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Assessment of the Physico-chemical Properties of Hydrocarbon Contaminated Soil

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ABSTRACT

The hydrocarbon levels and physico-chemical properties of the Ebocha -8 was determined six months after the spill incident to determine the extent of pollution. The affected area was mapped into (200m x 200m) quadrant and samples were collected using the grid method from three replicate quadrants at two depths, surface (0-15cm) and subsurface (15-30cm). An unpolluted site which is 50m away from the spill site but within same geographical location was also sampled and used as reference. The physico-chemical properties of soil such as pH, conductivity, moisture content, chloride, total acidity, sulphate were determined using standard analytical methods. Also the hydrocarbon level of the impacted soil was also determined at 95% confidence limit. The results for surface, subsurface and reference samples are: pH (6.50 ± 0.21, 6.48 ± 0.20 & 5.33 ± 1.16), Conductivity (2844.85 ± 157.2, 2072 ± 97.12 & 14.0 ± 4.95), moisture content (15.40 ± 1.09, 12.78 ± 0.81& 5. 82 ± 1.59), Total acidity (782.06 ± 33.62, 4328 ± 2.42 & 85.60 ± 30.37), Chloride (973.94 ±55.63, 366.06 ±17.29 & 56.00 ±17.76), Sulphate (1.06 ± 0.10, 0.25 ± 0.02 & 0.60 ± 0.37), Total Organic carbon (2.84 ± 0.13, 3.57 ± 0.12 & 3.56 ± 0.75), Total Organic Matter (4.90 ± 0.22, 6.15 ± 0.21 & 6.14 ± 1.30) mg/kg and Total Hydrocarbon Content (19837.12 ±1465.05, 1672.37 ± 113.67& 50.0 ± 10) mg/kg. The high values of the results from surface and sub- surface soils respectively are not unconnected with pollution. Immediate depollution measures and liming is therefore recommended to rehabilitate the impacted area.

Keywords: Oil spillage, depollution, hydrocarbon level, liming and Orashi river.

INTRODUCTION

The 'Niger Delta' located along longitude 3° to 9′ east and latitude 4° 30′ to 5° 20′ north is the most significant in the production of hydrocarbon in West Africa. This area has become synonymous to oil spillage as a result of the activities of oil exploration and prospecting industries. Over 18 billion barrels of crude oil and 300 oil fields operated by multinational oil companies exist in the region. This region is made of fragile ecological systems, house about 11,000km of ageing flow-lines and over 160 flow Stations connected to nine major terminals [8, 12]. The Ebocha-8 oil field is an onshore oil prospecting area in the Niger Delta, Nigeria. It has an extensive network of oil wells, oil pipelines, gas flow station and gas pipelines. Oil spillage affects the soil ecosystem and environment that are completely aquatic. It is known that oil sometimes floats on water surfaces where it is dispersed to shorelines by wind and wave action, also affecting the soil environment [3]. Oil pollution has deleterious effect on plant growth, soil macronutrients, microorganism and the terrestrial ecosystem in general [11]. A measure of the hydrocarbon level and comparing with baseline data set by regulatory agencies is therefore important to determine the extent of pollution considering the enormous amount of oil spilled into the environment especially on arable farmlands, swamps, creeks and rivers within the Niger Delta terrain which is the worst affected by the oil spillage.

MATERIALS AND METHODS

Site description.

Ebocha-8 field is in Obrikom, Ogba/Egbema-Ndoni local government area of Rivers state; it is located between the eastern coastline of the Orashi River and river Niger in the Niger Delta, *Fig 1* It is at the mangrove swamp forest of the Niger Delta, south-south Nigeria.

Sampling design and collection.

Sampling plots was erected at both the impacted and unpolluted (reference) site by grid system. A sampling area measuring 200 by 200m^2 was erected based on field reconnaissance delimited by area of oil spill (epicenter of spillage). The area was split into one hundred (100) grid plot. Thirty three percent (33%) of this plot was randomly selected and within each was mounted replicate quadrants from which soil samples were collected from surface depth (0 - 10cm) and subsurface (10 - 30cm) using a digger. A geographically similar virgin area located fifty meters adjacent to the oil polluted area was used as control (reference) samples. See plates 1 &2. The soil samples were then put into polyethylene bags, labeled accordingly and taken to the laboratory for analyses.

