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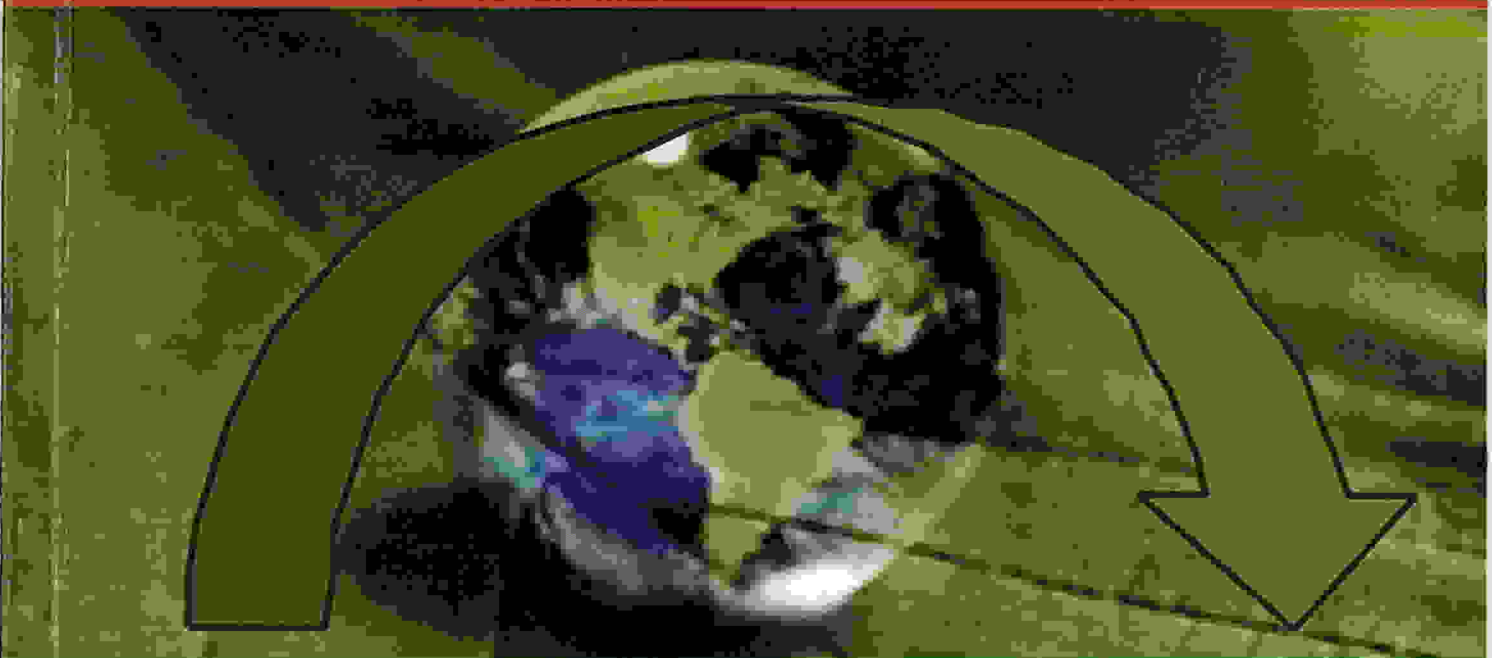

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Environmental Geochemistry and Heavy Metal Assessment in Soils, Surface and Groundwater from Eastern Niger-Delta, Nigeria using Multivariate Pollution Indices

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Abstract

In recent times, there have been increasing interests regarding heavy metal contaminations in the environments, apparently due to their toxicity and perceived persistency within the aquatic systems. Land and water are precious natural resources on which rely the sustainability of agriculture, industrialization and the civilization of mankind. They have been subjected to severe exploitation and contamination due to anthropogenic activities resulting from industrial effluent, refuse dumps, gas flaring, oil spillage and petroleum refining leading to the release of heavy metals into the environment. The results of the analyses indicate a low pH (3.84 – 7.74) and high concentrations of electrical conductivity (28.00 – 752.00), chloride (12.00 – 721.00) and heavy metals in the decreasing order of: Fe > Ni > Cu > Zn > Mn > Cd > V > Co > Pb > Cr > As > Hg. The heavy metal pollution index revealed that the metal pollution in the soil and water ranged from slightly polluted to very highly polluted. The poor sanitary condition coupled with the high degree environmental abuses in terms of oil spillage, gas flaring and industrial effluent in the area are responsible for the low pH, wide range in the concentration of EC, TDS, Chloride, E.coli, total coliform and heavy metals in the soil and water system in the area. Good sanitation, use of well-lined soakaway, treatment of industrial effluent before discharge and putting an end to gas flaring and oil spills are advocated. The use of environmentally friendly techniques such as bioremediation and phytoremediation in remediating the contaminated soil and water in the area is recommended.

Keywords: *Geochemistry; Heavy Metal; Assessment in Soils; Surface; Investigation.*

1.0 INTRODUCTION

Environmental quality indices are a powerful tool for development, evaluation and conveying raw environmental information to decision makers, managers, technician's or for the public (Praveena *et al.,* 2007). Heavy metal refers to any metallic chemical element that has a relatively high density and toxic at low concentrations. It refers to chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. They cannot be degraded or destroyed and can enter into human body through food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation is an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Heavy metals are required in trace amounts by living organism, some are essential for certain metabolic activities while others are essential components of enzymes and pigments in living system. Metals and their compound are indispensible to the industrial, agricultural and technological development of any country (Amadi *et al.*, 2012). Increase in industrial activities such as mining, tanneries, electronics, electroplating and petrochemical have resulted to heavy metal pollution of the environments. Studies have revealed that toxicity resulting from heavy metal discharge into the soil, surface and groundwater exceeds the combined total toxicity of radioactive and organic wastes (Badmus *et al*., 2007).

