Evaluation Of Heavy Metal And Total Hydrocarbon Levels In Hydrocarbons Polluted Ecosystem in the Niger Delta Region

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Abstract: These present study assessed the heavy metal and total hydrocarbon level in hydrocarbons polluted ecosystem in the Niger Delta region. GPS coordinates of each location was obtained using GPS 72H equipment (Garmin, Taiwan). Water samples were collected using sterile 250ml capacity media bottles. Sediment samples were obtained using Ponar grab sampler and aseptically transferred into 40z capacity Whirl- Pak bags (Nasco, USA). With the aid of sterile plastic hand trowel, mixed surface and subsurface soil samples were collected in duplicates and transported in ice-chest to the laboratory within six hours of collection. Data were analysed using SPSS and significant mean separated using LSD test at 5% probability level. The result shows that the concentration of heavy metals varied significantly among locations studied. The mean Lead (Pb) and Nickel (Ni) concentrations were significantly higher in polluted water samples than in the pristine samples whereas the mean Ni, V and Zn values were higher in the underlying sediment. The mean Cr, Co, Cd, Ni, V and Zn concentrations were significantly higher in polluted soil than in the pristine samples. It was concluded from the result that the level of heavy metal in polluted samples were significantly ($P<0.05$) higher than that of the pristine samples.
[Iwatt G.D., Antai S.P and Agbor R.B. **Evaluation Of Heavy Metal And Total Hydrocarbon Levels In Hydrocarbons Polluted Ecosystem in the Niger Delta Region.** *World Rural Observ* 2016;8(1):95-102]. ISSN: 1944-6543 (Print); ISSN: 1944-6551 (Online). http://www.sciencepub.net/rural. 13. doi:10.7537/marswro08011613.

Keywords: Heavy metal, hydrocarbon, water, sediment, soil

Introduction

Heavy metals" is a vague term used to depict elements that are metals or metalloids. Though, this term has been queried for many years (Phipps, 1981; Vanloon and Duffy, 2000), efforts to replace it by chemically sound terminology has unsuccessful (Nieboer and Richardson, 1980). Therefore "heavy metals" have so far been defined as a group of metals and metalloids with atomic density greater than 4g/cm^3, or 5 times or more, greater than water and are toxic or poisonous even at low concentration (Huton and Symon, 1986; Battarbee *et al*, 1988; Nriagu and Pacyna, 1989; Garbarino *et al,* 1995, Hawkes, 1997; Lenntech, 2004). Heavy metals when introduced into the environment in excessive amounts by human activities constitute a source of great danger to man's health (Wild, 1996; *Population* Reports, 2000). Mashi *et al* (2005) noted that out of 38 heavy metals, 12 are considered as those whose concentrations in the environment are easily influence by human activities and these include cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), mercury(Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), Lead (Pb), tin (Sn) and zinc (Zn). Heavy metals are naturally found in soils (Ojanuga *et al*, 1996). Those commonly associated with crude oil and petroleum products are Cr, Cd, V, Pb, Zn and Cu Chindah *et al,* 2009). Nigerian crude oil-Bonny light have been reported to Ni, Cu, Pb, Cd, Fe and Zn (Odokuma, 2009). Heavy metals are abundant in the natural environment but the anthropogenic sources contribute immensely its increased concentration thus, polluting the environment. The primary anthropogenic sources of heavy metals are point sources such as mines, foundries, smelters, and coal-burning power plants, as well as diffuse sources such as combustion by-products and vehicle emissions (Alloway, 1995; McDonald & Grandt, 1981). Human activity affects the natural geological and biological redistribution of heavy metals through pollution of the air, water, and soil. Alterations in chemical forms of heavy metals released to the environment by humans affects heavy metal's toxicity by allowing it to bio-accumulate in plants and animals, bio-concentrate in the food chain, or attack specific organs of the body (Kuhn and Koupelis, 2004). Heavy metals are associated with myriad of adverse health effects.

Materials And Method

Sampling locations

In the initial survey carried out 25 locations (13 soils and 12 aquatic) were identified for this study. All locations were situated in Akwa Ibom and Cross River States of Nigeria.

