

Physicochemical properties and metal speciation in gas flare-impacted soils in Ibeno, Nigeria

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Abstract

The physicochemical properties and metal speciation in gas flare-impacted soils in Ibeno, Nigeria was assessed in this study. During the study, surface soils were collected from five (5) communities impacted by gas flaring within Ibeno namely: Ukpenekang, Mkpanak, Atabrikang, Inua-Eyet Ikot, and Okorutip. Surface soils were also collected from a location outside Ibeno where there is no impact of gas flaring and used as the Control. These samples and Control were treated analytically and analysed for their physicochemical properties and the different fractions of the metals using standard procedures. Results obtained in the studied soils indicated that, the mean values of pH, organic carbon, electrical conductivity, and cation exchange capacity were all within their acceptable limits. The mean total concentrations of lead (Pb), cadmium (Cd), and nickel (Ni) were also within their recommended limits whereas, the mean total concentration of iron (Fe) was higher than the acceptable limit. However, the levels of all the physicochemical properties including the total concentrations of the trace metals in the studied gas flare-impacted soils were much higher than their levels in the control plot. Results of metal speciation in the studied soils revealed that, Pb and Cd existed predominantly in the acid extractable fraction, Ni in the reducible fraction while, Fe existed mainly in the residual fraction. Nevertheless, in the control plot Pb and Cd existed predominantly in the reducible fraction, Ni in the residual fraction while Fe existed in the residual fraction. The Principal component analysis revealed that anthropogenic factor impacted significantly on all the parameters determined except Fe. The Hierarchical cluster analysis confirmed that, all the parameters determined except Fe emanated mainly from the anthropogenic source and also indicated strong relationships among the parameters. The study revealed that, all the metals in the studied gas flare-impacted soils were in the moderate class of contamination factor. The ecological risk factor and potential ecological index of the metals were in the low ecological risk.

Keywords: Gas Flaring; Metal Speciation; Soil Pollution; Multivariate Analysis; Nigeria

1. Introduction

Gas flaring is a technique used by oil companies for the disposal of the waste gases associated with the processing of crude oil [1]. Notwithstanding the adverse economic and environmental problems related to this method of waste disposal, the technique is used by both the developing and developed countries of the world. This method of disposing waste gases by oil Companies is becoming one of the most challenging environmental problems globally. Gas flaring by petroleum industries discharges both organic and inorganic contaminants into the atmosphere which are eventually deposited in surface water bodies and soil environment [2, 3]. Studies have also revealed that, gas flaring has significant negative effect on the physicochemical properties of the soil [4, 5, 6]. Consequently, gas flaring has the potential of modifying the quality of the soil, reducing soil fertility and affect plant growth significantly [7, 8]. The acidic gases discharged during gas flaring causes acidic rain which impacts negatively on the air, soil, water environments and even

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rooftops as experienced in the Niger Delta Region of Nigeria [9, 10, 11]. Nwankwo and Ogagarue [12] opined that, gas flaring could also results in the high accumulation of toxic metals in both aquatic and terrestrial environments.

Gas flaring is one of the major causes of environmental degradation currently experienced in the Niger Delta Region of Nigeria. Over the years, Nigeria has made some legislations concerning the proper management of waste gases associated with the exploitation of crude oil however, the implementation of these laws has not been effectively done. Consequently, gas flaring has been going on unabated in the area and the associated environmental problems has also not been controlled properly.

This study was undertaken to investigate the extent of damage to the soil quality in Ibeno local government area of Akwa Ibom State by gas flaring. The impact of gas flaring on the physicochemical properties, total metal accumulation, and metal speciation in the soil of the study area were assessed. This research also evaluated the actual and major sources of the metals determined in the study area using Multivariate analysis. Previous research works concentrated on the impacts of gas flaring on the surface water, plants, and agricultural activities [13, 14, 15]. Reports have also shown that, researches carried out to evaluate the negative impact of gas flaring on soil focused on the concentrations of total metal without assessing the effect on metal speciation [16, 17]. Hitherto, parameters obtained in the study area were not subjected to Multivariate analysis and some pollution models to ascertain the actual sources of these soil properties and their potential risk in the environment. Thus, it is hoped that this study shall reveal comprehensively the extent to which gas flaring in Ibeno has affected the soil properties and determine the degree of environmental degradation caused.