Physico chemical Analyses.

Conductivity, Percent moisture content, pH, Chloride, Sulphate, Total acidity, were determined using standard laboratory methods as reported by Onojake [9]. Total Organic Carbon (TOC), Total organic matter (TOM) and Total hydrocarbon were also determined in the laboratory by chromic acid titrimetric method of Walkey and Black [16] as discussed below:

Estimation of Total organic carbon (TOC) and Total organic Matter (TOM).

One gram (1.0g) of soil samples was weighted into a 500ml volumetric flask. 10ml of $K_2Cr_2O_7$ and 20ml of conc. H_2SO_4 were added. 200ml of distilled water, 10ml of H_3PO_4 and five drops of diphenylamine indicator were added before titrating with 0.5N $(NH_4)_2SO_4Fe$. A blank titration was thereafter carried out and the % TOC was calculated as:

$$\%TOC = \frac{titre\ value\ of\ blank - titre\ value\ of\ sample}{weight\ of\ sample}$$
$$\%\,TOM = TOC(\%) \times 1.724$$
$$TOC\ is\ 58\%\ of\ TOM$$

Estimation of Total hydrocarbon (THC).

One gram (1.0g) of soil samples were air dried at room temperature for five days put a 500ml volumetric flask. 200ml xylene was added. The Xylene/soil mixture was shaken vigorously for 10min. The extract was filtered into 400ml cylinder. THC in xylene mixture was determined by a photometric method using a Fisher Electrophotometer II at a wavelength of 435nm. THC was estimated from calibration curve obtained by measuring absorbance of a 30.0ml of Bonny light crude oil with 50ml xylene solution.

Statistical analysis

Results were subjected to statistical analysis of mean; standard deviation and standard error (SE) at 95% confidence limit using the Microsoft excel software.

The confidence limit defines an interval around x that probably contains μ.

The confidence limit fixes the odds that the true mean will be within the defined limits.

It is given by the general expression:

$$CL\ for\ \mu = X \pm \frac{Z\delta}{N}$$

Where:
CL is the confidence limit
μ is exact value of the mean
X is mean of replicate data
Z is deviation from the mean
δ is standard deviation
N is number of measurement

$$Z = \frac{(X - \mu)}{\delta}$$

The value of Z for 95% confidence level is 1.96
See tables for results 1- 5 and figures as attached.

RESULTS AND DISCUSSION

The pH values of the impacted soils lies within the acidic range and may not support the growth of most crops that thrive on alkaline soil, this may lead to loss of macro minerals needed for plant growth. Thus acidification of soil depletes important nutrient elements such as potassium, calcium and magnesium [10]. Liming is therefore necessary to de-acidity the affected mat layer of soils for such soil to accommodate plant life. pH also affects the solubility and availability of soil constituents which may affect biological activity in the soil [15]. The increase level of moisture in the surface and sub-surface soils in not unconnected with intense rainfall and flooding which proceeded the period of sampling. The high moisture may lead to the problem of wetability and soil aeration, which may affect the nutrient status of the soil [3]. Consumption and carbon dioxide production in normal agricultural soils depends on soil moisture content and temperature [14]. When the soil is saturated and all the pore spaces are filled with water, there is no gaseous concentration gradient in the soil. Therefore, oxygen would not be able to diffuse to the plants roots from the atmosphere. Some of the plants roots become depleted of oxygen and this leads to changes in redox potential of the root zone [13]. Not much is known about the high level of conductivities in the oil spilled samples compared to the unpolluted, but this may be probably due the presence of ions from hydrocarbon introduced into the soil [6, 11]. When the conductivity of soil is high, it means that the salt content is high and vice versa. High hydrocarbon levels were observed from surface and sub-surface soil of the oil spilled site compared to the unpolluted site (table 2). Although the exact concentration of the hydrocarbon spilled was not immediately determined at the initial time of the oil spill, but it is generally believed that natural degradation of hydrocarbon in the environment primarily by bacteria and fungi is ongoing [5]. Large amount of hydrocarbon in soils discourages plant growth which in turn affects animals that depends on these plants for food and shelter [12]. Crops like yams, cocoyam's, vegetables do not thrive well in hydrocarbon contaminated soils. This is due to insufficient aeration of the soil because of the displacement of air from the spaces between the soils particles by crude oil which have adverse effect on plant growth, this can cause seeds sown on contaminated soil not to germinate even after 30days [3]. There is also on increase in the activity of anaerobic microbes which increases the stress to living organisms and soil animals like earthworms, nematodes and as such reduces their population density [1, 11]. Also there is considerable reduction on the plants covers such as Andropogin gayanus, and animals such as Rhabditis spp, and xiphinema spp reduce in population. Further studies by Gill and Nyuwuame [4] reveals that morphological and anatomical aberrations were discovered on the growth of Chromolaens odorata (L) [10]. This was revealed by the presence of hydrocarbon films in the epidermal and cortical regions of the root stem and leaves. Crude oil pollution overloads the soil with excess carbon leading to increased microbial population which tends to deplete the soil of nutrients[8].

