

Original Research Article

ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN LEACHATES AND SOILS OF CENTRAL BANK OF NIGERIA DUMPSITE ALONG UNIVERSITY OF AGRICULTURE ROAD- MAKURDI

Abstract-The concentrations of heavy metals (Cr, Pb, Cd, Hg and Se) in leachate from Central Bank of Nigeria Dumpsite platform and surrounding soil along University of Agriculture road, Makurdi, was determined using Atomic absorption spectrophotometry for Cr, Pb and Cd while cold vapour and hydride generation was used for Hg and Se. The soil samples were collected at different depths (cm) 0 – 20, 20 – 40, 40 – 60 and 60 – 80. The levels of all heavy metals in this study area were found to be higher than those of the control samples. The total mean concentration of the soil samples analysed for each metals concentration at different depths range from Cr (74.7 – 2.6 mg/kg), Cd (7.41 – 0.6 mg/kg), Hg (4.45 – 1.4 mg/kg), Se (2.04 – 1.2 mg/kg) and Pb (8.53 – 1.7 mg/kg). The concentrations in leachates were Cr (0.079 mg/L), Cd (0.010 mg/L), but Pb, Hg and Se were not detected. The concentrations of Cr and Cd determined in leachate were below the WHO standard limits. Similarly, the concentrations of Pb, Hg and Se in soil analyzed in this study were within the allowable permissible limits. However, the concentration of Cr and Cd were found to have higher permissible limits due to the increasing anthropogenic activities in the area.

Keywords: *Heavy metals, Leachate, Dumpsite, AAS, Soil.*

I. INTRODUCTION

Landfilling is the prime method of disposal in most of the countries globally because it is the most cost-effective option. Landfills pose a big predicament to the environment in which during landfill operations, different kinds of hazards including gas and leachate are deposited.

Landfill leachates have been reported to contain a wide range of heavy metals [1]. Leachate is a wastewater that can have negative public health and environmental impacts precisely, if it is allowed to infiltrate into groundwater. Waste is the oldest, growing problem in the whole wide world and its generation is one of the major concerns that threaten the surroundings [2]. Landfills are designed to check leachate from reaching the groundwater and also to accumulate and treat leachate through various wastewater treatment methods [3].

In Nigeria, leachate from refuse or open waste dumpsites are considered as good source of heavy metal pollution to both soil and aquatic surroundings [4]. Municipal landfill leachate is highly concentrated multifaceted effluents which contain dissolved organic matters, inorganic compounds such as ammonium, calcium, magnesium, sodium, potassium, iron, sulphates, chlorides and heavy metals such as cadmium, chromium, copper, lead, zinc, nickel and xenobiotic organic substances [5] which are also responsible for environmental pollution.

The leachate predicament is worsened by the fact that many landfills are deficient in an appropriate bottom liner or collection system; increasing the prospect of dissipation of leachate through the landfill layers to contaminate ground water as well [3]. It can also cause serious pollution problems when it gets in contact with the neighbouring soil, surface water and ground water leading to harmful effects on living organisms.

Exposure to toxic heavy metals like Pb and Cd has been reported to cause blood and bone disorders, kidney damage, decreased mental capacity and neurological damage [6, 7] in both human and animals. Sadly, in developing countries like Nigeria, awareness of the dangers of heavy metals to public health is deficient, therefore this research is imperative. The aim of this study was to determine the concentration of heavy metals in the leachate of Central Bank of Nigeria dumpsite along University of Agriculture Road-Makurdi and also to investigate their levels in soil around the dumpsite platform.

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II. MATERIALS AND METHODS

51 **Study Area:** Makurdi is the capital city of Benue State in North Central Nigeria and lies between Latitude 7° 44
52 N and Longitude 8° 54 N. The physiographic characteristics span between 73 - 167 m above sea level. In the
53 year 2007 Makurdi has an estimated population of 500,791 with a total land area of about 200 km² [8].

54 The study site is located along University of Agriculture Road Makurdi which lies between Latitude N 07° 45'
55 49.1" and Longitude E 008° 34' 46.2". The study location is surrounded by two communities: Ate- Akee
56 community in the West and Menne community in the East and a water dam 500 meter adjacent to it. The
57 population of these communities is about one hundred to one hundred and fifty persons and most of them are
58 peasant farmers. The CBN platform dumpsite was well constructed with cements and also has a dimension of 60
59 ft by 40 ft by 6 ft (18 m by 12 m by 1.8) with a proper drainage that leads to the flowing stream.

