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Research article

Petroleum Hydrocarbon Contamination of the Environment: A Case Study

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ABSTRACT

Hydrocarbon contaminated soils were investigated to assess the level of pollution. The physicochemical properties, trace metals and total petroleum hydrocarbon content of soil samples were determined in the laboratory by extraction and spectrophotometric techniques. Total petroleum hydrocarbons levels in soils under investigation were measured as high as 9.84×10^3mgkg^{-1} for soils under investigation. Multivariate statistical method was employed to evaluate the level of pollution of hydrocarbon contaminated soils. Principal component analysis carried out on soil showed that the eigenvalues of the two first principal components represent up to 67.2% of the total variance. A positive correlation of the first principal component with Cu, Cr, V, cation exchange capacity and total petroleum hydrocarbon shows pollution from oil spillage while correlation of the second principal component with Cr, Fe, V and DO shows both oil pollution and allochthnous inputs Cluster analysis shows that at about 68.56% similarity, all variables reveal a common source.

Keywords: Hydrocarbons, Multivariate analysis, allochthnous, principal components, Niger Delta

1. Introduction

Hydrocarbon contamination of soils and the mangrove ecosystem has become a wide spread global environmental issue since the discovery of crude oil and the use of its refined products as a source of energy. Crude oil and fuel spills are among the most extensive and environmentally damaging pollution problems constituting potential threats to human health and ecosystems.

One of the methods of knowing whether an area is contaminated or polluted is by estimating the total petroleum hydrocarbon content (TPH) of the impacted soil. Hydrocarbon contamination is the most contentious and recalcitrant of oil exploration and exploitation activities which have impacted negatively on arable agricultural farmlands, and in turn affected global food productivity, socio economic activities and human health in general.

Studies by Osuji and Onojake (2004) have shown that in an environment that is completely terrestrial, the penetration and spread of oil in the soil will depend on the nature and topography of the soil environment. However, adverse effects of the oil on soil biota will still 60 depend on the degree or extent of hydrocarbon contamination. Therefore the periodic monitoring, empirical records and analyses of typical and potential pollutants are essential for effective management of the impacted environment (Osuji and Ezebuiro, 2006).

In modern research, different statistical techniques such as the Pearson's correlation matrix, principal component analysis (PCA), cluster analysis (CA), and factor analysis (FA) have been used to evaluate and interpret complex data sets to better evaluate the a variety of environmental pollution sources (Xiaoyun *et al.,* 2010). Some of the recent studies which applied these methods include the work of Zhou *et al.,* (2007) and Boyacioglu and Boyacioglu (2007) who used the PCA and CA to classify the sampling sites and to identify the latent pollution source. These researchers showed that these methods could be used to assess the relationships between variables and possible pattern in distribution of measured data. Cluster analysis (CA) and factor analysis (FA) can be used to classify metals from different sources based on their similarity and to identify homogeneous groups of variable with similar properties. The application of different multivariate statistical techniques, such as principal component analysis (PCA) and factor analysis (FA), helps in the interpretation of complex data matrices to better understand the environmental and ecological status of the studied systems.

This study is aimed at using multivariate techniques which includes principal component analysis (PCA), Cluster analysis (CA) and Pearson's correlation matrix to describe and interpret the variation in the physicochemical parameters, total petroleum hydrocarbon and some trace metals of the soil within an oil spill contaminated site in Niger Delta, Nigeria in order to ascertain the level of pollution.

1.1 Multivariate Statistics

1.1.1 *Principal Component Analysis (PCA)*

PCA was performed on the values of the physicochemical properties, total petroleum hydrocarbons and metal content of the soil samples using Minitab 15.0 statistical analysis software. Principal component analysis (PCA) is one of the best statistical techniques for extracting linear relationships among a set of variables. Principal components are the linear combinations of original variables and are the eigenvectors. The Varimax rotation distributes the PC loading such that their dispersion is maximized by minimizing the number of large and small coefficients (Pradhan *et al.,* 2009). The PCA was applied in analyzing the data from an oil spill site.

1.1.2 Correlation Analysis

Pearson's correlation analysis was adopted to analyze and establish physicochemical characteristics, total petroleum hydrocarbons and inter-metal relationship of an oil spill contaminated soil. Correlation analysis is used to describe the degree of relationship between two continuous variables in a data set. The value ranges from −1 to +1. A positive correlation means that relatively high value on one variable will also have a high value on the other variable, and low value on one variable will also show low value on the second variable. On the other hand, a negative correlation means that relatively high value on one variable are paired with relatively low value on the other variable. A correlation of zero implies an absence of a correlation and there is no relationship between the two variables (Onojake *et al.,* 2011).

