Variation of Heavy Metal Concentration in Otofure, Edo State, Southern Nigeria

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Abstract

This study provides a critical assessment of heavy metal contamination at the Otofure dumpsite in Ovia North East Local Government Area, Edo State. Utilizing Atomic Absorption Spectrometry, soil samples from five distinct points and two depths (0-15 cm and 15-30 cm) were analyzed to determine the distribution of nine key heavy metals. Nine heavy metals were analyzed and they are Cadmium (Cd), Lead (Pb), Arsenic (As), Nickel (Ni), Iron (Fe), Chromium (Cr), Manganese (Mn), Copper (Cu)and Vanadium (V). The mean of the results includes Fe 96.08 - 65.88 Mg/kg, Cr 0.10 - 0.06 Mg/kg, Mn 15.34 - 11.82 Mg/kg, Ni 9.87 - 5.57 Mg/kg, Cd 0.05 - 0.01 Mg/kg, Cu 30.82 - 24. 36 Mg/kg, Pb 4.19 - 3.09 Mg/kg, V 31.06 - 20.13 Mg/kg and As 0.08 - 0.02 Mg/kg. Then the results obtained were compared with past research done on the dumpsite and national standards. The mean concentrations observed across the samples indicate varying levels for the heavy metals, with ranges such as 96.08 - 65.88 mg/kg for the most prevalent metal and considerably lower values like 0.05 - 0.01 mg/kg for others. Crucially, a comparative analysis of these findings against historical data for the dumpsite and relevant national environmental standards reveals a notable and encouraging trend: a significant reduction in heavy metal pollution. This positive environmental shift is directly attributable to two primary factors: a decreased influx of waste being deposited at the site and the ongoing efforts to reclaim the land for residential development. These results strongly suggest a future transformation of the Otofure dumpsite. The observed decline in contamination, coupled with the continued land reclamation initiatives, indicates a trajectory towards the eventual phasing out of the dumpsite, paving the way for its conversion into residential areas within the Otofure community. This development holds significant implications for local environmental health and land-use planning in Edo State.

Keywords: *Anthropogenic, Pollution, Contamination, Metal*

1. Introduction

Human activities have resulted in an unexpected accumulation of heavy metals in the various ecosystems. Over the last century, intensified emission of heavy metals are from anthropogenic sources. Heavy metals are non-biodegradable and persistent environmental contaminants, which may be deposited on the soil surfaces. Heavy metals pollution can be referred to as the quantities of the element in the soil higher than the normal allowable amount, (Alloway, 2013), thus

making it harmful to man and other living things in the area they occur. Heavy Metal(s) are widespread pollutants of great concern as they do not decompose or degrade and thus are persistent in the environment, (Tchounwou, 2012), thus, the impact on human health by natural materials such as rock, water and minerals are known for many years (Grandjean, 2006). Heavy metal pollution has emerged due to anthropogenic activity which is the prime cause of pollution, primarily due to mining the metal, smelting, foundries, and other industries that are metal-based, leaching of metals from different sources such as landfills, waste dumps, excretion, livestock and chicken manure, runoffs, automobiles and roadworks. Heavy metal use in the agricultural field has been the secondary source of heavy metal pollution, such as the use of pesticides, insecticides, fertilizers, and more. Natural causes can also increase heavy metal pollution such as volcanic activity, metal corrosion, metal evaporation from soil and water and sediment re-suspension, soil erosion, geological weathering (Briffa, *et al*, 2020).

Heavy metals are generally defined as metals with relatively high densities, atomic weights, or atomic numbers, and are toxic or poisonous even at low concentration (Duffus, 2002). Heavy metals contamination in man and its effect are as a result of the interrelationship between plants and animals through the food chain as the only means for survival. Also, humans can accumulate heavy metals via drinking of contaminated water or by direct inhalation or long exposure to heavy and toxic metals as in Zamfara State in Nigeria (Yi-Chun, *et al*, 2010).

The soil is able to accumulate these heavy metals without any obvious signs to its effect because of the ability of the soil to bio-accumulate. The use of dumpsite as farmland is a common practice in Nigeria because decayed and composted wastes enhance soil fertility (Ogunyemi, *et al,* 2003), these wastes contain heavy metals in different forms and various accumulation.