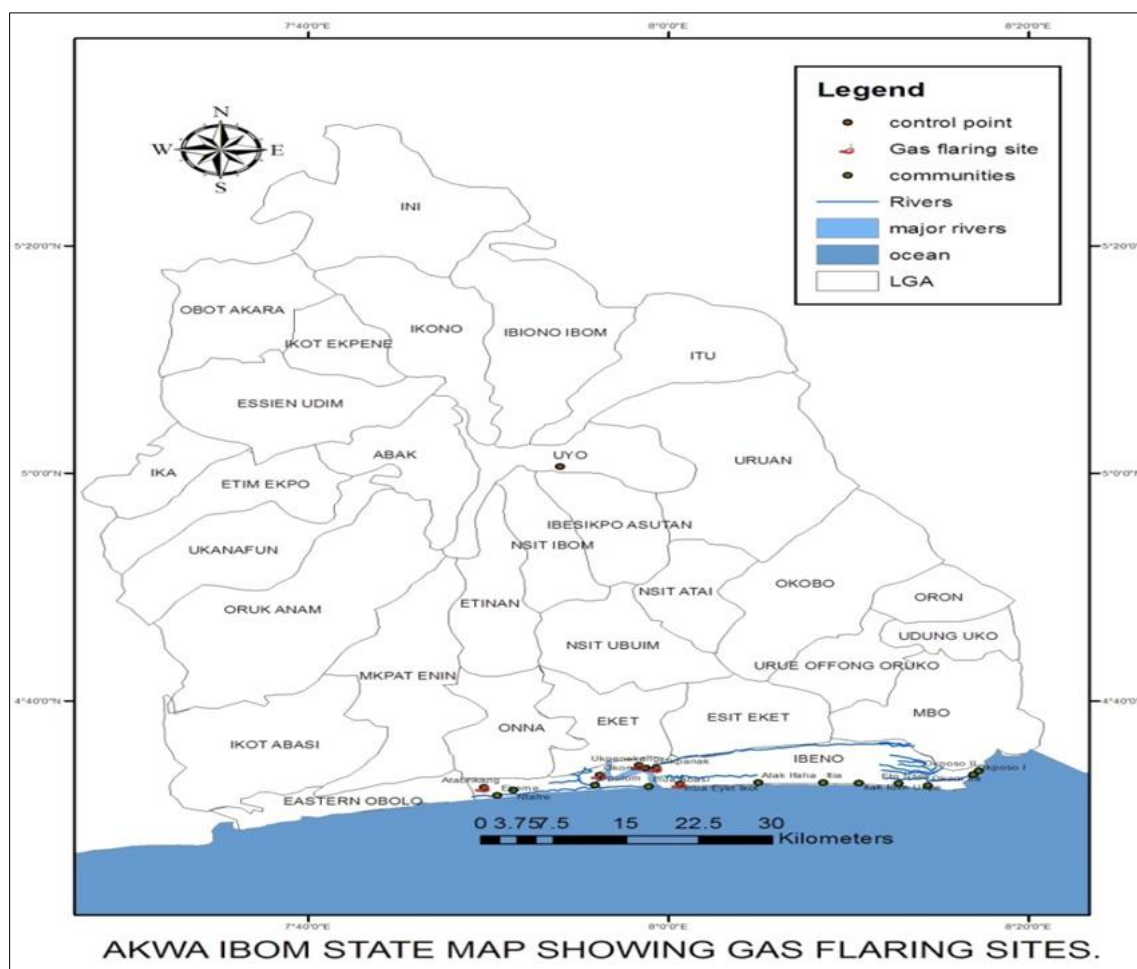
2. Material and methods

2.1. Study area

Ibeno is a local government in Akwa Ibom State, Nigeria that lies latitude $4^{\circ}33'N - 4^{\circ}36'N$ and longitude $7^{\circ}48' - 8^{\circ}17'E$ (Figure 1). It locates in the Mangrove Forest Belt of the Niger Delta Area of Nigeria, bounded to the south by Atlantic Ocean, to the west by Eastern Obolo Local Government Area, and to the north by Onna, Esit Eket and Eket [18]. Ibeno occupies more than 129 km² of Akwa Ibom State, the largest Atlantic coastline in the area. Ibeno has rainfall all the year round with the peak between May and September and the climatic condition of the area favours fishing and farming. The soil type in Ibeno is Anthrosol type according to the International Union of Soil Sciences World Reference Base (IUSS-WRB) Working Group classifications of soil [19]. This area of Akwa Ibom State is impacted significantly by the gas flared by the oil industries operating in the region. A physical evidence of the negative impact of gas flaring is noticed in the damaged rooftops of houses within the studied communities (Ukpenekang, Mkpanak, Atabrikang, Inua-Eyet Ikot, and Okorutip). The coordinates and source of contaminants to the studied locations and Control are shown in Table 1.

Table 1 Sample Locations and their sources of contaminants

Location		Coordinates		Probable source of contaminants
Symbol	Name	Latitude	Longitude	
S1	Ukpenekang	$4^{\circ} 34'N - 4^{\circ}14'N$	$7^{\circ} 58'E - 7^{\circ}46'E$	Gas flaring and oil-related wastes
S2	Mkpanak	$4^{\circ} 33'N - 4^{\circ} 59'N$	$7^{\circ} 59'E - 7^{\circ} 26'E$	Gas flaring and oil-related wastes
S3	Atabrikang	$4^{\circ} 30'N - 4^{\circ} 60'N$	$7^{\circ} 49'E - 7^{\circ} 52'E$	Gas flaring and oil-related wastes
S4	Inua Eyet Ikot	$4^{\circ} 30' E - 4^{\circ} 45'N$	$7^{\circ} 30'E - 8^{\circ} 00'E$	Gas flaring and oil-related wastes
S5	Okorutip	$4^{\circ} 32'N - 4^{\circ} 21'N$	$7^{\circ} 56'E - 7^{\circ} 21'E$	Gas flaring and oil-related wastes
CTL	Control Site (Uyo)	$5^{\circ} 50'N - 5^{\circ} 60'N$	$7^{\circ} 54'E - 7^{\circ} 55'E$	Not affected by gas flaring and other oil-related wastes