2. Materials and Methods

2.1 Description of study site

The study site Bodo city (figure 1) geographically lies within latitude 6° 73 N and longitude 5° 32 - 5°34E in Gokana local Government Area of Rivers State, Nigeria. Bodo creek complexes are vulnerable to crude oil pollution due to the networks of oil pipelines connecting Bodo west located in the mangrove swamp. This is a source of oil leakages to the environment. As the time of sampling, the total quantity of crude oil spilled into the environment was not known.

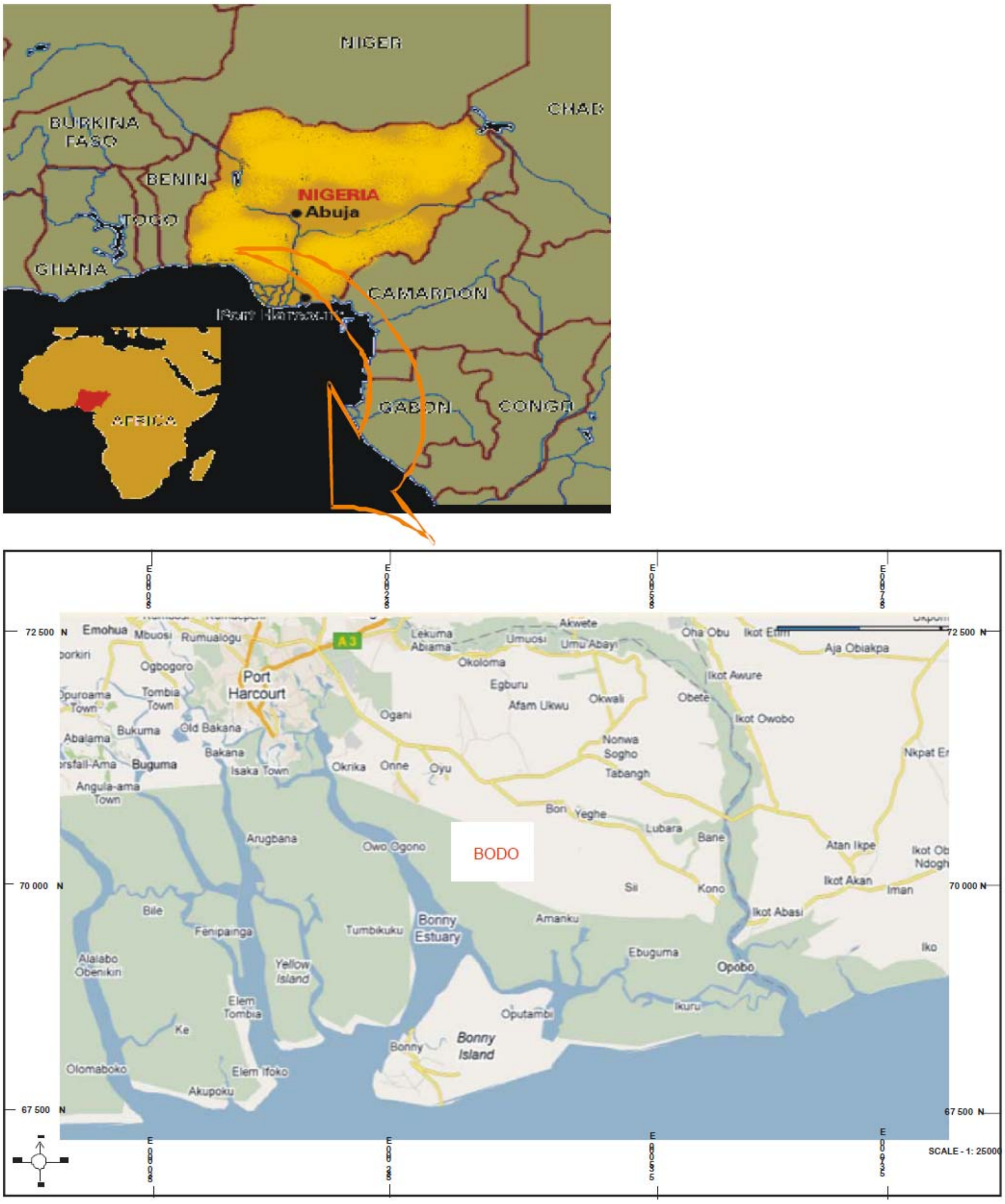

Figure 1. Map of study area showing Bodo city in Niger Delta, Nigeria.

