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## Heavy Metals and Total Petroleum Hydrocarbon Concentrations in Surface Water of Esi River, Western Niger Delta

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### ABSTRACT

Water samples from Esi river were analyzed for hydrocarbons and heavy metals to assess the impact of petroleum prospecting activities on the environment of the Western Niger Delta. Important results obtain are for O and G ( $11600 \pm 8600 \mu\text{g L}^{-1}$ ), TPH ( $4270 \pm 3000 \mu\text{g L}^{-1}$ ), Pb ( $39 \pm 33 \mu\text{g L}^{-1}$ ), Cd ( $2.4 \pm 3.1 \mu\text{g L}^{-1}$ ), Cr ( $42 \pm 17 \mu\text{g L}^{-1}$ ), Cu ( $16.1 \pm 7.4 \mu\text{g L}^{-1}$ ) and Zn ( $107 \pm 7.9 \mu\text{g L}^{-1}$ ), showing high concentrations of O and G and TPH. The nickel-vanadium ratio of 1.71 revealed that the measured oil residue had its source from oil drilled in the area. The concentration of Pb was also high relative to Nigerian and International guideline values for drinking water. The water is polluted and not fit for drinking.

**Key words:** Heavy metals, drinking water, Esi river, Ethiope river, oil and grease, total petroleum hydrocarbons

### INTRODUCTION

Heavy metal and petroleum hydrocarbon contamination often results from petroleum prospecting and processing activities (Forstner and Wittman, 1983; NRC., 1985; GESAMP., 1993; NRC., 2003). The degree of contamination may be significant where frequent spillages occur. The Niger Delta region of Nigeria is one of such areas (Hinrichson, 1990). The UNDP (2006) report indicates that between 1976 and 2001, about 7000 spill were recorded in the area which accounted for a loss of about three million barrels of oil, 70% of which were not recovered. Such spillages may lead to damage and loss of biodiversity, depletion of arable land, depletion of available potable water and blockage of waterways. In such circumstances, the concentrations of petroleum hydrocarbons and trace metals in water bodies are often observed to be elevated (NRC., 2003; UNDP., 2006; Luiselli *et al.*, 2004, 2006; Udoh and Akpan, 2010; Perez-Casanova *et al.*, 2010; Omo-Irabor *et al.*, 2011; Almeida *et al.*, 2013; Sung *et al.*, 2013). Oil spillages in their early stages also have direct adverse effects on human health (Lee *et al.*, 2009; Gwack *et al.*, 2012). The biodegradation of petroleum hydrocarbons is often made difficult and slow due to the presence of heavy metals, heavy metals show toxicity toward most species of biodegrading microorganisms (Almeida *et al.*, 2013; Kalita *et al.*, 2009; Plaza *et al.*, 2010; Nie *et al.*, 2010). Recovery of environments spilled with oil are even more difficult with mangrove forests, it takes up to three decade for a mangrove forest to recover (Ballou and Lewis III, 1989; Ballou *et al.*, 1989; UNEP., 2011). A number of studies in the Niger Delta area have focussed on the assessment of levels of petroleum residues (oil and grease, total petroleum hydrocarbon and polycyclic aromatic

Table 1: Incidents of oil Spills above 50 barrels up to December 1999 in the Esi river area (SPDC, 2001)

Date	Location	Volume of oil spilled bbL	Volume of oil recovered during clean-up bbL	SPDC official stated cause of spill	Class	Status of cleaning as at December 1999
1/6/93	Kokori flow station	60	0	Corrosion leak of L/P header	Corrosion	-
5/26/97	Eriemu well 13S	410	400	Master valves and survey valves opened by unknown person	Sabotage	-
7/25/84	Utorogu/UQCC delivery line	500	400	Corrosion leak of 16' utorogu delivery line within loc 16	Corrosion	-
8/3/99	Kokori 26/28/29 actual well yet to be determine	65	0	Bubbling of crude oil in a swamp location near wells 26/29/29	Sabotage/theft	Ongoing
9/11/83	Afiesere flare site	625	400	Carry over to the flare delivery closure/reopening	Production operations	Completed 11/10/98
10/4/98	Utorogu flow station	143	136	During routine cleaning of the flow-station saver pit on 04/10/98, crude oil was pumped and channeled to the 3" bund wall flush pipe to flare and un knowingly 68 m of the flush Pipe had been cut by unknown person(s)	Sabotage/theft	
11/3/96	Eriemu-UQCC trunk line	350	341	16" Eriemu-UQCC Delivery Line was cut by unknown person	Sabotage/theft	Ongoing
9/7/99	24" UQCC Rapele at Ekakpamre	200	103	Pipeline blown up with an explosive by unknown person(s)	Sabotage/theft	

UQCC: Ughelli quality control centre

hydrocarbons) and trace heavy metals in aquatic environments where oil spillages have occurred. Results have generally shown the concentrations to be elevated beyond background levels (Ibiebele, 1986; Ekundayo and Obuekwe, 2000; Anyakora *et al.*, 2005; Ayotamuno *et al.*, 2002; Osuji and Adesiyani, 2005; Olajire *et al.*, 2005; Davies *et al.*, 2006; Nduka and Orisakwe, 2009; Umoren and Udousoro, 2009; Sojinu *et al.*, 2010; Williams and Benson, 2010; Adeniyi and Owoade, 2010; Ossai *et al.*, 2010; Anyakora *et al.*, 2011; Nduka and Orisakwe, 2011; Akporido, 2013; Akporido and Asagba, 2013).

The Esi river is one river system in the western Niger Delta region which has been impacted by oil spillages and for which only scanty baseline environmental data is available. The river's drainage area includes the locations of several oilfields and other industries (Fig. 1). Esi river serves local residents for drinking, fishing, recreation and transportation.

Several major and minor oil spillages have occurred around Esi river (Table 1). Over 2890 bbl was spilled in the area around Esi river between 1983 and 1999 (SPDC., 2001). Yet, literature data on the degree of oil pollution in the area is severely limited.