Sample collection

Global positioning system (GPS) coordinates of each location was obtained using GPS 72H equipment (Garmin, Taiwan). Water samples were collection using sterile 250ml capacity media bottles. Sediment samples were obtained using Ponar grab sampler and

aseptically transferred into 40z capacity Whirl- Pak bags (Nasco, USA). With the aid of sterile plastic hand trowel, mixed surface and subsurface soil samples were collected in duplicates and transported in ice-chest to the laboratory within six hours of collection.

Estimation of total hydrocarbon (THC) and heavy metals concentrations.

THC was determined in the samples using the method of Odu *et al* (1988) and ASTM (1996) as described by Clinton *et al* (2009). Five grams of each sample was extracted twice with 25ml of toluene, filtered into 50ml flask and made up to 50 ml with toluene. Water sample was extracted thrice with 30ml of toluene, filtered and made up to 100ml with toluene. The absorbance of the filtrates was measured at 420nm wavelength using a spectrophotometer model PD-303UV (Apel, Japan) and THC concentrations calculated from the calibration graph. Heavy metals (Pb, Cu, Fe, Zn, Co, Cr, Cd, Ni and V) concentrations in soil and sediment samples were determined following digestion in aqua regia (3:1 HC1: $HN0_3$) (Nieuwenhuize *et al.,* 1991). Soil and sediment samples 2g each was taken in 250ml glass beakers and digested with 8ml of aqua regia on a sand bath for two hours (Chen and Ma, 2001). Following evaporation to near dryness, the samples were dissolved with 10ml of 2% HNO3, filtered and diluted to 50ml with distilled water. Heavy metals in extract were analyzed using an atomic absorption spectrophotometer (Unicam 969 Solaar). For heavy-metal determination in water samples, the method described by Olowu *et al* (2010) was adopted. Five (5) milliliters of concentrated hydrochloric acid was added to 250ml of water and evaporated to 25ml. The extract was transferred to a 50ml flask and made up to the mark with distilled water. Heavy metal contents were measured using AAS.

Statistical analysis

Analytical software (SPSS version 16, quick Calcs online GraphPad and Microsoft excel) were used in analyzing the data obtained from this study. Means of soil, sediment and water physicochemical parameters from sampled locations were compared using one way Analysis of Variance (ANOVA) and Duncan Multiple Ranged test used to test for significant difference among means.

Results

Total hydrocarbon (THC) and heavy metal analyses

The results of total hydrocarbon and heavy metals concentrations of pristine water samples are presented in Tables 1. The mean THC concentrations in pristine water samples ranged from 0.161±0.003 to 6.049±0.044mg/l while the mean heavy metal concentrations was in the range of 0.001 ±0.001 mg/1 to 1.139±0.036mg/l. THC and heavy metals concentrations varied significantly among samples (Duncan Multiple Range test, $P<0.05$). For petroleum hydrocarbon polluted water samples as presented in Table 2, the mean values of THC concentrations ranged from 6.026±0.023mg/l to 198.20±0.300mg/l while the values for heavy metals ranged from 0.001±0.001 mg/1 to 0.2910±0.002mg/l. THC contents and other heavy metal concentrations varied significantly (Duncan Multiple Range test, $P<0.05$) among polluted water samples with the exception of Cd concentrations which showed no significant variation (DMR, $P>0.05$). The mean THC and heavy metal concentrations of pristine and petroleum hydrocarbon polluted water samples. Though, the mean THC, Zn, V, Ni, Cd, Pb and Co concentration was greater in polluted than in pristine water sample, only the differences in mean THC, Pb, Ni, V and Fe were statistically significant ($p<0.05$). The mean Cr concentration was significantly higher ($p<0.05$) in pristine water than in polluted water samples. The mean Cu concentration was the same in both pristine and petroleum hydrocarbon polluted water samples. The order of heavy metal concentration in petroleum polluted water was Fe>Cd>Ni=Zn>V>Cr>Cu>Pb>Co. while in the pristine water samples the order of concentration was Fe>Zn>Cr>Cu>V=Ni>Pb>Co=Cd. The mean THC and heavy metal concentrations of the underlying sediment samples from the same locations as the water are presented in Tables 3 and 4 respectively. THC and heavy metal levels varied significantly with location in both polluted and pristine sediments. For the petroleum hydrocarbon polluted sediments (Table 3), the THC levels ranged from 110.09± 12.004 to 3267.90±34.656mg/kg while the levels of heavy metals were in the range of 0.001±0.000mg/kg and 2898.000±31.193mg/kg. The pristine sediment samples had THC levels ranging from 11.610± 1.214mg/kg to 228.89±3.413mg/kg (Table 4.13) while Heavy metal levels were in the range of 0.002±0.001 mg/kg and 3685.1±52.719mg/kg. The mean THC, Zn, Fe, V, and Ni levels were greater in polluted sediments than in pristine sediments with only the mean THC, Zn, V and Ni levels showing significant *($p<0.05$)* differences. The mean of mean Cu, Cd, Pb, Co and Cr levels were greater in pristine sediments than in polluted sediment with only Cu, Co and Cr levels showing significant difference *($p<0.05$).* The results of THC and heavy metal levels in petroleum hydrocarbon polluted and pristine soil samples are presented in Tables 5 and 6. THC concentrations in polluted soil samples ranged between 326.20±7.868-7303.5±8.351 mg/kg while heavy metals concentrations were in the range of 0.002±0.001