2.2 Field Reconnaissance and sampling

Field reconnaissance and sampling was carried out in order to delimit the area to be sampled. Sampling was carried out using the grid method reported by Osuji and Onojake (2004). Twenty soil samples were collected from surface and subsurface at the depth of 0 to 15 cm and 15 to 30 cm respectively. The soil samples were transferred into an acid-washed polyethylene bags and taken to the laboratory for analysis.

2.3 Physicochemical analysis

The pH, Conductivity, Turbidity, Dissolved oxygen, and salinity of soil samples were measured using the (U- 10, Horiba, LA-920, Kyoto, Japan) a state of the art instrument for simultaneous multi-parameter measurement. Soil samples were dried in an air circulation oven at a temperature of 60°C until a constant dry weight is achieved. The dried samples were crushed and sieved through a 63mm steel sieve attached to an electronic shaker to obtain a uniform particle size. Ten grams of the homogenous samples was weighed into clean, dry beakers and 20mL of de-ionized water was added and the slurry was stirred vigorously.

2.4 Spectrophotometric analyses

Pre extraction of cations in the soil samples was carried out with dithionite-126 citrate carbonate according to Hessler method as described by Osuji and Onojake (2004). Concentrations of As, Cu, Cr, Fe, Pb, Ba, Ni, V, Hg and cation exchange in the extract were determined using Perkin – 129 Elmer model 2280/2380 atomic absorption spectrophometer. The results are shown in table 2.

2.5 Estimation of Total Petroleum Hydrocarbon (TPH)

Total Petroleum Hydrocarbon (TPH) is defined as the measurable amount of petroleum-based hydrocarbon in an environmental media. GC-FID (EPA Methods 8015) is the most general method for determining hydrocarbons. FID is sensitive to most organic compounds and gives a linear response over a wide range of conditions. The samples were subjected to Gas chromatographic analysis after pre - extraction. This was achieved by using Shimadzu 14B series Gas Chromatograph, equipped with Flame Ionization Detector, 30m × 0.25 mm (fid) film thickness 0.25 μm fused silica capillary columns, coated with methyl silicone. The sample (1 μL) was injected in splitless mode by means of syringe through a rubber septum into the column. Detector (FID) and injector temperatures were kept at 250 and 280°C, respectively. The oven temperature was programmed from 60 to 280°C at 4°C /min with an initial hold time of 1 min and final hold time of 15 mins. Helium at a linear velocity of mL/min was used as carrier gas. The data were collected from retention time: 0-71 minutes

3. Results and Discussion

Results for some physicochemical characteristics and the total petroleum hydrocarbon content of the oil spill impacted site and their unpolluted site (reference) are contained in table 1. The physicochemical properties measured are pH, electrical conductivity, turbidity, salinity and dissolved oxygen. TPH concentrations obtained in this study presuppose a high level of contamination at the affected site. The hydrocarbon levels in soils under investigation were measured as high as $9.84 \times 10^3 \text{mgkg}^{-1}$ for oil spill impacted soils. The value is by far higher than the reference sample (collected 200 meters away from the oil spill site) with hydrocarbon level of 8.40×101 mgkg^{-1}. The measured values for impacted soils far exceed the maximum regulatory limit of 20 ppm for oil and grease contamination on land approved for the petroleum industries in Nigeria (DPR, 1991). The difference in level of total petroleum hydrocarbon for the study site and reference presupposes high level of crude oil contamination at the affected site. High hydrocarbon content causes oxygen deprivation and reduction in gaseous diffusion by the surface film of oil and these usually have far reaching implications for the flora and fauna of the affected area, and hence, soil fertility (Osuji and Ezebuiro, 2006). Also high hydrocarbon content of soils has been known to affect soil physicochemical properties, which in turn affect the agricultural potentials of such soils (Amadi and Dickson, 1993; Ezebuiro, 2004). Oil spillages have been reported to reduce the population density of soil microbes while some might utilize the excess hydrocarbon as an available source of energy, for growth and replication especially resistant strains of heterotrophs which are involved in hydrocarbon degradation (Odokuma and Okpokwasili, 1993).