The present study investigated the extent to which the Esi River and its adjoining areas have been impacted with crude oil spillages. The level of petroleum residue and heavy metals (copper, lead, nickel, cadmium, zinc, vanadium and chromium) in the river water was recently determined.

## MATERIALS AND METHODS

The Esi River has its source about 130 km northeast of the study area where several oil fields adjoin its drainage area (Fig. 1). Water sampling stations were governed by factors such as

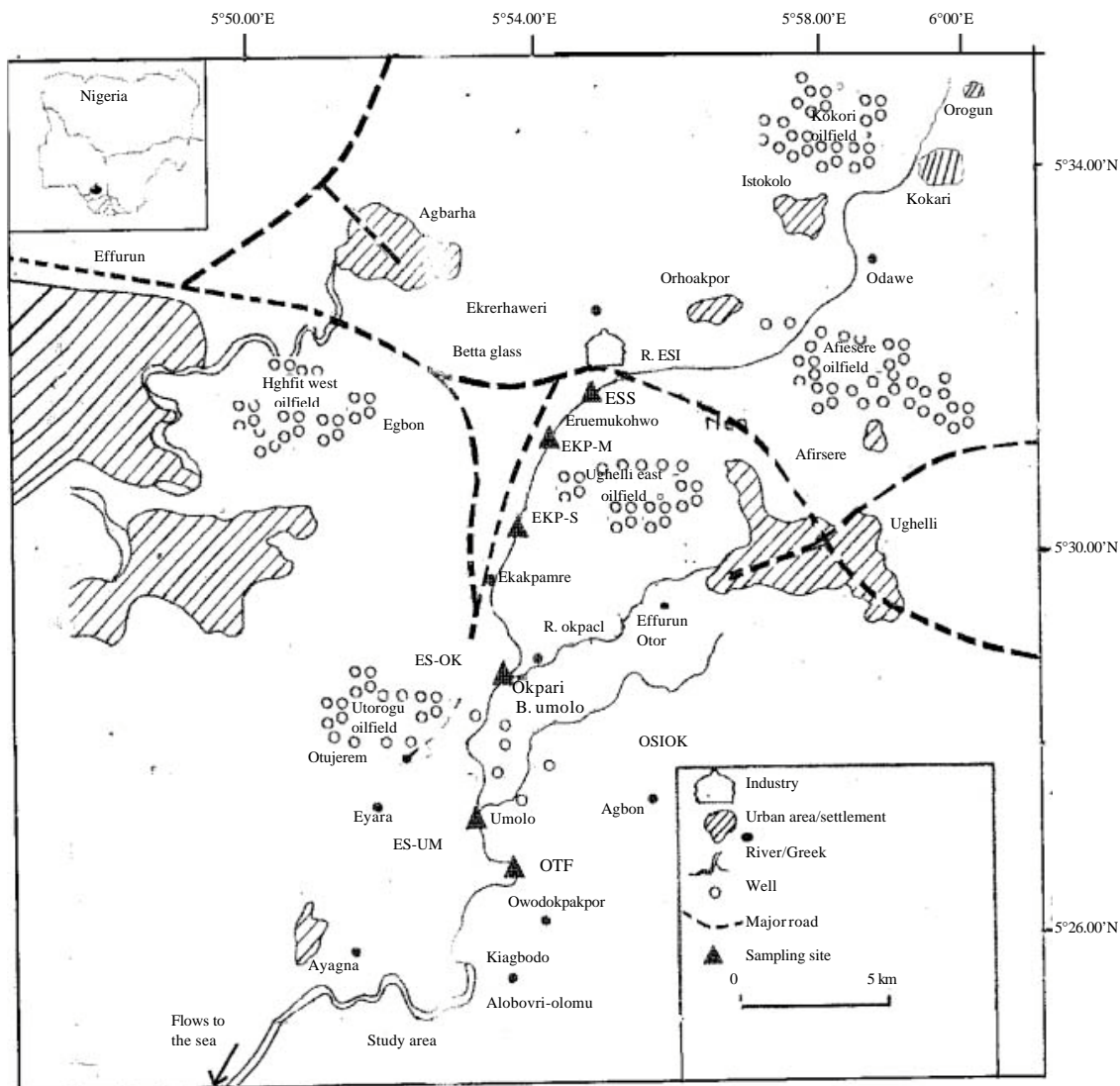


Fig. 1: Map of study area

recent incidents of spillages and confluences with other streams and rivers. Samples were collected quarterly during January 2002 to September 2003. Surface and at mid-depth, major sampling sites were: Ekakpamre Spill Site (ESS) (N 05°31.781' and E 005°54.871'), Ekakpamre middle town (Ekp-M) (N 05°31.175' and E 005°54.638'), Ekakpamre south Town (i.e., south of the town) (Ekp-S) (N 05°30.285' and E 005°53.407'), Esi and Okparsi rivers confluence (ES-OK) (N 05°28.629' and E 005°53.571'), Umolo stream and Esi river confluence (ES-UM) (N 05°27.143' and E 005°53.184') and Otujeremi Front (OTF) (N 05°26.734' and E 005°53.345'). Two control area sampling stations (BRB-N 05°49.451' and E 006°06.504'; AMB-N 05°48.038' and E 006°06.059') were located on a relatively cleaner river about 100 km away.

Samples for Oil and Grease (O and G) and Total Petroleum Hydrocarbons (TPH) determinations were collected with wide mouth glass bottles. Water samples for heavy metals determination were collected with plastic water bottles which have been washed with detergent, soaked in concentrated HNO<sub>3</sub> overnight and rinsed with distilled water. Samples for O and G and TPH determinations were preserved by adding concentrated HCl to pH<2 and water samples were analyzed within 28 days for heavy metal analysis by adding concentrated nitric acid to pH<2 (Anonymous, 1995).