However, the high hydrocarbon levels in the soil have adversely affected both man and animals which depend on such plants for food. The physico-chemical properties of the Ebocha-8 impacted soil which is altered as a result of spilled crude oil may affect plants, soil metabolic activities, the mobility of soil macro and micro nutrients and may aggravate their toxic potency in soils, thus liming, depollution measures and rehabilitation is highly recommended.

Correlation analysis: Pearson correlation coefficients for the data were evaluated to determine the level of inter relationship of the physico chemical characteristics and the hydrocarbon levels of the oil spill. The calculated correlation matrix of crude oil spilled soil samples shows positive values for some of the parameters as seen in table 4 showing that they are interrelated with each other. Most of the physico chemical properties showed significant positive correlations except few with the moisture content. There is a high positive correlation of 0.99 between TOC and TOM.This implies that TOC is derived from TOM.

Biplot of samples suggest that the high level of the physico chemical parameters above the reference values is due to oil spillage. The first factor accounts for 37% of the total variance and contains high concentration of Total hydrocarbon in the spill sample including high acidity (Table 5). The second factor accounts for 17.7 % of the variance and contains pH, and conductivity in high concentration. The third factor accounts for 13.1 % of the variance and contains moisture with high variable loadings on this factor.

RESULTS AND DISCUSSION

TABLE 1: RESULTS OF pH, CONDUCTIVITY AND MOISTURE CONTENT OF SOIL SAMPLES

	pH			CONDUCTIVITY(μScm^{-1})			MOISTURE CONTENT		
Samples	Surface samples	Sub- surface samples	Reference samples	Surface samples	Sub-surface samples	Reference samples	Surface samples	Sub-surface samples	Reference samples
1	6.83	6.49	5.01	1280.00	1560.00	10.00	13.10	12.80	7.20
2	6.67	6.38	5.52	2070.00	2340.00	20.00	5.30	20.70	4.20
3	6.39	6.49	5.17	5200.00	1570.00	10.00	14.00	11.10	5.70
4	6.40	6.48	5.35	3140.00	1530.00	10.00	5.50	9.80	5.90
5	6.53	6.50	5.61	2750.00	1540.00	20.00	10.60	10.90	6.10
6	6.71	6.47		2190.00	1550.00		12.50	2.00	
7	6.72	6.40		2190.00	2850.00		34.30	18.50	
8	6.79	6.65		2170.00	3070.00		14.90	22.60	
9	6.38	6.63		2570.00	3060.00		29.40	2.00	
10	6.88	6.57		1290.00	2980.00		2.20	13.80	
11	6.54	6.35		3200.00	1470.00		31.60	14.50	
12	6.78	6.35		3100.00	1460.00		6.20	5.10	
13	6.49	6.43		1370.00	1420.00		22.10	12.80	
14	6.58	6.65		5170.00	2900.00		5.30	16.60	
15	6.46	6.43		1380.00	1290.00		12.60	13.30	
16	6.60	6.57		2000.00	2590.00		17.40	16.70	
17	6.52	6.55		2930.00	2580.00		15.20	11.10	
18	6.46	6.50		2470.00	2500.00		1.90	12.10	
19	6.80	6.49		5050.00	2090.00		12.60	15.20	
20	6.38	6.51		2000.00	2350.00		9.00	5.10	
21	6.82	6.48		4040.00	940.00		50.50	10.40	
22	6.82	6.53		3290.00	1630.00		13.90	12.80	
23	6.82	6.50		2190.00	1650.00		11.10	13.00	
24	6.17	6.74		5920.00	2070.00		4.30	23.10	
25	6.60	6.68		3400.00	1960.00		16.20	11.40	
26	6.60	6.42		7030.00	2050.00		17.80	13.70	
27	6.46	6.40		1520.00	2040.00		31.50	8.10	
28	6.40	6.40		2930.00	1670.00		19.80	12.60	
29	6.47	6.40		4180.00	1900.00		18.30	40.00	
30	6.04	6.30		2360.00	2690.00		8.70	6.10	
31	5.90	6.45		2970.00	2080.00		8.00	7.70	
32	6.04	6.40		2900.00	2500.00		13.80	12.10	
33	6.40	6.30		2930.00	2500.00		18.60	8.90	
S.E @ 95%CL	6.50 ± 0.21	6.48 ± 0.20	5.33 ± 1.16	2844.85 ±157.2	2072 ± 97.12	14.00 ± 4.95	15.40 ± 1.09	12.78 ± 0.81	5.82 ± 1.59

