observation that most pollutant parameter had their highest average concentrations in the first three sampling station from the steel production company is in agreement with observation by other workers who had worked on similar environments (steel production areas) (Yang *et al.*, 2009, 2012; Wang *et al.*, 2011; Dheeba and Sampathkumar, 2012). The average concentration of Zn is however, highest at point E (147±12 mg kg^{-1}) and point F (147±9.3 mg kg^{-1}). This may be due to the effect of urbanization. There is much property development around this sampling station in recent times. Urbanization has been observed as a very important factor that increases the

Table 1: Average concentration of soil physicochemical parameters and heavy metals of each sampling station

	Sampling station						
Parameters	A	B	C	D	E	F	G
Physicochemical properties (%)							
pH	5.74±0.10	5.76±0.54	6.20±0.28	5.98±0.18	5.64±0.14	5.79±0.12	5.86±0.34
TOC	0.04±0.01	0.07±0.04	0.15±0.22	0.67±0.48	2.15±0.72	1.05±0.40	0.97±0.12
TOM	0.07±0.02	0.12±0.07	0.45±0.64	1.16±0.82	3.5±1.1	1.80±0.69	1.67±0.21
Sand	73.0±4.3	66.7±1.6	66.4±1.3	56.9±6.0	39±37	68.9±3.0	71.4±1.2
Silt	24.2±3.1	29.9±1.5	26.8±1.6	31.8±3.0	11.1±9.4	19.3±1.5	17.4±1.1
Clay	3.2±1.7	3.4±2.0	6.8±2.2	11.3±5.6	50±47	11.9±3.9	11.2±1.9
Heavy metals (μg g^{-1})							
Cu	21.4±6.6	12.6±5.4	31±11	12.8±3.4	18.4±5.1	15.4±2.3	16.3±1.7
Pb	176±66	114±47	109±34	112±21	115±21	135±8.1	124±8.4
Ni	69±57	132±14	61±34	24±18	2.1±1.6	8.1±2.0	10.3±3.7
Cd	5.3±2.2	7.8±3.4	15.0±8.0	0.38±0.74	12.3±6.1	13.6±4.0	10.0±1.4
Zn	117±7.6	83±16	32±13	122±26	147±12	147±9.3	135±11
Fe	4740±720	2980±470	5600±650	2510±360	2160±570	2020±260	1750±100

Table 2: Comparison of result for the determination of physicochemical and heavy metals on soil of study and control area

Parameter	Study area	Control area
Physicochemical properties (%)		
pH	5.85±0.32	6.49±0.08
TOC	0.73±0.79	0.02±0.03
TOM	1.3±1.3	0.09±0.04
Sand	63±17	89.2±3.9
Silt	22.9±7.9	7.8±2.8
Clay	14±23	1.2±0.91
Heavy metals (μg g^{-1})		
Cu	18.3±8.2	9.4±1.2
Pb	126±40	27±12
Ni	44±50	6.2±3.9
Cd	9.2±6.4	2.3±2.0
Zn	112±41	30±13
Fe	3110±1500	1630±65

Table 3: Concentration of physicochemical characteristics and heavy metals in soil in four seasons

Parameters	First rainy season	First dry season	Second rainy season	Second dry season
Physicochemical properties (%)				
pH	5.82±0.31	5.91±0.29	5.76±0.35	5.91±0.33
TOC	0.81±0.85	0.68±0.76	0.78±0.91	0.63±0.69
TOM	1.3±1.2	1.2±1.3	1.5±1.5	1.1±1.2
Sand	63±19	64±19	63±18	63±16
Silt	23.3±8.9	23.0±8.1	23.0±8.2	22.3±7.2
Clay	13±25	14±24	14±23	15±21
Heavy metals (μg g^{-1})				
Cu	18.1±7.5	15.4±5.2	25±11	15.1±4.7
Pb	131±42	119±36	142±44	113±36
Ni	45±54	40±49	52±57	38±46
Cd	9.3±5.7	7.8±5.1	12.6±8.6	7.0±4.4
Zn	114±39	106±42	126±39	102±43
Fe	3160±1500	2980±1500	3340±1500	2950±1500

concentration of pollutants in the environment (Wang *et al*., 2011; Yang *et al*., 2012). The differences in the concentrations of the pollutant parameters (i.e., the heavy metals) and the pH with the different sampling stations were found to be statistically significant (∞0.05) when the means of the concentrations of each metal in all the sampling station were compared using analysis of variance (ANOVA-single factor).

