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Trace Metals Associated with Oil Spillage: A case study

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ABSTRACT

Soil samples were collected from crude oil polluted sites in Bodo city in Niger Delta Nigeria following a field reconnaissance survey from different depths (0 – 15cm) surface and (15 – 30cm) subsurface. An uncontaminated sample was collected 50 metre away from the spill site but within the same geographical area was used as control sample. Trace elements such as, As, Cu, Cr, Cd, Fe, Pb, Ba, Ni, V, Hg and cation exchange capacity constituents of the oil contaminated and non contaminated soils were determined with Atomic absorption spectroscopy. Cu ranged from 0.50 – 13.41mg/kg, Cr ranged from 0.2 to 0.85mg/kg, Fe ranged from 6.18 – 8.74mg/kg, Ba ranged from 80 – 108mg/kg, Ni ranged from 0.61 – 4.80mg/kg, V ranged from 4.03 – 9.4mg/kg, cation exchange capacity ranged from 43.6 – 57.2 mg/kg in surface and subsurface soils respectively. As, Cd and Hg were less than 0.001mg/kg in all sample plots. The values of these trace elements were relatively higher at the epicenter of the spill and enhanced more at the surface soils signifying input from oil pollution. Principal component analysis of the soil was carried on the physicochemical and the trace element associated with crude oils. Results showed that the eigenvalues of the two first principal components represent up to 49.2% of the total variance. A positive correlation of the first principal component with Cu, Cr and cation exchange capacity shows pollution from oil spillage while a positive correlation of the second principal component with Cr, Fe, V and DO shows both oil pollution and allochthonous inputs.

Keywords: Oil Spillage, Trace metals, Bodo city, pollution and principal component analysis.

INTRODUCTION

Metal contamination of our environment is an increasing eco-toxicological problem due to their long residence time, non-biodegradability, irreversible nature of contamination and accumulation in food chain [6].

Trace elements or metals can be defined as metals occurring at 1000mg/kg or less in the earth crust. Depending on their densities, these elements can be classified as light or heavy. Elements with densities greater than $5g/cm^3$ are ‘heavy’ elements while those with densities less than $5g/cm^3$ are ‘light’ elements [9]. Main anthropogenic sources of heavy metals or trace elements contamination in our environment are mining, agricultural wastes, disposal of untreated and partially treated industrial effluents, fossils fuels, petroleum exploration, indiscriminate use of heavy metal-containing fertilizer, pesticides in agricultural fields and oil spillage [4][7][9]. Trace metals contamination are important due to their potential toxicity to the environment and human health when their concentrations reach certain levels The presence of heavy metals and residues from town and industrial waste and oil spillage has been found to be the causes of soil pollution. [1][5][12].

The incidental discharge of crude oils into the environment as a result of operational mishap, equipment failure, and intentional damage to pipelines conveying the crude oil is known as oil spillage. Oil spillage affects the soil ecosystem and environment that are completely aquatic. Oil pollution has deleterious effect on plant growth, soil macronutrients, microorganism and the terrestrial ecosystem in general [11].

The most contentious and recalcitrant of oil exploration and exploitation activities taking place in the Niger Delta is oil spillage, which in most cases have adversely affected the ecosystem especially arable agricultural farmlands, which in turn has affected food productivity, socio economic and impacted negatively on the health of the people in the region under study.

Owing to environmental and ecotoxicological impact of trace metal contamination, the present study is designed to investigate the concentration of some trace elements/metals contamination in Bodo city oil spill impacted site and to identify their effects on arable agricultural land within the area of the spillage.

EXPERIMENTAL SECTION

Description of study site.

The study site Bodo city (fig 1) geographically lies within latitude 6° 73′ N and longitude 5° 32′ - 5°34′ E 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 but investigation points to sabotage as the cause of the spillage.

