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ASSESSMENT OF HEAVY METAL POLLUTION IN SOILS OF IFIE COMMUNITY, WARRI, DELTA STATE, NIGERIA

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ABSTRACT

Twelve soil samples (11 soil samples and 1 control sample) were collected to assess the level of pollution and its distribution in soils around Ifie Community, Warri South, Delta State, Nigeria, including one control sample from Federal Government College Warri. An Atomic Absorption Spectroscopy (AAS) machine (model 210 VGP) was used and seven heavy metal parameters were analyzed: iron (Fe), nickel (Ni), chromium (Cr), lead (Pb), cadmium (Cd), zinc (Zn), and Copper (Cu). The following results were obtained: iron (110.5 - 201.5 mg/kg), nickel (20.5 - 47.5 mg/kg), chromium (1 - 23 mg/kg), lead (1 - 3.5 mg/kg), zinc (8 - 20 mg/kg), and copper (27 - 46 mg/kg). The heavy metal distribution patterns identified in this study from highest to lowest were as follows: iron, copper, nickel, zinc, chromium, lead, cadmium. Cadmium was below the detection level in all samples. The study findings indicate high nickel and copper levels, surpassed the World Health Organization's (WHO) target values, and high nickel levels exceeding the Conselho Nacional do Meio Ambiente(CONAMA) prevention values, suggesting that industrial and domestic activities in the area contribute to heavy metal pollution. The Contamination Factor (CF) and Geo-accumulation Index (GeoI) indicate moderate to considerable levels of Ni and Cu contamination, while statistical analysis shows that these two metals are most likely from the same source and influenced by the same factors.

KEYWORDS: Heavy metals, Ifie, Niger Delta, Soils

INTRODUCTION

Everyday, as society grows and industrialization accelerates, heavy metals are introduced into the soil. Heavy metals, being non-biodegradable and having high bioavailability, tend to accumulate in the soil in significant quantities. When heavy metals accumulate, they tend to cause an adverse effect on the environment referred to as pollution.
Olivier *et al.* (2021) stated that heavy metals are described as metals with comparatively high densities, atomic weights, or atomic numbers. Depending on the author and context, different criteria may be applied, and metalloids may or may not be included. A more comprehensive definition was suggested by Ali and Khan (2018) stating that "heavy metals" are defined as "naturally occurring metals with an elemental density higher than 5 g cm^{-3} and an atomic number higher than 20".

Soils are typically known as the loose combination of organic and mineral materials in one or more layers, subject to physical, chemical, and biological transformations near or at the Earth's surface. Generally it contains liquids, gases, and living organisms, providing support for plant life (Van Es, 2017). Heavy metals become a menace when there is a high level of accumulation.
Heavy Metal Accumulation can then be defined as the augmentation of heavy metals. This accumulation can be in soils or in water. Heavy metals can stay on the soils and accumulate because they have low mobility and high persistence in the environment. They can also bind to different soil components, such as organic matter, clay minerals, oxides, and carbonates, and form stable complexes that are difficult to dissolve or leach (Nnaji *et al*., 2023).

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Hence the type of soil and the amount of organic matter, clay mineral content, oxides and carbonates can also affect the rate of heavy metal accumulation. There are majorly two sources of heavy metals in the soil. They can be of naturogenic (natural) origin or they can be of anthropogenic (human caused) origin. Naturogenic sources of heavy metals include; atmospheric volcanic emissions, continental dust transport, and metal-rich rock weathering, volcanic eruptions. Anthropogenic sources of heavy metals include; mining activities, smelters, metal-containing chemicals and industrial use of waste sludge, fossil fuel combustion, military training, electronics (manufacturing use, and disposal). Higher heavy metal concentrations are also present in industrial waste-water, including chromium (Cr), zinc (Zn), nickel (Ni), cobalt (Co), cadmium (Cd), copper (Cu), and lead (Pb) (Khan *et al.,* 2021).

DESCRIPTION OF THE STUDY AREA

The study area, Ifie community is located in Warri South Local Government Area, Delta State, Nigeria. It falls within the latitudinal range of N5º 31' and N5º 34' and longitudinal range of E5º 41' and N5º 44' (Fig.1). It is bordered at the south by Warri River. Typically the area experiences two types of seasons a year, the rainy season and the dry season and the average yearly temperature hovers around 27ºC. The soils in this area are of varying types. Close to the creeks and water bodies we encounter very dark coloured soils with clay sized particles. Away from the water the soils are light coloured and majorly consist of sand sized particles. The region under study is drained by the Ifie River and various tributaries of the Warri River, which eventually flows into the sea. The predominant plant species in this vegetation are primarily mangroves, specifically Rhizophora racemosa (red mangrove) and Avicenia africana (white mangrove) (Wogu and Okaka, 2011). The area is a flat lying terrain which contain different water channels flowing through it. Some notable water bodies within the area are the Roth Creek, Keene Creek and the Crawford Creek (Fig. 2). Other water bodies exist within the area and they all flow towards the South which has a lower elevation. The Ifie River and its tributaries, along with other Warri River tributaries, drain the study area before flowing into the Warri River, which ultimately reaches the sea.