The concentrations of the heavy metals in the study area were also compared with their corresponding concentrations in the control area (Table 2). The results of these comparison shows that the concentrations of the heavy metals are higher in the study area than those of the control area. The differences in the concentrations of each of the heavy metals of the study area were found to be statistically significantly different from those of the control are when the means of their concentrations were compared using t-test (two sample, assuming equal variances). The concentrations of the heavy metals are generally higher in the rainy seasons (Table 3). These differences in concentrations in the rainy and dry seasons, with exception of those of Cu are not statistically significant, when the means of their concentrations were compared using analysis of variance (ANOVA-single factor). The average concentrations of

Table 4: Comparison of average concentrations of metals in five sampling stations with guideline values for land uses of the Canadian soil quality guideline for the protection of environmental and human health (CCME, 1999)

					Stations						
Parameters	Agricultural	Residential/ parkland	Commercial	Industrial	A	B	C	D	E	F	G
pH	6-8	6-8	6-8	6-8	5.74±0.10	5.76±0.54	6.20±0.28	5.98±0.18	5.64±0.14	5.79±0.12	5.86±0.34
Cu (mg kg^{-1})	63.0	63.0	91.0	91.0	21.4±6.6	12.6±5.4	31±11	12.8±3.4	18.4±5.1	15.4±2.3	16.3±1.7
Pb (mg kg^{-1})	70.0	140	260	600	176±66	114±47	109±34	112±21	115±21	135±8.1	124±8.4
Ni (mg kg^{-1})	159	199	599	599	69±57	132±14	61±34	24±18	2.1±1.6	8.1±2.0	10.3±3.7
Cd (mg kg^{-1})	1.40	10.0	22.0	22.0	5.3±2.2	7.8±3.4	15.0±8.0	0.38±0.74	12.3±6.1	13.6±4.0	10.0±1.4
Zn (mg kg^{-1})	200	200	360	360	117±7.6	83±16	32±13	122±26	147±12	147±9.3	135±11
Fe (mg kg^{-1})	-	-	-	-	4740±720	2980±470	5600±650	2510±360	2160±570	2020±260	1750±100

Cu in the four seasons studied are: First Rainy season (FR) (18.1±7.5 mg kg^{-1}), First Dry season (FD) (15.4±5.2 mg kg^{-1}), Second Rainy season (SR) (25±11 mg kg^{-1}), Second Dry season (SD) (15.1±4.7 mg kg^{-1}).

To be able to assess the pollution effect of each metal, the average concentration of each metal should be compared with soil guideline values for the metal. It is even better to compare these average concentrations with each metal's guideline values for different land uses. Soil Guideline Values (SGV) are 'trigger values' for screening-out low risk area of land contamination. They give an indication of representative average levels of chemicals in soil below which the long-term health risk are likely to be minimal. Exceeding SGV does not mean that remediation is always necessary, although in many cases some further investigation and evaluation of the risk will be carried out (Environment Agency, 2013). A very good soil quality guideline that provides these types of soil guideline values is the Canadian Soil Quality Guideline (SQGs) for the protection of the environment and human health by the Canadian council of ministers of the environment (Table 4) (CCME, 1999). The average levels of each metal and pH in each of the sampling stations were compared with guideline values for four different land uses (agricultural, residential/parkland, commercial and industrial land uses). The average pH of all the sampling stations with the exception of that for station C (6.20±0.28) fell below the acceptable pH range (6-8) for all the land uses (Table 4). This means that the acidity of the soils of this sampling stations are higher than acceptable levels. Such high acidity may increase the mobility of metal ions thus making them much more available for uptake by roots of plants. The average concentrations of Pb of all the sampling stations exceeded the guideline value for agricultural land use (70.0 mg kg^{-1}). The average Pb value for station A (176±66 mg kg^{-1}) also exceeded the residential/parkland guideline value (140 mg kg^{-1}).

