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Research Paper

Environmental Risk Assessment and Modeling of TPH and PAHS in OBRIKOM 15 Access Road Mini Manifold Spill

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ABSTRACT
From the anthropogenesis operations of petroleum hydrocarbon related activities in the Niger Delta region of Nigeria, the possibilities of environmental crisis and associated hazards is highly expected. BETX and PAHs as major constituents of petroleum hydrocarbon and their impacts on the environment had caused ecological imbalance with contamination/pollution resulting from crude oil spillages. Random sampling method was adopted and soil samples were collected using amber wide-mouth and vial glass bottles with the aid of soil auger at 0-4m depths and analysed using GC-FID, GC-MSD and APHA analytical techniques. The TPH and PAHs decreased with depth. The TPH measured values were up to 1,636.85mg/kg and PAHs as high as 5,702.21mg/kg in soil with below detectable level (BDL) of BTEX. CF values were between 0.059 to 0.327 and the DC value was 2.511 respectively, made Obrikom spill site soil lowly contaminated while the l-geo calculation values of PAHs was between 3.615 to 6.571 indicating strongly contaminated. The hypothesis testing calculation shows that the calculated value is less than the table value and therefore the hypothesis is upheld which states that there is no relationship between TPH and PAHs concentrations in Obrikom soil impacted site. The contour maps show decreasing values of TPH and PAHs from the point of spill and depth while variogram models revealed a continuous behavior having similar trends of identical exponential variograms.

Key words: *PAHs, TPH, pollution indices, environmental hazard, ecological imbalance.*

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I. INTRODUCTION

The Niger Delta region is the center of crude oil activities in Nigeria, and as such, the region had experienced pressure from anthropogenic activities from crude oil exploration, exploitation, production, transportation and storage. United Nations Environment Programme (2011) reported that the region is highly impacted with crude oil spillages judging from the Ogoniland studies, and so, crude oil spills are potential adverse effects on the ecosystem (Fattal et al. 2010). Is there environmental crisis? Off course, yes! Its degrading state threatened the well-being of ecosystems.

Rivers State is of the eastern Niger Delta region of Nigeria and its capital, Port Harcourt is the headquarter of the region. Obrikom the studied area is one of the communities in Ogba/Egbema/Ndoni local government area (LGA), which is the northern part of Rivers State. The LGA is of the rainforest ecological zone. The field trip to the site was made after the spill at Obrikom 15 Access Road Mini Manifold at Obrikom, ONELGA, Rivers State. At the site, physical observations of the environment were made followed by sample collection. The samples were analysed in the laboratory and the results were evaluated with the application of some contamination indices and the level of contamination/pollution determined. Fig 1 is the map of the study area.

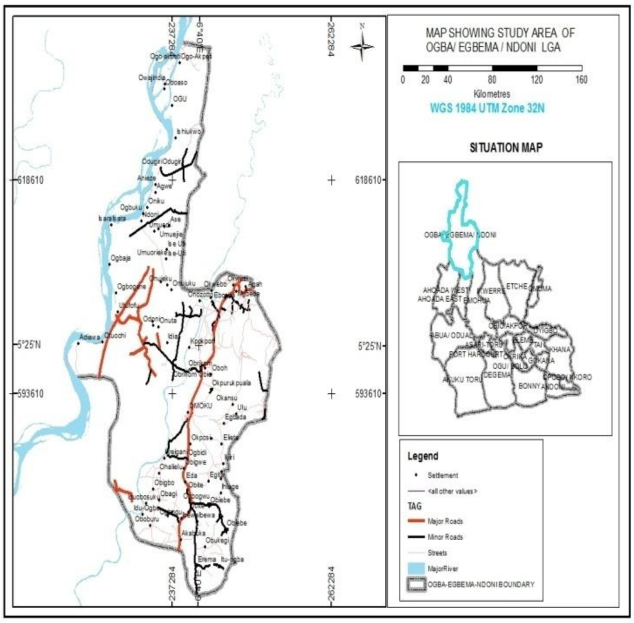

Fig 1: Rivers State showing ONELGA of the study area (Source: Rivers State Ministry of Land and Survey)

In this paper, PAHs, BTEX and TPH fractions of the petroleum hydrocarbon were studied.

II. MATERIAL AND METHOD

Materials

100ml glass beakers; 50ml, 100ml graduated cylinder, 500 ml/100ml Separatory funnels, Stainless steel Spatula, 250ml Erlenmeyer flasks; Glass funnels, Analytical balance capable of accurately weighing 0.0001g, Class ''A'' Volumetric flasks: 10, 25, 50 and 100ml; Class ''A'' Volumetric pipets: 1, 5ml, Microsyringe: 10 µL, Whatman No. 41 Filter Paper and 2ml glass vials with Teflon-lined rubber caps.

Reagent water: organic free water, Solvents: hexane, methylene chloride, and acetone, Sodium Sulphate (anhydrous), Certified TPH reference standard and Surrogate spike standard (Ortho-terphenyl /OTP).

