Original Research Article

Assessment of Heavy Metal Levels in the Neighbourhood of Gas Flaring Station in Obunagha, Bayelsa State, Nigeria

Erepamowei Young[1], Wurutuawei T. Silver[1], Ajoko Imomotimi Timipa[1*], Tarinimi Tamunosa Jim-Halliday[2], Christopher Unyime Ebong[3]

[1]Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria
[2]Department of Chemistry, Rivers State Universsity, Nkpolu-Oroworukwo, Port-Harcourt, P.M.B 5080
3Transition Minerals International Limited

*Corresponding author: Ajoko Imomotimi Timipa
Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria

Abstract

Gas flaring has the potential of polluting soil with heavy metals and consequently lead to poor fertility and reduced yield. This study investigates the impact of gas flaring on metal pollution of soil at Obunagha, Yenagoa Local Government Area of Bayelsa State. Soil samples were collected with soil auger at depths of 0-15 cm from distances of 200 m, 500 m, 1000 m, 2000 m, and 3000 m away from the flaring point of the Gbarain-Ubie Integrated Oil and Gas Plant. Physicochemical parameters such as pH, electrical conductivity and Cation Exchange Capacity were determined. Samples were extracted sequentially and heavy metals (Cr, Cd, Ni, Zn, Cu, Mn and Fe) were determined using flame atomic absorption spectrophotometer (FAAS). The pH values of the soil samples ranged from 4.63 ± 0.06 to 6.87 ± 0.06 indicating that the soils were acidic. The Electrical conductivity values ranged from 20 ± 0.00 to 39.7 ± 0.58 (µS/cm) while the Cation exchange capacity values ranged from 2.4 ± 0.01 to 6.95 ± 0.01 (meq/100 g), which are suggestive of the soil capacity to adsorbs metals. The results of the analysis of variance on heavy metals indicates non significance for $*P> 0.05$ while $**P< 0.05$ is significant. The closest distance (200 m) to the flaring point has the highest concentrations for all the metals studied while the farthest distance (3000 m) has the least concentrations. Also, the results revealed that the concentrations of all the metals studied decreased from the first fraction which is the water-soluble fraction to the sixth fraction (residual fraction). The concentrations of the metals analyzed for all the samples were higher than those recommended by DPR, WHO, and US EPA indicating that gas flaring activities in the study area has polluted the soil of the study area with the heavy metals studied.
Keywords: Gas flaring, Obunagha Community, Niger Delta, soil sample, Metal speciation, Heavy metals.

1. INTRODUCTION

Since Shell-Bp discovered crude oil in commercial quantities in 1956 at Oloibiri, Bayelsa State, it has been an important part of the Nigeria economy and has made gas flaring increased drastically in the Niger Delta region. The exploitation and exploration of oil has been of great gain to Nigeria but the negative results emanating from such production processes have been very disastrous. One of these is gas flaring, which locally and internationally threatens the world ecology, human health, agriculture, and water security by releasing toxins into the water, land, and air [1]. Gas flaring is the unscientific burning of excess hydrocarbon gathered in an oil/gas production flow station/site [2]. According to Olukoya [3], Nigeria has over 1,000 gas flaring stations,

making it the world's largest associated gas flarer. Interestingly, with this volume of gases flared, over 80% are not recovered. Gas flaring is an unavoidable part of the petroleum process confirming that there is hardly any oil producing nation which do not flare some percentage of her gas. However, statistics from various countries shows that Nigeria top the list of ten countries responsible for 75% of gas flaring emission in the world [4]. Approximately, the 75% of gas produced is flared annually causing considerate ecological and physical damage to other resources such as land/soil, water and vegetation. These gases are mostly emitted in the Niger Delta area of Nigeria. Mbaneme *et al.,* [5] states that gas flaring are major contributors to the emission of toxic gases and other pollutants. Like the combustion of other

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carbonaceous fuels, gas flaring produces oxides of carbon (COx), sulphur (SOx) and nitrogen (NOx), water vapor, volatile and non-volatile forms of trace metals (Pb, Cd, As, Hg, etc.). Ogwejifor [6], observed that incomplete combustion of the flared also produces greenhouse gases (such as methane), other gaseous pollutants (such as CO), and organic elemental participates (such as coke). Furthermore, gas flaring produces heat near flare stacks, a condition that may cause sleeplessness, especially at night (since the area is permanently bright red like day light) [7].

Studies have revealed that gas flaring has significant negative effect on the physicochemical properties of the soil. As a result, gas flaring has the ability to alter soil quality, diminish soil fertility, and have a substantial impact on plant growth [8]. However, because of the region's oil industry's environmental contamination, the soils in the Niger Delta region are among the worst [9].

In Obunagha Community, gas flaring is the major source of thermal pollution which occur 24hrs every day, for some years ago and this affects agricultural potentials, and other related activities in Obunagha and environs. Gas flaring has affected the soils found within gas flare areas. Obunagha Community is not exempted from this; the majority of the soils in the area have a tendency to discourage plant growth and are, thus, infertile. The pressure from gas flares causes the soil's acidity to rise since soil fertility depends on the presence of nutrients such as nitrogen, phosphorus, and potassium as well as other nutrient elements [9].

Flaring of associated gases results in the emission of pollutants that comprises of heavy metals, which are deposited into the soil as outfalls when the primary phase of the metals dissolves, subjecting the metal ions in solution to many pathways such as uptake by plants, mineral surfaces and organic matter. The occurrence of heavy metals in soil caused by weathering processes of parent materials is a natural phenomenon that occurs at trace (<1000 mg/kg) and seldom hazardous levels [10]. However, due to human activities that disrupt nature, most soils in urban and rural areas may accumulate one or more heavy metals above prescribed background levels, endangering plants, animals, human health, and ecosystems [11].