The average Cd concentrations of all the sampling stations with the exception of that of station D (0.38±0.74 mg kg^{-1}) exceeded the agricultural land use guideline value of Cd (1.40 mg kg^{-1}). The average concentrations of Cd of station C (15.0±8.0 mg kg^{-1}), station E (12.3±6.1 mg kg^{-1}), station F (13.6±4.0 mg kg^{-1}) and station G (10.0±1.4 mg kg^{-1}) also exceeded guideline value of Cd for residential/parkland land use (10.0 mg kg^{-1}). Based on all these observations, Pb and Cd are serious pollutants in the study area. The average concentrations of the heavy metals were also compared with guidelines values for other countries (Norway, Netherland, Switzerland and Japan), the Shell Development Company Limited (SPDC Ltd) guideline for Environmental Impact Assessment (EIA) processes (SPDC, 2004) and Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) (DPR, 2002) (Table 5). The results of the comparisons showed that the average

Table 5: Comparison of results with six other soil quality guidelines

	Heavy metals (mg kg^{-1})						
Guidelines	Cu	Pb	Ni	Cd	Zn	Fe	References
Norway	100	50.0	30.0	10.0	150	NS	Reimann *et al*. (1997)
Netherland (action level)	190	530	210	12.0	720	NS	Reimann *et al*. (1997)
Netherland (further investigation)	110	310	120	6.0	200	NS	Reimann *et al*. (1997)
Guideline for SPDC EIA Process (acceptable ranges)	5.00-50.0	5.00-50.0	5.00-50.0	0.70-3.00	10.0-120	100	SPDC (2004)
Switzerland (guide values)	50.0	50.0	-	0.80	200	NS	FOEFL (1987)
EQSSP (Japan land)	125 (Agric land)	NS	NS	1.00	NS	NS	EAGJ (1994)
EGASPIN target values	36.0	85.0	35.0	0.80	140	NS	DPR (2002)
EGASPIN intervention values	190	530	210	12.0	720	NS	DPR (2002)
Sampling stations							
A	21.4±6.6	176±66	69±57	5.3±2.2	117±7.6	4740±720	Present study
B	12.6±5.4	114±47	132±14	7.8±3.4	83±16	2980±470	Present study
C	31±11	109±34	61±34	15.0±8.0	32±13	5600±650	Present study
D	12.8±3.4	112±21	24±18	0.38±0.74	122±26	2510±360	Present study
E	18.4±5.1	115±21	2.1±1.6	12.3±6.1	147±12	2160±570	Present study
F	15.4±2.3	135±8.1	8.1±2.0	13.6±4.0	147±9.3	2020±260	Present study
G	16.3±1.7	124±8.4	10.3±3.7	10.0±1.4	135±11	1750±100	Present study

EAG: Environment agency of government, NS: Not specified, EQSSP: Environmental quality standards for soil pollutionm EGASPIN: Environmental guidelines and standards for the petroleum industry in Nigeria

concentration of Pb in all the sampling stations exceeded the Norway guideline value for Pb (50.0 mg kg^{-1}), SPDC Ltd. EIA process guideline range (5.00-50.0 mg kg^{-1}) and the target value of EGASPIN (85.0 mg kg^{-1}). The average concentration of Ni for station A(69±57 mg kg^{-1}) and station B (132±14 mg kg^{-1}) exceeded the Norway guideline value for Ni (30.0 mg kg^{-1}), the SPDC Ltd. EIA process guideline value (5.00-50.0 mg kg^{-1}) and EGASPIN target value (35.0 mg kg^{-1}).

