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Assessing The Extent and Nature of Heavy Metal Pollution in Kom-Kom Community, Rivers State, Nigeria

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Abstract: The persistent, toxic, and non-biodegradable nature of heavy metals have been recorded to negatively affect the environment. Given the reports of oil spill incidences in Kom-Kom community, a follow-up assessment and monitoring of the extent and nature of heavy metal pollution is necessary to determine the environment's health. Metal levels in soil and the African common toad, *Sclerophrys regularis* were assessed for Ni, Cd, Pb, Fe and Cu in 3 stations, S_1, S_2 and S_3 in Kom-kom community, Oyigbo local government of Rivers State, Nigeria during the rainy months. The samples were prepared and analysed using Micro Plasma Atomic Emission Spectrophotometer (Agilent 4210 MP AES). The physicochemical parameters (temperature, $_{P}$H and Electrical conductivity), and nitrate, sulphate and phosphate levels of soils were also analysed using standard methods. The mean values of metals in soils and biota ranged between 0.001±0.0001 to 0.001± 0.0002, Cd; 0.001±0.0001 to 0.001±0.003 Cu; 0.002±0.0002 to 0.002±0.0003, Pb, and 0.008±0.0002 to 0.008±0.0006 Ni showing no significant difference at $p<0.05$ in all metals. In soils, and skin of *Sclerophrys regularis,* accumulation pattern of heavy metal was in the order Fe>Ni>Pb>Cd≥ Cu in all three stations. Bio-concentration Factor values for all metals except Fe in the biota was found to have high contamination levels; Fe reported very high contamination. Contamination Factor and Pollution Load Index values for all metals showed low degree of contamination. All analysis in soil and biota reveals that the metals were within standard limit values. Continued measures against exposures and contamination is encouraged.

INTRODUCTION

The environment which includes our biophysical/natural, and social environment is the home to plants, animals, humans and every other life form that live in it. The interaction of both biotic and abiotic factors in the environment helps the normal functioning of the environment and this interaction directly and indirectly impacts on our health. Pollution which is the presence or release of any harmful substance into the environment, including the organisms and humans in them, is now a major global issue because of rapid industrialization and urbanization and the increasing human population. Pollution have been defined as the introduction of any contaminant into the environment that has the potential to create negative and hazardous impact on living things (Earth Science and Climate Change, 2020).

Environmental studies have become increasingly important due to recent increases in human population and industrial development, particularly in the Niger Delta. Heavy metal pollution is now a common occurrence and almost present in every ecosystem in the Niger Delta since it is the major hub of crude oil exploration in the country (Adekola, *et al.,* 2017). Rivers State is one of the nine Niger Delta States and the sixth most populous state in Nigeria. It is characterised by heavy rainfall, tropical rainforests, freshwater swamps, mangrove swamps and coastal sand ridges and is one of the significant oil producing states in Nigeria, producing more than 60% of the country's crude oil output and hosts many oil producing / servicing companies in various communities and Local governments one of which is Kom-Kom community in Oyibo Local government area (Nigeria Data Portal, 2006; Britannica, 2013; Onyejekwe *et al.,* 2019). As a result, it is quite likely to experience heavy metal pollution.

Heavy metal pollution levels can be determined scientifically in any environmental media. Organisms resident in the different environments can also be assessed to determine the levels of these pollutants in the environment. Such organisms serve as bioindicators and/or biomarkers of pollution. Heavy metals levels in the soil and biota can reveal the extent of pollution and the degree to which these metals can potentially impact adversely on the environment and the resident biota due to their characteristic nature. This study has assessed the levels of heavy metal contamination in soil and toad samples, especially from the Kom-Kom Community, Rivers State, Nigeria.