2.0 MATERIALS AND METHODS

2.1 Study Area Description

The study area lies within the eastern Niger Delta region of Nigeria between latitude 4°40^{I}N to 5°40^{I}N and longitude 6°50^{I}E to 7°50^{I}E (Figure1). It covers parts of Port-Harcourt, Aba and Owerri and a total area of approximately 12,056 km^2. The area is low lying with a good road network system and is drained by Imo, Aba, Kwa-Ibo and Bonny Rivers and their tributaries. The topography is under the influence of tides which results in flooding especially during the rainy season (Nwankwoaloa and Mmom, 2007). The prevalent climatic condition in the area comprises of the rainy (March to October) and dry (November to February) seasons characterized by high temperatures, low pressure and high relative humidity throughout the year. A short spell of dry season referred to as the 'August break' is often felt in August and is caused by the deflection of the moisture-laden current. Due to vagaries of weather, the August break sometimes occurs in July or September.

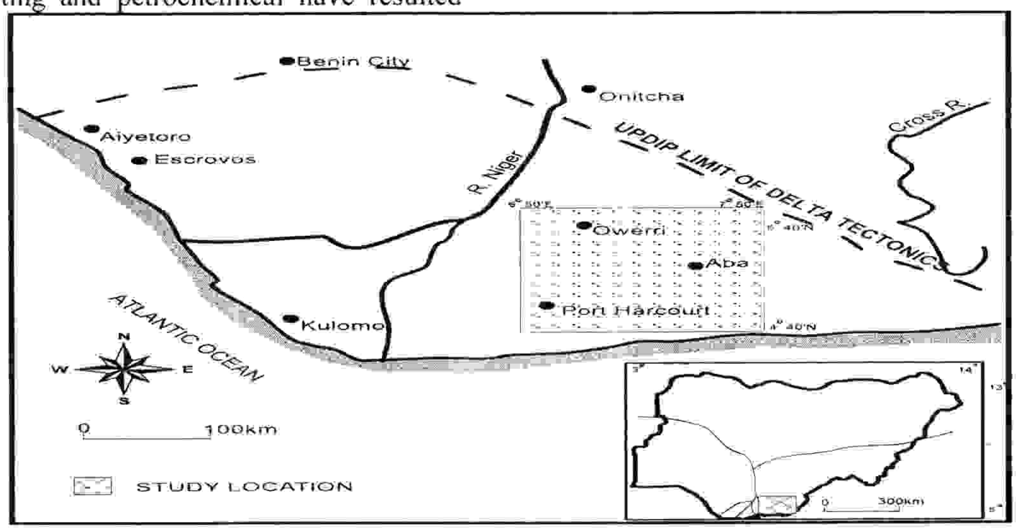

Figure 1. Map of Niger Delta showing the study area.

2.2 Sampling
A total of 85 soil samples, 30 surface water samples and 105 groundwater samples were strategically collected from different parts of eastern Niger Delta along Port-Harcourt-Aba-Owerri axis. The soil samples were taken at every 0.5m interval starting from the top soil to a depth of 2.5m. Sampling tools were washed and dried before the next sample was collected. The collected samples were stored in clean polythene ready for digestion and analysis. Pair of surface and groundwater samples was collected from existing rivers and boreholes in plastic and glass bottles. To each of these water samples in plastic bottles, two drops of concentrated HNO_3 acid were added for homogenization and prevention of adsorption of the metals to the walls of the plastic container and used for the heavy metal determination while the samples in the glass container were used for the determination of the anions. Prior to the collection of the water samples in the various bottles, the physical such as pH, conductivity, turbidity and temperature were measured in the field using pH meter, conductivity meter, turbidiometer and mercury thermometer respectively while the chemical parameters were analyzed in the laboratory using Atomic absorption spectrophotometer (Perkin Elmer, Model No. 2380) method in accordance with American Public Health Association (APHA, 2005).

2.3 Soil Digestion for Heavy Metals Analysis
The accurate measurement of trace metal concentrations is useful in environmental monitoring and research, as many of these elements have been identified as potentially hazardous pollutants. The use closed vessel microwave-assisted digestion systems under high temperature and pressure for acid digestion has now become routine as it allows shorter digestion times and good recoveries, even for volatile elements (Hassan *et al.*, 2007). In addition, it reduces the risk of external contamination and requires smaller quantities of acids, thus enhancing detection limits and the overall accuracy of the analytical method (Valeria *et al.*, 2003). Moreover, they are safer and simpler and provide more controlled and reproducible conditions than hot plate or block digesters (Singh *et al.*, 2002). For the digestion of soil samples, the samples were first dried at room temperature, grounded into powder and sieved with <2 mm sieve and stored in a plastic bag (Amadi, 2011). Then 0.25 g of the sample was added into the reference vessel where 2.5 mL of concentrated HNO3 and 2.5 mL of HF acids were added according to the USEPA Method 3050B for the analysis of heavy metals (USEPA, 1996). The vessel was then inserted into a carousel and into the microwave unit ready for digestion. The system was then programmed using the Ethos D control terminal equipped with software for 6 minutes of microwave digestion at 300 W power and another 5 minutes of microwave digestion using 500W power and then left for automatic ventilation for 10 minutes post digestion period. Afterwards, the digested solution was cooled and filtered using Whatman filter paper No.40 and 100 mL distilled water was added to it and stored in a container ready for analysis. Atomic absorption spectrophotometer (Perkin Elmer, Model No. 2380) was used for the sample analysis.