The pH of soils under study ranged from 6.00 to 6.80. The pH of the polluted soils is drifting toward the acidic range compared to that of the unpolluted sample with a pH of 7.10. These values are within the compliant limit set by regulatory body in Nigeria (DPR, 1999). Electrical conductivity (EC) Electrical conductivity of soils is a measure of the capacity of the soil to conduct or transmit electrical current; it is also an indirect measure of ionic concentration in the soil. EC ranged from 0.03 to 7.67 μScm^{-1} for the impacted soil. Most of these values are greater than the EC of unpolluted site with value of 0.03 μScm^{-1}. The low EC values shows that the salt contents are lower in the oil spill affected site and, therefore, corroborative of the level of contamination. This can be observed from the low and negative correlation of EC and some the metal ions in table 5. EC has a weak positive correlation with turbidity and DO. The changes in EC denote a changing composition of soil, which indicates treatment, may be require for these soils. Also the dissolved oxygen (DO) and turbidity of soil were also altered. These values ranged from 7.30 to 7.90 mg/kg and 200.00 to 596.00 NTU for the impacted soil samples and 8.10 mg/kg and 430.00 NTU for the reference sample. Dissolved oxygen in soil can be depleted as it is used in the oxidation of organic matter thereby reducing its magnitude in soil. This could be attributed to presence of organic matter pollution, and increased microbial activity (respiration) occurring during the degradation of the organic matter in polluted soils.

3.1 Correlation analysis

Pearson correlation analysis was employed for data to evaluate the level of inter-metal association with physicochemical properties of the oil spill impacted soils. The variables used are Cu, Cr, Fe, Ba, Ni, V, CEC, Temp., pH, EC, TURB, DO. The results are shown in Table 5. Some of the heavy metals show positive correlation with each other *e.g.*, Cu/Cr (r = 0.78); Cu/Ba (r = 0.32); Fe/V (r = 0.45); Ni/ V (r = 0.33); this suggests that each paired metals have identical source or chemical phenomena (Sekabira *et al.,* 2010). Some metals also show correlation with the physicochemical characteristics of the oil spill impacted soils. Table 5 shows that the pairs EC/Ni, Turb /Cu, pH/Ba, Turb/CEC, Fe/pH, DO/Fe, TPH/Ni, were significantly correlated suggesting their physicochemical associations, whereas the rest are either weakly or negatively correlated.

3.2 Analysis of variance

Analysis of variance (ANOVA) was done to determine the level of significance at $p < 0.05$ on the results obtained. All statistical analysis was performed using Minitab 15 English and Microsoft Excel software. The results of the single-factor ANOVA (tables 6 and 7) indicate that the sample sites show a significant effect on variation between groups of means for the physicochemical parameters and trace metals values respectively. It shows that the between sample mean square is greater than the within-sample mean square, and the *F*-test shows that this difference is highly significant. However, the results of physicochemical parameters within the sample sites shows $F = 41.218 > F\text{crit} = 2.167$ ($p < 0.05$); the same was observed for mean trace metal concentrations of elements within sample sites which also differed significantly F = 2093.37 > Fcrit = 1.876 (p < 0.05). The effects of the interaction between sample sites and trace metal concentration were highly significant, suggesting a transport phenomenon or mobility of the trace metals.

Table 1. Physico-chemical properties of an oil spill impacted site in Niger Delta, Nigeria.

Samp	Temp	pH	EC	TURB	SAL	DO	TPH
1	29.00	6.50	0.10	430.00	0.00	7.80	7878.27
2	29.00	6.00	0.83	200.00	0.00	7.60	4243.46
3	28.00	6.60	3.90	437.00	0.20	7.80	3875.35
4	29.00	6.60	5.60	596.00	0.10	7.30	2546.72
5	29.00	6.50	0.20	470.00	0.00	7.70	2852.87
6	30.00	6.00	0.20	436.00	0.00	7.60	1893.29
7	29.00	6.10	0.03	590.00	0.00	7.50	733.30
8	29.00	6.50	0.03	536.00	0.00	7.80	936.40
9	30.00	6.70	0.07	416.00	0.00	7.60	5118.20
10	29.00	6.80	2.20	422.00	0.10	7.60	6126.80
11	30.00	6.10	0.04	426.00	0.00	7.50	9836.26
12	29.00	6.20	1.40	200.00	0.10	7.60	7853.05
13	29.50	6.80	7.50	460.00	0.40	7.70	5234.41
14	30.00	6.30	2.30	440.00	0.10	7.80	2265.64
15	29.00	6.10	0.03	416.00	0.00	7.90	3289.93
16	30.00	6.20	0.02	396.00	0.00	7.60	2926.25
17	29.00	6.10	0.02	400.00	0.29	7.30	535.40
18	29.00	6.60	0.04	590.00	0.00	7.60	638.10
19	29.00	6.60	0.05	384.00	0.00	7.50	7134.00
20	29.00	6.80	5.30	450.00	0.30	7.60	9104.50
mean	**29.23**	**6.41**	**1.49**	**434.75**	**0.08**	**7.62**	**4251.11**
SE @95%CL	1.51	0.35	0.30	31.87	0.02	0.40	498.57
REFR.	30.00	7.10	0.03	430.00	0.00	8.10	84.02

Note: Mean ± SE at 95% confidence level. REFR, reference samples; EC, electrical conductivity; TURB, turbidity; SAL, salinity; DO, dissolved oxygen; THC, total hydrocarbon content. All computations were carried out using Microsoft Excel software.