MATERIALS AND METHODS

Description of study area

Kom-Kom community is a small settlement with farmlands, market places and few industries in Oyigbo Local government of Rivers State. The study area lie between longitude 4^{o} 40'0"N and 5^{o} 0'0"N and Latitude 7^{o} 10'0"E and 7^{o} 30'0"E. The area is surrounded by a few oil factories with pipelines passing through it as well as residential and business facilities. Shell Petroleum Development community operates an oil well in Oyigbo local government. Pipelines belonging to the Nigerian National Petroleum Corporation (NNPC) and Eastern Network Gas (Alscon pipeline) among others also pass through Kom-kom community in Oyigbo.

Sampling Stations and sample collection

Soil samples were collected in triplicates from three sampling stations.Three sampling stations were established in the area. Station 1 ($\mathbf{S_1}$) was the SPDC pipeline, Station 2 ($\mathbf{S_2}$) was the NNPC pipeline adjacent station 1 and station 3 ($\mathbf{S_3}$) was a bare land that served as the control station.

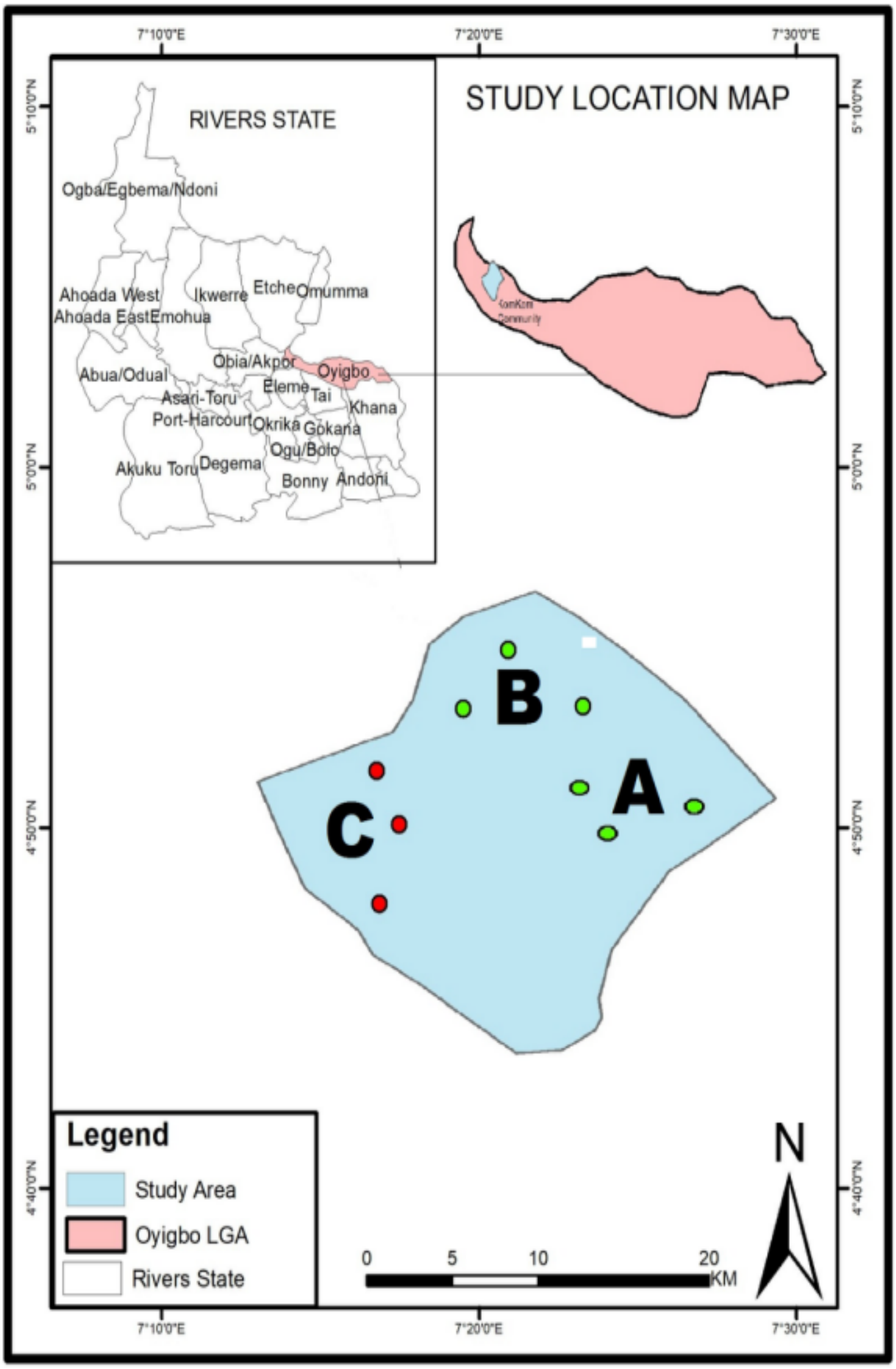

Fig. 1 Map showing sampling points in the three stations

Key: A= Station 1; B= Station 2, and C = Station 3 (Control Station)

Sampling Technique

Soil sampling and analysis

This study has been approved by the research ethics committee, University of Port Harcourt Centre for Research Management and Development. Triplicate soil samples were obtained once within the study period from the three stations. Surface litter was removed at the sampling spot and the sample was collected by driving the spade to a plough depth of 15cm, measured with a tape. An electronic handheld GPS (Global Positioning System) was used to record the coordinates of the sampling locations. *In situ* measurement of P^H, temperature and electrical conductivity of the soil samples was done. The temperature was measured using a probe. A solution was prepared with 100g of soil from each sample in 50mls of distilled water in a beaker and weighed manually; the mixture were poured into the P^H and conductivity metre (Myron ultrameter II) for assessment of the soil P^H and EC. A clean polyethene bag was used to collect and transport the labelled samples to the laboratory for additional analysis.