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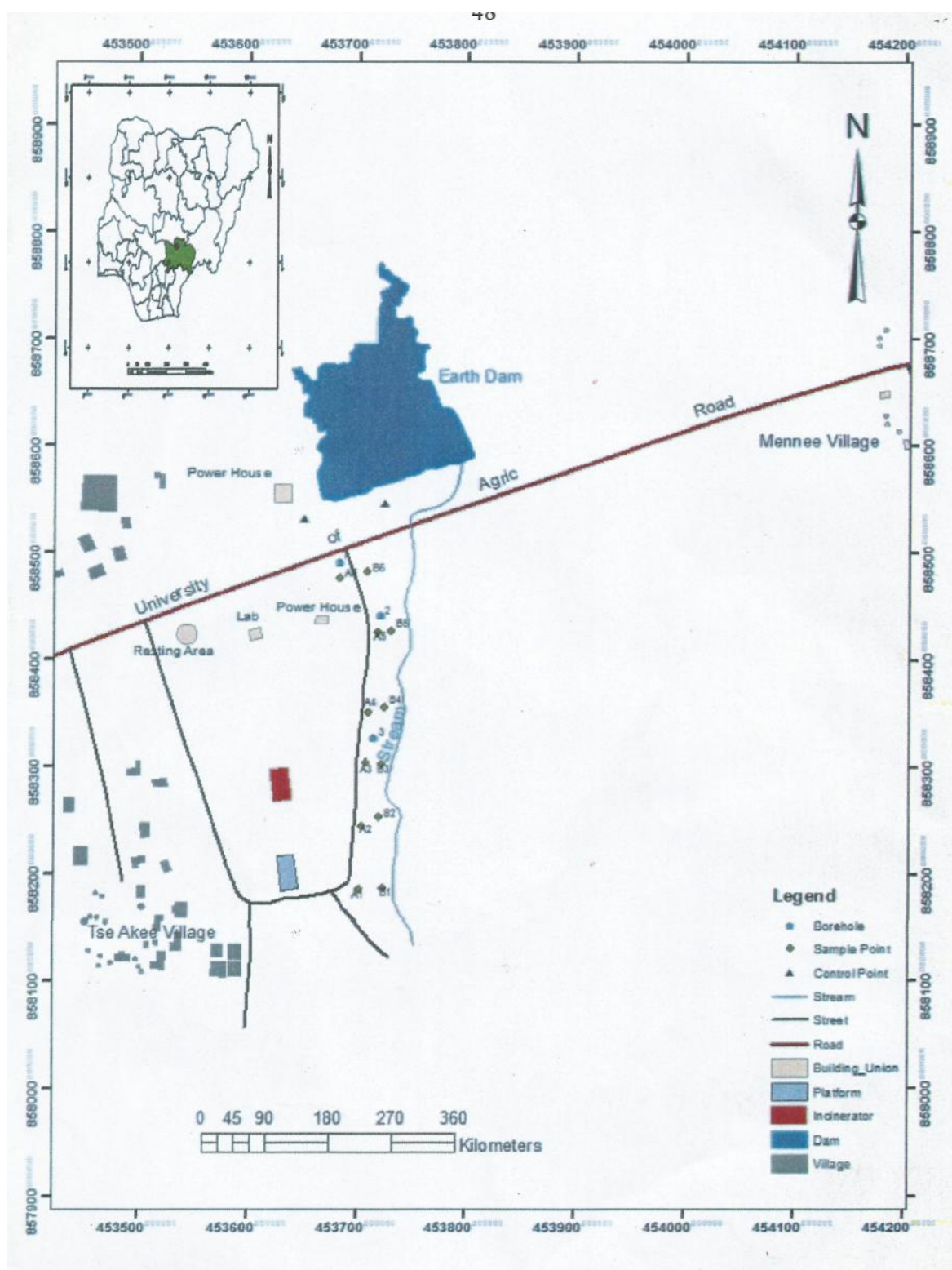


Figure 1: Map of Sampling Site showing the Dumpsite

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Sample Collection: A total of three leachate samples were collected with a clean plastic container from the leachate collection points within the dumpsite at ambient temperature. The leachate samples were collected on a monthly basis for three consecutive months (June – August, 2016). The soil samples were collected at six (6) different points from the dumpsites using hand trowel with the following sampling depths (cm) 0 – 20, 20 – 40, 40 – 60 and 60 – 80. The samples were collected into clean polythene bags. Soil sample were collected at about 600 m away from the CBN dumpsite as control sample.