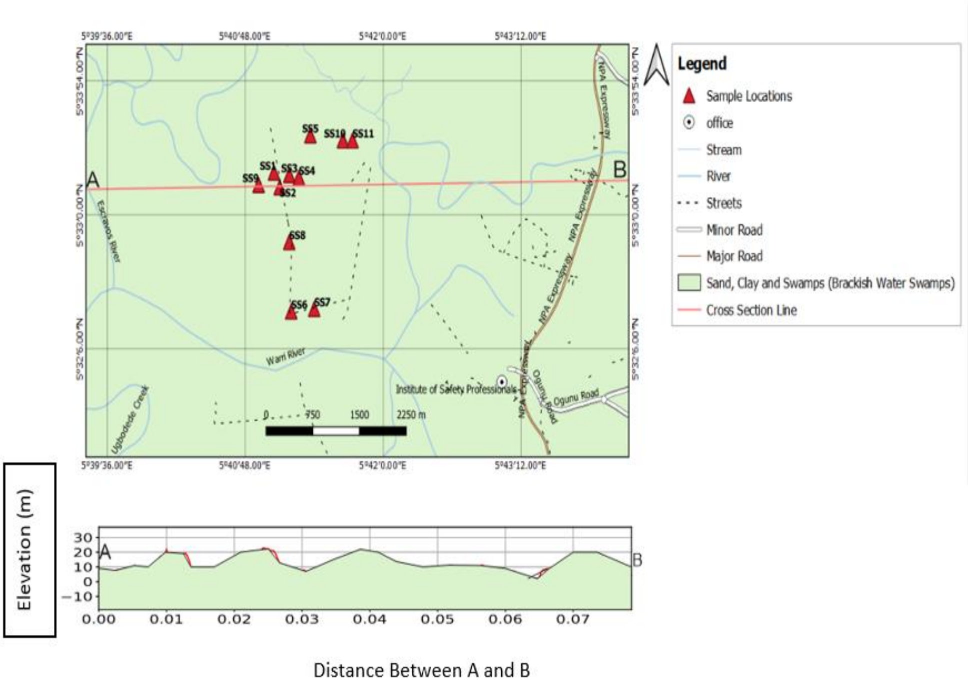

Figure 1: Geologic map of Ifie Community showing the sample sites and cross section profile of the area

Figure 2: Satellite View of Ifie community showing different sample site from Google Satellite.

LOCAL GEOLOGY

Ifie community lies within the Niger Delta Basin and it is on the Benin Formation. The Warri region is covered by sedimentary rocks from the Niger Delta, with an approximate thickness of 8000 meters. The primary lithologic formations, arranged from bottom to top, consist of the Akata formation, Agbada formation, Benin formation, and the Somebreiro-Warri Deltaic Plain Sands(Allen, 1965; Short and Stauble, 1967; Weber and Daukoru, 1975).The study region is situated directly above a Quaternary formation known as the Somebreiro-Warri Deltaic Plain Sand (Wigwe, 1975).This deposit comprises sands of fine to medium and coarse grains, interspersed with occasional layers of gravel, peat, or pockets of plastic clay. Typically, its thickness does not surpass 120 meters, and it is primarily unconsolidated. The water table is in close proximity to the ground surface, fluctuating within a range of 0 to 4 meters (Olobaniyi and Owoyemi, 2004).

METHODOLOGY

A randomized sampling method was employed to gather twelve soil samples from various points, each approximately 100 meters apart. This set included eleven samples from Ifie Community and one control sample from Federal Government College Warri. Federal Government College Warri was selected as a control site due to its lack of industrial activity, making it an ideal reference point for determining the background levels of heavy metals in the soil.

The soil sample was collected from an area with minimal human interaction, ensuring that the sample represents natural conditions with minimal contamination.

These samples were collected at a depth of22.5cm ± 7.5cm and each soil sample was carefully stored in new, uncontaminated aluminum foils and then transported to the University of Benin, Geology Department, located in Ugbowo, Benin City, Edo State, for onward analysis. The analysis utilized Atomic Absorption Spectrometry, employing a model210 VGP Atomic Absorption Spectrometer (AAS) machine. This method involves measuring the absorption of optical radiation by free atoms in the gaseous state, serving as a quantitative spectroanalytical technique for identifying chemical elements (Welz and Sperling, 2008).