O and G was determined by the Soxhlet extraction procedure. TPH was obtained from the O and G extract by re-dissolving in hexane and adding 4g of activated silica gel. This mixture was stirred with a magnetic stirrer for five min. Silica gel was filtered out and TPH obtained by distilling off the hexane and drying the residue to constant weight (Anonymous, 1995). Heavy metals (Cu, Pb, Cd, Zn, V, Cr and Ni) were determined by adding 5 mL concentrated nitric acid into 500 mL of water sample in a beaker. This was pre-concentrated and digested to near dryness. The residue was dissolved with a little distilled water and made up to the mark in a 50 mL volumetric flask. Metals were determined in the digest using flame atomic absorption spectrophotometer (Perkin Elmer AA 200, Waltham, USA). Sample and reagent blanks were analyzed for each batch of twenty samples. In addition to these, recovery studies were carried out.

## RESULTS AND DISCUSSION

Average of O and G levels were 116000±8600 µg L<sup>-1</sup> (ND-32600 µg L<sup>-1</sup>), while TPH levels averaged 4270±3000 µg L<sup>-1</sup> (ND-14900 µg L<sup>-1</sup>) (Table 2). Corresponding levels in control site samples were 1070±910 µg L<sup>-1</sup> for TOE and 506±610 µg L<sup>-1</sup> for TPH, respectively. These results are indicative of oil contamination in the study areas of the Esi river. Hydrocarbon levels around Ekakpamre Spill site which is located furthest upstream were lowest (2510±240 µg L<sup>-1</sup>) and the levels increased significantly beyond this point (to about 5000 µg L<sup>-1</sup>) (Table 3) due to further inputs from oily effluents/runoffs from oil wells at downstream points.

The levels of O and G and TPH are marginally higher at the surface than mid-depth (Table 4) but these differences are not significant. This may be as a result of turbulence which result in mixing during the prolong rainy periods. Seasonal variations in O and G and TPH level (Table 5) were found not to be statistically significant.

Table 2: Average concentrations of heavy metals, oil and grease and total petroleum hydrocarbons in study area and control area samples

	Concentrations (µg L <sup>-1</sup> )	
	Study area	Control area
Oil and grease	11600±8600	1070±910
Total petroleum hydrocarbons	4270±3000	506±610
Copper	16.1±7.4	22±25
Lead	39±33	19±18
Nickel	12±15	8.31±12
Cadmium	2.4±3.1	4.2±5.3
Zinc	107±220	204±280
Vanadium	7.0±7.9	6.3±1.3
Chromium	42±17	13±15

Table 3: Average concentrations of heavy metals oil and grease and total petroleum hydrocarbons at each of the sampling stations

Parameters	Concentrations ( $\mu\text{g L}^{-1}$ )					
	ESS	Ekp-M	Ekp-S	ES-OK	ES-UM	OTF
Oil and grease	7970±910	12600±700	14500±9100	17300±1200	7340±5800	11100±590
TPH	2510±240	5350±2900	4950±3000	4950±300	2880±2300	5630±410
Copper	13.6±8.1	19±11	10.4±1.8	17.8±7.4	17.2±6.1	15.8±4.5
Lead	17±12	42±54	47±56	51±22	51±22	30±13
Nickel	7.1±3.9	15±12	30±47	10.8±7.4	6.8±4.5	10.1±3.8
Cadmium	1.9±1.4	4.1±4.2	3.0±4.7	2.4±3.0	0.8±1.2	2.4±3.5
Zinc	27±41	21±17	22.8±32	167±240	185±330	178±310
Vanadium	7.0±11	15.0±8.4	6.3±2.4	9.9±6.7	3.9±5.7	6.3±4.8
Chromium	40.9±4.2	39±10	37±12	30±20	38.0±7.4	63±20

Table 4: Concentrations of heavy metals, O and G and TPH at half depth and at surface of Esi river

Heavy metals	Concentration ( $\mu\text{g L}^{-1}$ )	
	Mid-depth	Surface
Oil and grease	11400±8100	11800±9100
Total hydrocarbon	4300±2600	4230±2500
Copper	14.3±5.5	18.2±8.7
Lead	35±28	43±37
Nickel	12±19	10.6±7.7
Cadmium	2.0±2.9	2.7±3.3
Zinc	105±24	104±200
Vanadium	7.4±7.2	7.9±8.7
Chromium	41±20	42±14

Table 5: Seasonal concentrations of heavy metals, oil and grease and total petroleum hydrocarbons in surface water

Heavy metal	Concentrations ( $\mu\text{g L}^{-1}$ )			
	1st dry season	1st rainy season	2nd dry season	2nd rainy season
Oil and grease	18300±11000	14600±7400	7760±3700	5520±4500
TPH	4960±2600	4920±2500	3970±2800	3260±4200
Copper	18.2 ±9.2	12.5±2.5	14.8±6.5	18.7±8.3
Lead	45±28	36±32	30±20	44±46
Nickel	15±11	16±2.8	8.6±5.2	8.1±5.2
Cadmium	4.1±3.6	1.9±2.9	1.9±3.0	1.5±2.3
Zinc	31.5±5.4	10.5±1.0	380±320	5.4±3.0
Vanadium	10±11	5.5±2.8	9.0±9.6	9.7±5.8
Chromium	51±11	38±14	34±18	44±21

The average nickel-vanadium ratio was found to be 1.71. Nickel-vanadium ratio is an important factor used for fingerprinting the source of oil contamination in environmental media. The ratio obtained from this study is close to the ratio of 2.0 published for Forcados blend (COLG., 2011) which is the predominant oil type in the Western Niger Delta. This confirms the provenance of the hydrocarbons in the water as derived from crude oil related activities in the area. Also the following

Table 6: Comparison of levels of oil and grease, total petroleum hydrocarbon and heavy metals with maximum permissible levels of some drinking water quality standards