Nutrient parameters; Determination of Nitrate (NO_3^-), phosphate (PO_4^{3-}) and Sulphate (SO_4), was done using PG T60 U V Spectrometer. The sampled soil were weighed in 3 parts (5g, 2g and 5g), oven dried at 60°C and crushed for the analysis of the stated nutrient parameters. 20ml of 2 M KCl solution (extractant) was mixed with 5g of the crushed soil sample for analysis of nitrate. The mixture was swirled at room temperature for 10 minutes and filtered with whatmann No. 42 filter paper. Nitraver 5 powder was added 5mls of the filtrate. The mixture was shaken for 1 minute and kept standing for 5 minutes and the absorbance read using PG T60 UV Spectrometer (USEPA, 2013; Walsh *et al.,* 2019). Distilled 40ml H_2O_2 solution (extractant) was mixed with 2g of the crushed soil sample for analysis of phosphate. Whatmann No. 42 filter paper was used to filter the mixture; distilled water of 10mls, and colour development reagent (ammonium molybdate and Malachite Green) of 4ml was added to 5mls of the soil extract and made up to 25ml and swirlled. The mixture kept to stand for 10 minutes and the absorbance read using PG T60 UV Spectrometer (Adelowo and Agele, 2016, Wuenscher *et al.,* 2015). Acidified ammonium acetate extractant (25ml) was mixed with 5g of the crushed soil sample for analysis of sulphate. A rotary shaker was used to shake the mixture at 200 oscillations per minute and filtered with whatmann No. 42 filter paper. Distilled water of 15mls was added to 10ml of the filtrate; 1ml conditioning reagent was added and mixed properly by shaking for 3 minutes. A spoonful of barium chloride was added and allowed to sit for 1 minute. The absorbance was read using PG T60 UV Spectrometer (Singh *et al.,* 2011). For acid digestion, each soil sample was air-dried for one week, crushed with a porcelain mortar and pestle, and sifted through the 2mm sieve and weighed. 1g each of the soil samples was measured out and poured into a digestion tube and treated freshly prepared mixture of 5ml HNO_3, 0.5ml of H_2SO_4 and 1ml of $HClO_4$. The sample was swirled gently to achieve a homogenous mixture. The digestion tubes were placed on the digester till the temperature rose to 180°C. The digestate was kept to cool and filtered with whatman No.42 filter paper. Each of the digested sample was transferred into a clean stoppered plastic bottle and labelled accordingly. Concentrations of heavy metals (Ni, Cd, Pb, Fe, and Cu) in the digested samples were determined for using Micro Plasma Atomic Emission Spectrophotometer (Agilent 4210 MP AES) (Hettipathirana 2011). The data used for analysis were primary data obtained during soil sampling. Triplicate samples of soil were taken from each sampling station.