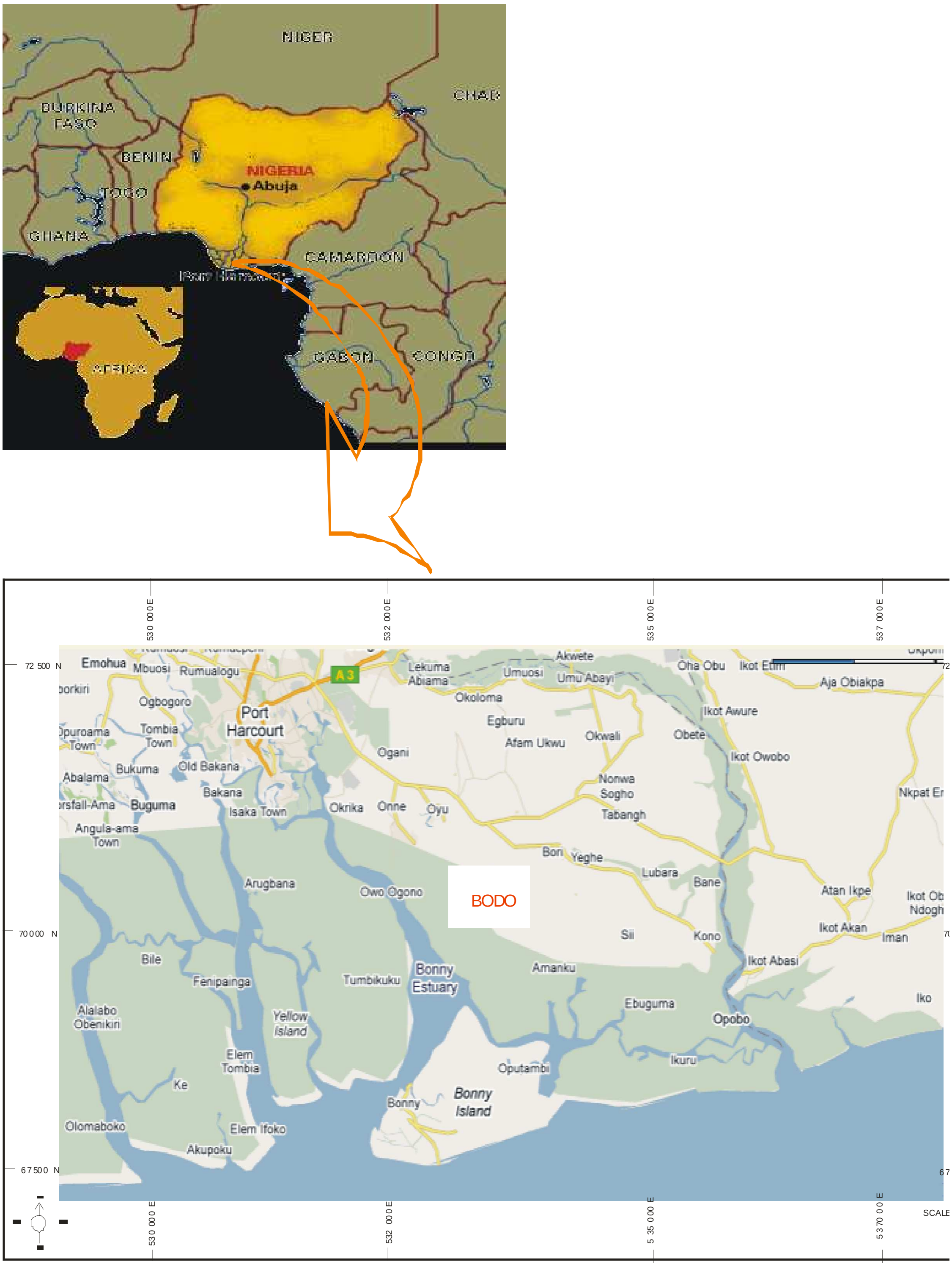


Fig 1 . Topographic map of study area showing sample collection site at Bodo oil field.