This research is centered on the comparison between recent work (This study) and previous work to check the level of heavy metal accumulation, if it has exceeded over the last decade.

2. Location of the Study Area

The study was conducted in Otofure dumpsite in Ovia North East Local Government Area, Benin city, Edo State, Nigeria. It is surrounded by the Oluku community to the north. It is geographically falls within the coordinates of N 6^{o} 27' 48.9'' and E 5^{o} 36' 04.1'' is experiencing influx of migrants within and around Benin City because of its strategic position as a satellite/commercial town with natural vegetation (Balogun and Onokerhoraye, 2017). The area has a length and breadth of 320 sqm by 320 sqm. The area was accessible by footpath and road network. The study area was covered by light vegetation and lots of waste such as plastic, polythene, paper etc. Upon the time of arrival, the waste in the dumpsite was burnt but traces of unsegregated wastes such as plastic, polythene, paper etc. could still be seen and the full extent of the dumpsite could be seen, this made collection of samples easy.

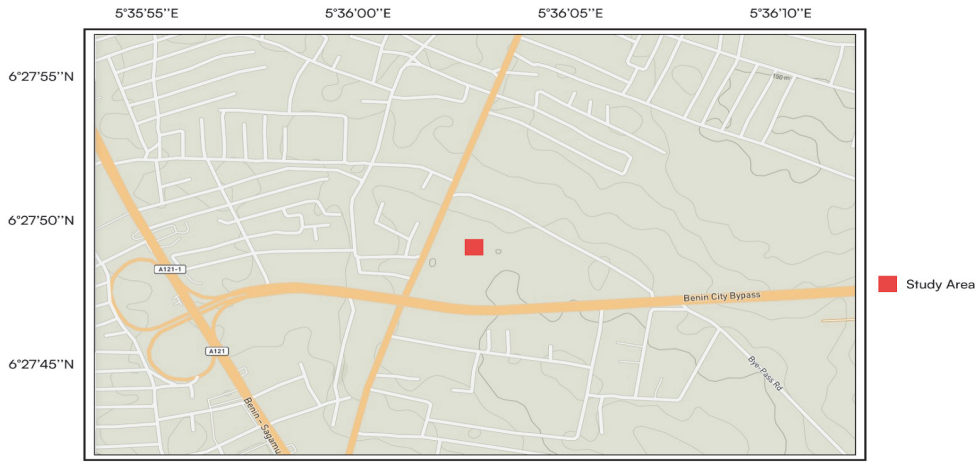


Figure 1: Location of the study area

3. Local Geology

The Niger Delta Basin is a large, highly productive extensional rift basin in southern Nigeria, broadly situated between latitudes 3°00'N and 6°50'N and longitudes 4°00'E and 8°80'E (Tuttle et al., 1999; Burke, 1972). It formed as a failed rift junction during the Mesozoic separation of the African and South American plates, with its structure largely influenced by gravity-driven deformation (Burke, 1972; Evamy et al., 1978). The Delta is bounded to the south by the Gulf of Guinea, to the north by older (cretaceous) sediments of the Anambra Basin, Abakaliki uplift and the Afikpo Syncline to the east and west by the Dahomey Basin and Cameroon volcanic line respectively. The Niger delta is a significant sedimentary basin in Nigeria and is characterized by a thick wedge of clastic sediments deposited over millions of years. The lithostratigraphy is broadly divided into three main diachronous formations, which represent a regressive sequence from marine to continental environment.

3.1 Akata Formation

According to Stauble and Short (1967), the Akate formation is the lowermost lithological division of the Niger Delta consisting of basically marine shales with clay and silt intervals in place. The Akata shales are under compacted and over pressured (Merki, 1972). The Akata ranges in age from the Paleocene - Recent and grades in the Agbada Formation.

3.2 Agbada Formation

The Agbada Formation overlies the Akata Formation and underlies the Benin Formation. It is a paralic sequence characterised by an alternation of sandstones, shales and siltstones. The Agbada Formation spans over 3500m (11500 ft) in thickness (Corredor *et al.,* 2005). The age of the Agbada Formation is in between the Eocene to Recent.