Method

Field trip to Obrikom oil field petroleum hydrocarbon spill site was made for both physical and empirical observations and samples were collected for laboratory analyses. Fig 2 below show Obirikom 15 Access Road Mini Manifold at Obrikom spill site visited. The substance that spilled was condensate gas and the cause of spill was loose nuts and bolts on the wellhead while the spill coordinates was N05^0 24' 52.4" E006^0 36' 23.4". The condensate gas emission gushed out from the wellhead like a fountain with high hissing sound.

Sampling, Preparation and Analysis

At each sampling station, soil samples were collected at 0-4m depths using stainless steel soil auger. The samples were put in 60ml amber wide-mouth glass jars with Teflon-lined screw caps. Auto sampler 20ml vials were used to collect samples for BTEX parameters. The coordinates of spill sites and sample points were determined using GPS. Fig 3 shows the sampling map.

Fig 2. Obirikom 15 Access Road Mini Manifold at Obrikom in ONELGA, Rivers State.

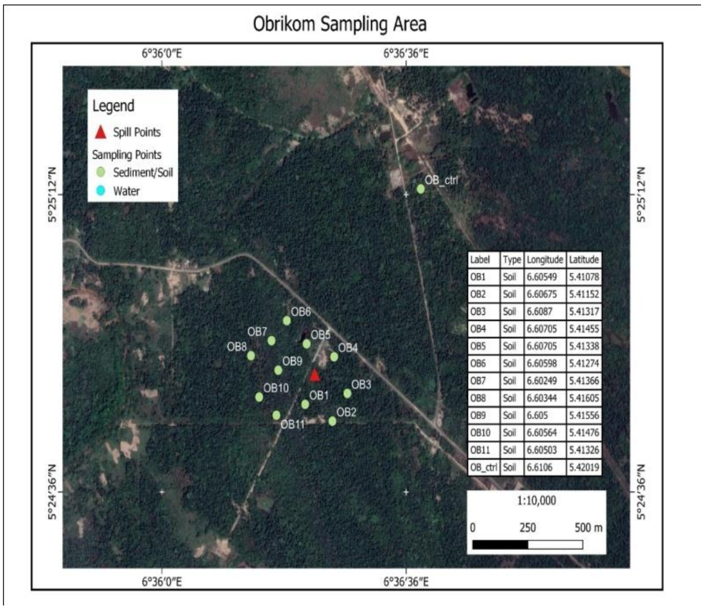

Fig 3: Sampling Map

A total of 12 soil samples were collected. The samples were cooled to 4 ± 2^{0}C immediately after sample collection. A chain of custody form was used to log in the sample names and other relevant data. Control sample was also collected at the same depth.

The soil samples were weighed and about 10g of a well mixed sample was put into solvent rinsed beaker and recorded the weight in the extraction log book and 50Ml of 1:1 Dichloromethane/acetone was added to the sample. After which, added 1mL of the surrogate spike standard to it and the beaker was covered with aluminium foil. Then, transfer the beaker to a mechanical shaker for about 1 hour. The sample was filtered through Whatman No.41 filter paper packed with 10g Na_2SO_4 and silica gel into Erlenmeyer flask, and concentrates the sample extract using a mechanical shaker to about 2 ml, then solvent exchange the extract with n-Hexane. Finally, re-concentrate the extract to 1 to 2mL and transfer by way of the pipette into the 2 ml auto sampler vial with Teflon lined caps.

The samples submitted for TPH analysis was extracted with methylene chloride, passed through sodium sulphate, solvent exchanged into hexane and concentrated in a mechanical shaker. The concentrated extract is then analyzed by a capillary column gas chromatograph equipped with a flame ionization detector (FID).The sample extracts from water/sediment samples were analyzed for TPH and PAH using a Gas Chromatograph with a Flame Ionization Detector (GC-FID) (Agilent 6890 and 7890A GC System) and Gas Chromatograph with a Flame Ionization Detector (Agilent 7820 GC System and 5975 series, 7890A and 5975C Inert XL MSD) respectively, sample injection is done with auto sampler using a 10 µl syringe. While Gas Chromatograph/ Mass Selective Detector (GC/MSD) 7890A 5975C Inert XL MSD; 7697A Headspace GC-MS was used for BTEX analyses.

All samples after collection were stored in a ice-cooled box and taken to laboratory and stored at 4°C in a refrigerator before analysis with GC-FID and GC-MSD; APHA 3110, ASTMD 1125 and APHA 2130. pH and temperature were measured in-situ using Hanna HI 98125 instrument.