Total metal concentrations give some signs of soil pollution or enrichment, but they don't account for metal mobility, thus they can't be used to assess metal toxicity hazards. Metal speciation, on the other hand, describes the various forms in which metals can be found, including their source, mode of distribution, mobility, and physicochemical and biological availability, all of which are impacted by a number of physical, chemicals, and biological factors [12].

The present study was designed to assess the extent of damage to the soil quality in Obunagha Community, Yenagoa Local Government area of Bayelsa State by gas flaring. In the research region, the effects of gas flaring on the physicochemical characteristics and metal speciation of the soil were evaluated. Thus, it is believed that the findings from this study will reveal the extent to which gas flaring in Obunagha Community has affected the soil properties.

2. MATERIALS AND METHODS
2.1. Description of Study Area
Obunagha community in Gbarain Clan, is located in Yenagoa LGA, Bayelsa State, Nigeria Fig 1), that lies latitudes 4°59'N - 5°28'N and longitudes 6°15'E - 6°21'E. The community is bordered on the north by Okolobiri, on the south by Tunuama, on the east by the Opokuma clan, and on the west by the Onopa village in Atisa Kingdom. This community is chosen for the study because it is hosting the Gbarain-Ubie Integrated Oil and Gas Project commonly called LNG in Bayelsa State. The project is owned by Shell Petroleum Development Company, Agip, Elf and Eni Joint Ventures. The Gbarain-Ubie Integrated oil and gas flow station has been functional for about a decade (2010) now and just like every other oil and gas flow station within the Niger Delta, unwanted (associated) gases from the facility are flared into the environment. Figure 1 is a map showing the Obunagha creek, LNG road, host community, and the gas flaring point. Figures 2a and 2b show the GPS maps (designated 200 m – 3000 m) of sampling sites.
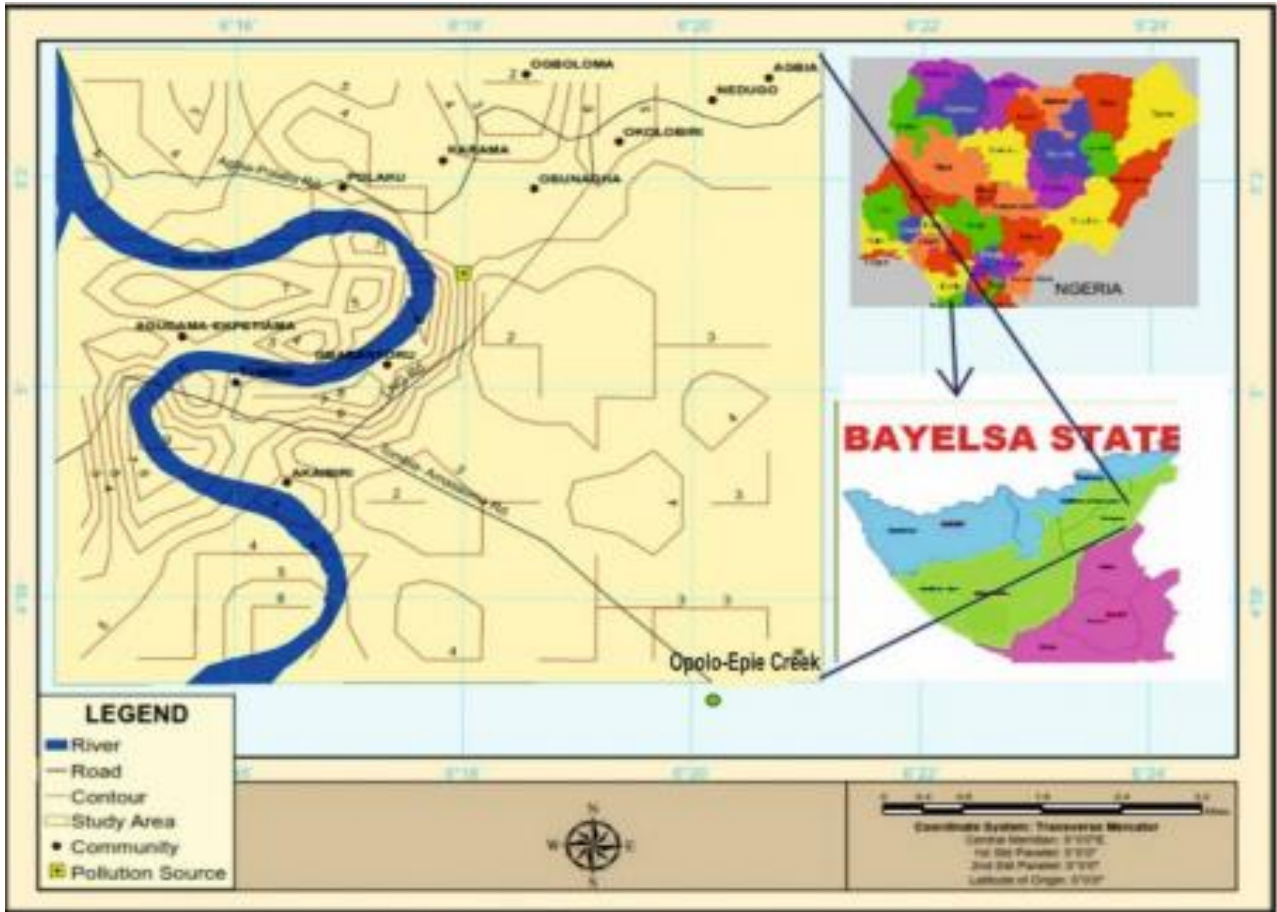
Fig 1: Map of the Study Area
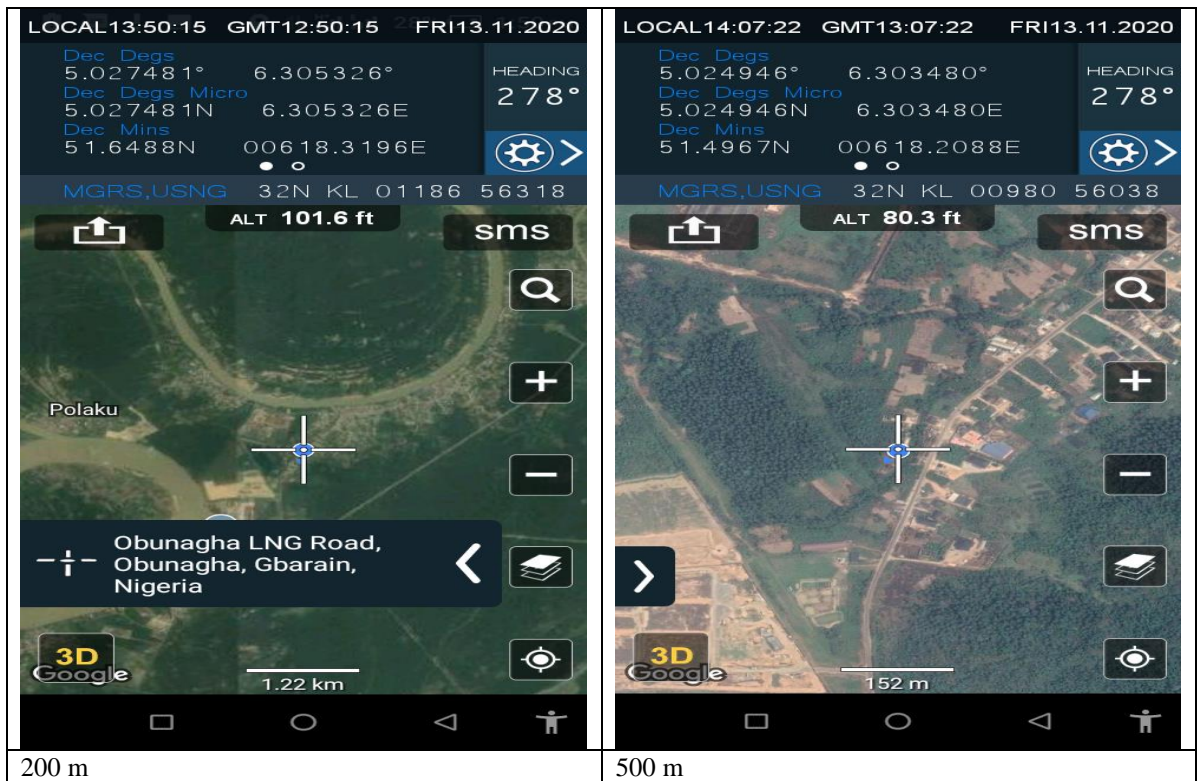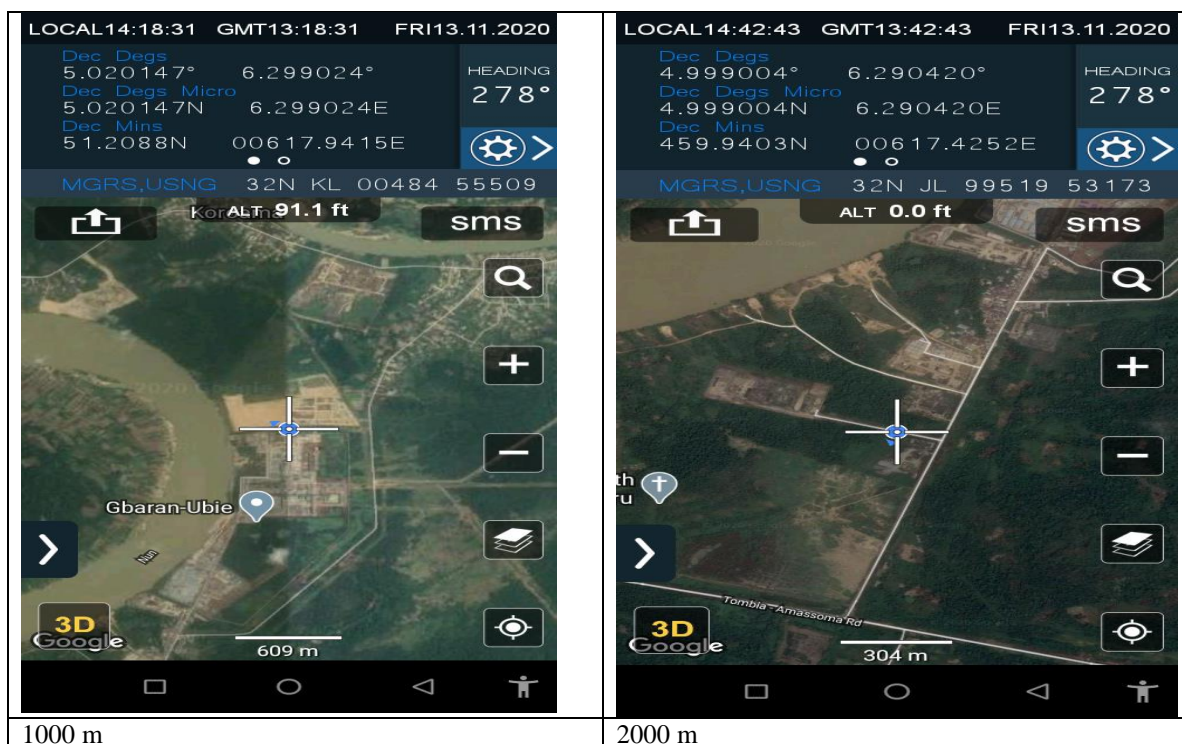
Fig 2a: GPS maps of the sampling sites; 200 - 2000 m away from the flaring point (indicated with a cross symbol on the maps)

Fig 2b: GPS map of the sampling site at 3000 m away from the flaring point (indicated with a cross symbol on the maps)