3.3 Benin Formation

Geologically, the study area falls on the Benin Formation which is the uppermost and the youngest formation of the Niger Delta and it made up of made up of yellow to white (sometimes cross bedded) sand, largely unconsolidated with pebbles, clays and sandy clays occurring in lenses (Short and Stauble 1967; Frank and Cordy 1967), very poorly consolidated sandstones, with little shales lense, coal and conglomerates from continental (Short & Stauble, 1967; Doust & Omatsola, 1990) and delta plain. These sediments were deposited in delta top environments such as alluvial plains, braided river systems and freshwater swamps. The Benin Formation represents the final stage of the Niger Delta's progradation.

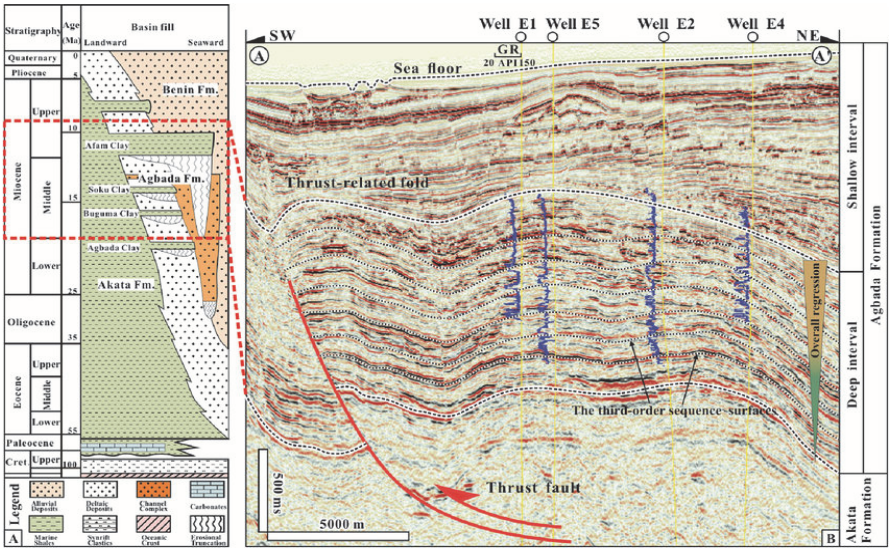


Figure 2: A map of the Niger Delta showing the Lithostratigraphy (Adapted from Zhang *et al.,* 2016)

4. Materials and Methods

This study employed both field and laboratory techniques. In the field, a total of 10 fresh samples were collected from 5 sampling points, the five sites investigated were; site 1 falls within N 6° 27' 47.0'' and E 5° 36' 04.8'', site 2 falls within N 6° 27' 47.2'' and E 5° 36' 05.0'', site 3 falls within N 6° 27' 46.2'' and E 5° 36' 06.8'', site 4 falls within N 6° 27' 43.3'' and E 5° 36' 08.0'' and site 5 falls within N 6° 27'42.5'' and E 5° 36' 06.8''using a machete and a soil auger at different depths of 0-15 cm and 15-30 cm. The samples obtained from the field were left to air dry in the laboratory before analysis was done. Drying was done by spreading the wet samples on a paper and left to dry at room temperatures for a period of 72 hours.