III. RESULTS AND DISCUSSION

Results

Table 1: Analytical Results for Soil Samples of oil spilled sites

SN	Parameter (mg/kg)	1 0-0.5m	2 0.5-1.5m	3 1.5-3m	4 3-4m	5 0-0.5m	6 0.5-1.5m	7 1.5-3m	8 3-4m	9 0-0.5m	10 0.5-2m	11 2-4m	12 0-0.5m
1	TPH	1582.53	1492.01	1108.76	1011.26	1,636.85	1561.61	1097.54	821.01	986.64	729.62	526.4	296.2
POLYCYCLIC AROMATIC HYDROCARBON (PAH) PROFILE													
1	Naphthalene	3411.021	3620.590	2345.093	1230.97	3381.980	1245.902	1106.794	976.192	3012.874	2589.102	216.2	NT
2	Acenaphthylene	2011.616	1558.659	987.093	1449.06	2172.903	1342.873	1209.972	951.116	1527.239	1275.098	307.1	NT
3	Acenaphthene	997.679	1064.939	735.027	875.390	1032.920	986.374	867.601	769.917	984.142	798.204	67.4	NT
4	Fluorene	826.091	817.024	800.726	724.638	822.903	809.427	759.110	749.921	789.123	723.901	351.6	NT
5	Phenanthrene	356.312	374.940	287.590	234.903	370.932	342.097	246.911	239.024	321.872	279.901	52.4	NT
6	Anthracene	466.611	473.477	409.367	324.187	467.241	236.094	374.010	376.092	408.901	356.920	50.2	NT
7	Fluoranthene	90.061	90.473	83.209	88.903	72.902	45.935	50.612	55.813	70.912	65.907	21.4	NT
8	Pyrene	50.912	53.659	48.903	51.907	53.390	52.139	49.011	48.921	48.902	45.896	16.6	NT
9	Benz(a) anthracene	28.988	30.554	23.091	24.908	31.782	29.906	25.621	25.022	28.902	26.921	10.9	NT
10	Benzo(b) fluoranthene	4.591	4.747	3.308	3.278	4.780	4.091	4.023	3.721	4.093	3.872	1.62	NT
11	Chrysene	16.932	18.324	15.904	15.904	17.902	13.983	8.966	7.911	15.951	12.892	2.81	NT
12	Benzo(a)pyrene	21.061	23.334	20.937	17.948	23.094	21.038	18.721	17.289	20.981	17.093	11.6	NT
13	Benzo(k) fluoranthene	8.662	8.975	7.0974	7.589	8.904	6.969	5.992	6.082	8.243	6.912	-	NT
14	Indeno(1,2,3-cd) pyrene	36.902	35.815	30.132	30.962	34.130	29.9053	31.061	33.712	30.012	27.906	-	NT
15	Dibenz(a,h) anthracene	50.677	48.656	45.936	46.923	49.925	40.984	42.092	47.920	42.902	41.962	-	NT
16	Benzo(g,h,i) perylene	7.871	7.524	6.189	6.836	7.612	5.934	6.092	5.521	6.672	5.819	-	NT
	Total PAH	**8385.987**	**8,231.69**	**5,859.61**	**2,757.28**	**8553.318**	**5,213.65**	**4806.598**	**4314.174**	**7321.721**	**6278.306**	**1109.8**	-
BTEX PROFILE BTEX PROFILE													
1	Benzene	BDL	BDL	NT	NT	BDL	NT	NT	BDL	NT	NT	BDL	NT
2	Toluene	BDL	BDL	NT	NT	BDL	NT	NT	BDL	NT	NT	BDL	NT
3	Ethylbenzene	BDL	BDL	NT	NT	BDL	NT	N	BDL	NT	NT	BDL	NT
4	M,p-xylene	BDL	BDL	NT	NT	BDL	NT	NT	BDL	NT	NT	BDL	NT
5	o-xylene	BDL	BDL	NT	NT	BDL	NT	NT	BDL	NT	NT	BDL	NT
	Total BTEX	-	-	-	-	-	-	-	-	-	-	-	-
	CF	0.316	0. 298	0. 222	0. 202	0. 327	0. 312	0.220	0.164	0.197	0.146	0.105	0.059
	DC = 2.511												
	I-geo	6.542	6.515	6.025	4.937	6.571	5.856	5.739	5.583	6.346	6.125	3.615	-

Table 2: Calculated values and table values of Obrikom Soil using PPMC

S/N	X (TPH)	Y(PAHs)	XY	X^2	Y^2
1	1582.53	5590.7	8847387	2504401	31255479
2	1492.01	5487.8	8187853	2226094	30115949
3	1108.76	3906.4	4331260	1229349	15259961
4	1011.26	1838.2	1858888	1027647	3378942.5
5	1636.85	5702.2	9333434	2679147	32515199
6	1561.61	3475.8	5427797	2438626	12080977
7	1097.54	3204.4	3156957	1204594	10268179
8	821.01	2876.1	2361323	674057.4	8272066.3
9	986.64	4881.2	4815938	973458.5	23825625

10	729.62	4185.5	3053854	532345.3	17518745
11	526.4	734.8	386830.3	2770096	540019.2
	12,554.19	**41883.04**	**51761521.4**	**15766815.4**	**185031142.7**

Using the variables in Table 1 and equation 1

Hypothesis: There is no relationship between TPH and PAHs concentrations in Obrikom soil spill impacted site.