Parameters	Results from	Nigerian drinking			Health Canada	Nigerian standard
	present study	water standards			(2012)	(FMoE and FEPA., 1991)
	(Esi river water)	SON (2007)	WHO (2011)	USEPA (2012)		
O and G ( $\mu\text{g L}^{-1}$ )	11600±8600	NS	NS	NS	NS	50.0
TPH ( $\mu\text{g L}^{-1}$ )	4270±3000	NS	NS	NS	NS	NS
Pb ( $\mu\text{g L}^{-1}$ )	39±33	10.0	10.0	15.0	10.0	50.0
Cd ( $\mu\text{g L}^{-1}$ )	2.4±3.1	3.00	3.00	5.00	5.00	10.0
Zn ( $\mu\text{g L}^{-1}$ )	107±220	3000	NS	NS	5000*	5000
V ( $\mu\text{g L}^{-1}$ )	7.0±7.9	NS	NS	NS	NS	10.0
Cr ( $\mu\text{g L}^{-1}$ )	42±17	50.0	50.0	100	50.0	50.0
Ni ( $\mu\text{g L}^{-1}$ )	12±15	20	70.0	NS	NS	50.0
Cu ( $\mu\text{g L}^{-1}$ )	16.1±7.4	1000	2000	1300	1000	100

ns: No standard specified, \*Not Maximum Acceptable Concentration (MAC)

pairs of parameters correlate strongly and their correlation coefficient are significant ( $\infty = 0.05$ ): Pb and Cu (0.505), Ni and Pb (0.505), Cd and Cu (0.456), Cd and Pb (0.485), Cd and Ni (0.634) and V and Cd (0.560). This indicates that members of each pair has identical source which may be from the oil prospecting and processing activities in the area through oil spillages.

The average concentrations of the heavy metals are Pb; 39±33  $\mu\text{g L}^{-1}$  (ND-160  $\mu\text{g L}^{-1}$ ), Cu; 16.1±7.4  $\mu\text{g L}^{-1}$  (ND-40.0  $\mu\text{g L}^{-1}$ ), Ni; 12±15  $\mu\text{g L}^{-1}$  (ND-100  $\mu\text{g L}^{-1}$ ), Zn; 107±220  $\mu\text{g L}^{-1}$  (1.00-819  $\mu\text{g L}^{-1}$ ), Cd; 2.4±3.1  $\mu\text{g L}^{-1}$  (ND-12.0  $\mu\text{g L}^{-1}$ ), V; 7.0±7.9  $\mu\text{g L}^{-1}$  (ND-35.0  $\mu\text{g L}^{-1}$ ) and Cr; 42±17  $\mu\text{g L}^{-1}$  (ND-100  $\mu\text{g L}^{-1}$ ) (Table 2). A comparison of the mean values of metals of all six study sampling stations (Table 3) using analysis of variance shows that the differences in concentrations for Cu, Pb and Cd for the six sampling stations are statistically not significant. The differences in the concentration of Zn, Ni, V and Cr are however statistically significant at 0.05 confidence level when tested with ANOVA single factor. There is no definite trend in the variation of all the metals with respect to distance of sampling stations from upstream to downstream.

A comparison of mean concentration of heavy metals of study area with those of the control area (Table 2) shows that the concentrations of heavy metals with the exception of the concentration of Zn are higher in the study area than in the control area. A paired t-test (Student t-test) however shows that the differences are not statistically significant at six degrees of freedom and at 95% confidence level.

Use of water for drinking purpose is one of the numerous uses to which the water of Esi River is put by the inhabitants close to the river in the absence of pipe-borne water or due to the high cost of other treated waters. A comparison of the concentrations of the parameters measured with national and international guidelines (Table 6) shows that the concentration of O and G (11600±8600  $\mu\text{g L}^{-1}$ ) is higher than the permissible limits of Federal Ministry of Environment (FMEnv) (formerly Federal Environmental Protection Agency [FEPA]) guidelines (50.0  $\mu\text{g L}^{-1}$ ) (FMoE and FEPA., 1991). The average concentration of Pb in Esi River (39±33  $\mu\text{g L}^{-1}$ ) exceeded the Minimum Permitted Levels (MPL) of Nigeria guidelines (10.0  $\mu\text{g L}^{-1}$ ) (SON., 2007), Health

Based Guideline (HBG) of WHO (2011) ( $10.0 \mu\text{g L}^{-1}$ ), Maximum contaminant level of USA water quality standards ( $15.0 \mu\text{g L}^{-1}$ ) (USEPA., 2012), Maximum allowable concentration Canadian water Quality Guideline ( $10 \mu\text{g L}^{-1}$ ) (Health Canada, 2012). The water is thus not suitable for drinking.

A comparison of average concentrations of parameters measured in the study area with guideline values for uses of water other than for drinking purpose (Table 7) shows the following: Average concentration of O and G ( $11600 \pm 8600 \mu\text{g L}^{-1}$ ) is higher than that specified for iron and steel water (Not detected) and also higher than the California State Water Quality Control Board (CSWQCB) 1963 guideline for recreational water ( $5000 \mu\text{g L}^{-1}$ ) (Van der Leeden *et al.*, 1990). The average concentration of Zn in Esi river ( $107 \pm 220 \mu\text{g L}^{-1}$ ) exceeded the Canadian water quality guidelines for power generation (Boiler feed water) ( $<10.0 \mu\text{g L}^{-1}$ ) (CCREM., 1987). The average concentration of Cu in Esi river ( $16.1 \pm 7.4 \mu\text{g L}^{-1}$ ) exceeded the Canadian water quality guideline for power generating (Boiler Feed water) ( $<10.0 \mu\text{g L}^{-1}$ ) (CCREM., 1987). The water of Esi River may not therefore be suitable for iron and steel industry, power generating industry and recreational water (it must however be cautioned here that these standards or guideline are not strictly enforceable in Nigeria, they have only been used here to assess the quality of water of Esi river).