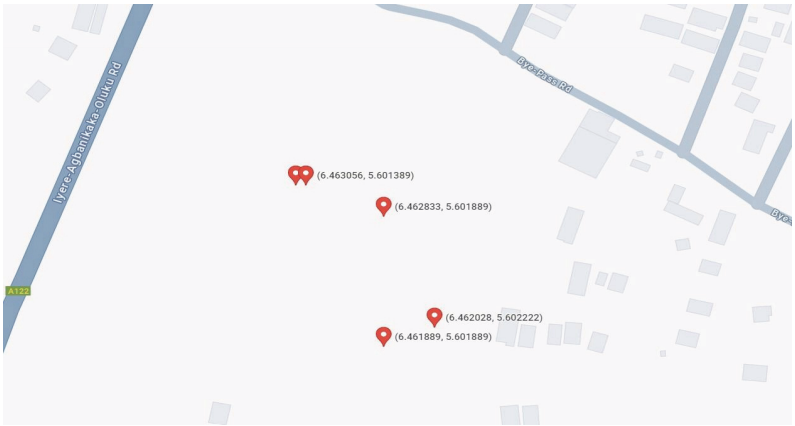


Figure 3: Location of the area of sample collection

4.1 Soil sample analysis

4.1.1 Procedure

In the laboratory, the 10 samples were prepared for Atomic Absorption Spectrometer analysis. Soil samples were ground using an agate mortar and sieved through a 2 mm sieve. An accurately weighed 2 g portion of the air-dried soil was transferred into a 150 ml beaker for digestion. A 20 ml of concentrated HNO3 was added and allowed to stand for 1 hour. After this, 15 ml of concentrated HClO3 was added. The mixture was digested at 200-225°C until it turned yellow or white, indicating reaction completion. The digest was dissolved in 0.1M HCl, then filtered using Whatman filter paper into a 250ml volumetric flask and left to mark. The digest was left to determine the various elements in the extract using the Atomic Absorption Spectrometer.

4.1.2 Analytical method

Samples under study were first digested using wet digestion method. Approximately 1.0 g of the digested sample was transferred into a 100 ml volumetric flask and about 10 ml of concentrated HNO3 was added, and the solution stood for a few hours. Then it was carefully heated over the laboratory plate till red fumes coming out of the flask completely ceased. The flask was allowed to cool at room temperature and then about 5 ml of chloric acid was added and the flask was heated again in the laboratory hot plate to evaporate till a small portion which was then filtered through whatman filter paper no 42. And the volume was made up to 100 ml using distilled water.

4.2 Atomic Absorption Spectrometry

The analysis was conducted using an atomic absorption spectrometer (AAS). The samples were converted into liquid form typically through dissolving or extraction. Then the sample is then nebulized, transformed into a fine mist, and introduced to a high - temperature flame. This intense heat breaks down the liquid and molecules into the individual atoms. The light source, often from a yellow cathode lamp containing the elements being analyzed , emits various wavelengths of light. As the light travels through the atomized sample, some of the light is absorbed by the target element at its characteristic wavelength. A detector at the other side of the flames measures the amount of light reaching it at each wavelength. The amount of light absorbed at the specific wavelength of the target element is proportional to the concentration of that element in the sample. By analyzing the amount of light absorbed at specific wavelengths, the AAS can determine the presence of certain elements and their concentration within the samples. Reagents used were of analytical grade, with nitric acid from Fisher Scientific. Solutions were prepared using ionized water. Glassware was washed, rinsed with distilled water, wrapped in aluminum foil, and sterilized at 160°C in a hot air oven.

5. Result and Discussion

5.1 Result from the Atomic Absorption Spectrometer

This section describes the vertical distribution of heavy metals within the soil profile, highlighting specific concentration trends.

The data indicates that Iron (Fe) consistently exhibits the highest concentrations in both the shallow (0-15 cm) and deeper (15-30 cm) topsoil layers, with values of 122 mg/kg at the surface and 81.5 mg/kg in the subsurface. This is ecologically significant as iron is a major component of earth's crust and commonly present in soils, but its high concentration can influence the mobility and bioavailability of other trace metals due to its role in various redox reactions and as an adsorbent. Conversely, the trace heavy metals Cadmium (Cd), Chromium (Cr) and Arsenic (As) are present at the lowest detected concentrations. Cadmium recorded the minimum concentration of 0.02 mg/kg in the surface layer, Chromium recorded the minimum concentration of 0.03 mg/kg in the surface layer while Arsenic showed the lowest at 0.01 mg/kg in the subsurface. These low levels are crucial because both Cd, Cr and As are highly toxic even at very low concentrations and are frequently associated with anthropogenic pollution. Their minimal presence suggests either limited external input or efficient immobilization within the soil profile at this specific site. The observed decrease in the concentration of Iron from the surface (122 mg/kg) to the subsurface (81.5 mg/kg) indicates a potential vertical attenuation or leaching effect, where some iron may be less concentrated at deeper horizons, possibly due to hydrological processes or varying soil mineralogy with depth. The distinct low concentrations of Cd, Cr and As,

particularly in the subsurface for As, warrant further investigation into the specific speciation and mobility of these elements to fully assess their environmental risk despite their low overall levels.