2.2. Materials

The materials used in this research include the following; De-ionized water, soil samples, soil auger and polyethylene bags (for soil samples collection), Magnesium chloride ($MgCl_2$), Acetic acid (CH_3COOH), Hydroxylamine hydrochloride ($NH_2OH.HCl$), Sulphuric acid (H_2SO_4), Nitric acid (HNO_3), Sodium ethanoate (CH_3COONa), Ammonium acetate (CH_3COONH_4),

Barium chloride dihydrate ($BaCl_2.2H_2O$), Magnesium sulphate ($MgSO_4$), Potassium chloride (KCl), pH meter, Conductivity meter, Filter paper- Whatman, masking tape, Glass wares such as beakers, volumetric flasks, measuring cylinders, stirring rods, funnels, conical flasks, reagent bottles, pestle and mortar, plastic sieve, etc. Analytical weighing balance, Water bath,

Centrifuge, Atomic Absorption Spectrometer (AAS model: S4 = 71096).

2.3. Collection of Sample

Test samples of soil were collected from the Gbarain-Ubie Integrated Oil and Gas Flow Station in Obunagha Community. With the aid of soil auger, soil samples were collected at depths of 0 to 15 cm. The collected samples were carefully labeled and stored in polyethylene bags for onward transfer to the laboratory. The sampling points are radial distances away from the flaring point: 200 m, 500 m, 1000 m, 2000 m, and 3000 m. A total of 15 samples (in triplicate) were sent to the lab for analysis.

2.4. Preparation of Sample

The soil samples were dried by air for roughly 8 days using plastic trays then labeled accordingly to those on the polythene bags. The soil samples that were air dried were crushed in a ceramic mortar and then sieved in a 2 mm plastic sieve. The finely sieved portions of the soil samples were kept in well labeled polythene bags which were used for the extraction.

2.5 Analysis of Samples

Soil samples collected at the gas flaring site were subjected to physical and chemical property tests from which properties such as pH, Electrical conductivity and Cation exchange capacity were measured.

2.5.1 pH Determination

20 g of each of the finely sieved soil samples were weighed into prewashed 100 mL beakers and then 40 mL volume of deionized water was introduced into each soil sample. For about 30 minutes, the mixtures were stirred at regular intervals. The pH values were obtained by immersing the electrodes in the mixtures and taking consistent readings.

2.5.2 Determination of Electrical Conductivity

20 g of each of the finely sieved soil samples were weighed into prewashed 100 mL beakers and then 40 mL of deionized water was added into each soil sample. At 30-minute intervals, the mixtures were stirred regularly. The electrodes were immersed into the supernatants from the mixtures and the stable readings were taken for the electrical conductivity values.

2.5.3 Determination of Cation Exchange Capacity

The Cation exchange capacity was assessed using the Barium Chloride Compulsive Exchange Method, AOAC [13]. In this method, 2 g of each of the finely sieved soil samples were weighed into funnels containing filter papers which were placed in prewashed 125 mL conical flasks. The soil samples were leached slowly by adding 20 mL of 0.1M $BaCl_2.2H_2O$, letting each addition permeate the soil before further additions. Following this, 60 mL of 2 mM $BaCl_2.2H_2O$ was added to the soil samples in six 10 mL portions, allowing for the soil to absorb each addition before adding more. The last 10 mL of the leachate from each soil samples was kept separately for pH determination. After taking the pH readings, the filter paper with the soil of each sample was transferred into 125 mL conical flasks that were pre-weighed and 10 mL of 5 mM $MgSO_4$ was added into each of the soil sample. Each of the pre-weighed 125 mL conical flasks containing the 10 mL portion of 5 mM $MgSO_4$ solution was swirled occasionally for an hour before weighing the flask for the final solution weight.

The 1.5 mM $MgSO_4$ solution conductivity was determined and it was within 300 µS or µmhos. Also, the conductivities of the sample solutions were determined and in cases where conductivities of the sample solutions were not more than 1.5 times of 300 µS or µmhos, 0.1 mL increments of 0.1M $MgSO_4$ was added until the conductivities of the sample solutions were within the 1.5 times 300 µS or µmhos range keeping record of the amount of 0.1 M $MgSO_4$ that was added to each sample solution.

2.6 Chemical fractionation of heavy metals in soil samples
2.6.0 Extraction

The fractionation of the metals was done using the extraction procedures of Salbu *et al.,* [14] which is an adapted modification of the Tessier *et al.,* [15] procedures. The procedure is designed to extract the heavy metals into six fractions as (F1) water soluble metals, (F2) exchangeable metals, (F3) bound to carbonate metals, (F4) bound to Fe-Mn oxides, (F5) bound to organic carbon metals and (F6) residual metals according to the following procedures: The procedure was carried out using 1 g of sieved dry soil sample.

2.6.1 Determination of Water-Soluble Metals (F1)

The samples were extracted with 20 mL of deionized water with occasional agitation. The extracts were centrifuged for 2 hours at room temperature to achieve good separation. The supernatant from the extraction were carefully decanted and was acidified with 0.5 mL concentrated HNO_3 and used to determine the water-soluble metals by flame atomic absorption spectrophotometer (FAAS). The solid residues from this fraction 1 were washed and used for F2 extraction.

2.6.2 Determination of Exchangeable Metals (F2)

The residue from the water-soluble fraction (F1) was extracted at room temperature for 1 hour with 8 mL of I M $MgCl_2$ at a pH of 7, with continuous stirring followed by centrifugation. The supernatants were acidified by addition of 0.5 mL concentrated HNO_3 and diluted to 20 mL with deionized water using a 20 mL standard flask and used for analysis. The final solution was used to determine the exchangeable heavy metals by FAAS. The residues from the soil samples in this fraction (fraction 2) were used for the fraction 3 procedures.