Atomic Absorption Spectroscopy (AAS) measures element concentrations by the light absorption of atoms at specific wavelengths. When some elements are exposed to their unique wavelengths, they absorb light, causing electron transitions to higher energy states. This process is used for quantitative analysis in AAS, which includes a light source, atomizer, monochromator, and detector to identify and measure elements based on absorbed light intensity and wavelength.

RESULTS AND DISCUSSION

Analytical results obtained from the AAS analysis of soil samples from Ifie Community are presented in Table 1.

The results reveal the presence of the following concentrations of heavy metals: iron ranges from 110.5 - 201.5 mg/kg, nickel ranges from 20.5 - 47.5 mg/kg, chromium ranges from 1 - 19 mg/kg, lead ranges from 1 - 3.5 mg/kg, copper ranges from 27 - 46 mg/kg, zinc ranges from 8 - 20 mg/kg. No concentration for Cadmium was recorded as it was below detection levels. The concentration of heavy metals from the control site at Federal Government College Warri are as follows: iron: 65.5, nickel: 19, chromium: 0.5, lead: 0.5, copper: 21.5, zinc: 7.5 while cadmium was below detection level.

Table 1: Concentration of Heavy Metals in the Soilsof Ifie Community

Site	**Fe**	**Ni**	**Cr**	**Pb**	**Cd**	**Cu**	**Zn**
SS1	181.5	20.5	11	2.5	BDL	29	9.5
SS2	201.5	33.5	19	3.5	BDL	31	20
SS3	119.5	31	9	1	BDL	36.5	17.5
SS4	158	24	23	1	BDL	27	11
SS5	154.5	25.5	11	2.5	BDL	32	16.5
SS6	193	38	2	1	BDL	34.5	12.5
SS7	199.5	40.5	2	3.5	BDL	46	12.5
SS8	135.5	42	1	1	BDL	45.5	11
SS9	110.5	30.5	8.5	1.5	BDL	36.5	10.5
SS10	128	39	3	2	BDL	37.5	8
SS11	119.5	47.5	1.5	3	BDL	44	11
MEAN	**154.6**	**33.8**	**8.3**	**1.8**	**-**	**36.3**	**12.7**
Range	110.5 - 201.5	20.5 - 47.5	1 - 23	1 - 3.5	-	27 - 46	8-20
Control Site	65.5	19	0.5	0.5	BDL	21.5	7.5

**All units in mg/kg *BDL: Below detection limit * - : Null / No Value *MEAN: Average Heavy Metal Value of Sample Sites *SS: Sample Site*