Fig 2. A section of Bodo oil spill showing superficial patches on the Niger Delta vegetation

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 [9] Twenty soil samples were collected from surface and sub surface at the depth of 0 to 15cm and 15 to 30 cm respectively. The soil samples were transferred into an acid-washed polyethylene bags and taken to the laboratory for analysis.

Methodology

Physico-chemical analysis

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

Spectrophotometric analyses.

Pre extraction of cations in the soil samples was carried out with dithionite-citrate carbonate according to Hessler method as described by Osuji and Onojake [9]. Concentrations of As, Cu, Cr, Fe, Pb, Ba, Ni, V, Hg and cation exchange in the extract were determined using Perkin – Elmer model 2280/2380 atomic- absorption spectrophometer. The results are shown in Table 3.

RESULTS AND DISCUSSION

Results of the physico-chemical properties and trace metals were calculated at 95% confidence limits using Microsoft excel software.

Table 1: Physico-chemical properties of surface samples of Bodo city oil spill impacted soils

Samp.	Temp	pH	EC	TURB	SAL	DO	TPH
1	29.00	6.50	0.10	430.00	0.00	7.80	7880.00
2	29.00	6.00	0.80	200.00	0.00	7.60	4240.00
3	28.00	6.60	3.90	437.00	0.20	7.80	3875.00
4	29.00	6.60	5.60	596.00	0.10	7.30	2550.00
5	29.00	6.50	0.20	470.00	0.00	7.70	2850.00
6	30.00	6.00	0.20	436.00	0.00	7.60	1890.00
7	29.00	6.10	0.03	590.00	0.00	7.50	733.00
8	29.00	6.50	0.03	536.00	0.00	7.80	936.00
9	30.00	6.70	0.07	416.00	0.00	7.60	5120.00
10	29.00	6.80	2.20	422.00	0.10	7.60	6130.00
Mean	29.00	6.40	1.30	453.00	0.04	7.63	3620.00
REFR.	30.00	7.10	0.03	430.00	0.00	8.10	84.00

Mean ±SE @ 95 confidence level. REFR.= Values of Reference samples. Temp (°C), EC(µScm^{-1}), TURB(NTU) every other parameter is in (mg/kg). All computations were done using Microsoft excel software.

Table 2: Physico-chemical properties of sub-surface samples of Bodo city oil spill impacted soils

Samp.	Temp	pH	EC	TURB	SAL	DO	TPH
1	30.00	6.10	0.04	426.00	0.00	7.50	9836.26
2	29.00	6.20	1.40	0.00	0.10	7.60	7853.05
3	29.50	6.80	7.50	460.00	0.40	7.70	5234.41
4	30.00	6.30	2.30	440.00	0.10	7.80	2265.64
5	29.00	6.10	0.03	416.00	0.00	7.90	3289.93
6	30.00	6.20	0.02	396.00	0.00	7.60	2926.25
7	29.00	6.10	0.02	400.00	0.29	7.30	535.40
8	29.00	6.60	0.04	590.00	0.00	7.60	638.10
9	29.00	6.60	0.05	384.00	0.00	7.50	7134.00
10	29.00	6.80	5.30	450.00	0.30	7.60	9104.50
Mean	29.35	6.38	1.67	416.20	0.12	7.61	4881.75

Mean ±SE @ 95 confidence level. REFR.= Values of Reference samples. . Temp (°C), EC(μScm^{-1}), TURB(NTU) every other parameter is in (mg/kg). All computations were done using Microsoft excel software.