2.6.3 Determination of Bound to Carbonate Metals (F3)

The residue obtained in the exchangeable fraction (F2) was solubilized with 8 mL of I M ammonium acetate acidified with acetic acid to pH 5. The mixture was shaking time was 5 hours at room temperature and centrifuged. The supernatants were acidified by adding 0.5 mL concentrated nitric acid and diluted into a 20 mL volumetric flask to the mark with distilled deionized water and used to determine the heavy metals bound to carbonates by FAAS. The solid residues from this fraction were used for fraction 4 extraction.

2.6.4 Determination of Metals Bound to Fe-Mn Oxides (F4)

The residues from carbonate bound fraction (F3) was dissolved in 20 mL of 0.04 M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% acetic acid (HOAc) and the mixture was heated in a water bath at 96^oC with intermittent agitation for 3 hours. The supernatant, after centrifugation, was acidified with 0.5 mL concentrated nitric acid and diluted into a 20 mL volumetric flask to the mark with distilled de-ionized water. Then the heavy metal bound to Fe-Mn Oxides was determined by using FAAS. The residues from the soil samples in this fraction were used for fraction 5 extraction.

2.6.5 Determination of Metals Bound to Organic Carbon (F5)

This fraction indicates heavy metals bound to various forms of organic carbon that can be released under oxidizing conditions. To the solid residue from F4 were treated 5 mL of 30% H_2O_2 and 3 mL of 0.02 M HNO_3 (adjusted to pH 2.0 with HNO_3). The mixture was heated to 85 °C for 2 hours using a water bath and occasionally. Then, 20% HNO_3 in 5 mL of 3.2 M ammonium acetate and 20 mL of deionized water was added to the resulting solution and the mixture was shaken for 3 hours. The supernatants were acidified with 0.5 mL concentrated nitric acid into a 20 mL volumetric flask and completed with distilled de-ionized water to the mark and used to determine the heavy metals bound to organic carbon by FAAS. The residues from the soil samples in this fraction were used for the F6 procedures.

2.6.6 Determination of Residual Metals (F6)

In this fraction, the residues from the organic bound fraction (F5) were extracted using 20 mL of 4 M HNO_3 and the mixture was heated to 80^oC using water bath for 2 hours. The mixture was cooled and centrifuged for three hours at 2000 rotations per minute. The extraction supernatants were acidified with 0.5 mL concentrated nitric acid to prevent the metals extracted from binding to the sample containers' walls. These were kept aside for the FAAS analysis.

Using flame atomic absorption spectrometry, the elemental measurement of Zn, Cr, Fe, Cd, Ni, Mn and Cu in various speciation fractions were carried out.

2.7. Statistical Analysis

In presenting the data, tables, statistical diagrams were employed. Subsequently, comparative analysis was made based on the data and presented on tables and statistical graphs. To investigate the variability of concentrations among samples, the outcomes were put through analysis of variance (ANOVA) with SSPS version 20 package

3. RESULTS AND DISCUSSION

3.1 Physicochemical parameters

Table 1 presents physicochemical characteristics of the soil samples. The soil pH measures the level of soil acidity or alkalinity in a solution or substance. The pH values for the soil samples ranged from 4.7 to 6.9, thus the soils found in the study area were acidic. The observed acidity level of soils could have been responsible for the poor utilization of the nutrients in the growth medium [16]. The low pH shows that gas flaring may have an impact on soil pH. The low pH around the flare sites could be attributed to acidic precipitation [17]. The pH values obtained in this study are consistent with the values reported by Uzoekwe [18], and Okeke & Okpala [19], who found that gas flaring changes the pH of the soil. Also, the acidic pH values shows that the metals under study are mobile as stated by Kumar and Srikantaswamy, [20] that the lower the pH values, the more mobile the metals will be in solution. Since at low pH (acidic) metals are more soluble and more bioavailable in the soil solution, the range of pH values obtained in this study will favour plant uptake of heavy metal and hence toxicity problems are possible [21].

Electrical conductivity (EC) is a measure of ionic concentration in the soils and is therefore related to dissolve solutes such as ions and salts. The electrical conductivity (EC) values for the soil samples were found to be between 20±0.00–39.7±0.58 µS/cm. This is due to the effect of gas flaring on the soil in the research region. The range of values obtained in this study are similar to the values reported by Uzoekwe's, [18] and Atuma & Ojeh, [9] findings, that reported electrical conductivity in the range of 0.031–1.120 mS/cm and 0.020–0.053 mS/cm respectively.

The soil Cation exchange capacity values ranged from 2.4±0.01 to 6.95±0.01 (meq/100 g), which are suggestive of the soil capacity to adsorbs metals. The values of cation exchange capacity found in this investigation are consistent with those reported by Ojeh [22], from the range of 2.01–5.17 meq/100 g at different gas flaring locations. Also, Uzoekwe [18], reported 3.245–7.405 at different locations.

Table 1: Values of soil pH, electrical conductivity and cation exchange capacity in relation to distance from flaring point

Properties	Distance (m) away from flaring point				
	200	**500**	**1000**	**2000**	**3000**
pH	4.97 ±0.06	4.93±0.06	4.63±0.06	6.87±0.06	4.77±0.06
Electrical conductivity (µS/cm)	30±0.00	39.7±0.58	20±0.00	30±0.00	20±0.00
Cation exchange capacity (meq/100 g)	5.15±0.01	3.46±0.01	4.5±0.01	6.95±0.01	2.4±0.01

3.2 Metal speciation

Water soluble fraction

Metal concentrations (mg/L) of Cr, Cd, Ni, Zn, Cu, Mn and Fe in this fraction ranged from 1.74–9.94, 0.32–1.01, 7.22–13.17, 1.16–3.17, 5.01–8.45, 1.05–2.46 and 1.57–4.15 respectively. The concentrations of the metals in this fraction are in the order of Ni > Cr > Cu > Fe > Zn > Mn > Cd. The concentrations of Zinc in this fraction at distances of 200 m, 500 m and 1000 m away from the flaring point are higher than the standards of DPR [23] and US EPA [24] but are within those of WHO [25] (Table 3). The concentrations of the other metals and those of zinc at distance of 3000 m away from the flaring point are above those of the governing bodies (Table 3) indicating the pollution of the soil in the research area.