TABLE 2: RESULTS OF TOTAL HYDROCARBON, CHLORIDE AND TOTAL ACIDITY

	TOTAL HYDROCARBON			CHLORIDE			TOTAL ACIDITY		
Samples	Surface samples	Sub- surface samples	Reference samples	Surface samples	Sub- surface samples	Reference samples	Surface samples	Sub- surface samples	Reference samples
1	5550.00	2750.00	50.00	300.00	330.00	40.00	600.00	65-20	140.00
2	3200.00	1250.00	50.00	800.00	300.00	60.00	800.00	54.00	96.00
3	27500.00	1900.00	50.00	890.00	300.00	60.00	520.00	19.40	56.00
4	27500.00	2000.00	500.00	1700.00	400.00	80.00	840.00	26.80	70.00
5	3575.00	2750.00	500.00	900.00	280.00	40.00	508.00	39.20	66.00
6	1125.00	1025.00		350.00	250.00		1000.00	38.80	
7	36750.00	2500.00		1000.00	500.00		840.00	31.20	
8	39500.00	250.00		700.00	600.00		1148.00	72.00	
9	36500.00	150.00		1000.00	270.00		888.00	30.08	
10	36250.00	2525.00		700.00	400.00		920.00	58.00	
11	5250.00	1075.00		1000.00	230.00		752.00	23.20	
12	42500.00	4025.00		700.00	400.00		640.00	24.00	
13	1825.00	1050.00		400.00	300.00		900.00	32.00	
14	29750.00	50.00		1400.00	450.00		936.00	56.00	
15	36500.00	2425.00		900.00	260.00		800.00	34.04	
16	11625.00	50.00		500.00	300.00		900.00	64.00	
17	34750.00	1750.00		1300.00	300.00		800.00	44.00	
18	30000.00	550.00		1600.00	400.00		800.00	30.00	
19	5125.00	2125.00		1000.00	400.00		584.00	80.00	
20	21500.00	3000.00		1800.00	400.00		800.00	22.00	
21	10875.00	2375.00		800.00	280.00		500.00	38.80	
22	1100.00	2175.00		900.00	380.00		688.00	36.00	
23	2525.00	700.00		450.00	320.00		696.00	21.60	
24	22250.00	1875.00		1300.00	460.00		1028.00	80.00	
25	29250.00	1000.00		1000.00	650.00		800.00	80.00	
26	36500.00	2500.00		1500.00	300.00		920.00	46.00	
27	28750.00	1075.00		1600.00	280.00		768.00	21.00	
28	2625.00	950.00		500.00	330.00		608.00	65.60	
29	26250.00	550.00		1000.00	490.00		900.00	48.00	
30	2525.00	4000.00		550.00	500.00		540.00	49.20	
31	1000.00	2150.00		400.00	300.00		584.00	26.80	
32	29500.00	650.00		1700.00	480.00		1040.00	43.20	
33	25250.00	2000.00		1500.00	240.00		760.00	28.00	
SE @ 95% CL	19837.12 ±1465.05	1672.73 ±113.67	230.00 ±142.62	973.94 ±55.63	366.06 ±17.29	56.00 ±17.76	782.06 ±33.62	4328 ±2.42	85.60 ±30.37