S1 = Ukpenekeang, S2 = Mkpanak, S3 = Atabrikang, S4 = Inua-Eyet Ikot, S5 = Okorutip, CTL = Control,

Figure 1 Map of Akwa Ibom State showing the studied locations

2.2. Sample collection, Treatment and Analysis

Surface soil (0 – 15 cm) samples were obtained from the designated locations and control plot in Figure 1 between September and November 2019 using soil Auger. A total of thirty sub-samples and five composite samples were used for this research. These samples and Control were air dried for three days, ground and sieved using a 2 mm Mesh. One gram (1g) of the soil sample was mixed with Aqua regia (HCl and HNO₃ in the ratio of 3:1) and digested on a hot plate. The concentrations of Pb, Cd, Ni, and Fe in the filtrates were obtained using an UNICAM SOLAR 969 Spectrophotometer [20].

2.3. Determination of Physicochemical Properties in soils from the studied locations and control plot

The pH of the studied soils and Control was determined using a pH Meter (Hanna Instrument model 211) following the procedures of Uyigue and Enujekwu [21]. Organic carbon (OC) in the soils from the studied locations and control plot was determined by the chromic acid digestion method of Walkley and Black [22]. The electrical conductivity (EC) of both studied soils and Control was obtained using Conductivity Meter (Model 30) following the procedures of Van Reeuwijk [23]. Cation exchange capacity (CEC) of the studied soils and Control was determined following the ammonium acetate (NH₄OAc) leachate procedures by Oviasogie *et al.* [24].

2.4. Sequential extraction of trace metals in soils from the studied locations and control plot.

This study employed the optimized BCR sequential extraction techniques by Rauret *et al.* [25] for the extraction of metals into the acid extractable, reducible, oxidisable, and residual fractions. The levels of these metals was analysed for in the different fractions obtained using UNICAM SOLAR 969 Spectrophotometer as reported by Rauret *et al.* [20].

2.4.1. Percentage recovery of trace metals in studied soils and Control was obtained using equation (1).

$$\% \text{ Recovery} = \frac{\sum n \text{ Sequential Extraction procedures}}{\text{Single Digestion with Strong Acids}} \times 100 \text{ --- (1)}$$

Where n stands for the level of a particular metal and the single digestion with strong acids denotes the total concentration of a particular metal obtained as reported by Saeedi and Jamshidi-Zanjani [26].

2.5. Determination of pollution status of trace metals in the studied soils and Control

2.5.1. Contamination Factor (CF)

Contamination factor of toxic metals in the studied agricultural soils was assessed by equation 2.

$$CF = \frac{C_m}{B_m} \text{ --- (2)}$$

Where CF is the Contamination factor; C_m represents the level of the metal in studied sample; B_m represents the background concentration in this study. According to Pekey *et al.* [27] contamination factor is categorized into four classes namely: $CF < 1$ = low contamination; $1 \leq CF \leq 3$, moderate contamination; $3 \leq CF \leq 6$, considerable contamination, and $CF > 6$ very high contamination.

2.5.2. Mobility Factor (MF)

Mobility Factor of the metals in the studied soils was determined using Equation 3.

$$MF = \frac{F_1}{F_1 + F_2 + F_3 + F_4} \times 100 \text{ --- (3)}$$

Where F_1 = acid extractable fraction, F_2 = reducible fraction, F_3 = oxidisable fraction and F_4 = residual fraction in modified BCR speciation procedures as reported by Gasparatos *et al.* [28].

2.5.3. Ecological risk index (E^i_r)

The ecological risk factor of trace metals determined in the studied soils was determined using Equation 4.

$$E^i_r = Tr \times CF \text{ --- (4)}$$

Where Tr is the toxic-response factor for the metals and CF is the contamination factor of the metals. Toxic response factors for metals according to Hakanson [29] are Pb (5.00), Cd (30.00), Ni (5.00), and Fe (0.00). The classes of ecological risk factor according to Cao *et al.* [30] are shown in Table 2.

2.5.4. Potential ecological risk index (RI)

The potential ecological risk index of metals in the different studied locations was determined using Equation (5).

$$RI = \sum E^i_r \text{ --- (5)}$$

Where $\sum E^i_r$ signifies the summation of multiple trace metals determined in studied soils as reported by Yang *et al.* [31]. The different categories of potential ecological risk index are indicated in Table 2.

2.6. Statistical Analysis

Statistical analysis of the results obtained in the study was performed using IBM SPSS Statistics 20 (IBM USA). Multivariate Analysis (Factor Analysis and Cluster Analysis), were carried out using Duncan's multiple range tests at 1% degree of probability. Factor analysis was done with eight (8) properties of the studied gas flare-impacted soils, and values from 0.549 and above were significant for the study. Cluster analysis was performed by Dendrograms to ascertain the similar groups of variables with common properties and source.