In a comparison of the results of determination of parameters in this study with results obtained for other rivers in Nigeria and in other countries which are polluted, it was found that most of the results were comparable with results obtained elsewhere. Some were however higher or lower than results obtained in other places (Table 8). The average concentration of O and G of Esi River,  $11600 \pm 8600 \mu\text{g L}^{-1}$  ( $\text{ND}-32600 \mu\text{g L}^{-1}$ ) is comparable with results obtained for Elechi Creek ( $90.0-1220 \mu\text{g L}^{-1}$ ) by Obire *et al.* (2003). It is also comparable with results for Benin river at Koko ( $2270 \pm 480 \mu\text{g L}^{-1}$ ) (Akporido, 2013). It is however lower than results obtained for Niger river drilling site ( $1100100 \mu\text{g L}^{-1}$ ) by Ayotamuno *et al.* (2002) and the New Calabar river in the petroleum prospecting area ( $10-5000000 \mu\text{g L}^{-1}$ ) (Odokuma and Okpokwasili, 1997). The average concentration of TPH in the study area  $4270 \pm 3000 \mu\text{g L}^{-1}$  ( $\text{ND}-14900 \mu\text{g L}^{-1}$ ) is comparable with results obtained for Niger river petroleum Prospecting area ( $1120-53900 \mu\text{g L}^{-1}$ ) by Ibiebele (1986) and Benin River at Koko ( $2010 \pm 340 \mu\text{g L}^{-1}$ ) (Akporido, 2013) but higher than that for Ponggion river estuary ( $0.35-1100 \mu\text{g L}^{-1}$ ) (Nayar *et al.*, 2004). The average concentration of Pb in Esi river  $39 \pm 33 \mu\text{g L}^{-1}$  ( $\text{ND}-160 \mu\text{g L}^{-1}$ ) is comparable with those results obtained for Elechi Creek ( $1.00-160 \mu\text{g L}^{-1}$ ) (Obire *et al.*, 2003), Benin river at Koko ( $146 \pm 55 \mu\text{g L}^{-1}$ ) (Akporido, 2013) and Crooked Creek ( $310 \pm 360 \mu\text{g L}^{-1}$ ) (Jennett and Foil, 1979). It is higher than results for Niger River (at Patani) (ND) (Asonye *et al.*, 2007) and Urashi River (ND) (Asonye *et al.*, 2007). It is however lower than those for Ogunpa/Ona ( $<10.0-8600 \mu\text{g L}^{-1}$ ) (Onianwa *et al.*, 2001), Bietri Bay and Ebrie Lagoon ( $2400-4800 \mu\text{g L}^{-1}$ ) (Koffi *et al.*, 2014) and New Calabar River ( $850 \mu\text{g L}^{-1}$ ) (Wegwu and Akiniwor, 2006). The mean concentration of Ni in Esi River ( $12 \pm 15 \mu\text{g L}^{-1}$ ) or the range ( $\text{ND}-100 \mu\text{g L}^{-1}$ ) is comparable with those for Elechi Creek ( $27.0-945 \mu\text{g L}^{-1}$ ) (Obire *et al.*, 2003). Ogunpa/Ona River ( $<1.00-27.0 \mu\text{g L}^{-1}$ ) (Onianwa *et al.*, 2001) but much lower than those for Tinto River ( $160,000 \pm 110,000 \mu\text{g L}^{-1}$ ) (Elbaz-Poulichet *et al.*, 1999) and Benin river at Koko ( $1880 \pm 630 \mu\text{g L}^{-1}$ ). The concentrations of the remaining parameters showed the same trend with the parameters discussed above when they were compared with results obtained for the other studies in Table 8 (i.e., some were comparable with these other results while some were either lower or higher).



Table 7: Comparison of mean values of oil and grease, total petroleum hydrocarbon and six heavy metals with internationally acceptable guideline for uses of water other than for drinking

Parameters	Food and beverage industry				CSWQCB 1963		CSWQCB 1963		Ontario min. of the environment 1984 water quality criteria for livestock (Van der Leeden <i>et al.</i> , 1990)
	Results from present study (Bsi river water)	Iron and steel industry (CREM, 1987)	Power generating industry (Boiler feedwater) (CREM, 1987)	(Food canning from dried, frozen, fruits, vegetables) (CREM, 1987)	FAO water quality guidelines for irrigation (Van der Leeden <i>et al.</i> , 1990)	water quality for the protection of aquatic life (Van der Leeden <i>et al.</i> , 1990)	Guideline for recreational water. Water contact-limiting threshold (Van der Leeden <i>et al.</i> , 1990)	environment 1984 water quality criteria for livestock (Van der Leeden <i>et al.</i> , 1990)	
O and G ( $\mu\text{g L}^{-1}$ )	11600±8600	ND	-	-	NS	-	5000	-	
TPH ( $\mu\text{g L}^{-1}$ )	4270±3000	-	-	-	NS	-	5000	-	
Pb ( $\mu\text{g L}^{-1}$ )	39±53	-	-	-	NS	100	-	100	
Cd ( $\mu\text{g L}^{-1}$ )	2.4±3.1	-	-	-	10.0	10.0	-	50.0	
Zn ( $\mu\text{g L}^{-1}$ )	107±220	-	<10.0	-	2000	100	-	25000	
V ( $\mu\text{g L}^{-1}$ )	7.0±7.9	-	-	-	100	-	-	100	
Cr ( $\mu\text{g L}^{-1}$ )	42±17	-	-	-	100	-	-	1000	
Ni ( $\mu\text{g L}^{-1}$ )	12±15	-	-	-	200	50.0	-	1000	
Cu ( $\mu\text{g L}^{-1}$ )	16.1±7.4	-	<10.0	-	200	20.0	-	500	