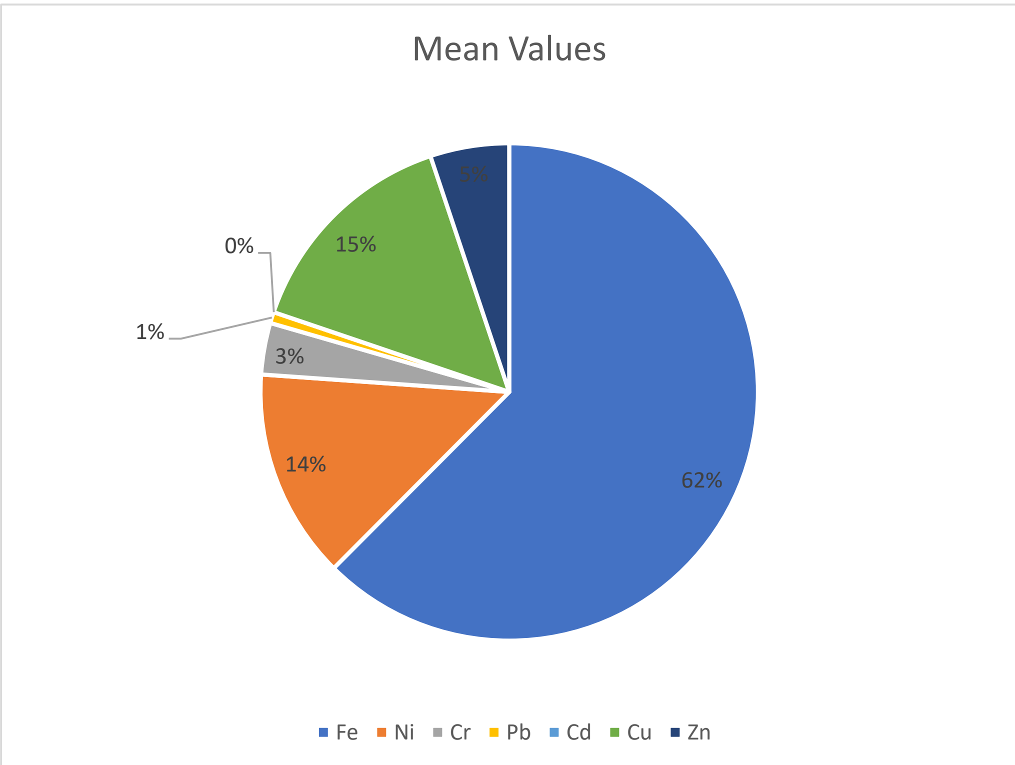

Figure 3: Pie Chart representation of the mean values of heavy metals in the study area

From the results shown in Table 1, the following could be deduced about the heavy metals concentrations:

1. Iron (Fe) Content

In the study area, iron concentration averages 154.6 mg/kg, with the highest value of 201.5 mg/kg obtained near a main road (SS2), likely due to petroleum tanker activity. Proximity to the road correlates with elevated iron levels in SS1, SS6, SS7, and SS8, all above 150 mg/kg. Lower concentrations in SS5, SS9, SS10, and SS11 may be due to their distance from the road and agricultural practices. Study sites SS3 and SS4 experience seasonal waterlogging, affecting metal distribution. Iron is the most abundant element in this region with a value of 62% as seen in the pie chart in (Fig. 3).

2. Nickel (Ni) content

Anthropogenic activities, notably fossil fuel combustion, have increased nickel (Ni) emissions, in the region. Nickel concentration in the area averages 33.8 mg/kg. Elevated Ni levels at SS11, SS7, and SS8 are linked to proximity to petroleum operations and a tank farm while SS11 exceeds World Health Organization (WHO) 1996 target values, suggesting local agricultural practices and rainfall may influence Ni distribution. The percentage of Ni among all the metals is 14%, which is slightly below Cu at 15% and Fe at 62% (Fig. 3).

3. Lead (Pb) and Chromium (Cr) contents

Chromium (Cr) and Lead (Pb) contamination in soil is linked to human activities like mining and traffic (Jin *et al*., 2020). The mean concentration of Cr and Pb are 8.3 mg/kg and 1.8 mg/kg in Ifie community respectively. High traffic and petroleum combustion contribute to these levels, especially near roads (SS4, SS2, SS1) and a poultry farm (SS5), which may introduce metals through manure (Akporido and Ipeaiyeda, 2014). Seasonal water logging can further affect metal mobility and bioavailability (Chen *et al*., 2021; Zwolak *et al*., 2019).

4. Copper (Cu) and Zinc (Zn) contents

Average soil concentrations of Zinc (Zn) and Copper (Cu) in the study area are 12.7 mg/kg and 36.3 mg/kg, respectively. The highest Zn (20 mg/kg) and Cu (46 mg/kg) levels are found near the main road and petroleum tank farm, indicating traffic and industrial activities as likely contamination sources. Despite this, both Zn and Cu levels remain below WHO permissible limits for soils.

5. Cadmium (Cd) Content

Cadmium (Cd) levels in the study area were below detection, suggesting minimal impact from potential sources like petroleum activities, industrial waste, and agricultural products.

Comparison of results with international standards

Table 2: Comparison of mean values of heavy metals in soils of Ifie Community with other authors and international standard permissible limits

Study Areas	Fe	Ni	Cr	Pb	Cd	Zn	Cu
Study Area (Ifie)	154.6	33.8	8.3	1.8	-	12.7	36.3
Control Sample (Federal Government College Warri)	65.5	19	0.5	0.5	-	21.5	7.5
(Adewuyi *et al.,* 2011)	-	42.61	50.60	49.52	0.05	185.26	45.24
(Ibekwe, 2023)	2657.67	14.82	3.34	1.79	2.16	43.26	9.77
WHO (1996) **Target value of soils**	-	35	100	85	0.8	50	36
CONAMA 2009 prevention values (Dos Santos and Alleoni, 2013)	-	26	75	72	1.3	300	60

*All units in mg/kg

Table 2 compares the mean values of heavy metal accumulation in soils reported by various authors in Delta State and surrounding areas with international standards. Ifie community has significantly higher amount of heavy metal concentration compared to the control sample collected from Federal Government College Warri. This is because the latter has very little sources of anthropogenic contamination. The absence of intense industrial (petroleum) activities is a major factor of the little concentration of heavy metals in the control sample.