$$r = \frac{n\Sigma xy - \Sigma x.\Sigma y}{\sqrt{n\Sigma x^2 - (\Sigma x)^2 \,.\, n\Sigma y^2 - (\Sigma y)^2}} \quad \text{------------------- } 1$$

$$r = \frac{11 \text{ x } 51761521.4 - 12554.19 \text{ x } 41883.04}{\sqrt{11 \text{ x } 15766851.4 - 12554.19^{2} \text{ x } 11 \text{ x } 185031142.7 - 41883.04^{2}}}$$

$$r = \frac{43569093.4624}{\sqrt{173434969.4 - 320785632005375700}} = \frac{43569093.4624}{\sqrt{-320785631840700}}$$

$$= \frac{43569093.4624}{566379406.3} = \mathbf{0.077}$$

Subjecting r to special t-test

$$t = \frac{r\sqrt{n-2}}{\sqrt{1-r^{2}}} = \frac{0.077\sqrt{11-2}}{\sqrt{1-0.077^{2}}} = \frac{0.077\sqrt{9}}{\sqrt{1-0.005929}} = \frac{0.077 \, x \, 3}{\sqrt{0.994}} = \frac{0.231}{0.997} = \mathbf{0.232}$$

DF = $N_1+N_2 - 2$ = 11 + 11 – 2 = 20 at 0.05 or 95% significant level = **2.09 critical value**

Decision: Since the calculated value of 0.232 is less than the critical value of 2.09, the hypothesis which states that there is no relationship between TPH and PAHs concentrations in Obrikom soil spill impacted site is accepted or upheld.

Applying Popoola *et al*., 2015 and Md Suhaimi *et al*., 2014 contamination factor (Cf) expressed as:

Cf = C_n/B_n ---------------------------- 2 where C_n = measured concentration; B_n = background value

Sample station 5:

$$Cf = \frac{1,636.85}{5000} = \mathbf{0.327}$$

Applying Atta *et al*., 2014 and Ite *et al*., 2018 degree of contamination (Dc) expressed as:

Dc = ∑Cf --- 3

= ∑Cf = (0.316 + 0.298 + 0.222 + 0.202 + 0.327 + 0.220 + 0.164 + 0.197 + 0. 146 + 0.105 + 0.059) = **2.511**

Applying index of geo-accumulation (l-geo) (Ghaleno et al. 2015) expressed as

$$\text{I-geo} = \log_2 \frac{Cn}{1.5 \text{ X } Bn} \quad \text{--------------- } 4$$

Sample station 2: $= \log_2 \frac{5487.80}{1.5 \text{ x } 40} = \log_2 91.4633 = \frac{\log 91.4633}{\text{Log}2} = \frac{1.9612}{0.3010} = \mathbf{6.515}$