mg/kg and 2863.1±43.028mg/kg. The mean THC and heavy levels from the different locations -aried significantly ($p<0.05$) (Table 5). As shown in Table 4.15, pristine soil samples had THC concentrations ranging from 10.350±0.563mg/kg to 134.750±1.391 mg/kg, with heavy metal levels ranging pristine soils whereas the mean Fe levels were insignificantly greater ($p=0.133$) in pristine than in polluted soils. The order of increase of mean heavy metal levels in polluted soil was Fe>Zn>Ni>V>Cr>Pb>Cu>Co>Cd while in the pristine it was Fe>Zn>Cu>Ni>V>Pb>Cr>Cd>Co.

Table 1: Inter-location comparison of THC and heavy metal concentration of pristine water samples

Physico-chemical parameters of samples			Location code			
	CR	ST	IT	EE	NS	OK
THC(mg/L)	6.049^{e}±0.044	0.161^{a}±0.003	2.006^{c}±0.006	0.434^{a}±0.323	1.273^{b}±0.369	$5.153^{(1}$±0.050
Zn(mg/L)	0.102^{f}±0.002	0.097^{c}±0.001	0.078^{d}±0.002	0.018^{a}±0.002	0.028^{c}±0.002	0.023^{b}±0.002
Cu(mg/L)	0.013^{c}±0.002	$0.006^{a,b}$±0.001	0.009^{b}±0.001	0.005^{a}±0.001	0.018^{d}±0.002	$0.007^{a,b}$±0.002
Fe(mg/L)	0.162^{b}±0.004	0.097^{a}±0.003	0.659^{d}±0.036	0.586^{C}±0.012	1.139^{e}±0.036	0.185^{b}±0.006
V(mg/L)	$0.009^{a,b}$±0.002	0.006^{a}±0.002	0.013^{b}±0.005	0.005^{a}±0.002	$0.009^{a,b}$±0.002	0.004^{a}±0.001
Ni(mg/L)	0.017^{C}±0.001	0.007^{b}±0.001	0.009^{b}±0.002	0.004^{a}±0.001	0.007^{b}±0.002	0.002^{a}±0.001
Cd(mg/L)	0.005^{c}±0.001	0.001^{a}±0.001	0.003^{b}±0.001	0.001^{a}±0.000	0.001^{a}±0.001	0.002^{a}±0.001
Pb(mg/L)	0.008^{d}±0.002	0.002^{a}±0.001	$0.007^{c,d}$±0.001	$0.003^{a,b}$±0.001	$0.005^{b,c}$±0.001	$0.004^{a,b}$±0.001
Co(mg/L)	0.003^{c}±0.001	$0.002^{a,b,c}$±0.001	0.001^{a}±0.000	$0.001^{a,b}$±0.001	$0.002^{b,c}$±0.001	$0.002^{a,b,c}$±0.001
Cr(mg/L)	0.022^{d}±0.001	0.17^{c}±0.001	0.026^{e}±0.001	0.005^{a}±0.001	0.014^{b}±0.001	0.007^{a}±0.001

ST=SateIite town stream, OK=Okon stream, IT=Itu bridge head, CR=Calabar River, NS=Nsidung beach, EE=Ekpo Eyo beach. Mean ±SD, Means with the same letter are not significantly different from each other (Duncan Multiple Range test, $P<0.05$).