3.0 RESULTS AND DISCUSSION
The results of the groundwater analysis are summarized in Table 1. A cursory examination of Table 1 reveals that majority of the groundwater samples in the area are characterized by low pH (3.84 – 7.74) and high concentrations of electrical conductivity (28.00 – 752.00), chloride (12.00 – 721.00) and heavy metals in the decreasing order of: Fe > Ni > Cu > Zn > Mn > Cd > V > Co > Pb > Cr > As > Hg. A close look at Table 1 shows wide range with corresponding high mean, standard deviation and variance values for chloride, EC, salinity, silica, sulphate and TDS. This is an indication that there are substantial differences in the

quality/composition of the groundwafer system in the aquifer within the study area. The arithmetic means were determined in order to know the central tendency for the physical, chemical and bacteriological parameters. The deviations in the normal concentration were analyzed using kurtosis test. An evaluation of the symmetry in the value distribution applying the skewness test was carried out and majority of the hydrologic data are positive skewed.

The pH value ranged between 3.84 and 7.74 with a mean value of 5.46 (Table 1). The pH is an important indicator of water quality and the extent of pollution. The mean pH of the groundwater falls below the acceptable range of 6.50-8.50 postulated by Nigerian Standard for Drinking Water Quality (NSDWQ, 2007). The low pH is an indication of acidity in the groundwater from the area and may be linked to acid-rain formation probably caused by non-stop gas flaring-where the gas associated with oil extraction is burnt off into the atmosphere, a method adopted by oil companies operating in the area, as means of getting rid of associated gas in the course of oil exploitation. In developed countries such as United Kingdom and United States of America, 99% of associated gas is used or re-injected into the ground, but in Nigeria, 99% of associated gas is flared, thereby making Nigeria one of the highest gas flarer in the world (World Bank, 2002). Temperature is a measure of the degree of hotness or coldness of a substance. It is an important water quality parameter which plays a major role in the distribution and abundance of organisms. Aquatic organism like other organisms is tolerant of certain ranges of temperature outside which they cannot function (Larry, 1995). Many biological processes in water are known to be influenced by changes in environmental temperature and chemical substances dissolve more readily as temperature increases, unlike most gases which become less soluble as temperature rises (Wooten, 1992).

Table 1. Statistical Summary of the Groundwater data from Eastern Niger Delta

Parameters (mg/l)	Range	Minimum	Maximum	Mean
Arsenic	0.015	0.001	0.016	0.007
BOD	5.03	3.20	8.23	5.60
Cadmium	0.12	0.07	0.19	0.14
Calcium	116.30	2.00	118.30	46.53
Cobalt	0.08	0.00	0.08	0.03
Chloride	709.00	12.00	721.00	275.20
Chromium	0.09	0.02	0.11	0.07
Copper	1.15	0.03	1.15	0.08
COD	5.18	7.80	12.98	10.60
E.Cond(μs/cm)	726.00	28.00	752.00	254.00
EC(cfu/100ml)	18.00	0.00	18.00	6.00
Iron	6.82	0.05	6.87	0.62
Lead	1.07	0.02	1.09	0.08
Manganese	0.77	0.01	0.78	0.19
Nickel	0.03	0.01	0.40	0.28
Nitrate	63.97	0.03	64.00	17.82
Ph	3.90	3.84	7.74	5.46
Strontium	3.59	0.91	4.50	3.02
TC(cfu/100ml)	48.00	0.00	48.00	15.00
Zinc	10.06	0.03	10.09	0.70

BOD-biochemical oxygen demand; COD-chemical oxygen demand; TC-total coliform; E.Cond-Electrical Conductivity EC-Escherichia coli; TSS-total suspended solid.

The electrical conductivity (EC) is a valuable indicator of the amount of materials dissolved in water. Its value ranged between 28.00 µs/cm to 752.00 µs/cm with an average value of 254.00 µs/cm (Table 1). The conductivity values are below the acceptable limit of 1000.00 µs/cm for safe water (NSDWQ, 2007). The concentration of Escherichia coli (E.coli) ranged between 0.00-18.00 cfu/100ml with an average value of 6.00 cfu/100ml while total coliform (TC) varied from 0.00-48.00 cfu/ml and a mean value of 15.00 cfu/ml (Table 1). Their presence in groundwater is an indication of faecal contamination. The practice of unlined pit-latrine and soakaway in shallow aquifer region exposes the groundwater to faecal contamination and good sanitary system is advocated for the area due to the vulnerability of its aquifer system. Faecal contamination causes water-borne diseases such as cholera, typhoid, meningitis and diarrhea as well as morbidity and mortality among children. It also causes acute renal failure and hemolytic anemia in adults (Khadse *et al.*, 2009).