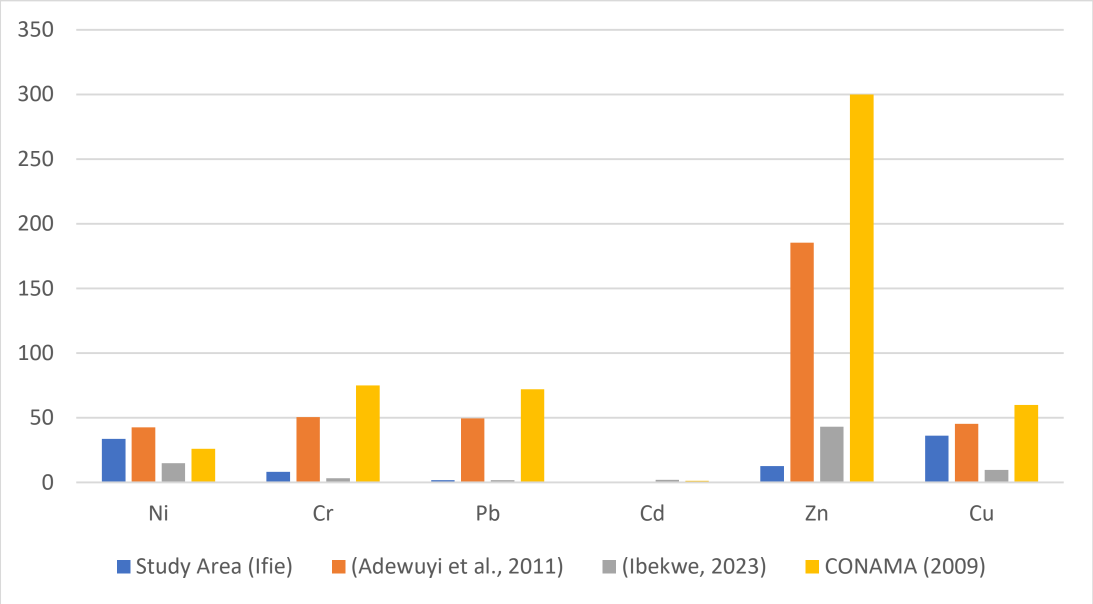

Figure 4: Bar chart comparison of mean values of previous work and CONAMA 2009 prevention values with this study

Adewuyi *et al.* (2011) found significant crude oil contamination in Ubeji's river sediments, with higher levels of Cr, Pb, Zn, and Cu compared to Ifie as shown in Figure 4. Nickel (Ni) levels were similar, and Cd was nearly undetectable in both locations, suggesting a greater negative impact of petroleum activities on the soils in Ubeji. Ibekwe (2023) reported very high Fe levels in the Obodo oil field, Warri, while Ifie showed higher levels of Ni, Cr, Pb, and Cu but lower Fe, Cd, and Zn. Lead (Pb) levels were similar in both studies. Ibekwe attributed these high heavy metal concentrations to oil and gas activities, recommending strict environmental regulations and remediation. Figure 4 also compares mean values from these studies with Conselho Nacional do Meio Ambiente (CONAMA) 2009 prevention values (Dos Santos and Alleoni, 2013). Nickel levels exceeded CONAMA's thresholds, indicating contamination, while Cu showed a rising trend. Cr, Pb, and Zn were below thresholds, and Cd was undetectable.

Most heavy metal values in Ifie were below WHO (1996) target values, with Cu slightly higher and Ni close to the target (Table 3). However, individual locations (Figure 5) showed Cu and Ni levels exceeding WHO targets, particularly near the main road and petroleum tank farm, indicating industrial activity-induced pollution.