Table 2: Inter-location comparison of THC and heavy metal concentration

Physico-chemical parameters of samples			Local ion code			
	F06	D06	H06	AO 6	Z06	C06
THC(mg/L)	6.026^{a}±0.023	4.007^{a}±0.006	157.92^{d}±1.175	35.590^{c}±3.182	198.20^{e}±0.300	10.990^{b}±0.8XS
Zn(mg/L)	0.058^{c}±0.003	0.074^{d}±0.004	0.03 l^{b}±0.003	0.08 l^{e}±0.001	0.029^{b}±0.004	0.009^{a}±0.00,'
Cu(mg/L)	0.018^{d}±0.002	$0.007^{a,b}$±0.001	0.005^{a}±0.002	0.01 l^{c}±0.002	$0.009^{b,c}$±0.003	$0.007^{a,b}$±0.001
Fe(mg/L)	0.29 l^{c}±0.002	0.195^{c}±0.003	0.283^{d}±0.004	0.059^{a}±0.001	0.112^{b}±0.005	0.290^{c}±0.002
V(mg/L)	0.015^{c}±0.001	0.069^{e}±0.002	0.038^{c}±0.003	$0.005^{a,b}$±0.001	0.008^{b}±0.002	0.004^{a}±0.00l
Ni(mg/L)	0.023^{b}±0.003	0.118^{d}±0.003	0.095^{c}±0.004	0.007^{a}±0.001	0.027^{b}±0.003	0.011^{a}±0.001
Cd(mg/L)	0.005^{a}±0.001	0.003^{a}±0.002	0.001^{a}±0.000	0.005^{a}±0.002	0.003^{a}±0.001	0.005^{a}±0.001
Pb(mg/L)	0.009^{c}±0.001	$0.007^{b,c}$±0.002	0.004^{a}±0.001	0.009^{c}±0.002	$0.005^{a,b}$±0.001	$0.007^{b,c}$±0.001
Co(mg/L)	0.007^{c}±0.001	$0.002^{a,b}$±0.001	0.001^{a}±0.001	$0.002^{a,b}$±0.001	0.001^{a}±0.000	0.003^{b}±0.001
Cr(mg/L)	0.002^{a}±0.001	0.009^{c}±0.001	0.006^{b}±0.001	0.018^{d}±0.002	o.on^{c}±o.ooi	0.005^{b}±0.001

A06=Utaewa-Jaja creek, C06=Location 1-Essene creek, D06=Location 2-Essene creek, F06=Ukan beach-Essene creek, H06=Imo River, Z06=Enen Idem. Mean ±SD, Means with the same letter are not significantly different from each other (Duncan Multiple Range test, $P<0.05$)

Table 3: Inter-location comparison of THC and heavy metal concentration of petroleum hydrocarbon polluted sediment samples