Table 2. Trace metal content of an oil spill impacted site in Niger Delta, Nigeria in ppm.

Samples	As	Cu	Cr	Cd	Fe	Pb	Ba	Ni	V	Hg	CEC
1	0.001	2.05	0.12	0.001	8.27	0.001	100.00	4.15	8.40	0.001	47.00
2	0.001	2.20	0.90	0.001	7.96	0.001	100.00	4.80	9.40	0.001	47.50
3	0.001	2.30	0.18	0.001	7.64	0.001	104.00	4.01	6.60	0.001	47.80
4	0.001	0.85	0.16	0.001	7.63	0.001	100.00	3.92	6.90	0.001	46.20
5	0.001	0.85	0.19	0.001	8.74	0.001	98.00	0.63	6.97	0.001	55.25
6	0.001	0.75	0.15	0.001	6.35	0.001	103.00	0.88	6.49	0.001	47.00
7	0.001	13.11	0.62	0.001	7.18	0.001	103.00	2.52	5.47	0.001	57.20
8	0.001	12.56	0.85	0.001	7.62	0.001	105.00	1.95	6.30	0.001	55.05
9	0.001	2.10	0.15	0.001	7.35	0.001	103.00	4.25	6.14	0.001	47.20
10	0.001	2.05	0.12	0.001	7.74	0.001	108.00	4.30	5.63	0.001	47.50
11	0.001	2.00	0.05	0.001	6.29	0.001	100.00	4.15	7.10	0.001	47.00
12	0.001	2.20	0.03	0.001	7.96	0.001	100.00	4.80	9.20	0.001	47.50
13	0.001	2.14	0.08	0.001	7.36	0.001	104.00	4.01	6.10	0.001	47.80
14	0.001	0.85	0.15	0.001	7.32	0.001	100.00	3.92	6.60	0.001	46.20
15	0.001	0.85	0.13	0.001	8.74	0.001	98.00	0.63	6.97	0.001	55.25
16	0.001	0.75	0.15	0.001	6.18	0.001	103.00	0.88	6.49	0.001	47.60
17	0.001	13.41	0.62	0.001	7.17	0.001	103.00	2.52	4.03	0.001	52.90
18	0.001	12.56	0.85	0.001	7.62	0.001	105.00	1.95	6.30	0.001	54.10
19	0.001	2.03	0.08	0.001	7.23	0.001	103.00	4.25	6.14	0.001	47.20
20	0.001	2.00	0.06	0.001	7.2	0.001	108.00	4.30	5.63	0.001	47.50
Mean	**0.001**	**3.88**	**0.28**	**0.001**	**7.4775**	**0.001**	**102.40**	**3.14**	**6.64**	**0.001**	**49.54**
SE @95%CL	0.00	0.65	0.04	0.00	0.44	0.00	5.40	0.30	0.45	0.00	2.84
REFR.	**0.001**	**0.90**	**0.01**	**0.001**	**5.60**	**0.001**	**70.00**	**1.04**	**3.20**	**0.001**	**56.20**

Table 3. Principal Component table for pH, Conductivity, Alkalinity, TSS, TDS, DO.

Eigenvalue	3.9368	2.6711	2.1227	1.4011	0.8079	0.6253	0.478	0.3135
Proportion	**0.303**	**0.205**	**0.163**	0.108	0.062	0.048	0.037	0.024
Cumulative	0.303	0.508	**0.672**	0.779	0.841	0.89	0.926	0.95

Table 4. Loading table of experimental variables on principal components for oil spill data sets.