Table 2 The different classes of ecological risk index and potential ecological risk index according to Cao et al. [30 and Yang et al. [31], respectively

Grade	E_i^r value	Grade of ecological risk of single trace metal	RI	Grade of potential ecological risk of the environment
A	$E_i^r < 40$	Low ecological risk	$RI < 150$	Low ecological risk
B	$40 < E_i^r \leq 80$	Moderate ecological risk	$150 < RI < 300$	Moderate ecological risk
C	$80 < E_i^r \leq 160$	Appreciable ecological risk	$300 < RI < 600$	High ecological risk
D	$160 < E_i^r \leq 320$	High ecological risk	$RI \geq 600$	Significantly high ecological risk
E	$E_i^r > 320$	Serious ecological risk		

3. Results and discussion

3.1. Physicochemical Properties of the studied soils and the control plot

The results for the physicochemical properties of the studied soils and the control plot are indicated in Table 3. The physicochemical properties of the studied soils varied with the locations (Table 3). The pH for the gas flared-impacted soils ranged from 4.38 to 5.74 with a mean value of 5.13 ± 0.45 (Table 3). This pH range is lower than 4.12 – 6.51 obtained by Umeda *et al.* [32] in gas flare-impacted soils. The mean pH value obtained in the studied soils is lower than 6.70 reported in the control plot. Consequently, the gas flare-impacted soils were more acidic than the soil in the control plot. This is consistent with findings by Uyigue and Enujekwe [21] in their research. This could be attributed to the impact of acidic gases discharged by the gases flared. Reports have shown that, pH of the soil has adverse effect on the availability of plant nutrients [33, 34]. However, the range of pH reported for the studied soils is within the acceptable range of 6.0 - 9.0 by WHO [35] and FEPA [36].

The electrical conductivity (EC) of the gas flare-impacted soils ranged between 0.12 and 0.27 dS/m with a mean value of 0.21 ± 0.05 dS/m (Table 3). The reported EC range is lower than 0.020 – 0.052 mS/cm obtained by Atuma and Ojeh [7] in gas flare-impacted soils. The mean EC value reported in the studied soils is higher than 0.08 dS/m obtained at the control soil. This is similar to the report by Atuma and Ojeh [7] in their study in soils impacted by gas flaring. Thus, the higher mean EC value in the gas flare-impacted soils could be attributed to the impact of gas flared. Nevertheless, the mean value of EC in the gas flare-impacted soils is within the acceptable limit of 100.0 μ S/cm by WHO [35].

Organic carbon (OC) contents of the gas flare-impacted soils ranged between 1.96 and 4.49 % with a mean value of 3.51 ± 1.07 % (Table 3). The obtained range is higher than 1.01 – 2.10 % reported by Atuma and Ojeh [7]. The mean OC value of the studied soils is lower than 7.26 % obtained at the control site. The higher OC contents in the control soil is consistent with the findings by Achieche *et al.* [37]. Consequently, gas flaring has a negative effect on the availability of soil organic carbon thereby affecting agricultural activities [14]. However, the mean OC value of the studied gas flare-impacted soils is within the acceptable limit of 5.00% by FEPA [36].

The CEC contents of the studied gas flare-impacted soils varied from 12.70 to 17.03 cmol/kg with a mean level of 14.74 ± 1.58 cmol/kg (Table 3). The CEC range reported in this study is higher than 3.245 – 4.095 meq/100g obtained by Uzoekwe [38] in a similar study. The mean CEC value of the gas flare-impacted soils is lower than 19.86 cmol/kg obtained in the control plot. This shows that the CEC of the soil increases with the soil pH as reported by Tomašić *et al.* [39]. Hence, gas flaring might have impacted negatively on the cation exchange capacity of the soil environment thereby affecting the availability of soil nutrients adversely. However, the mean CEC value reported in the studied gas flare-impacted soils is lower than the acceptable limit of 1000.0 cmol/kg by WHO [35].

Generally, the degree of variability of the physicochemical properties of the studied soils was low except for OC. This is confirmed by the low values of relative standard deviation (RSD) indicated in Table 3.

3.2. Distribution of total trace metals in the studied soils and the control plot

The concentrations of total trace metals determined in both the studied gas flare-impacted locations and the control plot are shown in Table 3. The concentrations of the total trace metals analysed for in the studied soils varied from one location to the other. The concentration of total Pb ranged from 8.24 to 13.29 mg/kg with a mean value of 10.73 ± 1.90 mg/kg (Table 3). The reported range is higher than 2.5 – 3.5 mg/kg obtained in the gas flared-impacted soils by

Achieche *et al.* [37]. The mean value of Pb obtained in the studied gas flare-impacted soils is also higher than 1.56 mgkg⁻¹ reported in the control site. This is in agreement with the report by Achieche *et al.* [37] in their study. Consequently, gas flaring activities in the area might have affected the accumulation of Pb in the studied soils. Nevertheless, the mean value of Pb obtained in the studied gas flare-impacted soils is within the permissible limit of 164.0 mgkg⁻¹ by NESREA [40].