Physico-chemical parameters of samples			Location code			
	F06	DO 6	HO 6	A06	Z06	C06
THC (mg/kg)	559.06^{c}±l 2.426	262.50^{b}±7.566	274.94^{b} ±5.037	137.30^{a}±3.764	110.09^{a}±12.004	3267.90^{d}±34.656
Zn(mg/kg)	19.733^{a}±1.107	122.73^{d}±0.306	71.583^{c}±0.369	18.586^{a}±0.577	47.616^{b}±0.398	148.21 ^{e}±l .934
Cu(mg/kg)	1.928^{b}±0.063	0.055^{a}±0.004	0.067^{a}±0.004	5.745^{c}±0.464	0.05 l^{a}±0.004	0.056^{a}±0.003
Fe(mg/kg)	2898.0^{d}±31.193	$2730.6^{b,c}$±23.585	2487.0^{a}±41.059	2900.0^{e}±l 1.786	2768.2^{C}±30.243	2716.5^{b}±5.095
V(mg/kg)	18.853^{b}±0.591	296.8 l^{d}±2.978	151.14^{c}±0.850	1.113^{a}±0.076	557.43^{e}±4.781	854.80^{f}±6.227
N i(mg/kg)	18.186^{b}± 1.099	419.53^0.569	158.78^{c}±4.597	0.220^{a}±0.034-	224.50^{d}±l 0.900	237.93^{c}±20.980
Cd(mg/kg)	0.437^{b}±.328	0.02 l^{a}±.002	0.027^{a}±0.003	0.018^{a}±0.004	0.016^{a}±0.004	0.019^{a}±0.003
Pb(mg/kg)	0.178^{b}±0.003	0.172^{b}±0.003	0.056^{a}±0.004	0.082^{a}±0.003	0.078^{a}±0.005	0.909^{c}±0.043
Co(mg/kg)	0.005°±0.001	0.001^{a}±0.000	0.001^{a}±0.000	0.003^{b}±0.001	0.002^{a}±0.001	0.004^{b}±0.001
Cr(mg/kg)	0.017^{a}±0.001	0.03 l^{b}±0.008	0.015^{a}±0.00l	0.046^{c}±0.004	0.114^{d}±0.002	0.128^{e}±0.002

A06=Utaewa-Jaja creek, C06=Location 1 -Essene creek, D06=Location 2-Essene creek, F06=Ukan beach-Essene creek, H06=Imo River, Z06=Enen Idem. Mean ±SD, Means in row with the same letter are not significantly different from each other (Duncan Multiple Range test)

Table 4: Inter-location comparison of THC and heavy metal concentration of pristine sediment sample

Physico-chemical parameters of samples	CRS	STS	ITS	EES	NSS	OKS
THC (mg/kg)	34.273[d]±1.870	228.89[f]±3.413	15.480[b]±0.590	120.000[e]±1.781	23.220[c]±1.017	11.610[a]±1.214
Zn(mg/kg)	17.173[c]±0.271	1.090[a]±0.271	51.633[d]±1.620	10.756[b]±0.280	66.283[e]±l .030	0.144[a]±0.057
Cu(mg/kg)	6.708[d]±0.371	2.314[a]±0.096	4.617[c]±0.374	10.453[e]±0.476	6.801[d]±0.264	3.777[b]±0.205
Fe(mg/kg)	3616.2[e]±105.809	77.312[b]±l 7.586	3685.l[c]±52.719	3322.8[d]±4.088	2189.3[C]±50.770	442.55[a]±5.997
V (mg/kg)	0.971 [a]±0.111	10.850[b]±0.340	0.785[a]±0.048	17.526[d]±0.865	13.210[C]± 1.435	0.386[a]±0.120
Ni(mg/kg)	1.993[a]±0.030	24.583[c]±l .588	1.971[a]±0.044	2.389[a]±0.535	18.016[b]±l. 144	0.886[a]±0.043
Cd(mg/kg)	0.585[c]±0.077	0.092[b]±0.003	0.093[b]±0.003	0.007[a]±0.001	0.118[b]±0.002	0.108[b]±0.002
Pb(mg/kg)	1.076[e]±0.066	0.436[d]±0.047	0.119[a,b] ±0.003	0.030[a]±0.001	0.173[b]±0.005	0.294[c]±0.007
Co(mg/kg)	0.005[b]±0.001	0.003[a]±0.001	0.005[b,c]±0.001	0.006[c]±0.001	0.008[d]±0.001	0.005[b,c]±0.001
Cr(mg/kg)	0.347[c]±0.046	0.583[d]±0.022	0.817[e]±0.030	0.002[a]±0.001	0.667[b]±±0.005	0.586[d]±0.047

ST=Satelite town stream, OK=Okon stream, IT=Itu bridge head, CR=Calabar River, NS=Nsidung beach, EE=Ekpo Eyo beach Mean ±SD, Means in row with the same letter are not significantly different from each other (Duncan Multiple Range test, P<0.05).