The average concentrations of Cd of all the sampling stations with the exception of that of station D (90.38±0.74 mg kg^{-1}) exceeded the guideline value of Cd of Netherland (further investigation) (6.00 mg kg^{-1}), SPDC Ltd. EIA process guideline range (0.70-3.00 mg kg^{-1}), Environmental Quality Standards for Soil Pollution (EQSSP) of the Environment Agency of Government of Japan (EAGJ, 1994) (1.00 mg kg^{-1}) and the target value of EGASPIN (0.80 mg kg^{-1}). In addition to this, the average concentrations of Cd in station C (15.0±8.0 mg kg^{-1}), station E (12.3±6.1 mg kg^{-1}) and station F (13.6±4.0 mg kg^{-1}) exceeded the Norway guideline value (10.0 mg kg^{-1}), Netherland (action level) (12.0 mg kg^{-1}) and the intervention value of EGASPIN (12.0 mg kg^{-1}). These latter sampling stations are seriously polluted with Cd. This inference can be made because the average value of in each of these sampling station even exceeded the intervention value of EGASPIN (12.0 mg kg^{-1}) (DPR, 2002). Concentrations of pollutants in excess of their intervention values in EGASPIN correspond to serious contamination with respect to such pollutants, this is because the intervention values of EGASPIN indicate the quality for which the functionality of soil for human, animal and plant life are or threatened with being seriously impaired. The average concentration of Zn in four of the sampling stations, station D (122±26 mg kg^{-1}), station E (147±12 mg kg^{-1}), station F (147±9.3 mg kg^{-1}) and

Table 6: Pearson (2-tailed) correlation of heavy metals in soil of study area

Heavy metals	Cu	Pb	Ni	Cd	Zn	Fe
Cu						
Pb	-0.090					
Ni	0.065	0.048				
Cd	-0.172	0.053	-0.240*			
Zn	-0.672**	0.209	-0.354**	-0.116		
Fe	0.715**	0.375**	0.402**	-0.034	-0.632**	

**Correlation coefficient significant (∞ = 0.01) *Correlation coefficient significant (∞ = 0.05)

station G (135±11 mg kg^{-1}) exceeded the SPDC Ltd. EIA processes guideline range for Zn (10.0-120 mg kg^{-1}). In addition to this the average concentrations of Zn in two sampling stations i.e., station E (147±12 mg kg^{-1}) and station F (147±9.3 mg kg^{-1}) also exceeded the EGASPIN target value for Zn (140 mg kg^{-1}).

The average concentrations of Fe in all the sampling stations very much exceeded the acceptable maximum value of iron as a nutrient in the soil by SPDC Ltd. EIA process guideline (100 mg kg^{-1}). The average concentrations of Fe in all the sampling stations are as much as seventeen times as high as this maximum guideline value of Fe (100 mg kg^{-1}). From the foregoing discussion, Cd, Pb and Fe are very serious pollutants in this study area. Ni and Zn are also serious pollutants in this study area but of lesser importance compared to the above three (i.e., Cd, Pb and Fe).

A pearson (2-tail) correlation of heavy metals in soil of the study area (Table 6) revealed that three of the heavy metals positively correlated strongly with Fe. They are Cu and Fe (0.715), Pb and Fe (0.375) and Ni and Fe (0.402). Their correlation coefficients are significant at 0.01 confidence level. This shows that the four metals (Fe, Cu, Pb and Ni) may have the same source. The source may be the steel production company (i.e., DSC). Zn did not correlate with Fe positively, this must be as already observed that the high average concentration of Zn may be as a result of intense urbanization taking place in this this portion of the study area. Construction of buildings most of the time involve the use of zinc galvanized roofing sheets. Similar explanation cannot, however, be given for the non-positive significant correlation of Cd with Fe. Cd did not also correlate strongly with Zn. It has been observed that Cd is a serious pollutant in most of the sampling stations.