ND: Not detected, NS: Not specified, FAO: Food and agricultural organisation, CSWQCB: California state water quality control board and CREM: Canadian council of resource and environment ministers

Table 8: Water quality characteristic of some other rivers compared with Esi river

Country	River	Major activities in the area	O and G	TPH	Cu	Pb	Ni	Cd	Zn	Cr	References
------( $\mu\text{g L}^{-1}$ )-----											
Nigeria (Niger delta)	Niger river (at Patani)	Petroleum prospecting	-	-	ND	ND	-	ND	1010	100	Asonye <i>et al.</i> (2007)
Nigeria (Niger delta)	New calabar river	Petroleum prospecting	10-5,000,000	-	-	-	-	-	-	-	Odokuma and Okpokwasili (1997)
Nigeria (Niger delta)	New calabar river	Petroleum prospecting	-	-	2080	850	-	560	6590	50.0	Wegwu and Akinwor (2006)
Nigeria (Niger delta)	Niger river	Drilling site	1,100,100	-	-	-	-	-	-	-	Ayotamuno <i>et al.</i> (2002)
Nigeria (Niger delta)	Urashi river (Ahoada-west)	Petroleum prospecting	-	-	ND	ND	-	ND	230	ND	Asonye <i>et al.</i> (2007)
Nigeria (Niger delta)	Niger river	Petroleum prospecting	-	1120-53900	-	-	-	-	-	-	Ibiebele (1986)
Nigeria (Niger delta)	Elechi creek	Petroleum prospecting	90-1220	-	1.00-58100	1.00-160	27.0-945	7.00-254	2.00-822	1.00-718	Obire <i>et al.</i> (2003)
Nigeria (Niger delta)	Ogupa/Ona (Ibadan)	Urban area	-	-	<1.00-39.0	<10.0-8600	<1.00-27.0	<1.00-23.0	<1.00-35.0	2.00-19.0	Onianwa <i>et al.</i> (2001)
Philippines	Ponggion river estuary	transportation	-	0.35-1100	-	-	-	-	-	-	Nayar <i>et al.</i> (2004)
Spain	Tinto river (Ria of huelva)	Industrial area	-	-	15200±1400	-	160,000±110,000	120±97	3440±33000	-	Elbaz-Poulichet <i>et al.</i> (1999)
U.S.A.	Crooked creek	Metal milling a smelting	-	-	24±19	310±360	-	730±350	2770±590	-	Jennett and Foil (1979)
Cote Divoire	Bietri bay and ebrie Lagoon	Industrial	-	-	9050-9680	2400-4800	-	20-260	12080-19870	-	Koffi <i>et al.</i> (2014)
Nigeria	Elechi creek	Petroleum prospecting	-	-	<1.00	-	<1.00	-	-	<1.00-2.00	Davies <i>et al.</i> (2006)
Nigeria	Benin river	Industrial area	2270±480	2010±340	-	146±55	1880±630	3.0±5.3	62±42	0.40±0.59	Akpoido (2013)
Nigeria	Esi river	Petroleum prospecting	11600±8600 (0.00-32600)	4270±3000 (0.00-14900)	16.1±7.4 (0.00-40.0)	39±33 (0.00-160)	12±15 (0.00-100)	2.4±3.1 (0.00-12.0)	107±220 (1.00-819)	42±17 (0.00-100)	Present study

## CONCLUSION

The study showed that hydrocarbon levels are high in all the sampling stations. These high concentrations of hydrocarbon and lead have obvious effect on human and animal health. Efforts should be made to control emissions of these pollutants into the environment. From the results of this study, there is an indication that Esi river in all locations is polluted with petroleum hydrocarbons that were derived from petroleum prospecting in the area. Furthermore comparison with standards for specific industrial purposes and for drinking showed that the river water is not adequate for drinking and for some of these non-drinking uses.

## REFERENCES

- Adeniyi, A.A. and O.J. Owoade, 2010. Total petroleum hydrocarbons and trace heavy metals in roadside soils along the Lagos-Badagry expressway, Nigeria. *Environ. Monit. Assess.*, 167: 625-630.
- Akporido, S.O., 2013. Quality characteristics of effluent receiving waters of Benin River adjacent to a lubricating oil producing factory, Nigeria. *Environ. Conserv. J.*, 14: 9-20.
- Akporido, S.O. and S.O. Asagba, 2013. Quality characteristics of soil close to the Benin River in the vicinity of a lubricating oil producing factory, Koko, Nigeria. *Int. J. Soil Sci.*, 8: 1-16.
- Almeida, R., A.P. Mucha, C. Teixeira, A.A. Bordalo and C.M.R. Almeida, 2013. Biodegradation of petroleum hydrocarbons in estuarine sediments: Metal influence. *Biodegradation*, 24: 111-123.
- Anonymous, 1995. *Standard Methods for the Examination of Water and Wastewater*. 19th Edn., APHA, AWWA and WEF, Washington, DC., USA.
- Anyakora, C., H. Coker and M. Arbabi, 2011. Application of polynuclear aromatic hydrocarbons in chemical fingerprinting: The Niger Delta case study. *Iran. J. Environ. Health Sci. Eng.*, 8: 75-84.
- Anyakora, C., A. Ogbeche, P. Palmer, H. Coker, G. Ukpo and C. Ogah, 2005. GC/MS analysis of polynuclear aromatic hydrocarbons in sediment samples from the Niger Delta region. *Chemosphere*, 60: 980-997.
- Asonye, C.C., N.P. Okolie, E.E. Okenwa and U.G. Iwuanyanwu, 2007. Some physico-chemical characteristics and heavy metal profiles of Nigerian rivers, streams and waterways. *Afr. J. Biotechnol.*, 6: 617-624.
- Ayotamuno, M.J., A.J. Akor and T.J. Igho, 2002. Effluent quality and wastes from petroleum drilling operations in the Niger Delta, Nigeria. *Environ. Manage. Health*, 13: 207-216.
- Ballou, T.G. and R.R. Lewis III, 1989. Environmental assessment and restoration recommendations for a mangrove forest affected by jet fuel. *Int. Oil Spill Conf. Proc.*, 1: 407-412.
- Ballou, T.G., S.C. Hess, E.E. Dodge and A.H. Knap, 1989. Tropical Oil Pollution Investigations in Coastal Systems (TROPICS): The Effects of Untreated and Chemically Dispersed Produce Bay Crude Oil in Mangrove, Seagrasses and Corals in Panama. In: *Oil Dispersants: New Ecological Approaches*, Flaherty, I.M. (Ed.). ASTM International, Philadelphia, ISBN-13: 9780803111943, Pages: 302.
- CCREM, 1987. *Canadian Water Quality Guidelines*. Canadian Council of Resource and Environment Ministers (CCREM), Canada.
- COLG., 2011. *Forcados lite crude oil specification/procedure*. Crude Oil Liners Group, Nigeria, USA.
- Davies, O.A., M.E. Allison and H.S. Uyi, 2006. Bioaccumulation of heavy metal in water, sediment and periwinkle (*Tympanotonous fuscatus var radula*) from the Elechi creek, Niger Delta. *Afr. J. Biotechnol.*, 5: 968-975.