Table 5: Inter-location comparison of mean THC and heavy metal concentration of petroleum hydrocarbon polluted soil samples

Physicochemical parameters of samples	A	B	C	D	E	F	G
THC (mg/kg)	7303.5[g]±8.351	3130.2[b]±6.009	326.20[a]±7.868	3270.3[C]±27.392	6577.8[f]±90.355	5267.6[e]±41.836	3613.3[f]±43.004
Zn(mg/kg)	0.082[a]±0.002	21.503[b]±0.443	43.673[c]±0.781	347.23[8]±18.036	167.16[d]±2.754	322.00'±10.428	219.60[c]±5.256
Cu(mg/kg)	2.809[b]±0.217	1.758[f]±2.402	7.550[c]±0.756	0.058[a]±0.003	0;053[a]±0.004	25.256[d]±0.890	41.233[e]±2.933
Fe(mg/kg)	1684.0[a]±34.56	2566.2[b]±29.362	2822.6[e]±22.47	2657.l[c]±47.387	2863.l[e]±43.028	2729.0[d]±6.885	2525.7[b]±12.667
V (mg/kg)	117.97[d]±2.402	0.096[a]±0.007	217.88[e]±2.429	226.12*'±3.93	19.646[c]±0.790	21.426[c]±.852	5.840[b]±0.317
Ni(mg/kg)	46.562[d]±.547	0.095[a]±0.005	51.094[c]±0.993	781.46[f]±4.343	8.609[c]±l .527	4.579[b]±0.551	2.118[ab]±0.019
Cd (mg/kg)	1.085[b]±0.111	0.009[a]±0.002	0.073[a]±0.016	0.347[a]±0.055	2.472°±.600	0.74[a]±0.009	0.044[a]±0.001
Pb(mg/kg)	2.178[b]±0.140	0.012[a]±0.003	67.45[fc]±0.91	45.333[e]±1.350	5.546[c]±0.452	0.104[a]±0.013	14.815[d]±0.612
Co(mg/kg)	0.002[a]±0.001	0.005[a]±0.001	0.002[a]±0.001	4.573[b]±0.539	0.015[a]±0.002	7.307[c]±0.789	0.005[a]±0.001
Cr(mg/kg)	5.447[a]±0.753	8.523[a]±0.958	18.353[b]±1.838	115.78[e]±3.71	24.58[c]±1.05	78.59[d]±2.636	7.367[a]±0.130

A= Soil near SPDC well head-Ikot Ada Udo, B= Tanker loading point, C=Crude oil distillation point, D=Auto-mechanic shop soil-Ikot Aba, E= NNPC depot, F= Auto-mechanic shop soil-Atekong, G=Diesel Depot-Bogobiri. Mean ±SD, Means in same row with the same letter are not significantly different from each other (Duncan Multiple Range test, P<0.05).

Table 6: Inter-location comparison of mean THC and heavy metal concentration of pristine soil samples

Physicochemical parameters of samples	CRD	NQ	UQ	ATM	BOT	EDET
THC (mg/kg)	134.750[c]±l .391	10.350[a]±0.563	11.270[a]±0.260	21.733[b]±0.232	27.346[c]±0.607	31.900°±0.131
Zn(mg/kg)	1I9.56[e]±0.665	36.393[c]±0.586	9.22 l[a]±0.221	61.076[d]±0.156	19.023[b]±0.071	130.500[f]±0.500
Cu(mg/kg)	20.650[e]±0.350	24.750[f]±0.250	1.585[b]±0.187	0.056[a]±0.004	10.017[c]±0.002	10.850[d]±0.150
Fe(mg/kg)	3742.10[c]±50.473	3650.80[c]±l 09.009	3739.40[c]±63.342	264.230[a]±0.873	3217.40[b]±2.500	3715.90[c]±12.519
V (mg/kg)	7.421[d]±0.514	0.117[a]±0.002	0.437[a,b]±0.054	0.546[b]±0.471	0.074[a]±0.005	0.994[c]±0.006
Ni (mg/kg)	10.520[c]±0.432	0.097[a]±0.003	0.102[a]±0.007	0.179[a]±0.004	0.047[a]±0.002	2.279[b]±0.152
Cd(mg/kg)	0.022[c]±0.007	0.008[a,b]±0.002	0.096[d]±0.004	0.020[c]±0.001	0.012[b]d=0.002	0.004[a]±0.001
Pb(mg/kg)	0.058[c,d]±0.002	0.002[a]±0.001	0.083[d]±0.003	0.040[b,c]±0.003	0.057[c,d]±0.004	0.030[b]±0.034
Co(mg/kg)	0.008[d]±0.001	0.005[a]±0.001	0.003[a]±0.001	0.127[c]±0.003	0.003[a]±0.001	0.005[a]±0.001
Cr(mg/kg)	0.161[d]±0.009	0.019[a]±0.003	0.029[b]±0.003	0.058[c]±0.003	0.019[a]±0.004	0.053[c]±0.002