TABLE 3: RESULTS OF SULPHATE TOTAL ORGANIC CARBON AND TOTAL ORGANIC MATTER

SULPHATE				TOTAL ORGANIC CARBON			TOTAL ORGANIC MATTER		
Samples	Surface samples	Sub- surface samples	Reference samples	Surface samples	Sub- surface samples	Reference samples	Surface samples	Sub- surface samples	Reference samples
1	0.36	0.33	0.15	3.54	3.72	3.48	6.10	6.14	6.00
2	0.26	0.70	0.12	2.61	3.54	3.60	4.50	6.10	6.21
3	0.74	0.22	0.14	2.40	3.66	3.48	4.14	6.31	6.00
4	0.98	0.19	1.32	2.28	3.60	3.72	3.93	6.21	6.41
5	0.15	0.15	1.29	3.66	3.00	3.54	6.31	5.17	6.10
6	0.70	0.14		3.60	2.92		6.21	5.03	
7	0.15	0.62		2.01	3.66		3.47	6.31	
8	0.17	0.12		2.01	3.60		3.47	6.21	
9	0.77	0.31		3.84	3.60		6.62	6.21	
10	0.33	0.15		2.16	3.51		3.72	6.05	
11	0.70	0.19		3.54	3.81		6.10	6.57	
12	0.27	0.36		2.61	3.47		4.50	5.98	
13	0.33	0.12		3.78	3.53		6.52	6.08	
14	2.64	0.43		2.40	3.42		4.14	5.90	
15	1.35	0.29		2.16	3.65		3.72	6.30	
16	6.22	0.29		3.84	3.60		6.62	6.21	
17	2.18	0.33		2.28	3.84		3.93	6.62	
18	1.77	0.63		2.46	3.54		4.24	6.10	
19	0.70	0.15		3.84	3.69		6.62	6.36	
20	1.39	0.12		2.28	3.48		3.93	6.00	
21	0.60	0.12		2.16	3.58		3.72	6.18	
22	0.73	0.57		3.75	3.78		6.47	6.52	
23	0.33	0.14		3.60	3.54		6.21	6.10	
24	1.49	0.11		2.58	3.64		4.45	6.28	
25	2.38	0.19		3.00	3.54		5.17	6.10	
26	0.74	0.11		1.92	3.54		3.31	6.10	
27	1.46	0.14		2.46	3.70		4.24	6.38	
28	0.83	0.19		3.48	3.54		6.00	6.10	
29	2.45	0.26		1.62	3.48		2.79	6.00	
30	0.22	0.22		3.60	3.65		6.21	6.29	
31	0.36	0.14		3.60	3.60		6.21	6.21	
32	0.14	0.15		2.46	3.78		4.24	6.52	
33	0.98	0.22		2.34	3.66		4.03	6.31	
S.E@ 95%CL	1.06 ± 0.10	0.25 ± 0.02	0.60 ±0.37	2.84 ±0.13	3.57 ± 0.12	3.56 ± 0.75	4.90 ± 0.22	6.15 ± 0.21	6.14 ±1.30

TABLE 4. CORRELATION COEFFICENT MATRIX BETWEEN PHYSICO-CHEMICAL PROPERTIES AND THE HYDROCARBON LEVELS

pH		Cond.	Moisture	Cl^-	SO_4^{2-}	T.acidity	T/H	TOC	TOM
pH	1.00								
Cond.	-0.47	1.00							
Moisture	0.14	-0.04	1.00						
Cl^-	-0.13	0.21	-0.05	1.00					
SO_4^{2-}	-0.09	0.13	-0.03	0.13	1.00				
T.acidity	0.08	-0.14	-0.15	0.28	0.23	1.00			
T/H	0.01	0.00	-0.02	0.53	0.12	0.46	1.00		
TOC	0.04	-0.08	-0.02	-0.56	-0.01	-0.35	-0.74	1.00	
TOM	0.04	-0.08	-0.02	-0.56	-0.01	-0.35	-0.74	0.99	1.00

T/H: Total hydrocarbon, TOC: Total organic carbon, TOM: Total Organic Matter.
Mean ±SE @ 95 confidence level. EC (μScm^{-1}), every other parameter is in (mg/kg). All computations were done using Microsoft excel software.