Table 1: Heavy metal data

Samples	Fe	Pb	Cr	Mn	Ni	Cd	Cu	V	As
S1 0-15 cm 15-30cm	102.4 73. 6	5.3 2.16	0.12 0.1	15.7 12.3	10.6 7.35	0.1 0.02	34.6 25.3	33.5 21.4	0.08 0.02
S2 0-15 cm 15-30cm	122.0 81.5	4.68 2.06	0.15 0.1	18.0 14.4	9.4 5.66	0.04 0.01	30.4 26.2	35.2 24.6	0.1 0.03
S3 0-15 cm 15-30cm	89.3 68.2	4.54 3.0	0.12 0.1	16.5 13.1	11.6 5.26	0.03 0.01	32.5 23.8	43.5 20.7	0.11 0.04
S4 0-15 cm 15-30cm	120.3 65.5	5.22 3.1	0.1 0.04	19.0 15.6	12.45 6.22	0.1 0.02	35.2 30.0	36.3 30.0	0.1 0.016
S5 0-15 cm 15-30cm	46.4 40.6	1.25 0.13	0.03 0.016	7.53 3.74	5.31 2.89	0.02 0.01	21.4 16.5	6.83 3.96	0.04 0.01
Mean 0-15cm 15-30cm	96.08 65. 88	4.19 2.09	0.10 0.06	15. 34 11.82	9.87 5.47	0.05 0.01	30.82 24.36	31.06 20.13	0.08 0.02

*All units are in Mg/kg *S1 - S5: Sample 1- Sample 5

5.2 Heavy metal analysis

This detailed analysis of heavy metal distribution in topsoil (0-15 cm) and subsurface (15-30 cm) layers provides crucial insights into contaminant mobility and the role of soil characteristics at the area of study. A consistent pattern emerges: for most analyzed heavy metals (Fe, Cd, Pb, As, Ni, Cu, Cr, V, Mn), concentrations are generally higher in the surface topsoil (0-15 cm) than in the subsurface (15-30 cm). This observed vertical attenuation is primarily attributed to the presence of clay substances identified at the 15-30 cm depth. Clay minerals, characterized by their high cation exchange capacity (CEC) large specific surface area, and layered structure, effectively adsorb and immobilize positively charged metal ions (Sposito, 2008; Bradl, 2005) This acts as a natural geochemical barrier or filter, limiting the downward percolation and mobility of heavy metals into deeper soil profiles and potentially reducing groundwater contamination risks.

5.2.1 Specific Element Interpretations

- Iron (Fe): As the most abundant element, originating significantly from decomposing landfill materials and the inherent stability of its oxides, Fe exhibits the highest concentrations across both depths (surface: 122 - 46.4 mg/kg; subsurface: 81.5 - 40.6 mg/kg). While highly prevalent due to its ubiquity and the stability of its oxide forms, the decrease with depth suggests some degree of surface accumulation and/or a slight reduction in concentration, possibly influenced by dilution or minor leaching processes that are, however, largely contained by the deeper clay layer.
- Cadmium (Cd) & Lead (Pb): These highly toxic trace elements, predominantly from anthropogenic sources, show clear evidence of surface accumulation and significant vertical attenuation. Cd concentrations notably decrease with depth (surface: 0.1 - 0.02 mg/kg; subsurface: 0.02 - 0.01 mg/kg . Similarly, Pb concentrations are distinctly higher at the surface (5.3 - 1.25 mg/kg) compared to the subsurface (3.00 - 0.13 mg/kg). The sharp drop with depth underscores the effectiveness of the surficial soil layers and the underlying clay in preventing the widespread vertical migration of these hazardous elements.