- Ekundayo, E.O. and O. Obuekwe, 2000. Effects of an oil spill on soil physico-chemical properties of a spill site in a typical udipsamment of the Niger delta basin of Nigeria. *Environ. Monitor. Assess.*, 60: 235-249.
- Elbaz-Poulichet, F., N.H. Morley, A. Cruzado, Z. Velasquez, E.P. Achterberg and C.B. Braungardt, 1999. Trace metal and nutrient distribution in an extremely low pH (2.5) river-estuarine system, the Ria of Huelva (South-West Spain). *Sci. Total Environ.*, 227: 73-83.
- FMoE and FEPA., 1991. Standards for water quality: Drinking water. Federal Ministry of Environment (FMoE) and Federal Environmental Protection Agency (FEPA), Garki Abuja, Nigeria.
- Forstner, U. and G.T.W. Wittman, 1983. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin, Germany, ISBN-13: 978-3540128564, Pages: 488.
- GESAMP., 1993. Impacts of oil and related chemicals and wastes in the marine environment. Group of Experts on the Scientific Aspects of marine Pollution (GESAMP), GESAMP Reports and Studies No. 50 International Marine Organization, London, UK.
- Gwack, J., J.H. Lee, Y.A. Kang, K.J. Chang, M.S. Lee and J.Y. Hong, 2012. Acute health effects among military personnel participating in the cleanup of the Hebei spirit oil spill, 2007, in Taean county, Korea. *Oson Public Health Res. Perspect.*, 3: 206-212.
- Health Canada, 2012. Guidelines for Canadian drinking water quality-summary table. Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario, pp: 1-22.
- Hinrichson, O., 1990. *Our Common Coast in Crisis*. Earths-Can Publications, London, UK., Pages: 84.
- Ibiebele, D.D., 1986. Point-source inputs of petroleum wastewater into the Niger Delta, Nigeria. *Sci. Total Environ.*, 52: 233-238.
- Jennett, J.C. and J.L. Foil, 1979. Trace metal transport from mining, milling and smelting watersheds. *J. Water Pollut. Control Fed.*, 51: 378-404.
- Kalita, M., K.G. Bhattacharyya and A. Devi, 2009. Assessment of oil field soil with special references to the presence of heavy metals: A case study in agricultural soil of Rudrasagar oil field, Assam. *India J. Environ. Prot.*, 29: 1065-1071.
- Koffi, K.M., S. Coulibaly, B.C. Atse and E.P. Kouamelan, 2014. Survey of heavy metals concentrations in water and sediments of the Estuary Bietri Bay, Ebrie Lagoon, Cote D'Ivoire. *Int. J. Res. Earth Environ. Sci.*, 1: 1-10.
- Lee, S.M., M. Ha, E.J. Kim, W.C. Jeong and J. Hur *et al.*, 2009. The effects of wearing protective devices among residents and volunteers participating in the cleanup of the Hebei spirit oil spill. *J. Prev. Public Health*, 42: 89-95.
- Luiselli, L., G.C. Akani, O.E. Politan, E. Odegbune and O. Bello, 2004. Dietary shifts of sympatric freshwater turtles in pristine and oil-polluted habitats of the Niger Delta Southern Nigeria. *Herpetol. J.*, 14: 57-64.
- Luiselli, L., G.C. Akani and E. Politano, 2006. Effects of habitat alteration caused by petrochemical activities and oil spills on the habitat use and interspecific relationships among four species of afro-tropical freshwater turtles. *Biodivers. Conserv.*, 15: 3756-3767.
- NRC, 1985. *Oil in the Sea: Inputs, Fates and Effects*. National Academy Press, Washington, DC., USA., ISBN-13: 9780309078351, Pages: 607.
- NRC., 2003. *Oil in the Sea III: Inputs, Fates and Effects*. National Academy Press, Washington, DC., USA., ISBN: 9780309084383, Pages: 265.