Exchangeable fraction

Metal concentrations of Cr, Cd, Ni, Zn, Cu, Mn and Fe in the exchangeable fraction ranges from 1.22–8.41, 0.17–0.79, 6.30–10.52, 0.68–2.61, 4.10–6.51, 0.42–2.04 and 0.43–2.40. The concentrations of the metals found in this fraction followed this pattern: Ni > Cr > Cu > Zn > Fe > Mn > Cd. As could be readily seen from the result Ni is highest in this fraction. The study revealed that the concentrations of all metals in this fraction were found to be above the safe limits set by DPR [23], US EPA [24] and WHO [25] (Table 3).

Bound to carbonate fraction

The analyzed metals (Cr, Cd, Ni, Zn, Cu, Mn and Fe) in the bound to carbonate fraction has concentrations ranging from 1.17–6.74, 0.10–0.53, 3.16–7.59, 0.53–2.02, 2.15–3.37, 0.09–1.67, 0.10–1.37 respectively. The concentrations were in this order: Ni > Cr > Cu > Zn > Mn > Fe > Cd. The analyzed concentrations are higher than those of the governing bodies.

Bound to Fe-Mn oxides fraction

The results of the sequential extraction of Fe-Mn oxides fraction in the soil samples are shown in Table 2. The bound to Fe-Mn oxides fraction has concentrations ranging from 0.82–6.20, 0.05–0.34, 2.29–5.89, 0.17–1.59, 0.82–3.83, 0.08–1.17 and 0.09–0.97 for the metals Cr, Cd, Ni, Zn, Cu, Mn and Fe respectively. The result shows that Cr is most abundant in this fraction. The concentration of heavy metals in this fraction displays the following decreasing trend: Cr > Ni > Cu > Zn > Mn > Fe > Cd. The data also showed that in this fraction all the heavy metals under study were higher than the recommended standards of DPR [23], WHO [24] and U.S EPA [25] (Table 3).

Bound to organic carbon fraction

The analyzed metals Cr, Cd, Ni, Zn, Cu, Mn and Fe have concentration range of 0.53–5.21, 0.04–0.30, 1.0–3.72, 1.0–1.04, 0.42–2.65, 0.05–0.91 and 0.03–0.57 respectively in the bound to organic carbon fraction. These concentration values are above the recommended values (Table 3). The concentrations for the metals are in the order of Cr > Ni > Cu > Zn > Mn > Fe > Cd.

The residual fraction

Table 2 shows the speciation of metals in soil samples. The results shows that the proportion of metals in the residual fraction was 0.22–3.92 for Ni, 0.03–0.19 for Zn, 0.31–1.94 for Mn, 0.02–0.74 for Cr, 0.06–1.59 for Fe, 0.02–0.37 for Cu and 0.00–0.20 mg/L for Cd. These concentrations were in this order: Ni > Mn > Cr > Fe > Cu > Zn > Cd. Zinc was found to be the most abundant in the residual fraction, which means that Zn is more mobile in this environment than other metals. The analyzed concentration values for all the metals were above the standards of the governing bodies (Table 3).

Table 2: Distribution of Cr, Cd, Ni, Zn, Cu, Mn and Fe in different fractions in soil samples, from Obunagha Community

Element	Distance (m)	Concentration (mg/L)					
		Fraction I n =3	**Fraction 11 n =3**	**Fraction III n =3**	**Fraction IV n =3**	**Fraction V n =3**	**Fraction VI n =3**
Chromium	200	9.94 ± 0.02	8.41 ±0.01	6.74±0.04	6.20±0.04	5.21±0.06	3.92±0.02
	500	6.81 ± 0.01	6.17 ±0.02	4.03±0.01	3.48±0.02	3.04±0.02	1.75±0.02
	1000	4.17 ± 0.01	3.87 ±0.02	2.18±0.01	1.83±0.04	1.07±0.07	1.00±0.01
	2000	3.66 ± 0.01	2.45 ±0.03	1.64±0.01	1.18±0.03	0.74±0.03	0.60 ±0.01
	3000	1.74 ± 0.04	1.22 ±0.05	1.17±0.02	0.82 ±0.01	0.53±0.03	0.22 ±0.01
Cadmium	200	1.01±0.10	0.79± 0.01	0.53±0.01	0.34±0.12	0.30±0.11	0.19±0.11
	500	0.67±0.01	0.42± 0.10	0.39±0.10	0.16±0.01	0.26±0.01	0.13±0.01
	1000	0.59±0.04	0.38± 0.11	0.21±0.11	0.10±0.01	0.10±0.02	0.10±0.04