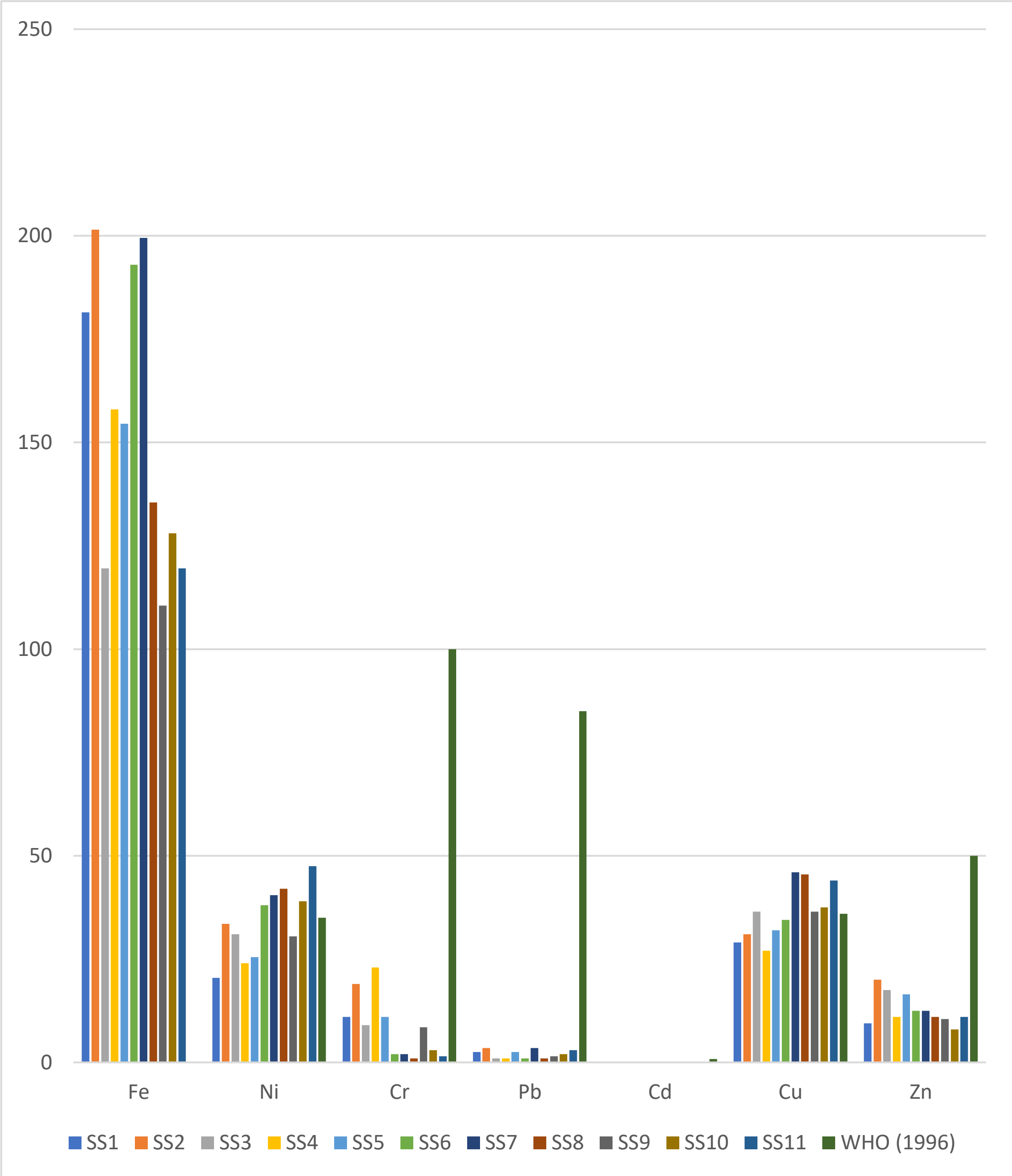

Figure 5: Heavy metal concentrations of the different sample sites in comparison to the (WHO 1996) target values.

Degree of Contamination

The Contamination Factor (CF) and Geo-accumulation Index (GeoI) are metrics used to assess the concentration trends of metals in soil quantitatively. The CF measures the level of contamination concerning either the typical composition of the Earth's crust for the specific metal or the background values obtained from areas with similar geological characteristics and without contamination (Tijani *et al.*, 2004). It is typically represented as:

$CF = C_m / B_m$

Where C_m represents the average concentration of metal m in the soil, and B_m denotes the background concentration (value) of metal m. This background concentration can be sourced from literature data, such as the average abundance in the Earth's crust, or obtained directly from a material with similar geological characteristics.

The Geo-accumulation Index (GeoI), introduced by Mueller in 1979 is a commonly employed method for assessing the extent of heavy metal pollution in both land and water ecosystems. It is expressed as:

$GeoI = \ln [C_m / 1.5 * B_m]$

Here, C_m and B_m retain the same meanings as previously described. The value 1.5 serves as an adjustment factor to account for potential differences in background concentrations resulting from variations in lithology. The Geo-accumulation Index (GeoI) is categorized into seven descriptive classes as presented in Tables 3 and 4.