A total of twenty five soil samples were collected. Three leachate samples were collected from the leachate collection points within the dump site area of CBN. The fourth leachate was 600 m upstream from the dumpsite as control sample. All the plastic containers that were used for collection of the leachate samples were rinsed using distilled water and the containers were tightly covered. The samples were appropriately labelled and samples for heavy metal determination were acidified with concentrated HNO_3 (1 mL/L of water sample) in order to keep the pH of the sample low subsequently preventing precipitation of the metal [9, 10]. All samples collected were stored at 4°C during transportation to the laboratory.

Sample Preparation and Analysis: The soil samples were air dried and were sieved with a 2 mm mesh size sieve. The glass electrode was used to determine the pH of the samples which involve taking the pH of 1:1 soil: deionized water extracted with calibrated pH meter followed by digestion of the samples using nitric and hydrochloric acids to desorb and extract the metal contents rapt in the soil particles [11].

Digestion procedure for leachates samples: A volume of 5.0 mL of leachate sample was transferred into a 250 mL beaker, 5 mL of concentrated nitric acid and 2 mL of 30 % (v/v) hydrogen peroxide were added. Then, samples were heated using a hot plate and these samples were added continuously to complete digestion for 30 minutes. The solutions were allowed to cool and then filtered through a Whatman No. 42 filter paper into a 100 mL standard volumetric flask and diluted to a final volume of 100 mL with deionized water [12].

Digestion of soil samples: Exactly 1.0 g of soil samples which had been dried and sieved (2 mm) was weighed into a 250 mL conical flask and 12 mL of freshly prepared aqua-regia (3 mL HNO_3 + 9 mL HCl) as described by [13] was added in a 250 mL beaker. The beaker was covered with a filter paper to enhance the digestion to take place under constant volume and the content was heated for 1 hour using a hot plate. The content was added continuously to enhance complete digestion and was allowed to cool and filtered using a Whatman No. 42 filter paper into a 100 mL standard volumetric flask. The filtrates were diluted to 100 mL with deionized distilled water and this procedure was repeated for all the soil samples for this study.

Mercury and Selenium Analysis by Cold Vapour Method and Hydride Generation: Using a FIAS-AAS system, a sample loop on the flow injection regulator is filled with the acidified sample, blank, or standard. The regulator was automatically switched to the injection position and the sample was mixed with a pumped stream of reductant, sodium borohydride for hydrides or stannous chloride for mercury to create the gaseous vapors. At the point of reaction with the reductant, selenium hydrides or elemental mercury vapour are created, along with hydrogen from the sodium borohydride, resulting in a two-phase mixture: vapour with the analyte in it and the used-up reductant [14].

Quality Control: Two blanks were prepared for the leachates namely A and B. Blank A comprises of 5 mL of concentrated nitric acid and 2 mL of 30 % (v/v) hydrogen peroxide which were heated for 30 minutes and the content was allowed to cool and then filtered through a Whatman No. 42 filter paper into a 100 mL standard volumetric flask and diluted to a final volume of 100 mL with deionised water whereas, blank B was 100 mL of deionised water. The contaminant present in blank A and B were subtracted from the contaminants present in all the leachates samples collected and digested for this study.

Similarly, two blanks were also prepared for soil samples coded C and D. Blank C comprises of 12 mL of freshly prepared aqua-regia (3 mL HNO_3 + 9 mL HCl) which was heated for 1 hour and the content was allowed to cool and then filtered through a Whatman No. 42 filter paper transferred into a 100 mL standard volumetric flask and diluted to a final volume of 100 mL with deionised water whereas, blank D was 50 mL of deionised

water. The contaminate present in blank C and D were subtracted from the contaminate present in all the soil samples collected and digested for this study to get the actual concentration of contaminants.