Statistical analysis

The data generated were analysed using descriptive statistics mean and standard deviation. Statistical Package for Social Sciences (SPSS Version 25.0) was used to conduct the Analysis of variance (ANOVA) to determine the mean differences ($p < 0.05$) between heavy metals and locations for Soil. Evaluation of data variability was done using the coefficient of variation and F-ratio test. The mean concentrations of the heavy metals were compared with the DPR (2002) standard limits for heavy metals soils.

Quantification of the extent metal accumulation

Bio-concentration factor

The extent of metal accumulation in the toads sampled in each station was measured by determining the bio-concentration factor (BCF).

$$BCF = \frac{\text{Heavy metal concentration in sampled toads}}{\text{Heavy metal concentration in soil}}$$

BCF (contamination) value > 1 = high

< 1 = No metal enrichment

$1 \leq BCF \leq 3$ = Moderate

$3 \leq BCF \leq 6$ = Considerable

BCF > 6 = Very high

Pollution Load Index

Mathematically, it is expressed based on the previous method by Lacutusu, (2000) as:

$CF = C_{metal} / C_{background\ value}$

$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \ldots \times CFn)}$

Where,

CF = contamination factor,

n = number of metals

C_{metal} = metal concentration in polluted soil

$C_{Background\ value}$ = background value of the metal.

PLI Value <0.1 =Very slight contamination (This will have no negative effect on biota/environment)

0.10 - 0.25 = Slight contamination

0.26 - 0.5 = Moderate contamination

0.51 – 0.75 = Severe contamination

0.76 – 1.00 = Very severe contamination

1.10 – 2.00 = Slight pollution (This will have a potentially negative effect on the environment/biota)

2.10 – 4.00 = Moderate pollution

4.10 – 8.00 = Severe pollution

8.10-16.00 = Very severe pollution

>16.00 = Excessive pollution

RESULTS

Physicochemical characteristics and nutrient concentrations

The mean values of Temperature, pH, and Conductivity of sampled soil from all study locations and mean concentrations of soil sulphate, nitrate and phosphate are presented in Tables 1 and 2, respectively.

Temperature

The mean temperature across all stations ranged between 28.9°C ± 0.1°C and 29.6°C ± 0.3°C with the highest mean temperature recorded in station 1 which is surrounded by vegetation; including crop plants and trees, and also has an oil pipeline running through it. Station 3 recorded the lowest temperatures. However, the temperature across all stations were well within NESREA recommended limits (Table 1).

pH

The mean pH values recorded were within the range of 6.34 ± 0.01 and 6.52 ± 0.02 revealing that the area within the study period was slightly acidic with a gradual increase in pH observed in station 1 (neutral). The pH however was observed to be within NESREA recommended limits.

Electrical conductivity

The overall mean electrical conductivity values ranged from 116.3 $\mu S \cdot cm^{-1}$ ± 0.07 $\mu S \cdot cm^{-1}$ to 249.8 $\mu S \cdot cm^{-1}$ ± 0.17 $\mu S \cdot cm^{-1}$. The highest value is recorded in station 1 and the lowest in station 2. The values recorded were found to be within NESREA standard limits for soil conductivity.