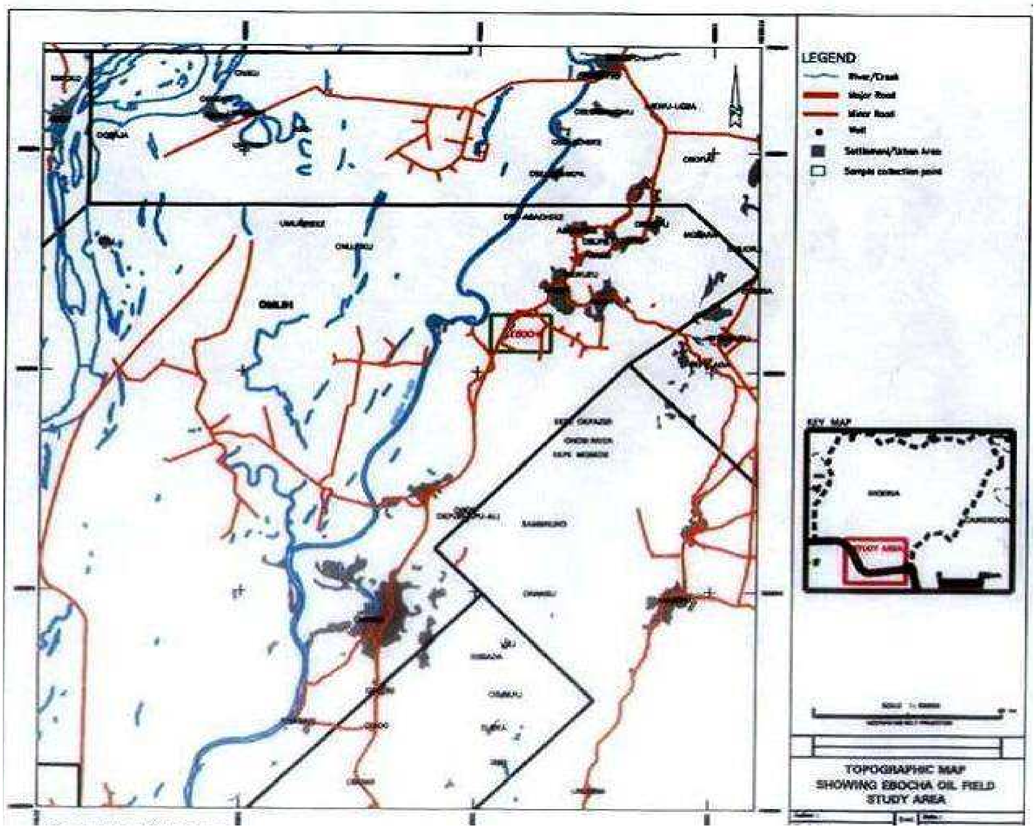
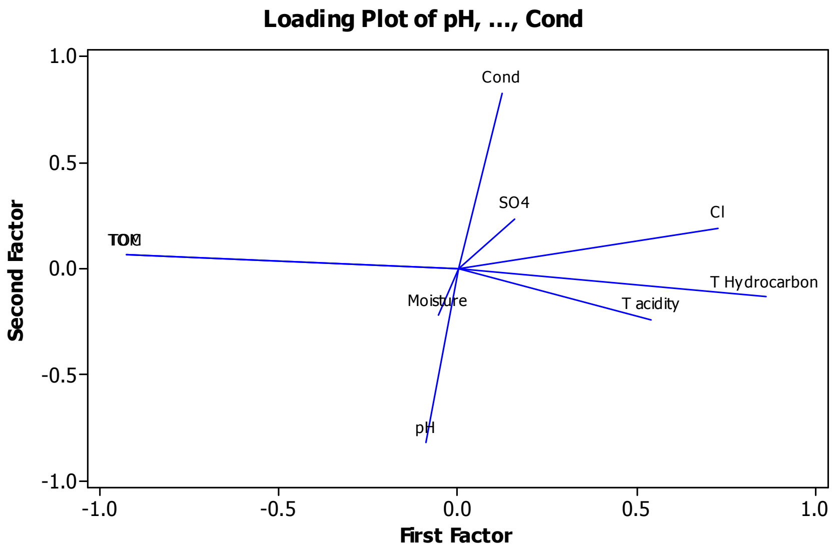