Surface water in the area were sampled and analyzed for relevant physical, chemical and microbial analysis (Table 2). Some of the rivers in the area have witnessed various degree of pollution by oil spills and industrial effluent without any form of treatment. The results when compared with the Nigerian Standard for Drinking Water Quality (NSDWQ, 2007) and subjected to geostatistical techniques such as Heavy Metal Pollution Index (HMPI) shows that both the surface and groundwater in the area have experienced varying degree of pollution and needs treatment before used for domestic purposes. During the fieldwork, it was observed that the surface water, especially those in the creeks contains floating oil, ranging from thin sheen to thick dark oil. This has also led to the extinction of many species of fishes as well as destruction of fishing habitat, as fishermen in the area are stripped of their viable profession. In parts of Ogoni and Eleme axis, hydrocarbon was found in soils at depth of about 4.0 m and because there is no continuous clay layer across the entire Eastern Niger Delta, the hydrocarbon pollution has reached the shallow groundwater table as refined crude oil was recovered from sampled public wells in the area.

3.1 Heavy Metal Pollution Index (HMPI)

Heavy Metal pollution index (HMPI) is a method of rating that shows the composite influence of individual parameters on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance individual quality considerations. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the water (Amadi, 2011). It is also a combined physio-chemical and microbial index which makes it possible to compare the water quality of various water bodies (Tamasi & Cini, 2004; Prasad & Kumari, 2008). It has wide application and it is used as the indicator of the quality of sea (Filatov. *et al.*, 2005) and river water (Amadi *et al.*, 2013; Lylko *et al.*, 2001; Mohan *et al.*. 1996), as well as drinking water (Nikoladis *et al.*, 2008; Amadi *et al.*, 2010). The HMPI represents the sum of the ratio between the analyzed parameters and their corresponding Nigerian Standard for drinking water Quality values (Table 3 and 4). Water quality and its suitability for drinking purpose can be effectively studies using the metal pollution index concept (Amadi *et al.*, 2012). The results of the calculated HMPI indicates that the surface and groundwater regimes in the area are polluted by each of the analyzed heavy metals in variable degree ranging from slightly polluted to very highly polluted (Tables 3 and 4). The poor sanitation in the area coupled with the high class environmental abuses in terms of oil spillage, gas flaring and industrial effluent are the possible sources of the observed heavy metals in the water system in the area. Some rivers in the area as well as soils were abandoned due to pollution by oil spillage (Plates 1and 2) and the natural ecosystem destroyed.

$$MPI = \sum_{i=1}^{n} \left[\frac{C_i}{(MAC)_i} \right]$$

where: C_i: mean concentration
MAC: maximum allowable concentration

Soil quality determines the sustainability and productivity of agro-ecosystems. The soils in the area are largely defined by their acidity (pH: 3.17–7.12). The acidity is partly natural, being a characteristic of the soils of Sombriero–Deltaic sediment and partly anthropogenic due to prolonged effect of gas flaring and oil spillage in the region. The low nutritional status (organic matter content) of the soils due to the low pH (mean value 5.20), is an important constraint on the capacity of the soils for agricultural use, hence the use of agro-chemical. The high concentration of total organic carbon, total hydrocarbon concentrations (THC) and heavy metal contents found in the soil are attributed to oil spillage in the area. The excessive use of agro-chemical in intensive agriculture has led to the enrichment of soil in the area with heavy metal and reduced the soil cohesiveness leading to an increase of erosion. Their enrichment is a function of soil pH, grain size, organic matter, cation exchange capacity (CEC) and hydraulic conductivity (Nachtergaele *et al.,* 2002).

Table 2: Statistical Summary of Soil and Surface Water from Eastern Niger Delta.

Parameters	Soil (mg/kg)		Surface Water (mg/l)	
	Range	Mean	Range	Mean
pH	3.17– 7.12	5.20	5.32–7.30	6.10
TDS	10.80–78.50	46.50	484.00–1524.00	1340.20
Conductivity	17.00–187.00	120.70	28.00–2950.00	1410.00
Na	146.30–398.10	265.60	22.32–328.60	230.40
Cl	24.00–400.00	160.50	107.00–1315.00	816.80
Fe	20.33–252.72	232.40	0.01–2.46	0.92
Mn	0.42–108.00	21.25	0.01–0.08	0.05
Zn	1.62–20.94	10.98	0.02–0.80	0.45
Cu	1.46–15.30	9.70	0.03–1.28	0.82
Cr	0.06–1.86	0.88	0.02–0.14	0.76
Cd	1.08–24.58	10.76	0.07–0.20	0.13
Ni	0.50–18.24	11.62	0.01–0.15	0.82
V	0.44–20.56	12.58	0.005–0.018	0.011
Pb	0.32–1.86	0.78	0.01–0.14	0.06
Hg	0.03–0.07	0.05	0.002–0.005	0.003
As	0.01–0.07	0.03	0.001–0.004	0.002
TOC	15.10–84.65	43.30	0.10–2.40	1.70
THC	2.98–39.80	14.18	0.68–5.24	1.06
BOD	1.56–38.90	17.64	1.00–5.80	3.78
COD	4.25–51.05.	23.96	0.20–11.20	4.94
TBC	1.0×10^{2}–6.0×10^{5}	2.5×10^{3}	0.00–715.00	60.00

Total Bacteria Count: Soil (cfu/g), Water (cfu/l); THC-total hydrocarbon content; TOC-total organic carbon; BOD-biochemical oxygen demand; COD-chemical oxygen Demand.

Table 3: Calculated metal pollution index for Groundwater in the area.