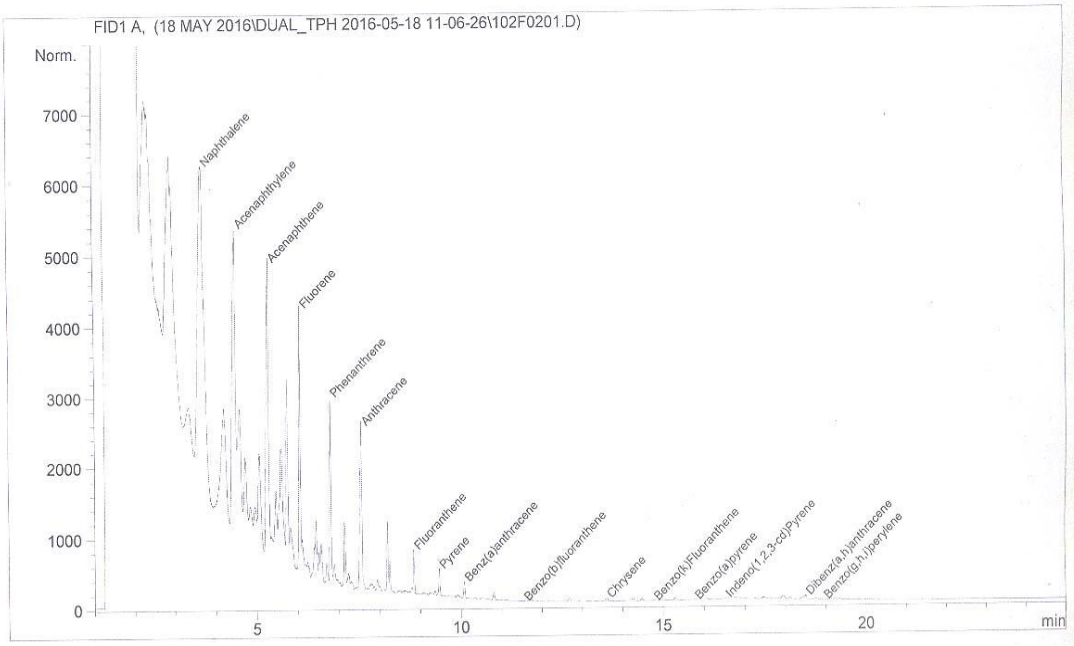

Fig 4: GC-FID of PAHs in soil

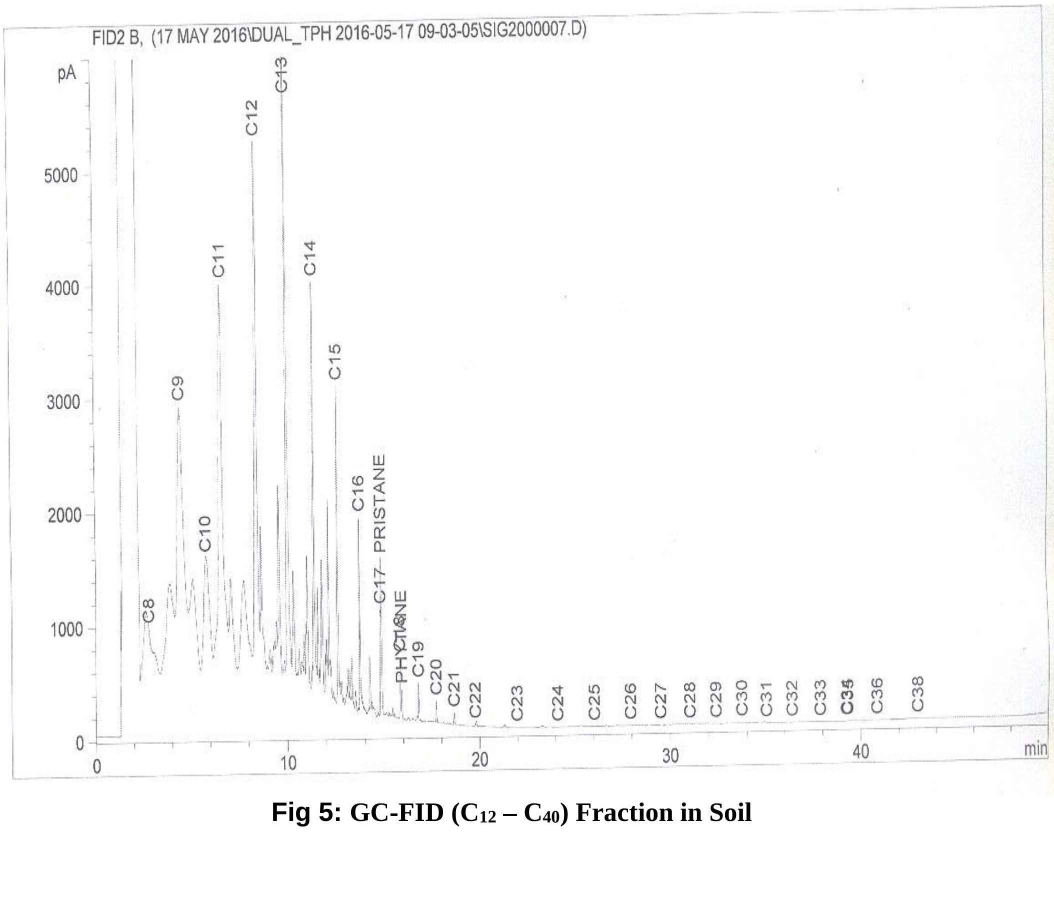

Fig 5: GC-FID (C_{12} – C_{40}) Fraction in Soil

Areal distribution of PAHs and TPH in Soil

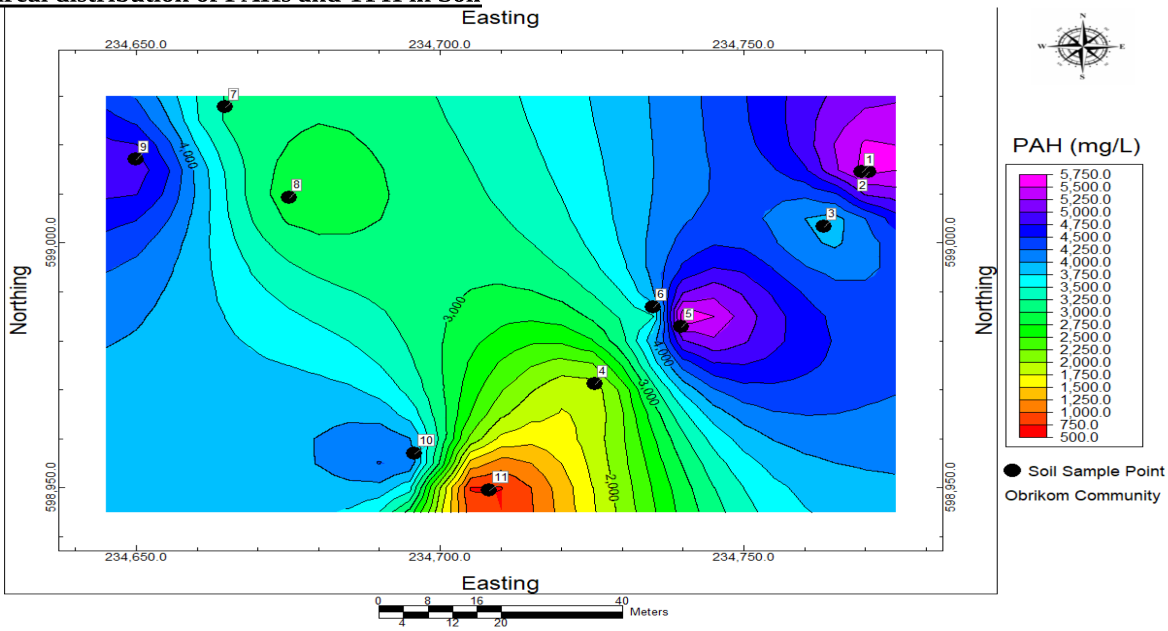

Fig 6: Soil PAHs Contour Map

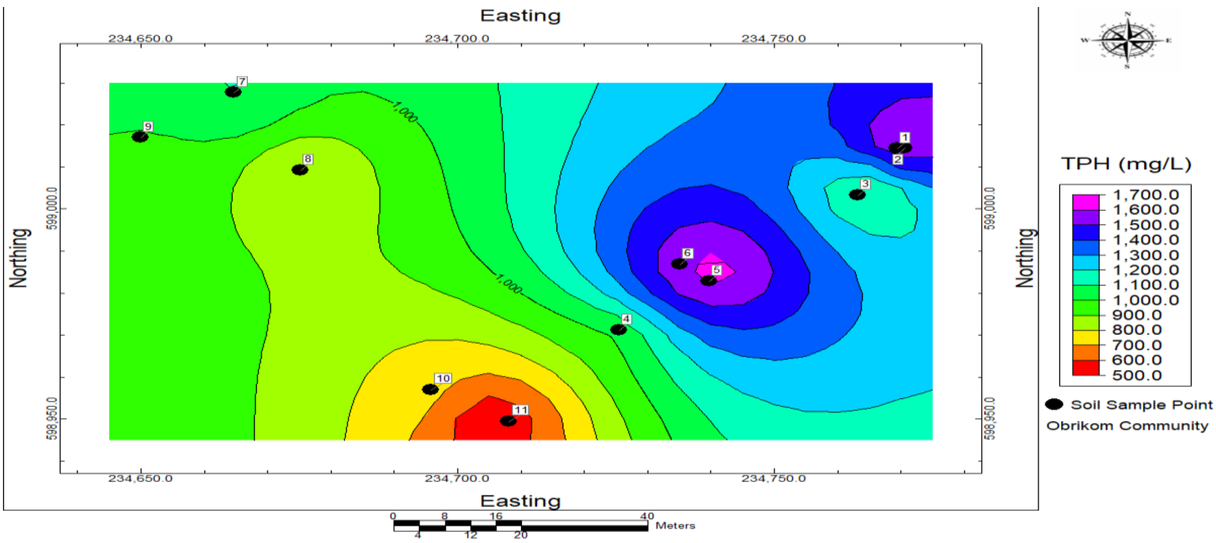

Fig 7: Soil TPH Contour Map

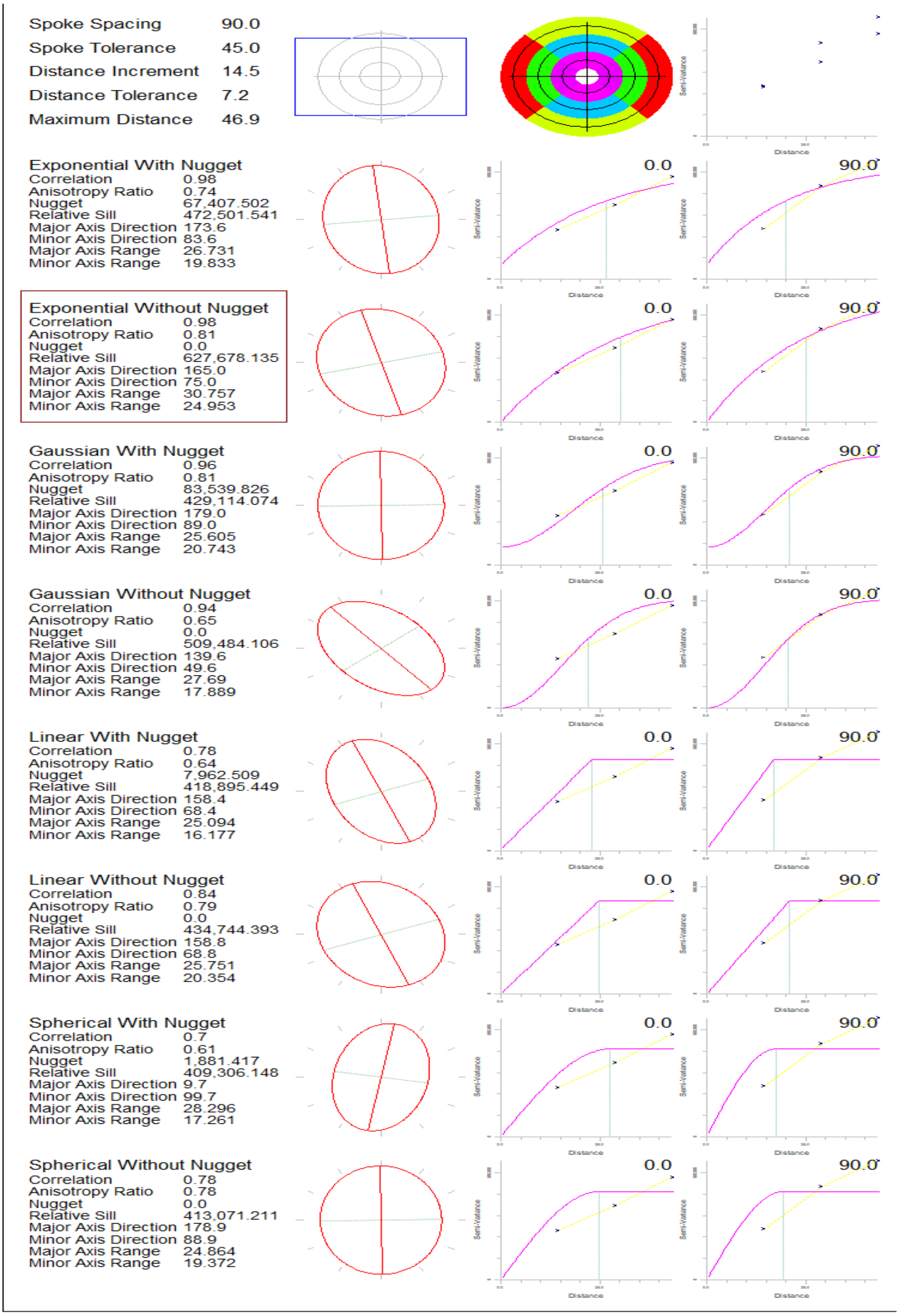

Fig 8: Soil PAHs Variogram

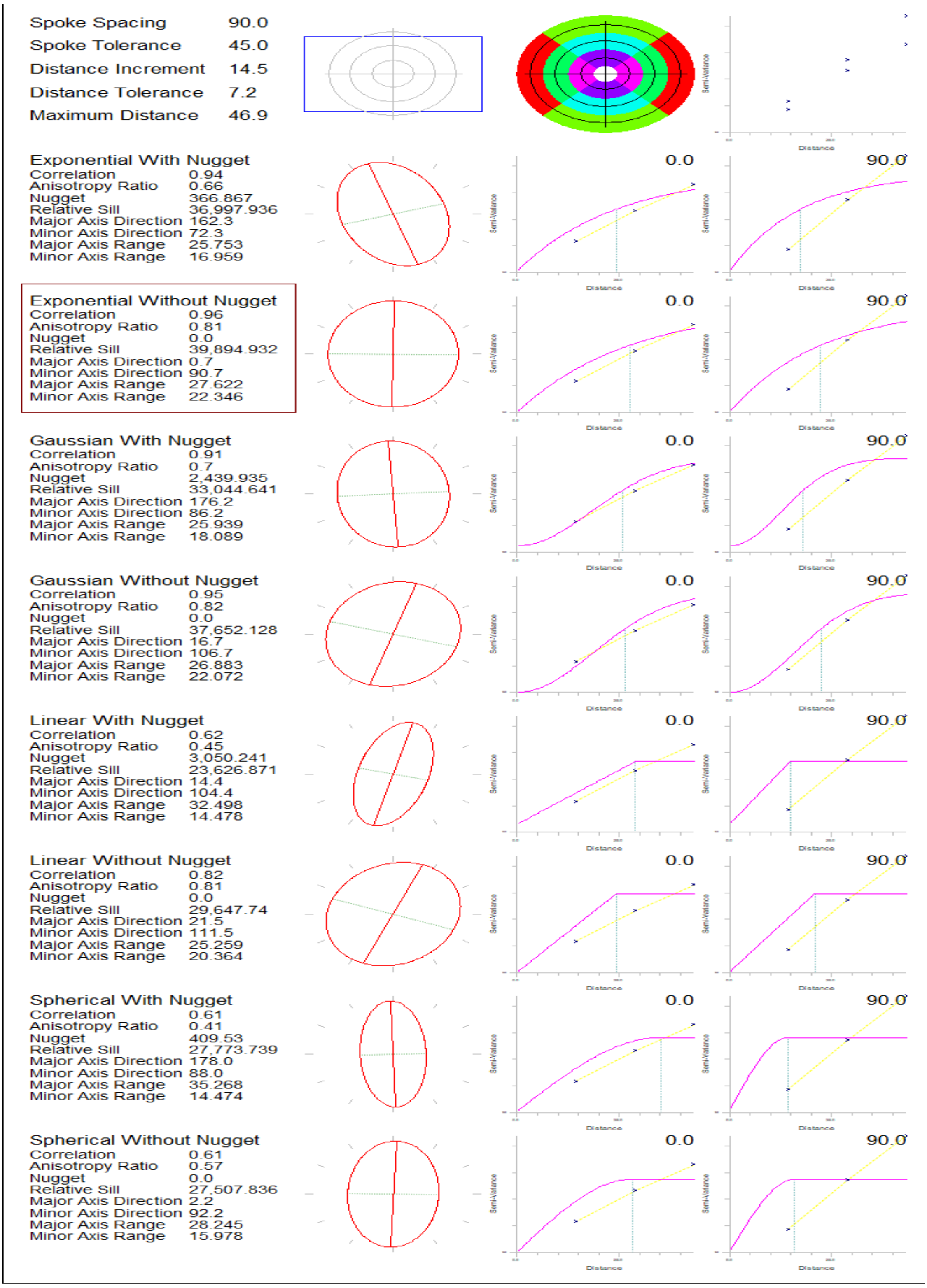

Fig 9: Soil TPH Variogram

IV. Discussions

Fig 4 and fig 5 are the PAHs and TPH chromatographs respectively from the soil samples. The soil has a maximum TPH level of 1,636.85mg/kg (Table 1) which was within the DPR acceptable limit of 5000mg/kg and the maximum total PAHs was 5,702.21kg which was above DPR acceptable limit of 40mg/kg (DPR, 2018). Applying contamination indices of CF and DC [13], the soil was lowly contaminated with a maximum CF of 0.327 and DC of 2.511. Also, applying l-geo, the soil was extremely polluted with a maximum l-geo of 6.571

(Table 1). These indices were also applied by [14]; and [11]. BTEX was below detective level (BDL) in all samples.