FIG 1. TOPOGRAPHIC MAP OF STUDY AREA SHOWING EBOCHA FIELD

Factor Analysis: pH, Moisture, SO_4^{2-}, TOC, TOM, T Hydrocarbon, Cl^-, T acidity, Conductivity

Table 5: Unrotated Factor Loadings and Communalities of physic chemical characteristics and Total hydrocarbons of Ebocha 8 spill site

Variable	Factor1	Factor2	Factor3	Communality
pH	-0.087	0.820	-0.041	0.682
Moisture	-0.054	-0.223	0.531	0.334
SO_4^{2-}	0.159	0.237	-0.666	0.525
TOC	-0.928	0.065	-0.227	0.917
TOM	-0.928	0.065	-0.227	0.917
T Hydrocarbon	0.862	-0.133	-0.025	0.761
Cl	0.729	0.194	0.029	0.569
T acidity	0.541	-0.239	-0.571	0.675
Cond	0.123	0.831	0.152	0.729
Variance	3.3393	1.5895	1.1798	6.1085
% Var	0.371	0.177	0.131	0.679



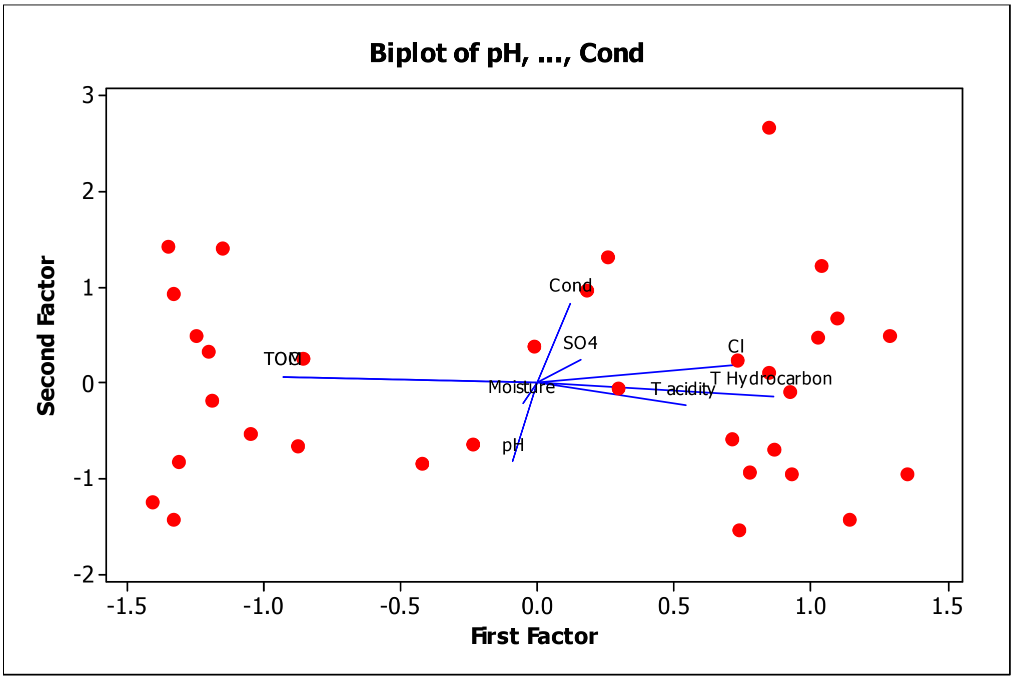


Fig 2: Loading plot and Biplot of physico chemical parameters.

Table 6: Factor Score Coefficients

Variable	Factor1	Factor2	Factor3
pH	-0.026	-0.516	-0.035
Moisture	-0.016	-0.140	0.450
SO_4^{2-}	0.048	0.149	-0.564
TOC	-0.278	0.041	-0.192
TOM	-0.278	0.041	-0.192
T Hydrocarbon	0.258	-0.084	-0.021
Cl	0.218	0.122	0.025
T acidity	0.162	- 0.150	-0.484
Cond	0.037	0.523	0.129

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