Parameters (mg/l)	C_i	MAC_i	MPI Value	Rating
Arsenic	0.007	0.01	0.70	Lightly polluted
Cadmium	0.11	0.02	5.50	Highly polluted
Cobalt	0.02	0.01	2.00	Moderately polluted
Chromium	0.07	0.05	1.40	Moderately polluted
Copper	0.8	1.00	1.90	Moderately polluted
Iron	0.62	0.30	2.10	Moderately polluted
Lead	0.08	0.01	8.00	Highly polluted
Manganese	0.19	0.20	0.95	Lightly polluted
Mercury	0.003	0.001	3.00	Moderately polluted
Nickel	0.28	0.02	14.00	Very highly polluted
Zinc	0.17	3.00	1.57	Moderately polluted

< 0.01= Very lightly polluted; 0.01-1.0= Lightly polluted; 1.0-5.0= Moderately polluted; 5.0-10.0= Highly polluted; > 10.0= Very highly polluted

Table 4: Calculated metal pollution index for Surface Water in the area

Parameters (mg/l)	C_i	MAC_i	MPI Value	Rating
Arsenic	0.002	0.010	1.000	Lightly polluted
Cadmium	0.130	0.020	6.500	Highly polluted
Chromium	0.040	0.050	0.800	Lightly polluted
Copper	0.410	1.000	0.410	Lightly polluted
Iron	0.110	0.300	0.370	Lightly polluted
Lead	0.060	0.010	6.000	Highly polluted
Manganese	0.016	0.200	0.080	Lightly polluted
Mercury	0.003	0.001	3.000	Moderately polluted
Nickel	0.028	0.020	1.400	Moderately polluted
Zinc	0.160	3.000	0.046	Lightly polluted

< 0.01= Very lightly polluted; 0.01-1.0= Lightly polluted; 1.0-5.0= Moderately polluted; 5.0-10.0= Highly polluted; > 10.0= Very highly polluted

Plate 1: Contaminated river in the area.

Plate 2. Contaminated soil in the area.

3.2 Contamination Factor (CF) and Geo-accumulation index (Igeo)

Contamination factor (CF) and geo-accumulation index (Igeo) are quantitative check used to describe concentration trend of metals in soils. Contamination factor (CF) is a quantifier of the degree of contamination relative to either the average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area (Tijani *et al.*, 2004). It is expressed as:

$$CF = C_m / B_m$$

Where C_m is the mean concentration of metal m in soil and B_m is the background concentration (value) of metal m, either taken from the literature (average crustal abundance) or directly determined from a geologically similar material. Geo-accumulation index (Igeo) as proposed by Mueller (1979) and cited by Lokeshwari and Chandrappa (2006) have been widely used to evaluate the degree of heavy metal contamination in terrestrial and aquatic environments as expressed:

$$I_{geo} = \ln [C_m / 1.5*B_m]$$

Where C_m and B_m are as defined above, while 1.5 is a factor for possible variation in the background concentration due to lithologic differences. The Igeo is classified into seven descriptive classes as follows: <0 = practically uncontaminated; 0 – 1.9 uncontaminated to slightly contaminated, 2.0 – 3.9 = moderately to highly contaminated, 4.0 – 5.9 = highly to very strongly contaminated, 6.0 and above = very strongly contaminated (Table 5). The latter is an open-end class that is indicative of all values greater than 5, and Igeo of 6 is said to be indicative of 100-fold enrichment of a metal with respect to the baseline value (Mueller, 1979). The elevated concentration of the heavy metals showed a positive correlation with low pH and as well as high organic matter and clay content (Figure 6).

The present study has revealed that hydrocarbon pollution in the study area is widespread and worrisome as soil, groundwater and surface water have varying degree of pollution arising from benzene, a known carcinogen and a major component of the hydrocarbon (Achi, 2003). Diseases such as respiratory disorder, asthma and skin problem are the footprint of long term exposure to gas flaring and oil spills in the area. It has also been ascertained from the study that the environmental, socio-economic and health problems ravaging the host communities is due to pollution arising from hydrocarbon exploration, exploitation, refining and marketing.

Table 5: Metal contamination factor and geo-accumulation index of metals in soil from the dumpsite.

Parameters	C_m	B_m	CF	Igeo	Overall summary of contamination level
Cd	1.40	0.15	9.33	1.828	Moderately contaminated
Mn	18.12	95	0.025	0.842	Slightly contaminated
Cu	12.86	70	0.184	1.596	Moderately contaminated
Cr	1.34	12.2	0.011	2.920	Highly contaminated
Ni	2.94	80	0.037	3.709	Highly contaminated
Pb	1.08	1.6	0.068	3.101	Highly contaminated
As	0.05	3.0	0.010	1.007	Slightly contaminated
Zn	16.04	132	0.122	0.913	Slightly contaminated
Co	10.58	23	0.460	1.181	Slightly contaminated

CF- contamination factor;
Igeo- Index of Geo-Accumulation;
C_m- mean concentration of the metal in the soil;
B_m- average crustal abundance (background value) in an uncontaminated soil, adopted from (Dineley *et al.*, 1976).