The contamination factor of each of the heavy metals for each of the sites in each of the seasons studied is given in Table 7 (each of the surface and subsurface depths are taken to be sampling sites for this purpose). The contamination factors of Fe for all the sites are very high, 39.3 for site E surface in second dry season to 163 for site C subsurface in the second rainy season. Pb also has high contamination factors in all the sites, from 2.75 in site B surface in the second dry season to 13.6 in site A subsurface in the second raining season. The contamination factors of Cd were also high in some of the sites. They range from 0.002 in site D surface in the first rainy season to 3.10 in site C in the second rainy season. Ni has contamination factors which range from 0.01 each in site E surface and site E subsurface all in the first rainy season to 4.08 in site B surface in the second rainy season. Zn has contamination factors that are high in the last four sampling stations, they range from 0.03 each in site C surface in the first dry season and site C subsurface in the second dry season to 2.29 in site D (second rainy season). Cu appears to have the least polluting effect in the study area. Cu's contamination factors ranged from 0.30 in site B subsurface (second dry season) to 2.60 in site C surface (second rainy season).

Table 7: Contamination factors for each site in each of the seasons (each depth is also used as a site)

	Heavy metals (mg kg^{-1})																							
	Fe (40)				Cu (20)				Zn (70)				Pb (20)				Cd (10)				Ni (38)			
	FR	FD	SR	SD	FR	FD	SR	SD	FR	FD	SR	SD	FR	FD	SR	SD	FR	FD	SR	SD	FR	FD	SR	SD
Sites	(Seasons)																							
Site A surf	105.0	96.8	112.0	97.5	1.25	0.95	1.60	0.85	1.67	1.56	1.83	1.61	6.00	5.80	6.15	5.60	0.40	0.30	0.30	0.50	3.55	3.08	3.50	3.00
Site A subsurf	137.0	128.0	143.0	130.0	1.10	0.75	1.40	0.65	1.71	1.59	1.83	1.59	12.60	10.50	13.60	10.20	0.70	0.30	0.90	0.40	0.47	0.32	0.61	0.24
Site B surf	85.3	80.8	91.0	78.5	0.85	0.65	1.10	0.75	1.20	0.93	1.30	0.81	4.20	3.15	4.35	2.75	0.70	0.40	0.80	0.30	3.45	3.16	3.71	3.05
SiteB subsurf	68.5	61.8	73.8	57.0	0.45	0.35	0.60	0.30	1.37	1.21	1.49	1.21	8.45	7.25	8.75	6.65	1.00	0.80	1.40	0.80	3.74	3.37	4.08	3.13
Site C surf	126.0	125.0	128.0	122.0	1.85	1.35	2.60	1.02	0.43	0.30	0.61	0.27	4.35	3.55	4.95	3.15	1.10	0.80	1.60	0.60	0.87	0.71	1.18	0.52
Site C subsurf	156.0	151.0	163.0	150.0	1.40	1.10	2.00	1.00	0.57	0.41	0.79	0.30	7.10	6.60	7.75	6.20	2.10	1.50	3.10	1.20	2.53	2.21	2.89	1.87
Site D surf	66.5	55.8	71.0	57.5	0.70	0.50	0.90	0.55	1.57	1.34	1.74	1.24	5.20	4.45	5.65	3.95	0.002	0.01	0.02	0.10	0.26	0.21	0.37	0.18
Site D subsurf	71.8	54.0	74.0	51.8	0.65	0.50	0.85	0.45	2.20	1.81	2.29	1.71	6.90	5.95	7.00	5.8	0.003	0.01	0.20	0.02	1.18	0.79	1.39	0.74
Site E surf	40.3	39.0	45.3	39.3	0.95	1.00	1.35	1.05	1.97	1.92	2.14	1.83	4.75	4.55	5.70	4.30	0.78	0.75	0.80	0.60	0.01	0.05	0.08	0.11
Site E subsurf	62.8	68.8	66.8	70.0	0.60	0.65	1.05	0.70	2.07	2.21	2.31	2.27	6.35	6.60	7.05	6.55	1.40	1.50	2.40	1.60	0.01	0.05	0.05	0.11
Site F surf	46.3	43.5	47.5	42.8	0.70	0.70	0.95	0.65	2.11	1.97	2.36	1.99	6.60	6.65	7.40	6.25	1.40	1.20	2.00	0.90	0.18	0.24	0.29	0.26
Site F subsurf	55.3	54.3	60.5	54.0	0.75	0.70	0.95	0.75	2.04	2.09	2.21	2.00	6.85	6.55	7.30	6.45	1.30	1.20	1.90	1.00	0.13	0.16	0.21	0.24
Site G surf	43.0	41.8	46.8	42.8	0.75	0.75	0.95	0.80	1.99	2.01	2.14	1.90	6.40	6.05	6.95	5.90	1.20	0.90	1.00	0.80	0.16	0.13	0.26	0.21
Site G subsurf	45.5	42.3	47.8	40.3	0.70	0.80	0.90	0.85	1.89	1.77	2.10	1.67	6.20	5.95	6.60	5.65	1.00	1.20	0.90	1.00	0.37	0.34	0.39	0.29