Table 3: Index of Geoaccumulation (GeoI) for Contamination Level in Soil (Mueller, 1979)

GeoI Class	GeoI Value	Contamination Level
0	GeoI ≤ 0	Uncontaminated
1	0 <GeoI< 1	Uncontaminated to moderately contaminated
2	1 <GeoI< 2	Moderately contaminated
3	2 <GeoI< 3	Moderately to strongly contaminated
4	3 <GeoI< 4	Strongly contaminated
5	4 <GeoI< 5	Strongly to extremely contaminated
6	5 <GeoI	Extremely contaminated

Table 4: Contamination factor (CF) and level of contamination (Hakanson, 1980)

S/N	CF Value	Level of Contamination
1	CF < 1	Low contamination factor
2	1 < CF < 3	Moderate contamination factor
3	3< CF < 6	Considerable contamination factor
4	CF ≥ 6	Very high contamination factor

In Table 5, the mean heavy metal values from Ifie community was used as the C_m while the heavy metal values from the control site was used as the B_m.
The table indicates low to moderate contamination levels for the Heavy metals Fe, Ni, Pb and Cu. According to the CF values, Zn shows low level of contamination and in GeoI, it is uncontaminated. This is can be attributed to the high amount of Zn value from the control site to Ifie community. The Ifie community as shown in Table 6 has a very high level of Cr contamination, however both the mean value and the individual sample sites for Cr comfortably falls below both the WHO (1996) target values and the CONAMA 2009 prevention values. Ni and Cu show moderate to considerable level of contamination according to both the CF and GeoI. While the value for Cu in all the sample sites is lower than the CONAMA (2009) prevention values, the value for Ni is higher than the CONAMA (2009) prevention values in 8 out of the 11 sample sites. Ni and Cu in 5 out of 11 and 6 out of 11 sample sites respectively are above the WHO (1996) target values (Figure 6). This further establishes that there is moderate to considerable level of Ni and Cu contamination in the area.

Table 5: Metal contamination factor and geo-accumulation index of metals in soil samples from Ifie Community.

Parameters	C_m	B_m	CF	Level of Contamination (Using CF)	GeoI	Level of Contamination (Using GeoI)
Fe	154.60	65.50	2.37	Moderate	0.45	Uncontaminated to moderately contaminated
Ni	33.80	19.00	1.77	Moderate	0.17	Uncontaminated to moderately contaminated
Cr	8.30	0.50	16.6	Very high	2.40	Moderately to strongly contaminated
Pb	1.80	0.50	3.60	Considerable	0.87	Uncontaminated to moderately contaminated
Cd	-	-	-	-	-	-
Zn	12.70	21.50	0.59	Low	-9.3	Uncontaminated
Cu	36.30	7.50	4.84	Considerable	1.17	Moderately contaminated

Evaluation of contamination sources for heavy metals in soil samples through Correlation, Hierarchical Cluster Analysis, and Principal Component Analysis.

Table 7: Correlation of Heavy metals of studied soils

	Fe	Ni	Cr	Pb	Cu	Zn
Fe	1					
Ni	-0.16367	1				
Cr	0.228083	-0.73278	1			
Pb	0.431089	0.168873	0.008162	1		
Cu	-0.26697	0.85238	-0.82176	0.152319	1	
Zn	0.297217	-0.14349	0.396831	0.244364	-0.2118	1

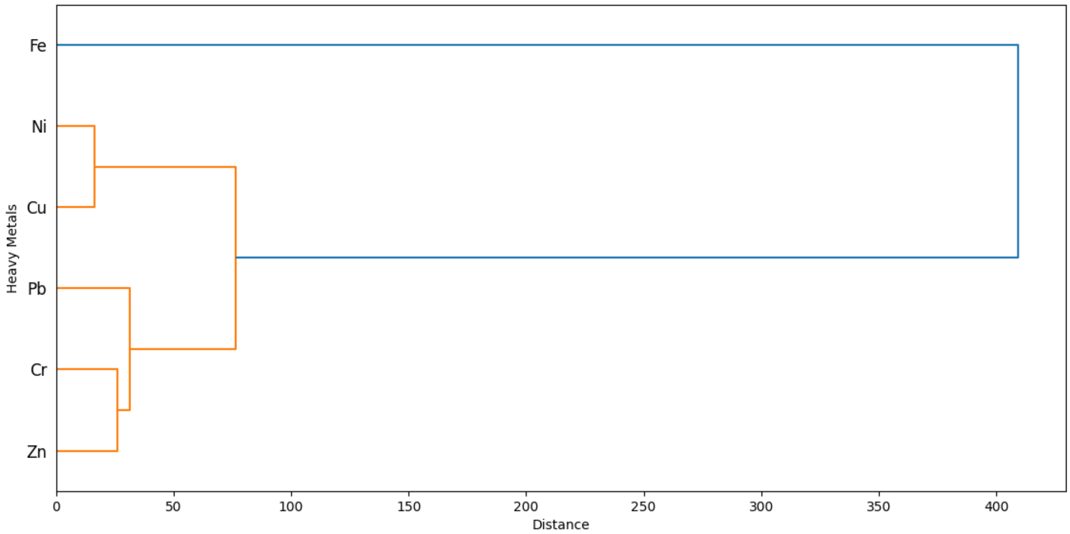

Figure 6: Dendrogram using average linkage between groups of soil samples, illustrating the contamination relationship among heavy metals.