Variable	**PC1**	**PC2**	**PC3**	**PC4**
Temp	0.091	-0.046	-0.55	-0.266
pH	0.12	0.434	0.345	-0.167
EC	0.212	0.356	0.213	-0.09
TURB	-0.276	0.304	0.049	-0.358
DO	0.05	0.211	0.323	-0.415
TPH	0.415	0.043	0.034	0.117
Cu	0.424	0.119	0.025	0.333
Cr	0.371	0.27	0.077	0.423
Fe	-0.017	0.233	0.588	-0.054
Ba	-0.065	0.499	0.014	0.126
Ni	0.330	0.177	0.119	0.482
V	0.349	0.419	0.154	0.174
CEC	0.434	-0.120	0.187	-0.093

Table 5. Pearson correlation coefficient matrix *(R)* for physicochemical characteristics and some heavy metal content of soil.

	Temp	pH	EC	Turb	DO	TPH	Cu	Cr	Fe	Ba	Ni	V	Ca Exch
Temp	1.00												
pH	-0.26	1.00											
EC	-0.19	0.56	1.00										
Turb	-0.05	0.34	0.15	1.00									
DO	-0.09	0.10	-0.04	-0.08	1.00								
TPH	0.06	0.26	0.21	-0.45	0.04	1.00							
Cu	-0.26	-0.11	-0.30	0.41	-0.25	-0.55	1.00						
Cr	-0.26	-0.25	- 0.33	0.16	-0.11	-0.62	0.78	1.00					
Fe	-0.59	0.20	0.02	-0.09	0.43	-0.03	-0.06	0.10	1.00				
Ba	-0.13	0.54	0.28	0.25	-0.12	0.03	0.32	0.13	-0.36	1.00			
Ni	-0.14	0.34	0.43	-0.36	-0.18	0.63	-0.21	-0.19	0.00	0.16	1.00		
V	-0.05	-0.26	-0.09	-0.56	0.32	0.36	-0.45	-0.06	0.45	-0.57	0.33	1.00	
CEC	-0.32	-0.20	-0.40	0.42	0.13	-0.58	0.69	0.56	0.36	-0.07	-0.64	-0.30	1.00

Table 6. Single factor ANOVA results for physicochemical properties.

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Temp	20	584.5	29.225	0.275658
pH	20	128.1	6.405	0.0805
EC	20	29.86	1.493	5.221685
TURB	20	8695	434.75	10687.88
Sal	20	1.59	0.0795	0.015142
DO	20	152.4	7.62	0.024842
TPH	20	85022.2	4251.11	8517473

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.01E+08	6	50216161	41.2179	4.51E-28	2.167423
Within Groups	1.62E+08	133	1218309			
Total	4.63E+08	139				

DF-degree of freedom; F-factor mean square SS- Sum of squares; MS- Mean square; $P < 0.05$

Table 7. Single factor ANOVA results of trace metals concentration.

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
As	20	0.02	0.001	1.98E-37
Cu	20	64.19	3.2095	17.80589
Cr	20	4.83	0.2415	0.066213
Cd	20	0.02	0.001	1.98E-37
Fe	20	149	7.45	0.437579
Pb	20	0.02	0.001	1.98E-37
Ba	20	1946	97.3	59.58947
Ni	20	60.63	3.0315	2.15415
V	20	131.07	6.5535	1.66174
Hg	20	0.02	0.001	1.98E-37
CEC	20	976.4	48.82	17.54774

Table 7.
Continued

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	188902.9	10	18890.29	2093.365	1.6E-203	1.876216
Within Groups	1885.993	209	9.023889			
Total	190788.9	219				

DF-degree of freedom; F-factor mean square SS- Sum of squares; MS- Mean square; $P < 0.05$

3.3 Using principal component analysis (PCA) and Cluster analysis *to interpret results*

Principal component analysis was performed on the physicochemical parameter and the trace elements of the polluted soil samples using the correlation matrix. Figure 2 is the loading plot of the principal component. From tables 3 and 4, the principal component analysis showed that the eigenvalues of the first two principal components represent up to 50.80% of the total variance (PC1 30.30%; PC2 20.50%) of the observations. This percentage rises up to 67.20% when taking into account three components. However, considering the large number of variables studied (12), for greater clarity, factor loadings on a PC1–PC2 axes plane was plotted (figure 2). To correctly interpret this graph, the factor loadings for each variable on the unrotated components must be taken into account, as shown in table 4. A close look at figure 2 and table 4 show that variables such as Cu, Cr, V, cation exchange capacity and total petroleum hydrocarbon of soil correlated positively and contributed to the construction of component 1. These observations show that the variables are linked to inputs from hydrocarbon pollution. The positive values on component correspond to important inputs from oil pollution while the negative values to low inputs. Variables in component 2 may be due to a combination of allochthonous and oil pollution. The variables with positive values include Cr, Fe, V and DO. The table also shows that the pollution levels of these variables are not so high but have altered the physicochemical properties of the soil.