- Arsenic (As): As a naturally occurring yet harmful element, As shows its highest surface concentration at 0.11 mg/kg and its lowest in the subsurface at 0.01 mg/kg. This vertical trend suggests that despite its natural presence, its transport into deeper layers is also restricted, likely by adsorption onto iron oxides, clay minerals, or organic matter.
- Nickel (Ni), Copper (Cu), Vanadium (V), and Manganese (Mn): These transition metals, derived from both natural mineral weathering and anthropogenic inputs (e.g., industrial activities, alloys), generally follow the trend of higher surface concentrations. Cu has a surface concentration of (35.2 - 21.4 mg/kg), which is consistently higher than subsurface (30.0 - 16.5 mg/kg). Ni has a surface concentration of (12.45 - 5.31 mg/kg) which is notably higher than the subsurface (2.89-7.35 mg/kg). V has a surface concentration of (43.5 - 6.83 mg/kg) generally exceeds subsurface (30.0 - 3.95 mg/kg). Mn has a surface concentration of (19.0 - 7.53 mg/kg) is higher than subsurface (15.6 - 3.74 mg/kg). The consistent higher concentrations at the surface suggest primary deposition from waste decomposition, followed by a filtering effect from the clay layer.
- Chromium (Cr) concentrations in the soil samples decreased from the surface (0.15 - 0.03 mg/kg) to the subsurface (0.1 - 0.04 mg/kg). This reduction with depth is attributed to the effective adsorption and immobilization of Cr by clay minerals, iron/manganese oxides, and organic matter, as well as the reduction of mobile Cr(VI) to immobile Cr(III) in the subsurface, preventing its downward migration.

In conclusion, the data highlights the landfill as a primary source of heavy metal input to the surface soil. Critically, the presence of clay substances at 15-30 cm depth acts as a crucial natural attenuator, significantly reducing the downward migration of most heavy metals and thus mitigating broader environmental contamination.

Table 2: Comparison of This study, Previous studies, NESREA

Study Areas	Depths	Fe	Pb	Cr	Mn	Ni	Cd	Cu	V	As
This Study	0-15 cm 15-30 cm	96.08 65.88	4.19 2.09	0.10 0.06	15.34 11.82	9.87 5.47	0.05 0.01	30.82 24.36	31.06 20.13	0.08 0.02
Aghewi *et al.*,(2019)	0-15 cm 15-30 cm	1.23 1.1	65.58 60.93	68.53 63.57	1.96 0.65	39.61 23.58	106.67 99.0	1.78 1.75	49.86 45.86	-
Imasuen and Omorogieva (2013)	0-15 cm 15-30 cm	-	49.41 32.71	50.30 37.71	-	27.31 17.90	38.91 26.61	-	-	13.92 10.40
NESREA (2009)		NS	164.00	100.00	NS	70.00	3.00	100.00	NS	NS

*All units are in Mg/kg *NS: Not Specified
*NESREA: National Environmental Standard and Regulation Enforcement Agency
* NESREA values are measured in ppm

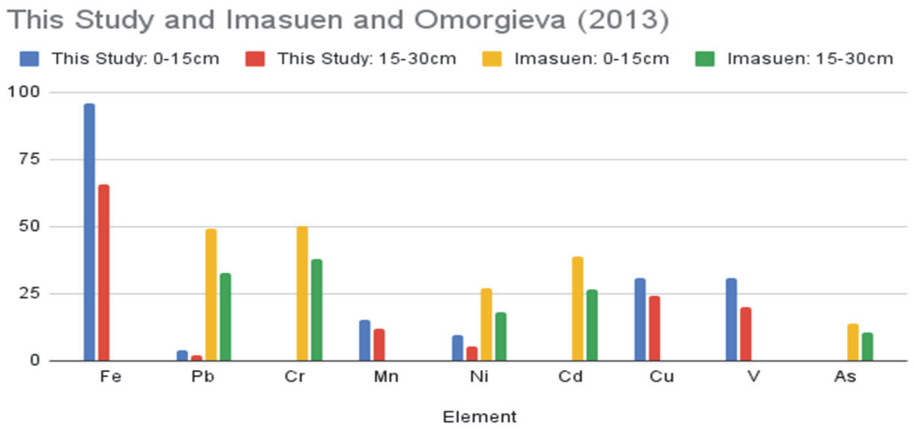
5.3 Comparative between Imasuen and Omorogieva (2013) and This Study

A comparative analysis was performed between the heavy metal concentrations observed in the current study and those previously reported by Imasuen and Omorogieva (2013) at the Otofure dumpsite. This temporal comparison focused on Lead (Pb), Chromium (Cr), Nickel (Ni), Cadmium (Cd), and Arsenic (As).