Table 8: Pollution load index of each sampling station and inference of pollution status of sampling station

Sampling stations	Pollution Load Index (PLI)	Inferred pollution status
A	4.03	Moderately polluted to highly polluted
B	3.89	Moderately polluted
C	4.03	Moderately polluted to highly polluted
D	1.19	Low pollution
E	1.71	Low pollution
F	3.28	Moderately polluted
G	3.16	Moderately polluted

Two sampling stations had the highest values of Pollution Load Index (PLI). They are station A with a PLI of 4.03 and station C also with a PLI of 4.03, these two stations were ranked to be moderately polluted to highly polluted (Table 8). This is not surprising because the contamination factors of most of the metals are high in these two sampling stations. These two stations are followed by station B with a PLI of 3.89 which is rated to be moderately polluted. Stations F and G had PLI of 3.28 and 3.16, respectively and both have been rate as being moderately polluted (Table 8). It can be seen that the PLI also has an averaging nature capable of aggregating all contaminants into one value. Site A and C are thus, the most polluted of all the sampling stations. This is also in line with the earlier observation that sampling stations near to the point of effluent discharge or near to the factory are more polluted with the heavy metals.

A comparison of the results obtained in this study with results obtained elsewhere in similar studies revealed that most results were comparable with results obtained elsewhere, some results were however, either higher or lower. The average value of pH of the study area, 5.85±0.32 (5.2-6.4) is comparable with results obtained for soils around Benin River lubricating oil factory (5.86±0.32). The average concentration of Pb, 126±40 mg kg^{-1} (55-271 mg kg^{-1}) is comparable with results obtained for soils around Benin river lubricating oil producing factory (227±160 mg kg^{-1}) (Akporido and Asagba, 2013), Niger Delta oil prospecting area (3.40-99.4 mg kg^{-1}) (Asia *et al*., 2007) and Effurun auto-mechanic village soil (68.4±9.9 mg kg^{-1}) (Akporido and Imah, 2009). It is much higher than results for Urashi river oil spillage affected soil (0.32-0.80 mg kg^{-1}) (Osuji and Onojake, 2004) and Tamil Nadu steel production area soil (8.00 mg kg^{-1}) (Dheeba and Sampathkumar, 2012). The value of lead is however much lower than the range of value obtained Arkansas River mining drainage affected soil (44-4900 mg kg^{-1}). The average concentration of Cd in study area, 9.2±6.4 mg kg^{-1} (ND-31 mg kg^{-1}) is comparable with results obtained for Benin River lubricating oil factory soil (2.0±2.9 mg kg^{-1}) (Akporido and Asagba, 2013) and Effurun auto-mechanic village soils (35±10 mg kg^{-1}) (Akporido and Imah, 2009). It is higher than results obtained for Urashi river oil spillage affected soils (<0.20 mg kg^{-1}) (Osuji and Onojake, 2004) and Niger Delta oil prospecting area (0.04-0.95 mg kg^{-1}) (Asia *et al*., 2007). It is however, lower than values obtained for Arkansas River mining drainage affected soils (3.00-110 mg kg^{-1}) and Guadalquiver River parkland area (230-340 mg kg^{-1}). The average concentration of Fe of study area, 3110±1500 mg kg^{-1} (1560-6500 mg kg^{-1}) is higher than value obtained for Tamil Nadu steel production area (44.9 mg kg^{-1}) (Dheeba and Sampathkumar, 2012). Results for the remaining heavy metals showed similar pattern when compared with similar studies elsewhere (Table 9).