In addition to ensure accuracy the AAS machine was calibrated using a known concentration of metals. These metals were run in the AAS machine to determine the absorbance and concentration. Calibration curves were obtained by plotting concentration against absorbance.

Data Analysis: The data was analysed using descriptive statistics. The summary statistics of Cr, Cd, Pb, Hg and Se concentration (mg/kg and mg/L) in both soil and leachates samples were expressed in mean values with their respective standard errors, minimum and maximum values. The results were also presented in tables and charts.

III RESULT AND DISCUSSION

Leachates: The results of the mean concentration of heavy metals in leachates expressed as mean is presented in Table 1

Table 1: The Monthly Concentration (mg/L) of Heavy Metals in Leachate samples and WHO Permissible Limits

Metals	June	July	August	Control	WHO
Pb	N.D	N.D	N.D	N.D	5.0
Hg	N.D	N.D	N.D	N.D	0.2
Cr	N.D	N.D	0.079	0.006	5.0
Cd	N.D	N.D	0.010	0.003	1.0
Se	N.D	N.D	N.D	N.D	1.0

N.D = Not detected

Table 2: Mean concentration (mg/L) of heavy metals in leachate

Elements	Minimum	Maximum	Mean \pm S.D
Pb	N.D	N.D	N.D
Cr	0.006	0.079	0.05 \pm 0.03
Hg	N.D	N.D	N.D
Cd	0.003	0.010	0.01 \pm 0.00
Se	N.D	N.D	N.D

N.D = Not Detected

In the same vein, the variation of metal concentrations and months shows that some of the metals such as Pb, Cr, Hg, Cd and Se were not detected in early rainy season but as the intensity of the rain increases, Cr and Cd that were hanging on the platform were detected (Table 1). In CBN dumpsite metal concentration in leachates samples increases with an increase in rain intensity due to left over traces on the platform. Also some of these metals could not be detected because concentration of these metals are below detection limit or not present at all. However, the finding is in agreement with the research work reported by [15]. The concentration of Cd is below

the permissible limit of 1.0 mg/L WHO [16], due to the reduction in the volume of the leachate for ultimate treatment. This result is in agreement with the result presented by [17].