The concentrations of total Cd in the studied gas flare-impacted soils varied between 1.87 mgkg⁻¹ to 2.50 mgkg⁻¹ with a mean concentration of 2.14±0.24 mgkg⁻¹ (Table 3). The range obtained in this study is lower than 2.050 – 3.116 mgkg⁻¹ reported by Uyigue and Enujekwu [21] in gas flare-impacted soils. Results in Table 3 show higher levels of Cd in the studied gas flare-impacted soils than in the control site. This is in agreement with the results reported by Ejiogu *et al.* [41] in their study on gas flare-impacted soils and a Control. Thus, gases flared in the studied communities might have contributed significant quantity of Cd to the adjoining soil environment. However, the mean Cd value reported for the studied gas flare-impacted soils is within the recommended limit of 3.0 mgkg⁻¹ by NESREA [40].

Total Ni levels in the studied gas flare-impacted soils as shown in Table 3 range between 1.92 and 2.40 mgkg⁻¹ with a mean value of 2.15±0.20 mgkg⁻¹. This range is lower than 15.10 – 20.40 mgkg⁻¹ obtained in gas flare-impacted soils by Achieche *et al.* [37]. The mean concentration of Ni in the studied gas flare-impacted locations is higher than 0.87 mgkg⁻¹. This is an indication of anthropogenic input of the metal from gas flaring into the studied soil environment. The higher concentrations of Ni in the studied gas flare-impacted communities than in the control site is consistent with the findings by Uyigue and Enujekwu [21]. Nevertheless, the mean value of Ni obtained in the studied gas flare-impacted communities is within the permissible limit of 70.0 mgkg⁻¹ by NESREA [40].

Total Fe concentrations in the studied gas flare-impacted soils varied from 1530.09 to 1664.49 mgkg⁻¹ with a mean value of 1593.03 ±43.12 mgkg⁻¹ (Table 3). The reported range is higher than 1045.19 – 1083.96 mgkg⁻¹ obtained by Enuenwemba *et al.* [42] in a similar research work. Results in Table 3 also indicate higher levels of Fe in the studied gas flare-impacted locations than in the control site. This is consistent with the findings by Uyigue and Enujekwu [21] in a related study. This is also an indication of substantial anthropogenic addition of Ni to the soil environment by the gases flared in the area. The mean value of Fe reported in the studied gas flare-impacted soils is higher than the recommended 400.0 mgkg⁻¹ for Nigerian soil by FEPA [36]. The high level of Fe reported in this study may not be attributed solely to the anthropogenic activities but the high availability of Fe in Nigerian soils could also be a factor [43]. This corroborates the higher level of Fe in the control site than the recommended limit as shown in Table 3. The results of the speciation of trace metals has also confirmed that, health problems associated with Fe toxicity may not manifest in the area as the metal existed mostly in the inert (residual) fraction.

Table 3 Physicochemical Properties and total trace metals of the studied soils and Control

	pH	EC (dS/m)	OC (%)	CEC (cmol/kg)	Pb (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Fe (mg/kg)
S1	5.24	0.27	1.96	14.08	13.29	2.50	2.38	1581.02
S2	4.38	0.20	4.18	12.70	12.17	2.25	1.97	1664.49
S3	5.35	0.22	4.49	16.06	10.99	1.89	2.40	1588.59
S4	4.95	0.22	4.43	13.81	8.24	2.18	2.06	1600.95
S5	5.74	0.12	2.50	17.03	8.94	1.87	1.92	1530.09
Min	4.38	0.12	1.96	12.70	8.24	1.87	1.92	1530.09
Max	5.74	0.27	4.49	17.03	13.29	2.50	2.40	1664.49
SD	0.45	0.05	1.07	1.58	1.90	0.24	0.20	43.12
\bar{x}	5.13	0.21	3.51	14.74	10.73	2.14	2.15	1593.03
RSD (%)	9.0	24.0	31.0	11.0	18.0	11.0	9.0	3.0
CTL	6.70	0.08	5.26	19.86	1.56	0.69	0.87	634.97

S1 = UkpeneKang, S2 = Mkpanak, S3 = Atabrikang, S4 = Inua-Eyet Ikot, S5 = Okorutip, CTL = Control, Min = Minimum, Max = Maximum, SD = Standard Deviation; \bar{x} = Mean, RSD = Relative Standard Deviation

Generally, the mean concentrations of Pb, Cd, and Ni reported in this study were within their acceptable limits however, their existence should be closely monitored to forestall associated negative implications as they are very toxic even at low concentrations. The results for the total concentrations of the metals in both the studied locations and control site followed the order: Fe > Pb > Ni > Cd. The degree of variability of these metals among the different locations investigated is also low as affirmed by their low RSD values in Table 3.