Sulphate, Nitrate and Phosphate

The mean values for Sulphate ranged between 53.31 mg/kg ± 0.01 mg/kg and 187 mg/kg ± 2.0 mg/kg and station 3 recorded the highest value among others (Table 2). The mean values for Nitrate ranged between 1.0 mg/kg ± 0.001 mg/kg and 1.534mg/kg ± 0.010mg/kg and station 1 recorded the highest value among others. The mean values for Phosphate ranged between 81.87 mg/kg ±0.010 mg/kg and 112.95 mg/kg ± 0.016 mg/kg and station 3 recorded the highest value than other stations.

Heavy metal, bio-concentration factor, contamination factor and pollution load index analysis

The results of the laboratory and data analysis for heavy metal, Bio-concentration factor, Contamination Factor and Pollution Load Index analysis are presented in Tables 4.3-4.6. The metal concentrations soil and toads were found to be within the same values and range, differing only in values for iron Fe.

Mean concentrations of metals in soils and biota

The mean concentrations of Ni, Cd, Pb, Fe and Cu in soil and Toad samples from the three stations are presented in Tables 3 and 4 respectively. The mean values of metals in soils and biota ranged between 0.001±0.0001 to 0.001± 0.0002 for Cd; 0.001±0.0001 to 0.001±0.003, Cu; 0.002±0.0002 to 0.002±0.0003, Pb, and 0.008±0.0002 to 0.008±0.0006, Ni. Station 3 recorded the highest concentration value. The results obtained also revealed that all the metals were within permissible limits in the soil. The levels of Heavy metals in the soil were observed to be in the order Fe>Ni>Pb>Cd≥ Cu. The result of the statistical analysis suggests that the concentrations of heavy metals in the study are within regulatory standard values.

Bioconcentration values of metals in biota

The bio-concentration values for Ni, Cd, Pb, and Cu showed moderate contamination in all the stations. The concentration values for Fe revealed very high contamination in all stations. The Contamination Factor and pollution load index for the sampled the metals showed low degree of contamination

Table 1. Mean values of physicochemical parameters of soils from the 3 sampled stations. Values are triplicate samples collected once.

Parameters	Station 1	Station 2	Station 3	NESREA 2009 standard limit
Temperature	29.6°C	29.1°C	28.9°C	< 40°C
P^H	6.52	6.43	6.34	6-9
Electrical conductivity	249.8 $\mu S \cdot cm^{-1}$	116.3 $\mu S \cdot cm^{-1}$	173.9 $\mu S \cdot cm^{-1}$	1000 $\mu S \cdot cm^{-1}$

Table 2. Mean values (mg/kg) of Sulphate, Nitrate and Phosphate concentrations in soils in all three stations.

Parameter	Station 1	Station 2	Station 3	NESREA limit
Sulphate	88.08	53.31	187	500
Nitrate	1.534	1	1.517	20
Phosphate	81.87	88.05	112.95	5.0

NESREA**-** National Environmental Standards and Regulations Enforcement Agency, 2011 limit for nutrients in soil

Table 3. Mean concentrations (mg/kg) of Heavy metals in Soils from the three sample stations

Heavy Metal	station 1	station 2	station 3	DPR background value
Cadmium	0.001±0.0001[a]	0.001±0.0002[a]	0.001±0.0002[a]	0.8
Copper	0.001±0.0001[a]	0.001±0.0002[a,b]	0.001±0.0003[b]	36
Iron	2270±0.71[a]	1211±1.73[c]	2174±1.58[b]	NA
Lead	0.002±0.0002[a]	0.002±0.0002[a]	0.002±0.0003[a]	85
Nickel	0.008±0.0002[a]	0.008±0.0006[a]	0.008±0.0003[a]	35

NB: Each value is expressed as mean ± standard deviation; dissimilar superscripts (a, b, c) implies significant differences at $p<0.05$; NA- Not available