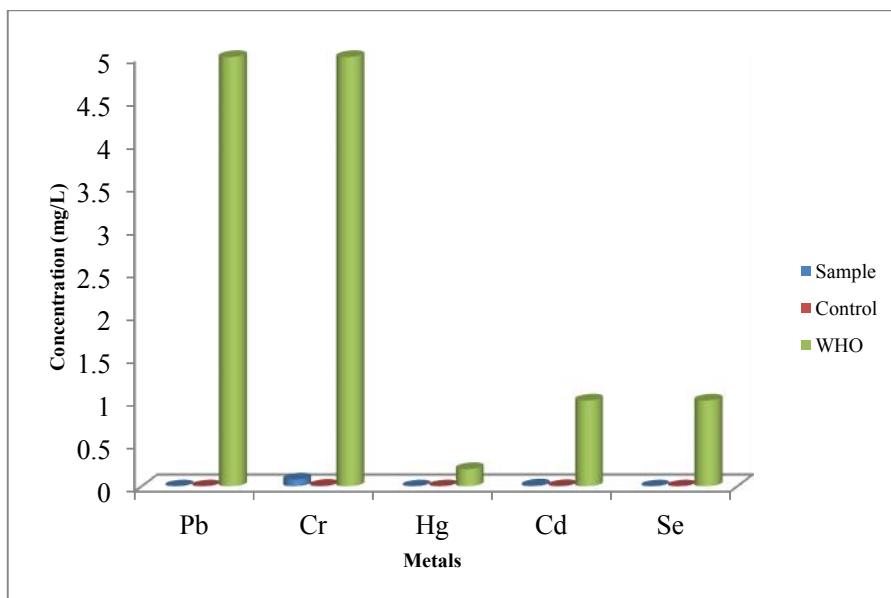


Figure 2: Variation of heavy metal concentration in different months

SOIL

The mean concentration (mg/kg) of heavy metals analysed in soil at different depths at the CBN dumpsite. Chromium ranges between 70.7 – 77.2 mg/kg with an overall mean value of 73.3 ± 2.5 mg/kg at 0 – 20 cm depth. Cadmium at 0 – 20 cm depth ranges between 6.47 to 8.02 mg/kg with an overall mean value of 7.08 ± 0.6 mg/kg. Mercury ranges between 2.15 to 5.95 mg/kg with an overall mean value of 3.63 ± 1.4 mg/kg at 0 – 20 cm depth. Selenium has a range of 1.54 to 3.60 mg/kg with an overall mean value of 2.09 ± 0.8 mg/kg at 0 – 20 cm depth. Lead ranges between 5.87 to 10.3 mg/kg with an overall mean value of 7.59 ± 1.7 mg/kg at 0 – 20 cm depth. However chromium has the highest value, whereas selenium has the lowest value in this depth.

Chromium at 20 – 40 cm depth ranges between 77.2 to 83.7 mg/kg with an overall mean value of 80.0 ± 2.26 mg/kg. Cadmium ranges between 8.02 to 9.58 mg/kg with an overall mean value 8.67 ± 0.5 mg/kg at 20 – 40 cm depth. Mercury ranges between 5.95 to 9.74 mg/kg with an overall mean value of 7.53 ± 1.3 mg/kg at 20 – 40 cm depth. Selenium ranges between 0.65 to 3.6 mg/kg with an overall mean value 2.68 ± 1.5 at 20 – 40 cm depth. Lead ranges between 10.3 to 14.7 mg/kg with overall mean value 12.1 ± 1.5 mg/kg at 20 – 40 cm depth. However chromium has the highest mean concentration value and selenium has the lowest value in this depth.

Chromium ranges between 67.5 to 75.1 mg/kg with an overall mean value 70.3 ± 3.0 mg/kg at 40 – 60 cm depth. Cadmium ranges between 5.26 to 7.51 mg/kg with an overall mean value 6.38 ± 0.7 mg/kg at 40 – 60 cm depth. Mercury ranges between 0.26 to 4.68 mg/kg with an overall mean value 1.93 ± 1.7 mg/kg at 40 – 60 cm depth. Selenium ranges between 0.65 to 3.60 mg/kg with an overall mean value 1.33 ± 1.2 mg/kg at 40 – 60 cm depth. Lead ranges between 3.67 to 8.81 mg/kg with an overall mean value 5.63 ± 2.0 mg/kg at 40 – 60 cm depth. Highest concentration in this depth is chromium whereas the lowest value concentration is selenium.

Chromium ranges between 71.8 to 78.3 mg/kg with an overall mean value 75.1 ± 2.6 at 60 – 80 cm depth. Cadmium has a range of 6.73 to 8.28 mg/kg with an overall mean value 7.51 ± 0.61 at 60 – 80 cm depth. Mercury ranges between 2.79 to 6.58 mg/kg with an overall mean value 4.68 ± 1.5 mg/kg at 60 – 80 cm depth. Selenium ranges between 0.65 to 3.64 mg/kg with an overall mean value 2.04 ± 1.3 mg/kg at 60 – 80 cm depth.

Lead ranges between 6.61 to 11.0 mg/kg with an overall mean value 8.81 ± 1.7 mg/kg at 60 – 80 cm depth. Chromium has the highest mean concentration whereas Selenium has the lowest value in this depth.

Table 3: Mean concentration (mg/kg) of heavy metals in the soil at different depths (cm) around CBN dumpsites.

Soil depth (cm)	Elements	Minimum	Maximum	Mean \pm SD
0 – 20	Cr	70.7	77.2	73.3 ± 2.5
	Cd	6.47	8.02	7.08 ± 0.6
	Hg	2.15	5.95	3.63 ± 1.4
	Se	1.54	3.60	2.09 ± 0.8
	Pb	5.87	10.3	7.59 ± 1.7
20 – 40	Cr	77.2	83.8	80.0 ± 2.3
	Cd	8.02	9.58	8.67 ± 0.5
	Hg	5.95	9.74	7.53 ± 1.3
	Se	0.65	3.67	2.68 ± 1.5
	Pb	10.3	14.7	12.1 ± 1.5
40 – 60	Cr	67.5	75.1	70.3 ± 3.0
	Cd	5.26	7.51	6.38 ± 0.7
	Hg	0.26	4.68	1.94 ± 1.7
	Se	0.65	3.60	1.33 ± 1.2
	Pb	3.67	8.81	5.63 ± 2.0
60 – 80	Cr	71.8	78.3	75.1 ± 2.6
	Cd	6.73	8.28	7.51 ± 0.6
	Hg	2.79	6.58	4.68 ± 1.5
	Se	0.65	3.64	2.04 ± 1.3
	Pb	6.61	11.0	8.81 ± 1.7