Table 6: Pearson Correlation Coefficient Matrix for Heavy Metals in Soils from the Dumpsite

	Cd	Mn	Cu	Cr	Ni	Pb	Ar	Zn	Co	pH	OM	C + S
Cd	1.000											
Mn	0.109	1.000										
Cu	0.065	-0.112	1.000									
Cr	0.252	0.041	0.141	1.000								
Ni	0.354	0.678**	0.101	0.093	1.000							
Pb	0.327	-0.113	0.818**	0.008	0.334	1.000						
As	0.080	0.199	0.249	0.118	-0.333	0.090	1.000					
Zn	0.153	0.205	0.788**	-0.044	0.534*	0.637**	0.110	1.000				
Co	0.433*	0.084	0.211	0.208	0.360*	0.016	0.186	0.127	1.000			
pH	0.106	-0.112	0.024	0.091	0.119	0.095	0.112	0.085	0.101	1.000		
OM	0.598*	0.724**	0.028	0.284	0.284	0.195	0.220	0.054	0.066	0.841*	1.000	
C + S	0.045	0.293	0.123	0.031	-0.023	0.545*	0.151	0.049	0.137	0.521	-0.192	1.000

**Correlation is significant at the 0.01 level (2-tailed);
*Correlation is significant at the 0.05 level (2-tailed);
OM-Organic Matter; C + S-Clay + Silt.

Apart from the high concentration of benzene already established, crude oil also contains toluene, ethylbenzene and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). These compounds are known carcinogens and therefore dangerous to health (Achi, 2003). The negligence by the authorities concerned in cleaning up oil spill enables rainfall to wash the oil away into neighbouring farmlands and rivers while some infiltrates into the shallow groundwater system. This explains why we have high concentration of total hydrocarbon content (THC) in the soil, groundwater and surface water samples analyzed. The study has also confirmed that the heavy metals in the crude oil are the major sources of heavy metal pollution in the environment (soil, groundwater and surface water). Hydrocarbon pollution is more pronounced in the southern part (Port-Harcourt area) than the northern part (Owerri area) because the southern portion has more creeks, oil wells, flow station, oil pipeline and gas flaring point than the northern portion (Amadi and Nwankwoala, 2013). Geologically, the southern part is composed of mainly friable sand with minor clay intercalation that is not continuous while in the northern part, the clay layer is continuous as the clay layer from Ogwashi-Asaba Formation and Afam clay are encountered and this serves as impervious layer and natural attenuation mechanism for pollutant migration.

Since the water level in the study area is shallow and natural attenuation mechanism such as advection, adsorption and dispersion are entirely absent due the local geology (Benin Formation that is porous and permeable formation) by implication, the soil, surface and groundwater in the area are in serious danger once there is a pollution such as oil spill, as it will easily infiltrate downward. The Department of Petroleum Resources of Nigerian National Petroleum Cooperation (NNPC) estimated 1.89 million barrels of petroleum were spilled into the Niger Delta between 1976 and 1996 out of a total of 2.4 million barrels spilled in 4,835 incidents (Daily Trust, 2008). The United Nations Development Programme (UNDP, 2011), report states that there have been a total of 6,817 oil spills between 1976 and 2001, which account for a loss of three million barrels of oil, of which more than 70% was not recovered (Daily Trust, 2008). The Nigerian National Petroleum Corporation places the quantity of petroleum spilled into the environment yearly at 2,300 cubic metres with an average of 300 individual spills annually (Tell Magazine, 2008).

However, because this amount does not take into account "minor" spills, the World Bank argues that the true quantity of petroleum spilled into the environment could be as much as 10 times the officially claimed amount (Tell Magazine, 2008). It also reported that between 9 million and 13 million barrels of crude oil have been spilled in the Niger Delta since 1958. By multiplying this number by over 50 years of oil exploration in the region, it can be imagined what the host environment may look like. The accumulation effect is what has left crude oil in soil at greater depth while it freely floats in wells in the area. Surface water and vegetation also had their own share as the heavy rainfall lead to oil spill been washed away into the farmlands and rivers. When oil reaches the root zone, the crops and other plants begin to experience stress and later die, while those that survive has very low yield unlike the non-impacted farmlands and this has become a routine observation in the study area. This problem is further compounded by the use of aquifers and rivers in the area as a repository for human and industrial waste and this lead to the generating a contamination plume map for the area.

The UNEP (2011) investigation of parts of the area revealed that all air samples analyzed, benzene was found with concentration ranging from 0.156 to 48.3 μg/m^3 and this is about 10 times higher than the maximum permissible limit of World Health Organization (WHO, 2006) and the United States Environmental Protection Agency (USEPA, 1998) and attributed the cancer epidemic in the area to the accumulated effect of long term exposure to benzene.

The findings underline that the people of Eastern Niger Delta, especially host communities to oil installations are exposed hydrocarbon pollution either in the air through long term non-stop gas flaring, in drinking water through oil spill and acid rain, or through direct contact with contaminated soil, sediments, fishes, plants and surface water. Since oil exploration and exploitation has been going on in the area for the past 50 years, it is a possibility that many people from the host communities have lived with chronic oil pollution throughout their lives. A schematic illustration of the devastating effects of oil spills and gas flaring on the environment are shown in Figures 2 and 3 respectively. According to UNEP, (2011), it will take several years to clean-up the polluted soils in Ogoniland. The present study reveals that the heavy metal pollution is not limited to the soil, but extends surface water, groundwater and rani-water (Fig.4).