Element	Distance (m)	Concentration (mg/L)					
		Fraction I n =3	Fraction 11 n =3	Fraction III n =3	Fraction IV n =3	Fraction V n =3	Fraction VI n =3
	2000	0.50±0.10	0.21± 0.01	0.15±0.01	0.09±0.03	0.08±0.01	0.06±0.02
	3000	0.32±0.10	0.17± 0.12	0.10±0.02	0.05±0.01	0.04±0.01	0.03±0.01
Nickel	200	13.17±2.11	10.52±1.23	7.59 ± 2.12	5.89 ±2.01	3.72±1.99	1.94 ±0.55
	500	11.05±0.21	9.38 ±2.54	5.87 ± 0.55	4.16 ±1.87	3.21±1.47	1.30 ±0.11
	1000	8.24±2.54	8.86 ±1.05	5.14 ± 2.45	3.60 ±0.21	1.62±0.02	0.86 ±0.01
	2000	7.62±0.27	8.13±0.11	3.84 ± 0.22	3.05 ±0.01	1.15±0.21	0.57 ± .22
	3000	7.22±0.88	6.30±0.88	3.16 ± 0.03	2.29 ±0.55	1.0 0.12	0.31 ±0.01
Zinc	200	3.17 ± 0.60	2.61 ± 0.11	2.02 ± 0.12	1.59 ±0.11	1.04 ±0.11	0.74 ±0.11
	500	2.37 ± 0.51	2.20 ± 0.12	1.65 ± 0.11	1.0 0.01	0.85 ±0.22	0.37 ±0.02
	1000	2.03 ± 0.21	1.55 ± 0.01	1.14 ± 0.14	0.75 ±0.01	0.31 ±0.01	0.10 ±0.04
	2000	1.47 ± 0.11	1.14 ± 0.52	0.84 ± 0.11	0.35 ±0.03	0.15 ±0.44	0.05 ±0.02
	3000	1.16 ± 0.01	0.68 ± 0.03	0.53 ± 0.02	0.17 ±0.01	1.0 ±0.21	0.02 ±0.02
Copper	200	8.45 ± 1.22	6.51 ± 0.22	3.37 ± 0.01	3.83 ±0.44	2.65 ±0.21	1.59 ±0.01
	500	7.21 ± 2.11	6.01 ± 1.47	5.14 ± 1.25	3.01 ±0.11	2.02 ±0.11	1.04 ±0.14
	1000	6.40 ± 0.01	4.90 ± 0.57	4.64 ± 0.24	1.21 ±0.01	1.36 ±0.14	0.52 ±0.11
	2000	5.85 ± 0.22	4.90 ± 0.21	2.75 ± 0.11	1.0 0.10	0.76 ±0.21	0.28 ±0.01
	3000	5.01 ± 0.40	4.10 ± 1.02	2.15 ± 0.32	0.82 ±0.04	0.42 ±0.01	0.06 ±0.01
Manganese	200	2.46 ± 0.11	2.04 ± 0.11	1.67 ± 0.01	1.17 ±0.04	0.91 ±0.03	0.37 ±0.01
	500	2.00 ± 0.01	1.64 ± 0.12	1.08 ± 0.21	0.81 ±0.01	0.62 ±0.04	0.16 ±0.02
	1000	1.85 ± 0.04	1.19 ± 0.10	0.43 ± 0.02	0.51 ±0.21	0.27 ±0.02	0.07 ±0.01
	2000	1.37 ± 0.01	0.74 ± 0.01	0.20 ± 0.02	0.20 ±0.12	0.11 ±0.01	0.03 ±0.01
	3000	1.05 ± 0.01	0.42 ± 0.10	0.09 ± 0.01	0.08 ±0.01	0.05 ±0.04	0.02 ±0.01
Iron	200	4.15 ± 1.02	2.40 ± 0.02	1.37 ± 0.09	0.97 ±0.02	0.57 ±0.01	0.20 ±0.01
	500	3.26 ± 0.21	2.02 ± 0.21	0.76 ± 0.05	0.73 ±0.07	0.36 ±0.02	0.05 ±0.02
	1000	2.86 ± 0.11	1.48 ± 0.08	0.53 ± 0.12	0.42 ±0.02	0.18 ±0.02	0.01 0.01
	2000	2.19 ± 0.11	1.02 ± 0.02	0.13 ± 0.01	0.31 ±0.15	0.05 ±0.01	0.01 0.01
	3000	1.57 ± 0.01	0.43 ± 0.14	0.10 ± 0.01	0.09 ±0.03	0.03 ±0.01	n.d

n = Number of samples, n.d: not detected Fraction I: water soluble metals, Fraction II: Exchangeable metals, Fraction III: Metals bound to carbonates, Fraction IV: Metals bound to Fe-Mn oxide, Fraction V: bound to organic carbon metals, Fraction VI: residual metals

Table 3: DPR (2002), WHO (1993) and US EPA (2010) Limits/ Standards for Metals Studied

Metal	DPR Limits	WHO Standards	US EPA Standards
Cr	0.03 mg/ L	0.10 mg/ L	0.10 mg/ L
Cd	--------	0.003 mg/ L	0.005 mg/ L
Ni	--------	0.05 mg/L	0.05 mg/ L
Zn	1.50 mg/ L	5.0-15 mg/ L	2.0 mg/ L
Cu	1.00 mg/ L	1.00-1.5 mg/ L	1.00 mg/L
Mn	-------------	0.4 mg/ L	0.05 mg/ L
Fe	1.00 mg/ L	0.3 mg/ L	0.3 mg/ L

STATISTICAL TREATMENT OF SPECIATION DATA

Table 4: Results of the Analysis of Variance on the data – chromium

CHROMIUM										
Fraction 1 (Water soluble)						Fraction 2 (Exchangeable metals)				
Distance	200	500	1000	2000	3000	200	500	1000	2000	3000
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 3 (bound to carbonate metals)						Fraction 4 (bound to Fe-Mn oxide metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**

	200	500	1000	2000	3000	200	500	1000	2000	3000
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 5 (bound to organic carbon metals)						Fraction 6 (residual metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000						**	**	**	**	*

Distance: Distance away from flaring point in meters. *$P > 0.05$; **$P < 0.05$

Table 5: Results of the Analysis of Variance on the data – cadmium

CADMIUM										
Fraction 1 (Water soluble)						Fraction 2 (Exchangeable metals)				
Distance	200	500	1000	2000	3000	200	500	1000	2000	3000
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 3 (bound to carbonate metals)						Fraction 4 (bound to Fe-Mn oxide metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 5 (bound to organic carbon metals)						Fraction 6 (residual metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000						**	**	**	**	*