Based on Table 6 and Figure 6, we can analyze the relationships and clustering of heavy metals. There is a strong positive correlation between Ni and Cu (0.8523), indicating they likely share a common source of contamination, likely related to petroleum activities in the area. Both metals have strong negative correlations with Cr (-0.7328 for Ni and -0.8218 for Cu), suggesting different sources or behaviors in the soil compared to Cr. Cr and Zn show a moderate positive correlation (0.396831), while Cr and Pb have a weaker positive correlation (0.008162), implying shared sources or similar environmental transport mechanisms. In the clustering analysis, Ni and Cu form a distinct cluster, reinforcing their close relationship and common sources. Cr and Zn cluster together closely, with Pb joining them next, suggesting these metals share similar patterns and possibly originate from similar processes or contamination sources. The primary clusters identified are (Ni, Cu) and (Pb, Cr, Zn), indicating different influencing factors or sources of contamination for these metal sets. Fe is distinct from all other metals, as indicated by its separate clustering branch, suggesting it is influenced by a unique source or environmental condition different from the other metals.

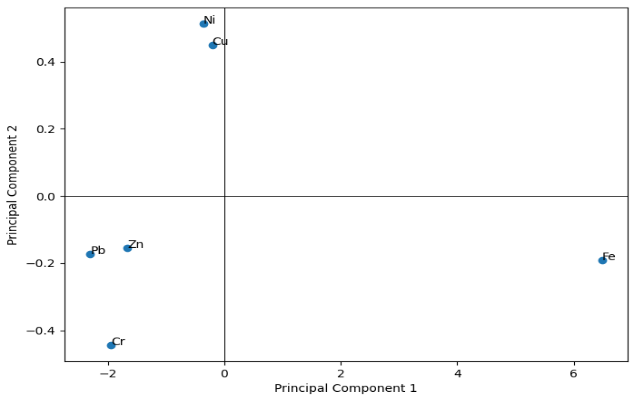

Figure 7: Principal Component Analysis Biplot of Heavy Metals Data (Gotten from Varimax Rotation Method)

The plot shown in Figure7 shows the relationships between heavy metals based on the first two Principal Components (PC1 and PC2), with PC1 explaining the most variance. Fe is significantly separated along the PC1 axis. Ni and Cu cluster together in the positive region of PC2, suggesting a shared contamination source influenced by different factors than PC1. Cr, Pb, and Zn are near the origin, indicating multiple or less dominant contamination sources.

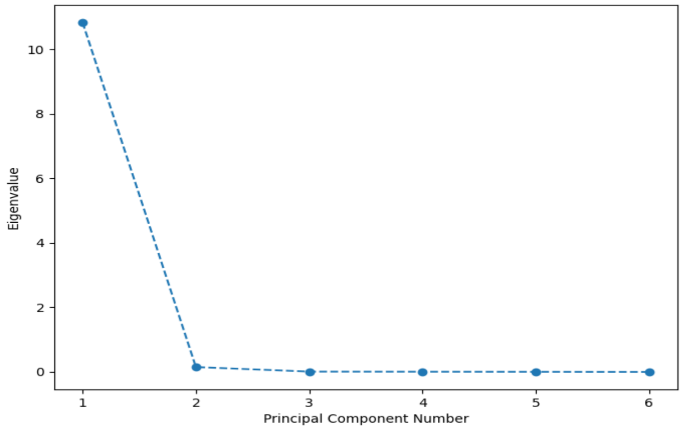

Figure 8: Scree plot of Eigenvalue against component number (gotten from extraction method)

Figure 8 displays the eigenvalues of the principal components showing the variance each explains. The higher the eigenvalue, the more variance that component explains (George and Ajayakumar 2024). The steep decline after the first component shows that only the first two components are meaningful and should be considered for analysis.

CONCLUSION

The results on the study of the analysis of heavy metals in the soils indicate that the mean concentrations of Cr, Pb, Cd, and Zn in all samples fall below the target values but the mean value for Cu exceeded the target values in some locations while only the mean value for Ni exceeds the prevention values set, signaling varying levels of Ni and Cu contamination. These exceeded mean values correlated with CF and GeoI indicated moderate to considerable levels of Ni and Cu contamination while statistical analysis showed that these two metals are most likely from the same source and influenced by the same factors. The elevated levels also suggests potential pollution sources, potentially linked to the proximity of a petroleum tank farm in the area and the frequent passage of petrol tankers and trucks to gain access to petroleum products.

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