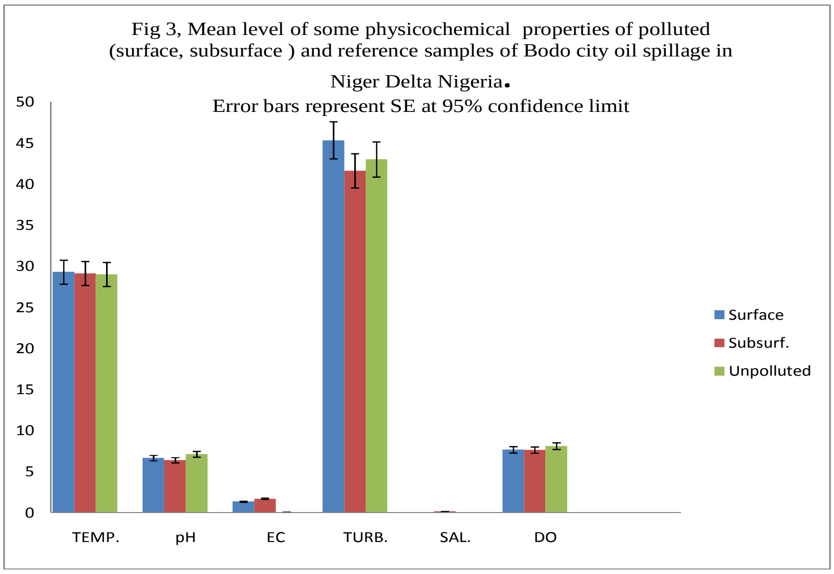
Table 3: Trace metal content of Bodo city oil spillage in Niger Delta Nigeria for surface samples ppm

Samples	As	Cu	Cr	Cd	Fe	Pb	Ba	Ni	V	Hg	Ca Exch
1	0.001	2.05	0.12	0.001	8.27	0.001	80.00	4.05	8.40	0.001	46.20
2	0.001	2.20	0.90	0.001	7.96	0.001	98.00	4.30	9.40	0.001	43.90
3	0.001	2.30	0.18	0.001	7.64	0.001	83.00	3.39	6.60	0.001	47.30
4	0.001	0.25	0.16	0.001	7.63	0.001	100.00	4.05	6.90	0.001	44.30
5	0.001	0.49	0.19	0.001	8.35	0.001	92.00	0.61	6.90	0.001	53.40
6	0.001	0.50	0.14	0.001	6.35	0.001	97.00	0.79	6.31	0.001	46.00
7	0.001	10.66	0.20	0.001	7.18	0.001	100.00	2.02	5.84	0.001	57.20
8	0.001	12.59	0.47	0.001	7.46	0.001	96.00	1.73	5.47	0.001	55.05
9	0.001	2.10	0.15	0.001	7.35	0.001	82.00	4.20	5.42	0.001	43.60
10	0.001	2.05	0.12	0.001	7.74	0.001	94.00	4.08	5.27	0.001	44.80

Table 4:Trace metal content of Bodo city oil spillage in Niger Delta Nigeria for subsurface samples in ppm

Samples	As	Cu	Cr	Cd	Fe	Pb	Ba	Ni	V	Hg	Ca Exch
1	0.001	2.00	0.05	0.001	6.29	0.001	100.00	4.15	7.10	0.001	47.00
2	0.001	2.20	0.03	0.001	7.96	0.001	100.00	4.80	9.20	0.001	47.50
3	0.001	2.14	0.08	0.001	7.36	0.001	104.00	4.01	6.01	0.001	47.80
4	0.001	0.85	0.15	0.001	7.32	0.001	100.00	3.92	6.60	0.001	46.20
5	0.001	0.85	0.13	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	6.18	0.001	103.00	0.88	6.49	0.001	47.60
7	0.001	13.41	0.62	0.001	7.17	0.001	103.00	2.52	4.03	0.001	52.90
8	0.001	12.56	0.85	0.001	7.62	0.001	105.00	1.95	6.30	0.001	54.10
9	0.001	2.03	0.08	0.001	7.23	0.001	103.00	4.25	6.14	0.001	47.20
10	0.001	2.00	0.06	0.001	7.20	0.001	108	4.30	5.63	0.001	47.50