The concentrations of these specific heavy metals (Pb, Cr, Ni, Cd, As) reported by Imasuen and Omorogieva (2013) were markedly higher than the values obtained in the present investigation. This significant reduction in heavy metal levels over the decade strongly indicates a decrease in active waste deposition and associated pollutant loading at the Otofure dumpsite. The Otofure dumpsite currently receives significantly less municipal waste, a change directly correlated with its ongoing reclamation and conversion into residential areas. This cessation of active dumping naturally reduces the continuous input of heavy metals. Over time, heavy metals within landfill environments are subject to leaching and migration. Percolating rainwater facilitates the dissolution of soluble metal species, enabling their advective and diffusive transport out of the primary waste matrix and into surrounding soil and potentially groundwater. This efflux contributes to a reduction in the overall concentration of heavy metals within the original contaminated footprint.

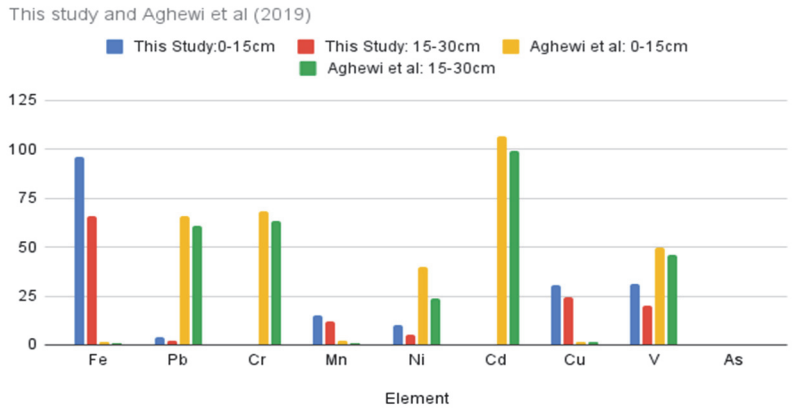
The predominant cause of heavy metal accumulation at this site, historically, remains anthropogenic activities, specifically the large-scale disposal of diverse waste streams laden with metallic contaminants. It is pertinent to note that the Imasuen and Omorogieva (2013) study did not include analyses for Iron (Fe), Manganese (Mn), Copper (Cu), and

Vanadium (V), thus precluding a direct temporal comparison for these specific elements.



5.4 Comparative between Aghewi et al., (2019) and This Study

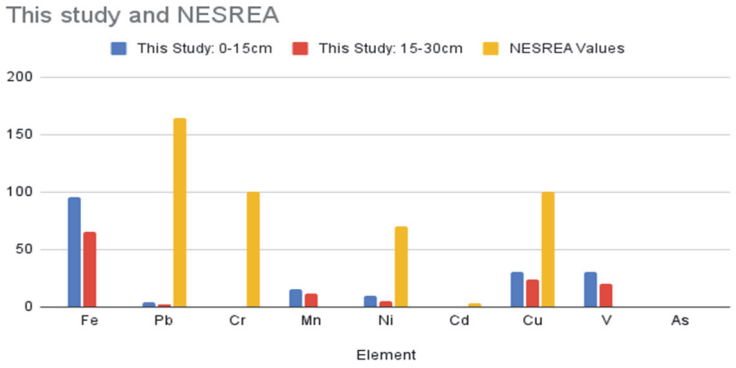
A comparative analysis was conducted between the heavy metal concentrations found in the current study and those reported by Aghewi et al. (2019) at the Otofure dumpsite, near Benin City. The objective was to ascertain changes in heavy metal accumulation patterns, primarily attributed to anthropogenic activities. For the commonly analyzed heavy metals, the Aghewi et al. (2019) study reported elevated concentrations of Lead (Pb), Chromium (Cr), Nickel (Ni), and Cadmium (Cd) when compared to the present study's findings. Conversely, Iron (Fe), Manganese (Mn), and Copper (Cu) exhibited reduced levels in the Aghewi et al. (2019) data compared to the current investigation. While the current study analyzed Vanadium (V), Aghewi et al. (2019) did not, and Arsenic (As) was not analyzed by Aghewi et al. (2019), precluding a direct comparison for these elements. This observed difference suggests a historical shift in waste composition at the dumpsite over the past six years. The higher concentrations of Pb, Cr, Ni, and Cd previously observed infer a period of more significant deposition of waste streams rich in these specific elements. Potential anthropogenic sources contributing to such elevated heavy metal loads include industrial discharges, the combustion of municipal solid waste (MSW), and the improper disposal of specific vanadium-containing industrial byproducts (though the V comparison is constrained by the data availability from Aghewi et al.). The current study's higher Fe, Mn, and Cu levels might indicate an increased influx of waste types rich in these metals in more recent times, or differential leaching/mobilization patterns over the six-year period.