3.3. Speciation of Trace Metals in the studied locations and control site

The results for the speciation of trace metals determined in this study are shown in Table 4. The results revealed that, Pb existed mostly in acid extractable fraction in the studied gas flare-impacted soils with a total composition of 45.4 %. However, Pb existed mainly in the reducible fraction in the control site with a composition of 39.5 %. This disparity between the studied locations and the control site could be attributed to the impact of gas flaring. Consequently, gas flaring is encouraging the high bioavailability and mobility of this toxic metal (Pb) in the studied gas flare-impacted communities which is very risky to those exposed to it either directly or indirectly. This should be properly controlled to forestall the human health associated with Pb toxic as reported by ATSDR [44]. The results in Table 4 show the percentage recovery of Pb in the studied locations and control site as 90 and 80 %, respectively. The mobility factor of Pb in the studied locations is 45 % but 21 % in the control site. The high bioavailability of Pb in the studied soils is shown in the obtained order: Aex > Red > Ox > Res while the control site followed a trend of Red > Ox > Aex > Res.

Cd existed predominantly in the acid extractable fraction in the studied gas flare-impacted locations with a high percentage composition of 43.0. Conversely, Cd existed mostly in the reducible fraction in the control site with a high percentage composition of 57.4. This is an indication of the impact of gas flaring on the bioavailability of Cd in the communities investigated. The high bioavailability of Cd in the studied locations should be closely monitored to avoid Cd toxicity and its associated human health implications as reported by ATSDR [45]. The percentage recovery of Cd as shown in Table 4 for the studied gas flare-impacted soils and control site are 89 and 85, respectively. The mobility of Cd in the studied soils and control plot are 43 and 29 %, respectively. The higher bioavailability of Cd in the studied gas flare-impacted soils than in the control plot is also revealed in the followings trends: Aex > Red > Ox > Res (Studied soils) and Red > Aex > Ox > (control plot).

Table 4 Results for speciation, percentage composition, % recovery and mobility factor of metals

	AEX F1	%	RED F2	%	OX F3	%	RES F4	%	TMF	TM	% REC	MF %
Pb	21.94	45.4	11.39	23.6	8.32	17.2	6.64	13.8	48.29	53.63	90	45
Cd	4.07	43.0	2.68	28.3	1.73	18.3	0.99	10.4	9.47	10.69	89	43
Ni	1.35	14.0	3.42	35.5	2.06	21.4	2.81	29.1	9.64	10.73	90	14
Fe	654.69	8.7	1113.95	14.8	2187.20	29.2	3551.04	47.3	7506.88	7965.14	94	9
CONTROL												
Pb	0.64	20.7	1.22	39.5	0.71	23.0	0.52	16.8	3.09	3.87	80	21
Cd	0.29	28.7	0.58	57.4	0.12	11.9	0.02	2.0	1.01	1.19	85	29
Ni	0.07	6.5	0.19	17.6	0.36	33.3	0.46	42.6	1.08	1.27	85	7
Fe	76.71	7.3	108.57	10.4	323.21	31.0	535.81	51.3	1044.30	1134.97	92	7

Aex = Acid extractable, Red = Reducible, Ox = Oxidisable, Res = Residual, TMF = Total metal fraction, TM = Total metal, % Rec = Percentage recovery, MF = Mobility factor

Ni existed principally in the reducible fraction in the studied soils with percentage composition of 35.5 but in the control plot as residual fraction with a composition of 42.6 %. This could be attributed to the anthropogenic impact of gases flared in the studied soils. The findings also revealed that a change in the soil chemistry that favours a reduction process could release more Ni into the readily available fraction in the studied soils than in the control plot. The distribution of Ni into the different fractions in the studied gas flare-impacted soils and control plot followed the orders: Red > Res > Ox > Aex and Res > Ox > Red > Aex, respectively. The recovery rates of Ni in both the studied gas flare-impacted soils and the control plot are 90 and 85 %, respectively (Table 4). The results in Table 4 also indicate a higher bioavailability level of Ni in the studied gas flare-impacted soils than in the control plot with values of 14 and 7 %, respectively.

Fe existed primarily in the inert (residual) fraction in both the studied gas flare-impacted soils and Control with percentage compositions of 47.3 and 51.3 %, respectively. This confirms the non-bioavailability of Fe in both the studied soils and Control notwithstanding their high concentrations. The low mobility factors of Fe in both the studied gas flare-impacted soils and control plot (9 and 7 %, respectively) verifies the low bioavailability of the metal. This may have attributed to the separate cluster illustrated for Fe in Figure 4 and confirms the high contribution of natural factor to the accumulation of Fe in both the studied soils and the control plot. The results in Table 4 also reveal the insignificant impact of anthropogenic factor (gas flaring) on the accumulation of Fe in the studied communities. The non-bioavailability of Fe in both the studied soils and control plot is further confirmed by the common trend of Res > Ox > Red > Aex. The recovery rates of Fe in the studied gas flare-impacted and control plot are 92 and 94 %, respectively.

Generally, the recovery percentages for the trace metals determined was very high and this attest to the reliability of the analytical techniques used and results obtained.

3.4. Contamination Factor (CF)

Results for the contamination factor (CF) of each of the metals determined at each location are shown in Figure 2. Contamination factor for trace metals in the studied gas flare-impacted soils was used to measure the impact of each of these metals on the soil environment [46]. The mean values of CF for Pb, Cd, Ni, and Fe as shown in Figure 2 are 2.77, 1.80, 1.69, and 1.40, respectively. Following the classifications of CF by Wang et al. [47], all the metals were in the moderate class of contamination. However, the CF values of Pb at locations S1 and S2 (Ukpenekang and Mkpanak, respectively) were in the considerable contamination class. The high degree of contamination of Pb at these locations could be attributed to their closeness to the point source. The degree of metal enrichment in the studied locations followed the order: Pb > Cd > Ni > Fe.