The areal distribution of PAHs and TPH in the soil shows spatial variability/continuity distribution of the composition of the spilled oil. Fig 6 is PAHs contours map and Fig 8 is the PAHs variogram showing anisotropy of 0.81, no nugget effect, sill of 627.6 and range of 30.7. While Fig 7 is the TPH contour map and fig 9 is the TPH variogram also no nugget effect, anisotropy of 0.81, sill of 39.8 and range of 27.6.The contour maps displayed decreasing concentration of TPH and PAHs from the points of spill and also, decreases with depth in lithology.

V. Conclusion

The major components of petroleum hydrocarbon are the TPH, PAHs and BTEX (ASTDR, 2009). The soil samples were not polluted with TPH but PAHs polluted the Obrikom soil. The hypothesis testing proved that the high concentration of PAHs may be as a result of accumulated spill incidences and not just this particular spill visited. TPH and PAHs values show decreasing with depth. From the obtained variograms, no nugget effect was seen, meaning that there was no significant measurement error or variation. Therefore, it revealed a continuous behavior (the apparent nugget effect). The obtained variograms shows similar trends of identical exponential variograms.

Conflict of Interest

This research work was carried out by me. The content, field work and laboratory analysis, results and interpretations were all my original work.

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REFERENCES

[1]. ATSDR (Agency for Toxic Substances Disease Registry) (2009). Interaction Profile for Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX). US Department of Health and Human Services, Atlanta, GA. Available at www.atsdr.cdc.gov/interactionprofiles/ip05.html

[2]. Atta E. R. and Zakaria Kh. M. (2014): Evaluation of some radioactive materials and heavy metals in marine environment of Alexandria Coastline, Egypt. Journal of Environmental Protection, 2014,5, 1618-1629

[3]. Fattal P., Maanan M., Tillier I., Rollo N., Robin M., and Pottier P. (2010). Coastal Vulnerability to oil spill pollution: the case of Noirmoutier Islan (France). Journal of Coastal Research, 26(5), 879-889.

[4]. Environmental Guidelines and Standards for the Petroleum Industries in Nigeria (EGASPIN) (2018). Issued by the Department of Petroleum Resources, Nigeria. (Revised edition, 2002).

[5]. Ghaleno R. O., Sayadi M. H. and Rezaei M. R. (2015): Potential ecological risk assessment of heavy metals in sediments of water reservoir case study: Chah Nimeh of Sistan. International academy of ecology and environmental sciences, 2015, 5(4): 89-96