DPR- Department of Petroleum Resources (2002) limits for heavy metals in soils

Table 4. Mean concentration (mg/kg) of heavy metals in *Sclerophrys regularis* from the three sample stations

Heavy Metal	station 1	station 2	station 3
Cadmium	0.001±0.0001[a]	0.001±0.0002[a]	0.001±0.0002[a]
Copper	0.001±0.0001[a]	0.001±0.0002[a]	0.001±0.0002[a]
Iron	8.6±0.014[a]	1.829±0.001[c]	5.079±0.001[b]
Lead	0.002±0.0002[a]	0.002±0.0002[a]	0.002±0.0003[a]
Nickel	0.008±0.0002[a]	0.008±0.0006[a]	0.008±0.0003[a]

NB- Each value is expressed as mean ± standard error; dissimilar superscripts (a, b, c) implies significant differences at $p<0.05$; Standard limit values for *Sclerophrys regularis* is not provided by regulatory bodies

DISCUSSION

Physicochemical parameters

The physicochemical parameters of any environment principally determine its health and ability to support and sustain life in that environment.

Temperature

The mean pH value for soils observed in this study was classified as neutral. These values agreed with the findings of Onyejekwe *et al.,* (2019). The mean pH values from stations 2 and 3 are slightly lower than the value recorded in station 1. This may be a result of anthropogenic activities in both sites since human activities are frequent in the area. As adduced by Olayinka *et al*., (2017), the decomposition of organic materials from human activities releases carbon (IV) oxide and reacts with water to form weak acidic conditions which reduces soil pH.

pH

The mean temperature values recorded in all stations were within standard limits. From the Table 1, station 3 recorded the highest temperature in all. Station 3 which is the control station is a residential location and with a lot of domestic human activities. This high temperature value may be responsible for the low concentration of heavy metal in that station as a result of the increased degradation rates as stated by Bartha and Bossert (1984) and Cooney, (1984).

Conductivity

The mean values for electrical conductivity in soil from the sampled stations were also found to be well within the permissible limits. The values across stations differed significantly with station 1 recording the highest value followed by station 3 and station 2. The high value recorded for station 1 is assumed to result from presence of heavy metals in the area. This assumption agrees with the statement of Osakwe and Okolie, (2015). The values recorded in this study are lower than that of Onyejekwe *et al.,* (2019). Only station 1 recorded similar values.

Nutrient Concentration

The result of the analysis showed that all the nutrients were within the recommended values of NESREA (2011). Across stations, the highest mean concentration of sulphate was observed in station 3 followed by stations 1 and 2; the highest value for Nitrate was observed in station 1 followed by station 3 and 1; Phosphate recorded the highest value in station 3 followed by station 2. Mean concentrations recorded in Sulphate and Phosphate in station 3 are significantly different from stations 2 and 1. This high concentration from station 3 is assumed to result from the activities in that residential site. The inhabitants of this area engage in subsistence agricultural activities around their houses and may have introduced either natural or synthetic fertilizers to the soil. This result agrees with the report of Isiuku and Enyoh, (2020); Adesuyi *et al.*, (2015); and FAO, (2018).

Metal Profiles in the matrices

This study revealed that the levels of heavy metals in the two matrices from the three stations are within standard values with slight variation across the stations (Table 3 and 3.4). These slight variations across the stations are assumed to result from the nature of anthropogenic activity in the station. Stations 2 and 3 which experience frequent human interference had slightly higher concentrations in soils and biota than station 1 for all sampled metals except for Fe. In soil, Cd had the same concentration in stations 2 and 3, only slightly lower by 0.0001 in station 1; Cu and Fe showed highest concentrations in station 3, next to station 2 and 1; Ni recorded the highest value in station 2, next to station 3 and 1; Pb recorded the highest value in station 3, next to station 2 and 1 (which had the same value). In biota, station 3 recorded the highest value for Pb and Ni, and the lowest in Fe. In station 2, the highest values were recorded for Ni; in station 1, the highest value was recorded for Fe and, Pb and Ni. It is suspected that these levels may increase if these anthropogenic activities continue without caution. This is assumption is so because according to USDA (2000), as human activities increase, the soil becomes more exposed to these metals to levels beyond what the environment can repair.