The pH concentration is generally low and it could be attributed to acid rain arising from the long term non-stop gas flaring and indiscriminate oil spills that have characterized the area. Heavy metal concentrations are in the order of: Fe > Ni > Cu > Zn > Mn > Cd > V > Co > Pb > Cr > As > Hg and this similar trend were observed in other geomaterials analyzed. It has been established from this study that the heavy metal pollution is more on soil, followed by rainwater, groundwater and surface water respectively based on their concentration trend. Similar trend was observed in the vicinity of dumpsites in the area. It is believed that crude oil activities and leachate from dumpsite are the possible sources of these pollutants in the aquifer and groundwater system in the area. Solution of these gases in the rainwater under relatively high partial pressure of the gases raises the concentration of the bicarbonate and sulphate ions in the antecedent rainwater that subsequently recharges the groundwater. The paucity of carbonate in the soil and water samples can be attributed to the intense biochemical reaction in the soil and geologic materials especially near gas flaring points could have led to the dissolution of carbonate rich materials and more concentration of bicarbonate ions.

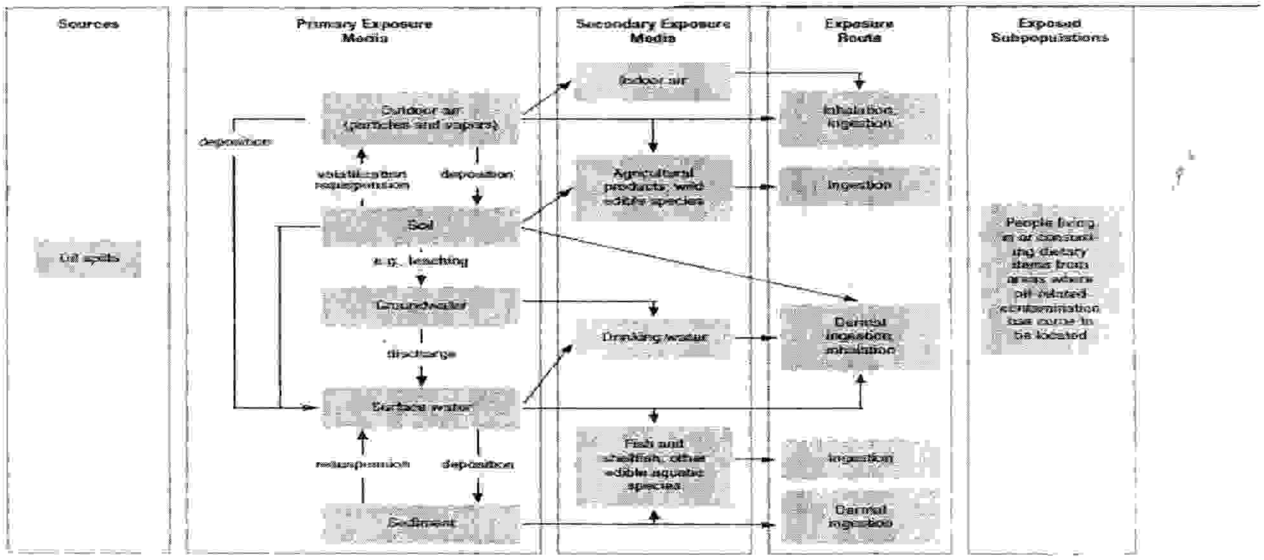

Figure 2. Schematic diagram showing the impacts of oil spills on the environment (UNDP, 2011).

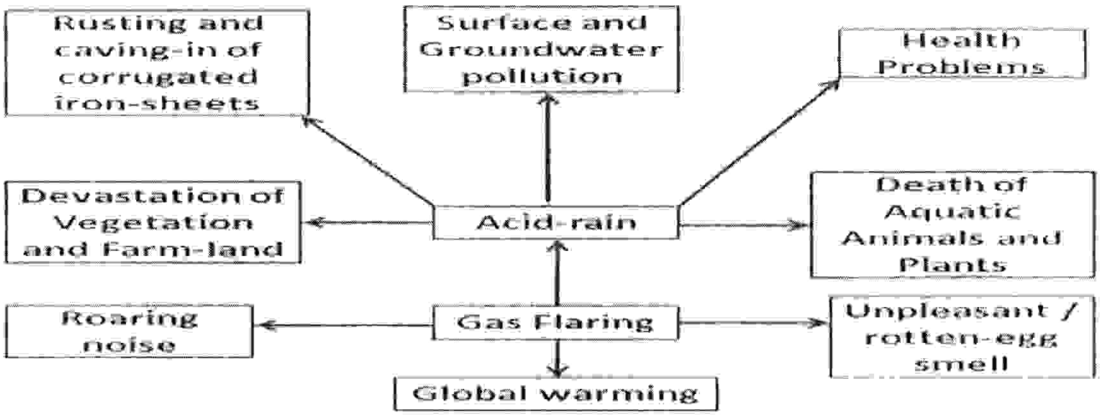

Figure 3. Schematic illustration of the impacts of gas flaring on the environment (Amadi, 2013).

The general pattern of distribution of the geochemical constituents with high values in the vicinity of gas flaring and flow stations and low values at distances far away from the hot spot (Figures 4 and 5) clearly indicate that the enrichment of the ions are associated with the envisaged anthropogenic activities domiciled in the area. Hydrocarbon exploration, exploitation, refining and marketing has brought high class environmental degradation to the area and the footprint are shown by the hydrocarbon pollution of soil, sediments, air, groundwater, surface water and rainwater in the area. Fishing, farming and other socio-economic activities in the area has been crippled by same hydrocarbon pollution while the natural mangroves and vegetation has also been destroyed by the same culprit. The field observations and scientific investigation found that hydrocarbon pollution in the study area is widespread and multi-dimensional in nature as many components of the environments such as land, air and water are polluted and this has had its own share on the health of the people.