Table 9: Comparison soil metal levels around the Udu river (part of Warri river) with those from studies elsewhere

River/location	Country	Major activities in the area	pH	Metal level (mg kg^{-1}) Cu	Pb	Ni	Cd	Zn	Fe	References
Urashi river (Obiobi/Obrikom)	Nigeria	Oil spillage Area (Surface)		0.15-0.30	0.32-0.80	0.53-18.0	<0.20	-	-	Osuji and Onojake (2004)
Niger delta area	Nigeria	Oil prospecting area		5.10-49.3	3.40-99.4	1.60-13.6	0.04-0.95	11.1-274	-	Asia *et al*. (2007)
Benin river (Koko)	Nigeria	Lubricating oil manufacture	5.86±0.32	-	227±160	0.07±0.22	2.0±2.9	562±510	-	Akporido and Asagba (2013)
ESC area	Iran	Steel production		9.20	-	-	-	10.0	-	Hoodaji *et al*. (2010)
Effurun	Nigeria	Auto-mechanic village area		102 ± 18	68.4 ± 9.9	121 ± 51	35 ± 10	-	-	Akporido and Imah (2009)
Arkansas river Leadville colorado	USA	Mining Drainage affected area		14-1200	44-4900	-	3-110	44-12000	-	Levy *et al*. (1992)
Tamil Nadu	India	Steel production/ Industrial area		1.87	8.00	-	-	12.0	44.91	Dheeba and Sampathkumar (2012)
Guadalquiver river (marshes)	Spain	Parkland	-	-	-	-	230 - 340	3150 - 126000	-	Ramos *et al*. (1994)
Udu river (DSC area)	Nigeria	Steel Manufacturing	5.85±0.32 (5.2-6.4)	18.3±8.2 (6.00-52.0)	126±40 (55 -271)	44±50 (ND-155)	9.2±6.4 (ND-31)	112±41 (19-165)	3110±1500 (1560-6500)	Present study

ESC: Esfahan steel company, DSC: Delta steel company

CONCLUSION

This study determined selected physicochemical parameters and selected heavy metals in soil around a steel manufacturing company by the Udu section of Warri River. The average concentrations of Fe, Pb, Cd, Ni and Zn were found to be high in most of the sampling stations and these average concentrations exceeded guideline value in most cases. The Pollution Load Index (PLI) of sampling stations A and C are the highest. Station A and C each has a PLI of 4.03 each, respectively. They have been rated as having pollution status of "moderately polluted to highly polluted". Station B is next to these two and has PLI of 3.89 and rated to have pollution status of "moderately polluted". The study has also shown that the pollution observed in most sampling stations soil may have its source in the steel plant located in the area. This is so, because some of the metals correlated very strongly with Fe. Sampling stations near to the steel plant or point of discharge effluent are most polluted with metals which correlated positively significantly with iron. These heavy metals may have entered the soil from effluent from the steel plant which entered into the river and got to the banks of the river by overflow of water from the river. This water is further carried inland by storm water runoff. Metals from the plant may also have entered the soils of the study area through atmospheric emission from the steel plant aided by atmospheric wash down during the rainy periods. Environmental authorities in Nigeria should ensure that effluents of industries are properly treated and that atmospheric emissions from industrial plant are reduced to minimum.

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