3.4 Cluster analysis

Cluster analysis was performed on the data using Single linkage and correlation coefficient distance. Cluster analysis rendered a dendrogram (figure 3), where the variables of the oil spilled polluted site was grouped into three statistically significant clusters. Three (3) groups of elemental associations with eigenvalue > 1 were extracted in the analysis. At about 68.56% similarity, all variables were fused together except temperature that reveals nearly the same relationship among the parameters which connotes identical source from oil pollution. At about 68.56% similarity, pH, EC, Ba, TPH and Ni while, Turbidity, Cu, Cr, CEC, DO, Fe, and V, Ni were fused into clusters because of their relative concentrations at oil spill impacted site and their similarity coefficients. This also shows common characteristics features and natural background source of these variables.

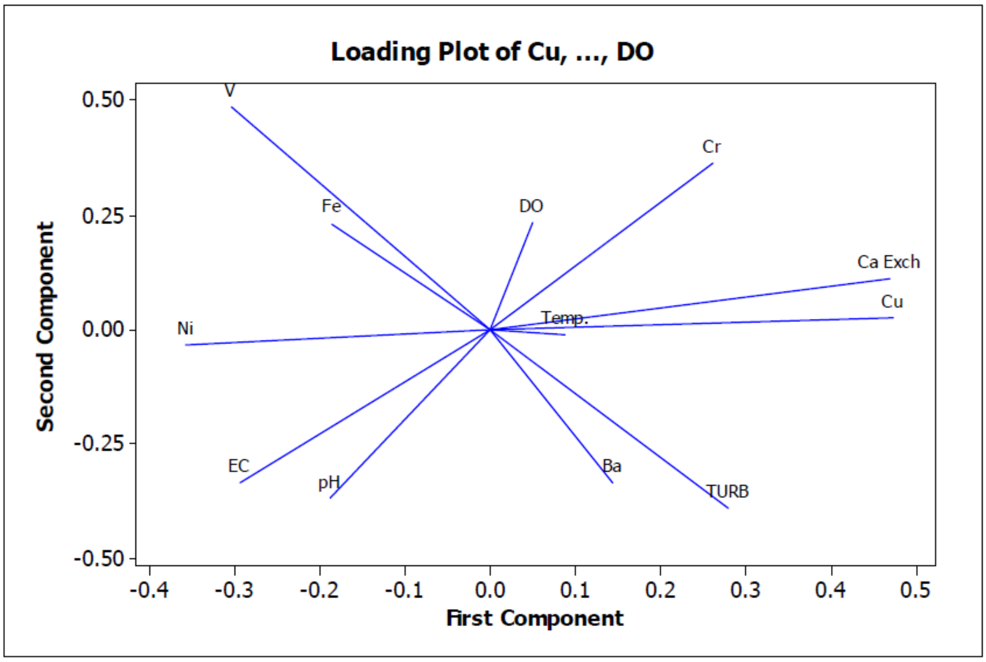

Figure 2. Loading plot of the principal component analysis.