- Nayar, S., B.P.L. Goh and L.M. Chou, 2004. The impact of petroleum hydrocarbons (diesel) on periphyton in an impacted tropical estuary based on in situ microcosms. *J. Exp. Mar. Biol Ecol.*, 32: 213-232.
- Nduka, J.K. and O.E. Orisakwe, 2009. Effect of effluents from warri refinery petrochemical company WRPC on water and soil qualities of contiguous host and impacted on communities of delta state, Nigeria. *Open Environ. Pollut. Toxicol. J.*, 1: 11-17.
- Nduka, J.K. and O.E. Orisakwe, 2011. Water-quality issues in the Niger Delta of Nigeria: A look at heavy metal levels and some physicochemical properties. *Environ. Sci. Pollut. Res.*, 18: 237-246.
- Nie, M., N. Xian, X. Fu., X. Chen and B. Li, 2010. The interactive effect of petroleum hydrocarbon spillage and plant rhiosphene on concentrations and distribution of heavy metals in sediments in the Yellow River Delta, China. *J. Hazard. Mater.*, 174: 156-161.
- Obire, O., D.C. Tamuno and S.A. Wemedo, 2003. Physico-chemical quality of elechi creek in port harcourt, Nigeria. *J. Appllied Sci. Environ. Manage.*, 7: 43-50.
- Odokuma, L.O. and G.C. Okpokwasili, 1997. Seasonal influences of the organic pollution monitoring of the new Calabar river, Nigeria. *Environ. Monit. Assess.*, 45: 43-56.
- Olajire, A.A., R. Altenburger, E. Kuster and W. Brack, 2005. Chemical and ecotoxicological assessment of polycyclic aromatic hydrocarbon: Contaminated sediments of the Niger Delta, Southern Nigeria. *Sci. Total Environ.*, 340: 123-136.
- Omo-Irabor, O.G., S.B. Olobaniyi, J. Akunna, V. Venus, J.M. Maina and C. Paradzayi, 2011. Mangrove vulnerability modelling in parts of Western Niger Delta, Nigeria using satellite images, GIS techniques and Spatial Multi-Criteria Analysis (SMCA). *Environ. Monitor. Assess.*, 178: 39-51.
- Onianwa, P.C., A. Ipeyeda and J.E. Emurotu, 2001. Water quality of the urban rivers and streams of Ibadan Nigeria. *Environ. Educat. Inform.*, 20: 107-120.
- Ossai, C.I., U.I. Duru, I.A. Ossai and I.M.T. Arubi, 2010. An appraisal of soil pollution in oil and gas production environment: A case study of heavy metals concentration in Ebocha and Akri oil fields. *Proceedings of the International Oil and Gas Conference and Exhibition, June 8-10, 2010, Beijing, China*, pp: 492-497.
- Osuji, L.C. and S.O. Adesiyon, 2005. Extractable hydrocarbons, nickel and vanadium contents of ogbodo-isiokpo oil spill polluted soils in Niger Delta, Nigeria. *Environ. Monitor. Assess*, 110: 129-139.
- Perez-Casanova, J.C., D. Hamoutene, S. Samuelson, K. Burt, T.L. King and K. Lee, 2010. The immune response of juvenile Atlantic cod (*Gadus morhua* L.) to chronic exposure to produced water. *Mar. Environ. Res.*, 70: 26-34.
- Plaza, G.A., G. Nalecz-Jawecki, O. Pinyakong, P. Illmer and R. Margesin, 2010. Ecotoxicological and microbiological characterization of soils from heavy-metal-and hydrocarbon-contaminated sites. *Environ. Monit. Assess.*, 163: 477-488.
- SON., 2007. Nigeria standard for drinking water quality. Nigerian Industrial Standard 554: 2007, Standards Organization of Nigeria (SON), Lagos, Nigeria, pp: 1-30.
- SPDC., 2001. Environmental incident report listing by spill date. Shell Petroleum Development Company (SPDC), Nigeria.
- Sojinu, O.S., J.Z. Wang, O.O. Sonibare and E.Y. Zeng, 2010. Polycyclic aromatic hydrocarbons in sediments and soils from oil exploration areas of the Niger Delta, Nigeria. *J. Hazard. Mater.*, 174: 641-647.

- Sung, K., K.S. Kim and S. Park, 2013. Enhancing degradation of total petroleum hydrocarbons and uptake of heavy metals in a wetland microcosm planted with *Phragmites communis* by humic acids addition. *Int. J. Phytorem.*, 15: 536-549.
- UNDP., 2006. The Niger Delta human development report. United Nation Environmental Programme, Abuja, Nigeria, pp: 1-218. [http://web.ng.undp.org/reports/nigeria\\_hdr\\_report.pdf](http://web.ng.undp.org/reports/nigeria_hdr_report.pdf).
- UNEP., 2011. Environmental assessment of ogoniland. United Nation Environment Programme (UNEP), Nairobi, pp: 1-246. [http://postconflict.unep.ch/publications/OEA/UNEP\\_OEA.pdf](http://postconflict.unep.ch/publications/OEA/UNEP_OEA.pdf).
- USEPA., 2012. 2012 edition of the drinking water standards and health advisories. EPA 822-S-12-001, Office of Water, U.S. Environmental Protection Agency, Washington, DC., USA.
- Udoh, F.D. and N.M. Akpan, 2010. Effect of oil spillage on alakiri community in okrika local government area of rivers state, Nigeria. *J. Ind. Pollut. Control*, 26: 139-143.
- Umoren, I.U. and I.I. Udousoro, 2009. Fractionation of Cd, Cr, Pb and Ni in roadside soils of Uyo, Niger Delta Region: Nigeria using the optimized BCR sequential extraction technique. *Environmentalist*, 29: 280-286.
- Van der Leeden, F., F.L. Troise and D.K. Todd, 1990. *The Water Encyclopedia*. 2nd Edn., CRC Press, Boca Raton, FL., ISBN-13: 9780873711203, Pages: 824.
- WHO, 2011. *Guidelines for Drinking-water Quality*. 4th Edn., World Health Organization, Geneva, Switzerland, ISBN: 9789241548151.
- Wegwu, M.O. and J.O. Akiniwor, 2006. Assessment of heavy-metal profile of the new Calabar river and its impact on Juvenile *Clarias gariepinus*. *Chem. Biodivers.*, 3: 79-87.
- Williams, A.B. and N.U. Benson, 2010. Interseasonal hydrological characteristics and variabilities in surface water of tropical estuarine ecosystems within Niger Delta, Nigeria. *Environ. Monit. Assess.*, 165: 399-404.