5.5 Comparative between NESREA and This Study

The analytical results indicate that the concentrations of most analyzed heavy metals are within the established permissible limits set by the National Environmental Standards and Regulations Enforcement Agency (NESREA). This suggests compliance with current environmental guidelines for these specific contaminants in the assessed soil matrices.

However, a direct comparative assessment for Iron (Fe) and Vanadium (V) against NESREA standards cannot be explicitly made. This is due to the absence of specific regulatory target limits or permissible thresholds for Fe and V within the current NESREA guidelines. Therefore, while their measured concentrations are reported, their environmental risk or compliance status relative to Nigerian federal regulations cannot be definitively determined based solely on NESREA's published limits for these two elements. Interpretation for Fe and V would require comparison with other international standards, background concentrations, or ecological risk assessment frameworks.



6. Conclusion

6.1 Summary

This study assessed heavy metal concentrations in soil from the transitioning Otofure dumpsite in Benin City, Nigeria, using five samples collected at 0-15 cm and 15-30 cm depths. Nine heavy metals were analyzed by Atomic Absorption Spectrometry, with mean concentrations of Fe (96.08-65.88 mg/kg), Cr (0.10-0.06 mg/kg), Mn (15.34-11.82 mg/kg), Ni (9.87-5.57 mg/kg), Cd (0.05-0.01 mg/kg), Cu (30.82-24.36 mg/kg), V (31.06-20.13 mg/kg), and As (0.08-0.02 mg/kg). These levels are generally within NESREA permissible limits (e.g., Pb: 164 ppm; Cr: 100 ppm; Ni: 70 ppm; Cd: 3 ppm;

Cu: 100 ppm), and a temporal comparison shows overall reduced levels compared to past data. Despite regulatory compliance, the study highlights ecological and human health risks due to bioaccumulation in cassava plants and aquatic contamination via a standing water body connected to the Ikpoba Hill River, emphasizing the long-term dangers of heavy metal consumption. Therefore, proactive phytoremediation (phytoextraction, rhizofiltration) and advanced water treatment (membrane filtration, ion exchange, biosorption) are recommended to mitigate metal transfer into the food chain and protect public health during the site's conversion to residential use.

6.2 Recommendation

Continuous environmental monitoring of the Otofure dumpsite in Benin City, Nigeria, is imperative, particularly given its ongoing conversion into residential areas, to proactively detect and prevent any future increases in soil heavy metal concentrations, thereby safeguarding public health and ecological integrity. The prevalent informal practice of waste burning poses a significant environmental hazard, directly elevating soil heavy metal levels via ash and particulate deposition, while simultaneously releasing harmful atmospheric pollutants that degrade air quality, impact the stratospheric ozone layer, and exacerbate climate change. Consequently, it is crucial for governmental authorities to implement robust public awareness campaigns to eradicate waste burning and foster the adoption of environmentally sound waste management alternatives, including comprehensive integrated waste management systems (emphasizing reduction, reuse, recycling, and composting), properly engineered sanitary landfills with leachate and gas control, and, where appropriate, controlled waste-to-energy technologies with advanced emission controls, to ensure a sustainable and healthy environment for the transitioning community.

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