The metal profile for all sampled metals in the soils and toads recorded the same values differing only in values for iron Fe as a result of its abundant nature in the earth's crust. The results obtained are in agreement with those of previous studies conducted within the same area (Onyejekwe *et al.,* 2019; Nwaichi *et al.,* 2021). All sampled metals were observed to be within permissible limits except for Fe which is suspected to be high; however, standard regulatory limits for Fe in biota is not given. These high values could be as a result of the abundant nature of the metal in natural (soil) environments (Gambrell, 1994).

The low concentrations of Ni, Cd, Pb, and Cu in biota may be a result of natural attenuation by oil-degrading soil microbes. These oil-degrading microbes are said to be ubiquitous; with the ability to degrade petroleum products, reducing their concentration in the soil and making them less toxic. Oil biodegradation occurs over a range of pH values, but is generally optimum at near-neutral to slightly alkaline conditions (pH 6.5-8) (Das and Chandran, 2011; Igiri *et al.,* 2018). The sampled soils in all three samples fall within the range of 6.3-6.5 hence the assumption. Some factors that may justify the low levels of heavy metals could be the temperature, electrical conductivity, and nutrients in the soil (Attah and Melkamu, 2013) in addition to the remediation exercise conducted after the spill.

Bio-concentration factor

The bio-concentration factor, BCF Cd, Pb, Ni, and Cu in the biota was found to have moderate contamination levels and Fe is reported to hold very high contamination when compared with standard bio-concentration values. The BCF reported uniform values for all metals except for Fe (Table 4.5). The significant variation in concentration of Fe seen across the stations is likely to result from the activities that go on in each of the stations. Station 1 which is a remote site will scarcely any human interference recorded the least concentration. The highest value was observed in station 2 and is assumed to result from the anthropogenic activities such as indiscriminate dumping and littering of waste This assumption agrees with the statement of Ali *et al.,* (2019), that “the BCF values of metal concentrations in biota are inversely related to the metal concentration in the environmental medium”. The findings of Enuneku *et al.,* (2018) also revealed that accumulation of heavy metals in biota in higher concentrations than the environment is largely from anthropogenic sources.**Contamination factor and pollution load index**

The contamination factor (CF) and pollution load index (PLI) values do not show any variability across stations (Table 4.6). Comparing values of CF and PLI developed by Lacutusu (2000), the metals showed low degree of contamination. This signifies that the extent of pollution in the area is between moderate to low as at the period of study. This however does not suggest that high levels of pollution are not possible since increased anthropogenic activities can expose the soil to contamination as seen in the case of Benson *et al.,* (2016), which showed moderate contamination owing to anthropogenic inputs, such as fossil fuel combustion, fertilizer inputs and waste dump.

CONCLUSION

Concentration of the sampled heavy metals in the environment have been reported to be within permissible limits when compared with DPR standard for soils. The order of concentrations are as follows Fe>Ni>Pb>Cd≥ Cu. The bio-concentration values of the metals detected moderate contamination; the pollution load indices for biota showed no trace of pollution/contamination when compared with standard PLI values. The recorded low levels of heavy metals could be credited to the remediation activity carried out in the area after the explosion incident in 2019. From the general assessment, the level of metals in soil and biota reveals that the extent of pollution is moderate. Owing to the industrial activities that are done in the area, the toxic nature of the associated heavy metals and health effects of these metals, it is important that regular assessment of the levels of heavy metals are carried out. Proper measures against exposures and contamination should also continue.

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Institutional Review Board Statement: Not applicable

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