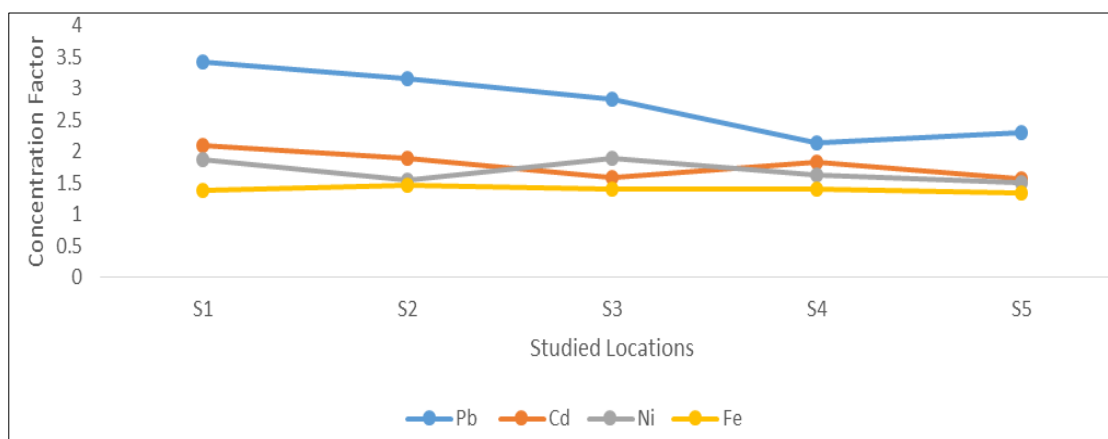


Figure 2 Contamination Factor (CF) of Trace Metals in the studied Soils

3.5. Ecological risk factor (E_r) and Potential ecological risk index (RI)

Results for the ecological risk factor (E_r) for individual element determined in the studied gas flare-impacted soils are illustrated in Figure 3. The mean values of the ecological risk factor of the metals as indicated in Figure 3 are as follows: (Pb) 13.86, Cd (53.88), Ni (8.44), and Fe (0.00). Consequently, all the metals belong to the low ecological risk class according to Cao *et al.* [30]. Despite the low ecological risk class of these metals, their presence in the studied environment should be closely monitored to avoid bioaccumulation and associated health implications as all the metals except Fe are highly toxic [48].

Potential ecological risk index (RI) indicates the toxicity and environmental response to the risks related to the trace metals assessed in the studied gas flare-impacted soils [31]. Results for the RI values of the metals at the studied locations are shown in Figure 3. The RI values for the trace metals in the studied locations varied from 71.35 to 89.50. Thus, the potential ecological risk index of the soils investigated belong to the low ecological risk category [31]. However, the trend should be properly monitored to forestall risks associated with metal toxicity in the studied locations.

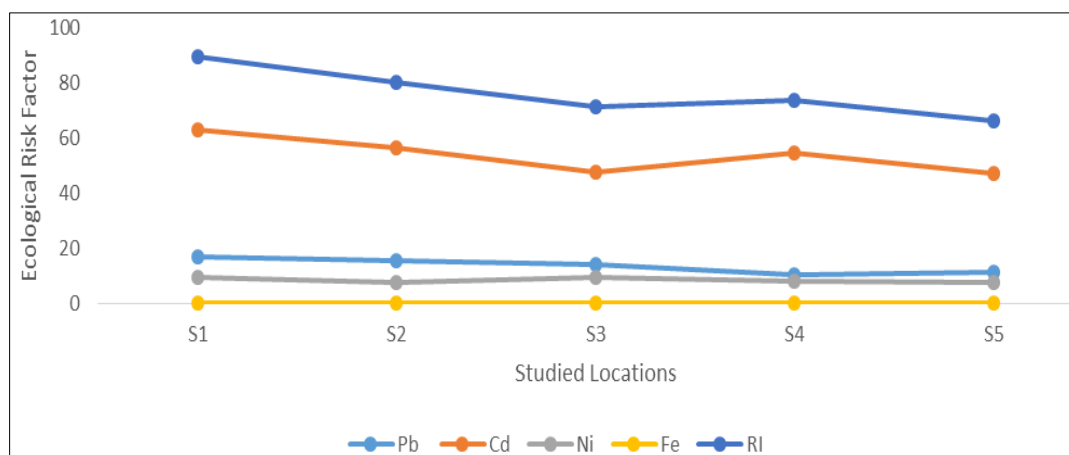


Figure 3 The Ecological Risk Factor ((Er) and Ecological Risk Index (RI) of Trace Metals in the studied Soils

3.6. Multivariate Analysis

The multivariate analyses employed for the source identification and existing relationship among the parameters determined in the studied gas flare-impacted soils include Principal component analysis (PCA) and Hierarchical cluster analysis (HCA) as indicated below.