The physicochemical properties of soil are important parameters that enhance the mobility of trace elements in soils (fig 3). The physico - chemical parameters have shown temporal and spatial variations. The temperature of the surface and subsurface soil samples are higher than the subsurface, the pH of the polluted soils is drifting toward the acidic range compared with the unpolluted sample, and the Electrical conductivity (EC) of polluted soils is a measure of the dissolved salt in a soil sample. The changes in conductivity denote a changing composition of soil, which indicates treatment, may be require for these soils. Also the turbidity and dissolved oxygen (DO) of soil were also altered. 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 [13]. The results of the physico-chemical properties are represented graphically in fig 3.



The amount of Cu in polluted soils ranged from 0.75 to 2.56mg/kg with a mean of 1.78 ± 0.31mg/kg. Cr values ranged from 0.12 to 0.90 mg/kg with mean of 0.34mg/kg, Fe ranged from 6.35 to 8.74mg/kg with mean of 7.65mg/kg, Ba ranged from 98 to 108mg/kg with mean of 102.4mg/kg, Ni ranged from 0.63 to 4.80mg/kg with mean of 3.14mg/kg. V varied from 5.47 to 9.4mg/kg with mean of 6.83 mg/kg. There was no significant difference in the values of As, Pb, Cd and Hg in the unpolluted soil samples as they are less than 0.001mg/kg. The cation exchange capacity ranged from 46.2 to 57.2 with a mean of 49.77mg/kg.

The enhance level of Ni, Cu, Cr, Fe, Ba and V in the soils may result in enhanced absorption by plants leading to possible bioaccumulation by plants and animals which may depend on them for survival thus leading to toxic reactions along the food chain [9]. The result of this research may not provide enough scientific evidence that the enhance level of Ni, Cu, Cr, Fe, Ba and V in soil under investigation is solely due crude oil spillage, but rather it is suggested that intense rainfall, flooding and weathering activities which are the characteristics of the area under investigation may lead to significant mobilization and redistribution of most trace elements in the soil. The hydrocarbon levels in soils under investigation were measured as high as 3.6204 $\times 10^4$mg/kg and 4.8817$\times 10^4$mg/kg for surface and subsurface soils respectively. Such increases in V and Ni content have been reported by Volkman et al., [12] as one the gross properties of biodegraded petroleum. 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 [10]. It has also been observed by Amadi and Dickson, [3] that high hydrocarbon content of soils may affect the physico-chemical properties of the soil which may in turn affect the agricultural potentials and productivities of such soils.

Table 5, Loadings of the principal components 1 and 2 Eigenanalysis of the Correlation Matrix