S.D = Standard Deviation

Cr: Our research findings shows that chromium has the highest concentration from all collected soil samples at a depth of 20 – 40 cm with a mean concentration value of 80.0 ± 2.3 (mg/kg). This result is higher than the control value of 11.5 mg/kg, however the permissible limit of chromium varies from one country to another country. For example, the permissible limit of chromium concentration in the soil for United Kingdom is 400 mg/kg, for Sweden 60 mg/kg, Netherland 30 mg/kg, Luxembourg 100-200 mg/kg, France 150 mg/kg Germany 60 mg/kg and Austria 100 mg/kg (Table 1) European Commission Director General Environment [18]. Therefore, the chromium concentration in this research work in the soil sample is higher than some of the permissible limit in the following countries like Netherland, Germany and Sweden. The chromium concentration is at variance with [15]. The level was however found to be within the normal range in soils as reported by [19] is as shown in Table 5. The values of Cr obtained in this study were lower than 900 – 2000 mg/kg reported by [20] in a similar work in impact of municipal solid waste disposal in Ado Ekiti metropolis, Ekiti State, Nigeria.

On the other hand Chromium (Cr) concentration obtained in this study area disagrees with 3.63 ± 2.46 mg/kg mean concentration reported by [21] in Environmental Fate of Heavy Metals in Soil of Ido-Osun Waste Dump Site, Osogbo, Osun, Nigeria. The Chromium (Cr) concentration obtained in this study area also disagrees with that of [10] who reported low level Cr concentration (23.40 ± 7.45 mg/kg) in a similar study around CBN waste dumpsite in Makurdi, Benue State Nigeria. Chromium is one of the heavy metals whose concentration in the environment is steady increasing due to industrial growth, especially the development of metal chemical and tanning industries. Sources of chromium might be due to wastes from household chemicals and cleaners, diesel engines utilizing anti-corrosive agents, rubber, candles and matches etc. Although there is no risk of chromium contamination on a global scale, local permeation of the metal to soil, water or the atmosphere might result in excessive amounts of this pollutant in biogeochemical circulation [22]. As observed by [23] nonbiodegradability of chromium is responsible for its persistence in the environment; once mixed in soil, it undergoes transformation into various mobile forms before ending into the environmental sink. Although Cr toxicity in the environment is

relatively rare, it still presents some risks to human health since chromium can be accumulated on skin, lungs, muscles fat, and it accumulates in liver, dorsal spine, hair, nails and placenta where it is traceable to various health conditions [24].

Pb: In this study lead concentration has the second highest mean value mean concentration at different depths as shown in table 3. The mean value of Lead (Pb) in the soil is higher than the control level of 2.60 mg/kg away from the dumpsite. The Maximum Allowable Limit of Lead concentration varies widely with countries. The Pb values obtained are within the allowable limits in several countries, while on the other hand the values are below the allowable limits in several countries. The value of Lead in this study is lower than the mean concentration 48.60 - 36.72 mg/kg of Lead (Pb) reported by [25] in a similar work in Ado – Ekiti and Ijero Ekiti Nigeria. The Lead value obtained in this study is lower than the mean range 12.43 – 2.63 mg/kg of Lead reported by [10] in a similar around CBN waste dumpsite in Makurdi, Benue State Nigeria. On other hand mean level of Lead in this study was higher than what was obtained by [26, 27].

The pollution of soil by Lead is very serious problems that have been given much attention by environment chemist. This is due to the fact that lead is cumulative pollutant [28] and the continuous disposal of Lead contains waste into the environment should be discouraged. Lead is known as poisoning in human as well as chronic neurological disorder especially in fetuses and children [29, 1]. Sorting and recycling of wastes should be intensified to reduce the quantity of these toxic metals in the dumpsites.