CRD= Calabar road, NQ= Navy quarters, UQ=UNICAL quarters, ATM=Atimbo, BOT=UNICAL botanical garden, EDET=Edem Edet.Mean ±SD, Means with the same letter are not significantly different from each other (Duncan Multiple Range test, P<0.05).

Discussion

Petroleum polluted soils, water and sediments in this study recorded considerable high values of total hydrocarbon. The high values were expected considering the high oil bunkering activities, indiscriminate disposal of spent oil and oil spillage that characterized the sampling sites. The mean THC values for polluted water (63.789 mg/1) and sediment (768.632mg/kg) exceeded the FEPA limit of 10m/l for water and l00mg/kg for sediment respectively. These values indicate gross petroleum pollution. The values obtained for the pristine aquatic ecosystems were below the FEPA limit. Furthermore the THC values for the studied soil ecosystems showed that the mean value of 4312.620mg/kg for polluted soil was also above the recognized biogenic value of 50mg/kg reported by DPR (1991) while that of the pristine was below the limit. The total hydrocarbon values obtained in this study are environmentally significant and indicative of gross contamination which could in turn stimulate a wide variety of environmental issues. Several studies have reported bioaccumulation of hydrocarbon and heavy metal in sediment and in organisms in aquatic ecosystem for a long period after oil spills and related activities (Lim *et al*., 1998; Etesin, 2002; Chindah *et al,* 2004). In this study the mean heavy metal levels in petroleum hydrocarbon polluted aquatic ecosystems were seen to be higher than that of the pristine sites. The mean Pb, Cd, Ni and V levels though higher in polluted water than in pristine water were below the DPR regulatory limits. We attribute these low levels of heavy metal in water to dilution effect and tidal movement. On the other hand, considerable heavy metal levels were observed in underlying sediment samples from the same study locations. Location along the Essene creek which were heavily polluted with crude oil had high levels of Pb, V and Ni. The high concentration of heavy metals recorded in the sediment confirms its absorption property which makes it act as sink and source of pollutant in the aquatic ecosystems (Pekey, 2006). Heavy metals levels in soil obtained in this study show that soil ecosystem polluted with petroleum hydrocarbon had appreciable concentrations as compared to the pristine soil. The levels of Cu and Zn were above the normal content interval but below the maximum allowable limit whereas Ni and V levels exceeded the maximum allowable limit in soil (Kloke, 1980). This finding corroborates other studies (Osuji and Onojake, 2004; Osuji and Adesiyan, 2005; Onojake and Okonkwo, 2011) that have reported enhanced heavy metals in petroleum polluted soil ecosystems in Niger Delta areas in Nigeria. In an event of petroleum pollution of the environment, microbial population is usually the first line of defense (Walker and Colwell, 1973) and the concept of using hydrocarbon utilizing microorganisms as indicator of hydrocarbon pollution has been supported by several studies (Hood *et al.,* 1975; Walker and Colwell, 1976). In this study, bacteria density (culturable heterotrophic and hydrocarbon utilizing bacteria) was greater in petroleum polluted soil, water and sediments than in their pristine counterpart. The results corroborate those of Piehler *et al* (2002), Syvokiene and Micheniene (2004) and Youssef *et al* (2010) who reported greater bacterial abundance and high proportion of hydrocarbon utilizing bacteria in petroleum polluted sites than in non polluted areas. Indicator organisms are typically used to demonstrate the potential presence or absence of groups of pathogens in samples. In this study, total coliforms and faecal coliform counts were determined from soil, water and sediment samples from both pristine and petroleum hydrocarbon polluted ecosystems. A considerable population density of total coliforms and faecal coliforms was recorded indicating input of faecal matter into the aquatic ecosystem. Faecal coliform level in the polluted and pristine water studied exceeded the optimal average count of 100 cfu/100 ml for freshwater while some locations had faecal coliform count exceeding l000cfu/lOOml for bathing water (WHO, 2003). Generally, total coliform levels were lower in sediment samples. This may probably be due to the dissolution of faecal matter in water with less sedimentation. This result corroborates the high level of human presence and activities that characterized the studied locations and the likelihood of direct defaecation into the water body. This high level of faecal bacteria contamination may be due to the fact that organic nutrient present within the faeces provided a favourable environment for the growth or survival of faecal bacteria (Davies *et al.,* 1995). Total coliform levels in the studied soil ecosystems were high with relatively low faecal coliform counts. The result reflected non pollution with human faecal matter but rather the few faecal coliform count recorded may have been of animal origin. A greater percentage of bacteria isolated from petroleum hydrocarbon polluted ecosystems in this study were tolerant to the seven heavy metals (Pb, Mi, Cr, Cd, Co, Cu and V) tested than those from the pristine ecosystems. The differences in tolerance rate were statistically significant (p 0.000l). In addition to the observed differences, bacteria from petroleum hydrocarbon polluted ecosystems were able to tolerate multiple heavy metals (MHT5, MHT6 and MHT7) than those from the pristine ecosystems. This difference is due to the selective pressure from the metal content of the growth environment. Microorganisms have evolved several mechanisms to