3.7. Principal Component Analysis (PCA)

The Principal Component Analysis (PCA) was employed to establish the actual sources of the metals determined in the studied soils [49, 50]. Components with Eigenvalues of one and above were considered while parameters with values of 0.549 and above were used for the explanation of the results in Table 5. The PCA indicated three major factors with Eigenvalues greater than one with strong 93.98% of the total variance (Table 5). Factor one (PC1) contributed 51.41% of the total variance with strong positive loadings on Fe, Cd, EC, Pb but with significant negative loadings on CEC and pH (Table 6). This signifies the negative impact of both the natural and anthropogenic activities (gas flaring) on the quality of the studied gas flare-impacted soils [51, 52]. Factor two (PC2) contributed 28.57% of the total variance with significant positive loadings on Pb and Ni but with strong negative loadings on OC (Table 6). This represents specifically the negative impact of anthropogenic activities in the study area on the soil environment as reported by Mugoša *et al.* [51]. Factor three (PC3) contributed 13.99% of the total variance with significant positive loadings on Ni and OC (Table 6). This is the negative effect of the industrial activities on the quality of the studied gas flare-impacted soils [53].

Table 5 Total Variance Explained for parameter determined in the studied soils

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.113	51.413	51.413	4.113	51.413	51.413	3.653	45.657	45.657
2	2.286	28.573	79.986	2.286	28.573	79.986	2.297	28.716	74.374
3	1.119	13.988	93.975	1.119	13.988	93.975	1.568	19.601	93.975
4	.482	6.025	100.000						
5	1.002E-015	1.252E-014	100.000						
6	3.164E-016	3.955E-015	100.000						
7	1.413E-017	1.766E-016	100.000						
8	-1.111E-016	-1.389E-015	100.000						

Extraction Method: Principal Component Analysis.

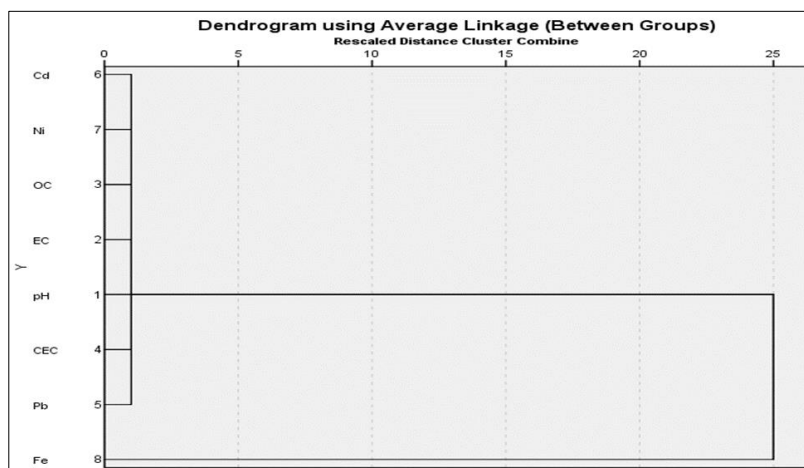
Table 6 Matrix of the principal components in the studied soils

Component			
	PC1	PC2	PC3
CEC	-0.934	0.243	0.205
Fe	0.861	-0.463	0.079
pH	-0.856	0.506	0.075
Cd	0.799	0.376	0-.393
EC	0.766	0.490	0.318
Pb	0.648	0.549	0-.085
Ni	0.262	0.743	0.616
OC	0.232	-0.723	0.651

Extraction Method: Principal Component Analysis

3.8. Hierarchical Cluster Analysis (HCA)

The pair-wise associations among the physicochemical properties of the studied gas flare-impacted soils indicated two major clusters as shown in Figure 4. Cluster one links Cd, Ni, OC, EC, pH, CEC, and Pb together while cluster two links Fe only. Cluster one shows the significant impact of gases flared on Cd, Ni, OM, EC, pH, CEC, and Pb on the studied soils whereas, cluster two reveals that, a greater proportion of Fe might have been contributed by the natural source as reported by Ebong *et al.* [54]. This corroborates the occurrence of Fe in the residual form in both the studied gas flare-impacted soils and the control site.

**Figure 4** Hierarchical clusters of the parameters determined in the studied soils

4. Conclusion

This research revealed the negative impact of gases flared by oil Companies on the physicochemical properties of the soil within the studied communities. Results obtained has also shown that, gas flaring may have contributed substantial quantities of metals reported in the studied soils. The results of metal speciation confirmed that, gas flaring has the potential to modify the forms of metals in the studied soils. The Principal component analysis and Hierarchical cluster analysis attributed the relative high levels of the physicochemical properties of the studied gas flare-impacted soils to the anthropogenic source. The study has also shown that, Pb and Cd were readily available in the studied gas flare-impacted soils than in the control plot. Generally, the negative impact of gas flaring on the fertility of the studied gas flare-impacted soils has been exposed.

Compliance with ethical standards

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Disclosure of conflict of interest

We wish to state clearly that, there is no conflict of interest regarding this Study and the related article.

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