Cd: The mean concentration of cadmium varies from depth to depth (Table 3) in dumpsite with a control value of 0.76 mg/kg. The concentration value Cd is higher than the control value. The concentration values of cadmium obtained in this study was found to be above the critical permissible concentration in the various countries (Table 4). The study by [20] reported higher cadmium Level of 219 – 330 mg/kg which is higher than this current research work. On the other hand the result of Cd concentration recorded in this study disagrees with that of [30] who reported low level of Cd concentration (0.60 - 0.14) mg/kg in heavy metals in Soils of auto- mechanic shops and refuse dumpsites in Makurdi Nigeria. The Cd concentration obtained in this study also disagrees with that of [10] who recorded low level of Cd concentration (0.69 – 0.09) mg/kg in a similar work around CBN waste dumpsite in Makurdi, Benue State Nigeria.

This difference in metal concentration could be accounted for due to location and nature of waste disposal. In all the dumpsites cadmium batteries, metal scraps, PVC plastics, motor oil and disposal sludge etc, are being dumped from the industrial and residential areas, which might have contributed to the large concentration of the metal [31, 32]. The primary health risks of long term exposure are lung cancer and kidney damage, [1].

Hg: The mean concentration level of mercury varies from depth to depth at the dumpsites while the control value was recorded as zero concentration. The mercury (Hg) values obtained are within the permissible limits in various countries. The mean value concentration of mercury in this study is higher than the mean concentration (0.29 ± 0.22 mg/kg) reported by [33] in India. On the other hand, Hg concentration obtained in this disagrees with that of [10] with 0.05 – 0.06 mg/kg mean concentration in a similar work around CBN waste dumpsite Makurdi, Benue State Nigeria.

The anthropogenic distribution of mercury in this location could be attributed to the disposal of batteries, fluorescent bulbs, thermometer, electrical gear and waste mercury compounds in the dump. If you examined the biological pathway of mercury contamination in human, mercury is not commonly found in plant products but it can enter human bodies through vegetables and other crops. Significantly high exposure to mercury could cause brain and kidney damage, lungs irritation, eye irritation, skin rashes, vomiting and diarrhoea [29].

Se: In this study selenium has the lowest mean concentration among all the five metals. The mean concentration value of selenium is higher than the control value of 0.22 mg/kg. The mean concentration value selenium obtained in this study is below the maximum permissible limit in soil which suggests that there is little anthropogenic contribution [29]. The value of selenium obtained in this study disagrees 0.038 – 0.037 mg/kg mean concentration reported by [10] around CBN waste dumpsite Makurdi, Benue State Nigeria.

Selenium is not distributed evenly across the planet, rather concentrations differ markedly depending on local conditions and an understanding of these variations is essential to aid the amelioration of health problems associated with selenium deficiency and toxicity [34].

Table 4: Permissible Limits of Heavy Metals in Soil (mg/kg) of Selected Countries

Countries	Cadmium	Chromium	Lead
Austria	1 – 2	100	100
Germany	1	60	70
France	2	150	100
Luxembourg	1 – 3	100 – 200	50 – 300
Netherland	0.5	30	40
Nigeria	3	100	100
Sweden	0.4	60	40
United kingdom	3	400	300

Source: [18]

Table 5: Concentration ranges of metals (mg/kg) in soils

Metal	Normal range in soils
Cr	5 – 1500
Hg	0.01 – 0.5
Cd	0.01 – 2
Pb	2 – 300

Source: [19]

IV CONCLUSIONS

The results show that chromium (Cr) had the highest concentration in both soil and leachate, with selenium lowest concentration in soil sample. Also the results revealed that some of the heavy metal concentrations in leachate were beyond the detection limit. This may be attributed to their high affinity to be sorbed to the soil which is accounted to their non-detection to the leachate. The metals concentrations in this study area have been found to be higher than their control collected 600 m upstream from the CBN dumpsite. The heavy metals concentration of soil in these dumpsite at different depths were all within the WHO acceptable limit in the dumpsite except Cd which was above the permissible limit and Se which was below the limit. The concentrations of heavy metals in leachate were all below permissible limit of FEPA and WHO. This suggests a less significant risk to this population in the environment. Consequently, it is imperative to continually assess and monitor the levels of heavy metals in the environment due to anthropogenic activities for evaluation of human exposure and for sustainable environment.

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