tolerate the uptake of metal ions in other to survive heavy metal toxicity. This mechanisms include surface binding or reduced uptake, increased efflux, intracellular sequestration, enzyme detoxification and active transport (Laddaga *et al.,* 1985; Summers, 1986; Nies, 1992; Misra, 1992; Diels *et al*., 1995; Bruins *et al.,* 2000). A high tolerance rate of bacteria isolates from polluted ecosystems to heavy metals particularly nickel, vanadium and chromium which are known to be associated with petroleum (Osuji and Onojake, 2004; Chindah *et al.,* 2009) suggests that petroleum hydrocarbon pollution of the ecosystem could select for bacteria community tolerance to these metals with co-occurrence of resistance to antibiotics. Bacterial heavy metal cross-resistance has been reported by several authors. Dugal and Gangawane (2012) reported cross-resistance to zinc exhibited by cadmium-resistant *Pseudomonas* species isolated from heavy metal contaminated soil. The heavy metal tolerant bacteria isolates in this study were also found to be resistant to antibiotics. Though the antibiotics resistance rates among isolates from petroleum polluted ecosystems were higher than that of isolates from the pristine ecosystems, the trend was marginal. This suggests that other factors such as the use of antibiotics in agricultural practices (Cabello, 2006) or direct human impact may have contributed to the observed antibiotics resistance among isolates from the pristine ecosystem. We could not establish a direct link or correlation between resistance to a specific antibiotic and a particular heavy metal possibly because we studied a mixed population of bacteria from different geographical sites and habitats. However, studies have shown relationship between tolerance to some heavy metals and multiple antibiotic resistance among bacteria species. Lazar *et al* (2002) in their studies reported multiple tolerance to high levels of Cd^{2+}, Cu^{2+}, Cr^{3+} and Ni^{2+} among multiple antibiotics resistant *E.coli* strains isolated from polluted waters. Also, Kimiran- Erdem *et al* (2007) demonstrated dual resistance of 100 species of environmental entero-cocci to zinc, iron, cadmium, cobalt, chromium, and some antibiotics. Bacterial dual resistance to heavy metals and antibiotics in contaminated ecosystems in Nigeria has been reported by Oyetibo *et al.* (2010). This dual or co-resistance to heavy metal and antibiotics is made possible because multiple genes encoding for metal and antibiotics resistance are commonly found on the same plasmid or transposons (Summers, 2002). In other cases, dual resistance could be due to single enzyme that functions as efflux pump for multiple metals and antibiotics (Perron *et al.,* 2004; Tokunga *et al*., 2004).

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3/24/2016