Distance= distance (m) from flaring point. *$P > 0.05$; **$P < 0.05$

Table 6: Results of the Analysis of Variance on the data – nickel

Fraction 1 (Water soluble)						Fraction 2 (Exchangeable metals)				
Distance	200	500	1000	2000	3000	200	500	1000	2000	3000
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 3 (bound to carbonate metals)						Fraction 4 (bound to Fe-Mn oxide metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 5 (bound to organic carbon metals)						Fraction 6 (residual metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000						**	**	**	**	*

Distance= distance (m) from flaring point. *$P > 0.05$; **$P < 0.05$

Table 7: Results of the Analysis of Variance on the data – zinc

ZINC									
Fraction 1 (Water soluble)						Fraction 2 (Exchangeable metals)			
Distance	200	500	1000	2000	3000	200	500	1000	2000	3000
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 3 (bound to carbonate metals)						Fraction 4 (bound to Fe-Mn oxide metals)			
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 5 (bound to organic carbon metals)						Fraction 6 (residual metals)			
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	*	**	**	**	**	**	**	**	**	*

Distance= distance (m) from flaring point. $*P> 0.05$; $**P< 0.05$

Table 8: Results of the Analysis of Variance on the data – copper

COPPER									
Fraction 1 (Water soluble)						Fraction 2 (Exchangeable metals)			
Distance	200	500	1000	2000	3000	200	500	1000	2000	3000
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 3 (bound to carbonate metals)						Fraction 4 (bound to Fe-Mn oxide metals)			
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 5 (bound to organic carbon metals)						Fraction 6 (residual metals)			
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000						**	**	**	**	*

Distance= distance (m) from flaring point. $*P> 0.05$; $**P< 0.05$

Table 9: Results of the Analysis of Variance on the data – manganese

MANGANESE									
Fraction 1 (Water soluble)						Fraction 2 (Exchangeable metals)			
Distance	200	500	1000	2000	3000	200	500	1000	2000	3000
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 3 (bound to carbonate metals)						Fraction 4 (bound to Fe-Mn oxide metals)			
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**

1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 5 (bound to organic carbon metals)					Fraction 6 (residual metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	*	**	**	**	**	**	**	**	**	*

Distance= distance (m) from flaring point. $*P> 0.05$; $**P< 0.05$

Table 10: Results of the Analysis of Variance on the data – iron

IRON										
Fraction 1 (Water soluble)						Fraction 2 (Exchangeable metals)				
Distance	200	500	1000	2000	3000	200	500	1000	2000	3000
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 3 (bound to carbonate metals)						Fraction 4 (bound to Fe-Mn oxide metals)				
200	*	**	**	**	**	*	**	**	**	**
500	**	*	**	**	**	**	*	**	**	**
1000	**	**	*	**	**	**	**	*	**	**
2000	**	**	**	*	**	**	**	**	*	**
3000	**	**	**	**	*	**	**	**	**	*
Fraction 5 (bound to organic carbon metals)						Fraction 6 (residual metals)				
200	*	**	**	**	**	*	**	**	**	**	*
500	**	*	**	**	**	**	*	**	**	**	**
1000	**	**	*	**	**	**	**	*	**	**	**
2000	**	**	**	*	**	**	**	**	*	**	**
3000	*	**	**	**	**	**	**	**	**	*	**

Distance= distance (m) from flaring point. $*P> 0.05$; $**P< 0.05$

3.3 Statistical Treatment of Speciation Data

The results of the analysis of variance on the data are tabulated on tables 4-10. The results of the analysis of variance on chromium, cadmium, nickel, zinc, cobalt, manganese and iron indicates non significance for $*P> 0.05$ while $**P< 0.05$ is significant.

The closest distance to the flaring point (200 m away from the flaring point) in all the samples has the highest concentrations for all the metals studied and the least concentrations are found in the farthest distance from the flaring point (3000 m away from the farming point) obeying the distance decay concept. This is in line with Ojeh (2012) [22] research where he reported decrease in the concentrations as the distance away from the flare stack increases. In addition, he reported that the impact of gas flaring is dependent on the volume of gas flared, wind speed, temperature, height and type of flare stack. The results indicates that the metals analyzed in the soil collected from the Gbarain-Ubie Integrated Oil and Gas flow station in Obunagha are due to anthropogenic activities which is gas flaring in this research. This result is also consistent with the study of Ratuzny *et al.*, [27] and Kabala and Singh [28], which states that heavy metal contaminated soils and anthropogenic inputs tend to reside in the first four fractions of the sequential extraction procedures while metals from natural occurrence in parent rocks resides in the residual fraction. The concentrations of Ni, Cr, Cu, Fe, Zn, Mn, and Cd from the soil samples analyzed are of higher level than the standards recommended by DPR [23], WHO [25] and US EPA [24], agreeing to the contamination of the study location which may be attributed to the gas flaring plant located in the site.

CONCLUSION

Based on the results from the present study, it can be concluded that the analysis of soil samples collected from the host community (Obunagha) of the Gbarain-Ubie Integrated Oil and Gas flow station revealed that the heavy metals determined were found in appreciable concentrations. The study further demonstrates that Cr, Cd, Ni, Zn, Cu, Mn, and Fe were readily available in the gas flare-impacted soil. The assessment from soils around the flaring points (200 m, 500 m, 1000 m, 2000 m, 3000 m) at Obunagha indicates that the concentrations of heavy metals decreased moving away from the flaring point.

RECOMMENDATIONS

It is evident from the study that gas flaring is a potential source of heavy metal pollution and therefore, in order to promote sustainable development in the study region, we advise the government and oil companies to continue to monitor, assess, and manage the oil drilling environment. Also, the residents of Obunagha community should be enlightened on the dangers inherent in exposure to gas flaring.

Conflict of Interest: There are no conflicts of interest.

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