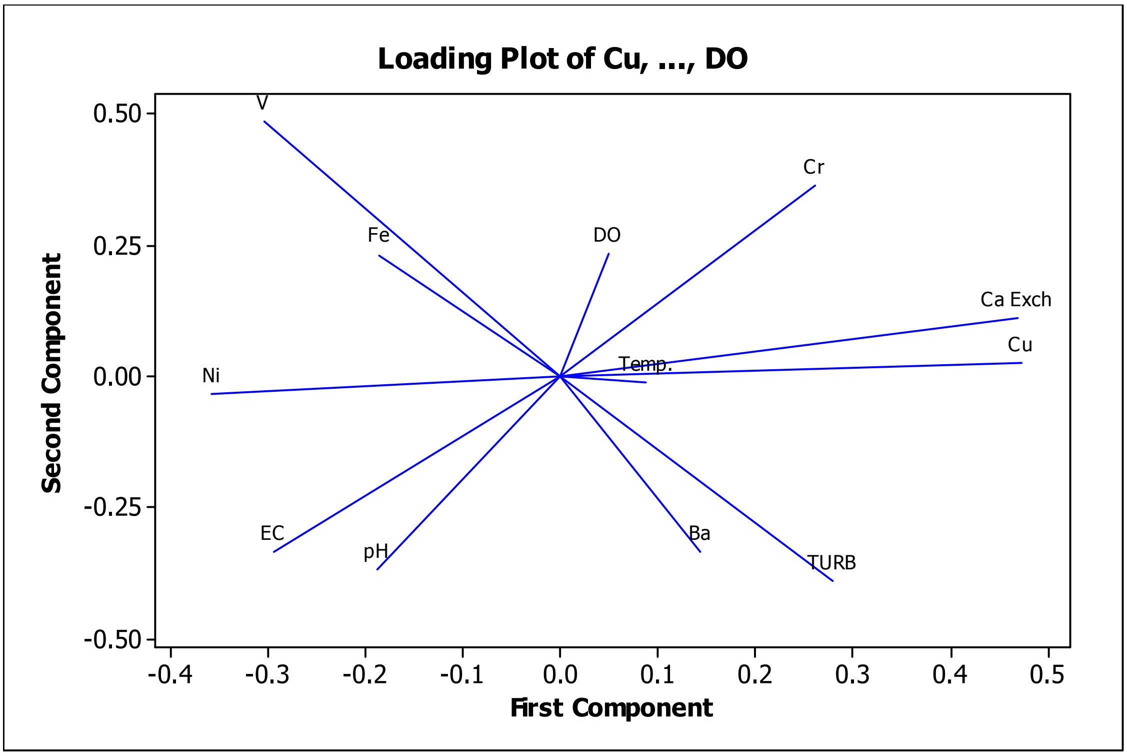
Eigenvalue	3.2574	2.6452	2.0285	1.4920	1.3887	0.6447	0.2944	0.1868
Proportion	**0.271**	**0.221**	**0.169**	0.124	0.116	0.054	0.025	0.016
Cumulative	0.271	0.492	**0.661**	0.785	0.901	0.955	0.979	0.995

Variable	PC1	PC2
Cu	0.473	0.025
Cr	0.26	0.361
Fe	-0.186	0.231
Ba	0.144	-0.335
Ni	-0.358	-0.035
V	-0.305	0.485
Ca Exch	0.47	0.11
Temp.	0.088	-0.013
pH	-0.188	-0.369
EC	-0.295	-0.335
TURB	0.279	-0.39
DO	0.049	0.233

Using principal component analysis (PCA) to interpret results

Fig 4 is the loading plot of the principal component analysis of the physicochemical parameter and the trace elements of the polluted soil samples. From table 5, the principal component analysis showed that the eigenvalues of the first two principal components represent up to 49.20% of the total variance (PC1 27.10%; PC2 22.10%) of the observations. This percentage rises up to 66.10% 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 (Fig.4). To correctly interpret this graph, the factor loadings for each variable on the unrotated components must be taken into account, as shown in Table 5. A close look at fig 4 and table 5 shows that variables such as Cu, Cr and cation exchange capacity of soil correlated positively and contributed to the construction of component 1. These observation shows that the variables are linked to inputs from crude oil 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. This table also shows that the pollution levels of these variables are no so high but have altered the physicochemical properties of the soil.

Fig 4. The loading plot of the principal component analysis of the Phyisco -chemical parameters and the trace metals



CONCLUSION

From the analysis of data, it was observed that the Bodo oil spillage is responsible for part of the enhance levels of Ni, Cu, Pb, in the affected soils. The physicochemical properties, intense rainfall and weathering activities which are characteristic of the region under study are also contributory factors. It was also observed from the study of the trace metals in oil spill impacted sites, that the principal component analysis (PCA) can be employed in interpreting the inter-metal relationship with the physicochemical properties of the impacted soils. We observed a change in every relation linking analytical variables. By construction, PCA made with bar chart representation of these properties, makes these changes noticeable and become an easy and appropriate tool for such a description.

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