[6]. Hadiya Khalilova and Vagif Mammadov (2016): Assessing the Anthropogenic Impact on Heavy Metal Pollution of Soils and Sediments in Urban Areas of Azerbaijan's Oil Industrial Region. Pol. J. Environ. Stud. Vol. 25. No.1(2016). 159-166.

[7]. Ite, A. E., Thomas A. H., Clement O. O., Ekpedeme R. A., and Iniemem J. I. (2018). Petroleum Hydrocarbons Contaminations of Surface Water and Groundwater in the Niger Delta Region of Nigeria. Journal of Environmental Pollution and Human Health, 2018, Vol.6, No. 2, 51-61.

[8]. Md Suhaimi Elias, Mohn Suhaimi Hamzah, Shamsiah Ab Rahman, Nazaratul Ashifa Abdulla Salim, Wee Boon Siong, and Ezwiza Sanuri (2014): Ecological risk assessment of elemental pollution in sediment from Tunku Abdul Rahman National Park, Sabah. AIP Conference Proceedings 1799, 030008 (2017); 10.1063/1.4972918

[9]. Popoola S. Olatunde, Oyatola O. Otolorin, Appia J. Juliano and Ebohon J. Osiuare (2015): Distribution, Sources and Contamination Risk Assessment of Some Trace Metals in Bottom Sediments from Selected Locations in Lagos Lagoon, South Western Nigeria

[10]. United Nations Environmental Programme (2011). Environmental Assessment of Ogoniland.Nairobi Kenya: UNEP.DEP/1337/GE