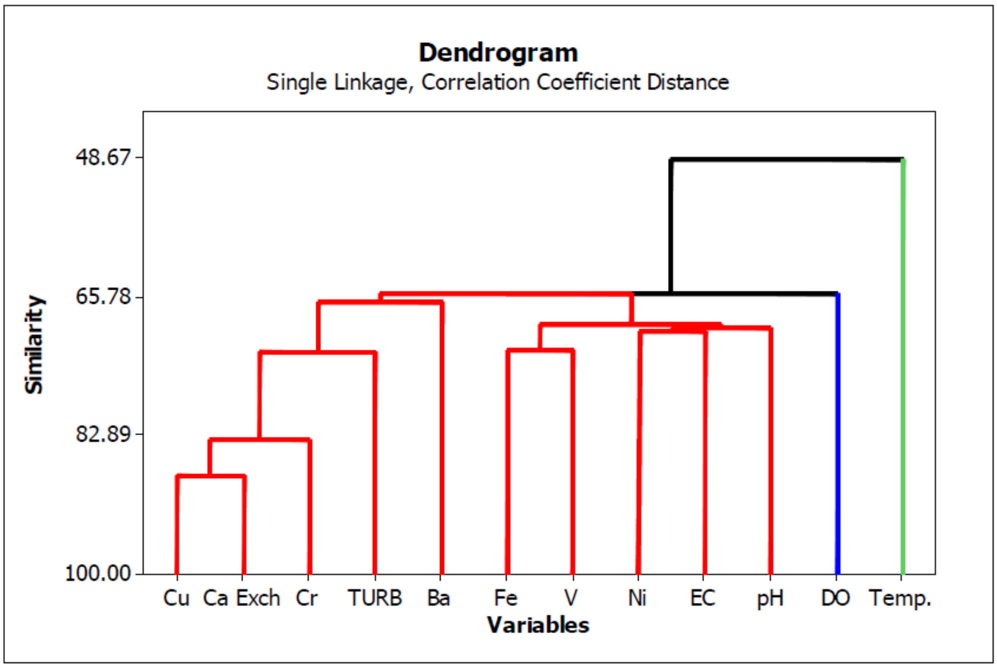

Figure 3. Dendrogram of the oil spill sample variables.

4. Conclusion

Multivariate statistical techniques have been successfully employed to analyze the physico chemical characteristics and some trace metals associated with crude oils within a contaminated area in the Niger Delta, Nigeria. These techniques have been used to derive information from the analyzed data set about the possible influences of oil spillage on physico- chemical properties of the impacted soils. The positive correlations between some of the parameters in the data set as seen on loading tables (tables 4 and 5) and Pearson's correlation matrix suggests that the major environmental pollution threats in the region were oil spillages. We finally concluded, based on the alteration of the physicochemical characteristics and the concentration of the trace metals, that the area under investigation has been impacted greatly by hydrocarbon contamination. The PCA scatter plots and dendrograms were used for the clustering of the variable also reveal a common or identical source. Multivariate statistical tools have great potential for assessing the relative importance of these parameters especially from petroleum hydrocarbon contamination.

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6. References

Amadi, A., Dickson, A. and Maate, G.O. 1993. Remediation of oil polluted soils: Effect of organic and inorganic nutrient supplements on the performance of maize (*Zea may L.*). *Water air soil pollution.* 66: 59 – 76.

Boyacioglu, H, and Boyacioglu, H. 2007. Water pollution sources assessment by multivariate statistical methods in the Tahtali Basin, Turkey. *Environ Geol* 54: 275–282

Department of Petroleum Resources (DPR) 1991. *Environmental Guidelines and Standards for Petroleum Industries in Nigeria*. Lagos 30 – 45

Ezebuiro, P. E. 2004. A review of effect of oil pollution in West African environment. *Journal Dis. environ.* 1: 62 – 68.

Odokuma, L.O. and Okpokwasili, G. C. 1993. Seasonal ecology of hydrocarbon utilizing microbes in the surface water of a river: *Environmental Monitoring and Assessment.* 27:175 – 191.

Onojake M.C., Ukerun, S.O. and Iwuoha, G. 2011. A Statistical Approach for Evaluation of the Effects of Industrial and Municipal Wastes on Warri Rivers, Niger Delta, Nigeria: *Water Qual Expo Health.* 3: 91– 99.

Osuji, L. C. and Onojake, C.M. 2004. Trace Heavy Metal Associated with Crude Oil: a Case Study of Ebocha- 8 Oil – spill Polluted Site in Niger Delta, Nigeria: *Chemistry and Biodiversity.* 1:1708 – 1715.

Osuji, L. C. and Ezebuiro, P. E. 2006. Hydrocarbon contamination of a typical Mangrove floor in Niger Delta, Nigeria: *International Journal of Environmental Science Technology.* 3 : 313–320.

Pradhan U. K., Shirodkar, P.V. and Shahu, B.K. 2009. Physicochemical characteristic of the coastal water off Devi estuary, Orissa and evaluation of its seasonal changes using chemometric techniques. *Current Science.* 96:1203–1209.

Sekabira K. H., Origa, O., Basamba, T. A. Mutumba, G. and Kakudidi, E. 2010. Heavy metal assessment and water quality values in urban stream and rain water: *International Journal Environmental Science and Technology.* 7:759–770.

Xiaoyun, F. C., Baoshan, Z., Hui, Z., Zhiming, Y. and Honggang, Z. 2010. Assessment of river water quality in Pearl River Delta using multivariate statistical techniques. In: International society for environmental information sciences 2010 annual conference (ISEIS) *procedia environmental sciences.,* 2: 1220–1234.

Zhang, Q., Zhongwu , L., Guangming , Z., Jianbing , L., Yong , F., Qingshui, Y., Yamei, W. and Fangyi, Y. 2009. Assessment of surface water quality using multivariate statistical techniques in red soil hilly region: a case study of Xiangjiang watershed China. *Environmental Monitoring and Assessment.* 152:123–131