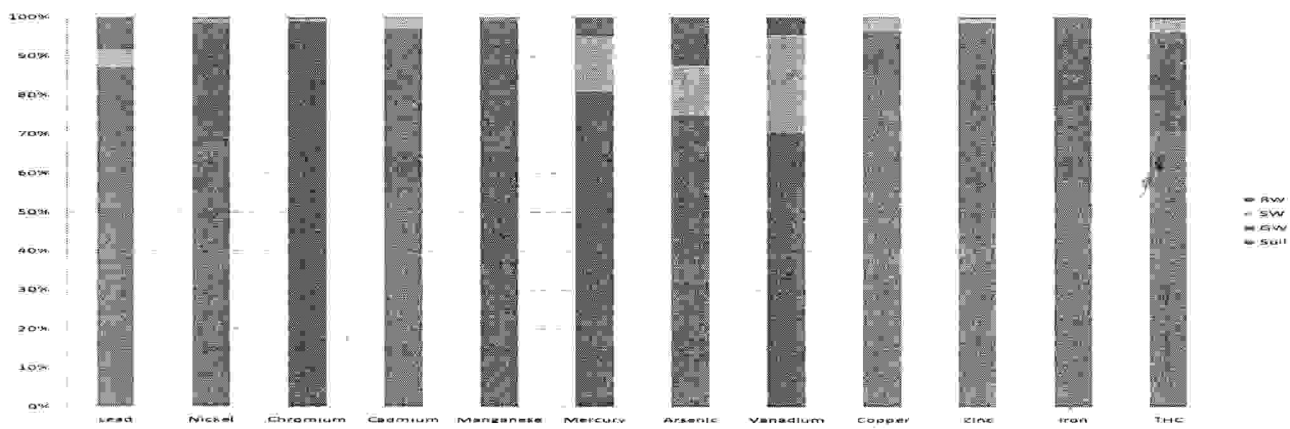

Figure 4: Component bar chart showing the relationship between Heavy Metal Concentration in Soil, Groundwater, Surface Water and Rainwater.

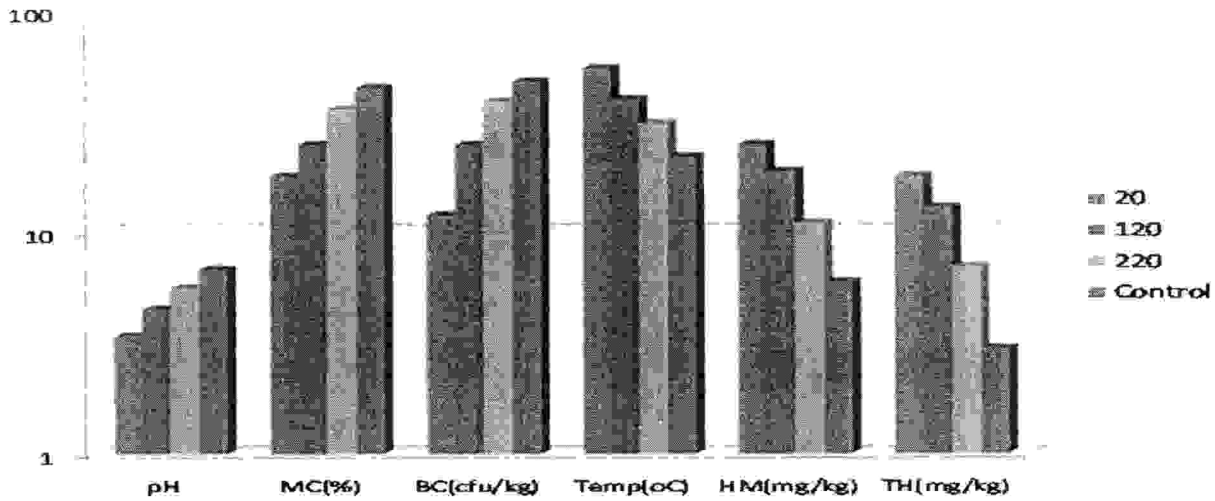

Figure 5: Multiple Bar Chart Showing the Relationship between Concentration of pH, Moisture Content (MC), Bacteria Count (BC), Temperature, Heavy Metals (HM) and Total Hydrocarbon (TH) in Soil and Distance from a Gas Flaring Station.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The environmental situation in eastern Niger Delta, Nigeria with emphasis on heavy metal pollution on soil and water resources was investigated in the present study. The study revealed the area is characterized by low pH, high content of electrical conductivity, total dissolved solids, chloride, total coliform, E.coli and heavy metals in the decreasing order of: Fe > Ni > Cu > Zn > Mn > Cd > V > Co > Pb > Cr > As > Hg. These are the signatures of decades of environmental abuses and neglect due to anthropogenic activities resulting from industrial effluent, refuse dumps, gas flaring, oil spillage and petroleum refining. The heavy metal pollution index showed that the level of metal pollution in the soil and water ranged from slightly polluted to very highly polluted. Good sanitary habit, use of well-lined soakaway, treatment of industrial effluent before discharge and eradication of gas flaring and oil spills are advocated. The use of environmentally friendly techniques such as bioremediation and phytoremediation in remediating the contaminated soil and water in the area is recommended.

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