

ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN LEACHATES AND SOILS OF CENTRAL BANK OF NIGERIA DUMPSITE MAKURDI

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Abstract- Leachates from dumpsite basically contain a wide range of heavy metals which has negative public health and environmental impacts once the leachates are allowed to infiltrate into groundwater. However, this is one of the oldest, growing problems threatening the surrounding globally. Therefore it is imperative to quantify the information on the environmental impact of heavy metals and suggesting various techniques that could be used to clean-up these metals from the environment to the barest minimum to ameliorate the plight of the people. 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. The concentrations of some heavy metals such as Chromium (Cr), Lead (Pb), Cadmium (Cd), Mercury (Hg) and Selenium (Se) in leachate from Central Bank of Nigeria Dumpsite platform and surrounding soil along University of Agriculture road, Makurdi, were determined using Atomic absorption spectrophotometry (Flame AAS) for Cr, Pb and Cd while cold vapour and hydride generation were used for Hg and Se respectively. 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 permissible limits. However, the concentration of Cr and Cd were found to be higher than the permissible limits due to the increasing anthropogenic activities in the area. Awareness of the pollution statuses of soil and leachate around the dumpsite need to be urgently created especially among people living in the surrounding environment. Proper and effective waste management plan should be developed and implemented.

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

1. INTRODUCTION

Leachate is a wastewater that can have negative public health and environmental impacts precisely, if it is allowed to infiltrate into groundwater. Leachate from dumpsite is one of the oldest, growing problems threatening the surroundings globally [1]. Dumpsites practice involves placing waste in one area with the main target of controlling pollution [1, 2]. In developing countries this concept is usually an unlined shallow hollow pit not deeper than 50 cm. Tse and Adamu [3] defined dumpsite as a pit that receive solid wastes in a more or less uncontrolled manner, making uneconomical use of the available space which gives room to waste pickers, Distasteful and hazardous smoke are produced during cleanup process using slow-burning fire. Hence, leachate of diverse composition are been generated, based on the nature of site construction and running practice adopted. Apart from that, the age of the dumpsite, climatic and hydrological conditions and surface water ingress into the dumpsite Tse and Adamu [3] plays a vital role in leachate infiltration, making it possible to move vertically and horizontally into the environment by

direct discharge into streams and natural water bodies around the dumpsite. In Makurdi, leachate from refuse or open waste dumpsites are considered as good source of heavy metal pollution to both soil and aquatic surroundings Odukoya *et al.* [4] because open waste disposal is a common practice by the inhabitants. 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 Lohe *et al.* [5] which are also responsible for environmental pollution.

Over the years, various detection and removal methods have been projected and implemented by different researchers with the basic motive of cutting down the rate of environmental pollution to bring about a sustainable and eco-friendly development. A very good examples are fluorescent-based sensors and electrochemical sensors for detection purposes, immobilized enzyme-based catalytic systems and photocatalytic systems for degradation purposes, along with other physiochemical-based process, etc. are the most widely used, though each have certain advantages and disadvantages [6,7,8]. 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 [9]. 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 [10]. 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 Esakku *et al.*, Yurtsever and Sengil [11, 12] 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

2. MATERIALS AND METHODS

2.1 Reagents

HCl (May and Baker Bagaenman England, M.S 0231), HNO₃ (BDH-Chemical Ltd Poole England, 29335), H₂SO₄ (Fisons Plc. Scientific Equipment Division Loughborough LE11 Org.England, No.1830), NH₄OH (BDH Chemicals Ltd Poole England, 6902600), K₂CrO₇ (BDH Chemicals Ltd Poole England, No. 29605).

2.2 Equipments: Hot Plate, Glass electrode pH meter, Digital Weighing meter and AAS (Biotech Engineering Management Co. Ltd, FAAS Phonenix 986).

2.3 Reagents for Cold Vapour Method and Hydride Generation: Potassium borohydride (KBH₄) 2g Potassium borahydride, 0.2g sodium hydroxide and 200ml distilled water were used as carrier liquor (add 5ml HCl into 500ml volumetric flask and dil to 500ml with water) Blank (add 20ml sulfuric acid into 500 mL volumetric flask and diluted to 500 mL plus sulfuric acid potassium permanganate and dilute to 500 mL to obtain a light purple solution).

2.4 System Conditions: Carrier gas flow rate: 100 mL/min , KBH₄ concentration: 0.5-1.5% (medium 0.1%NaOH), Linearity range:10-80ng/mL, Sensitivity: 0.5ng/ml/1%A.

2.5 Study Area

Makurdi is the capital city of Benue State in North Central Nigeria and lies between Latitude $7^{\circ} 44' N$ and Longitude $8^{\circ} 54' N$. The physical geography of the area ranges between 73 - 167 m above sea level. In the year 2007 Makurdi has an estimated population of 500,791 with a total land area of about 200 km^2 [13]. The study site is located along University of Agriculture Road Makurdi which lies between Latitude $N 07^{\circ} 45' 49.1''$ and Longitude E $008^{\circ} 34' 46.2''$. The study location is surrounded by two communities: Ate- Akee community in the West and Menne community in the East and a water dam 500 meter adjacent to it. The population of these communities is about one hundred to one hundred and fifty persons and most of them are peasant farmers. The CBN platform dumpsite was well constructed with cements and also has a dimension of 60 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.

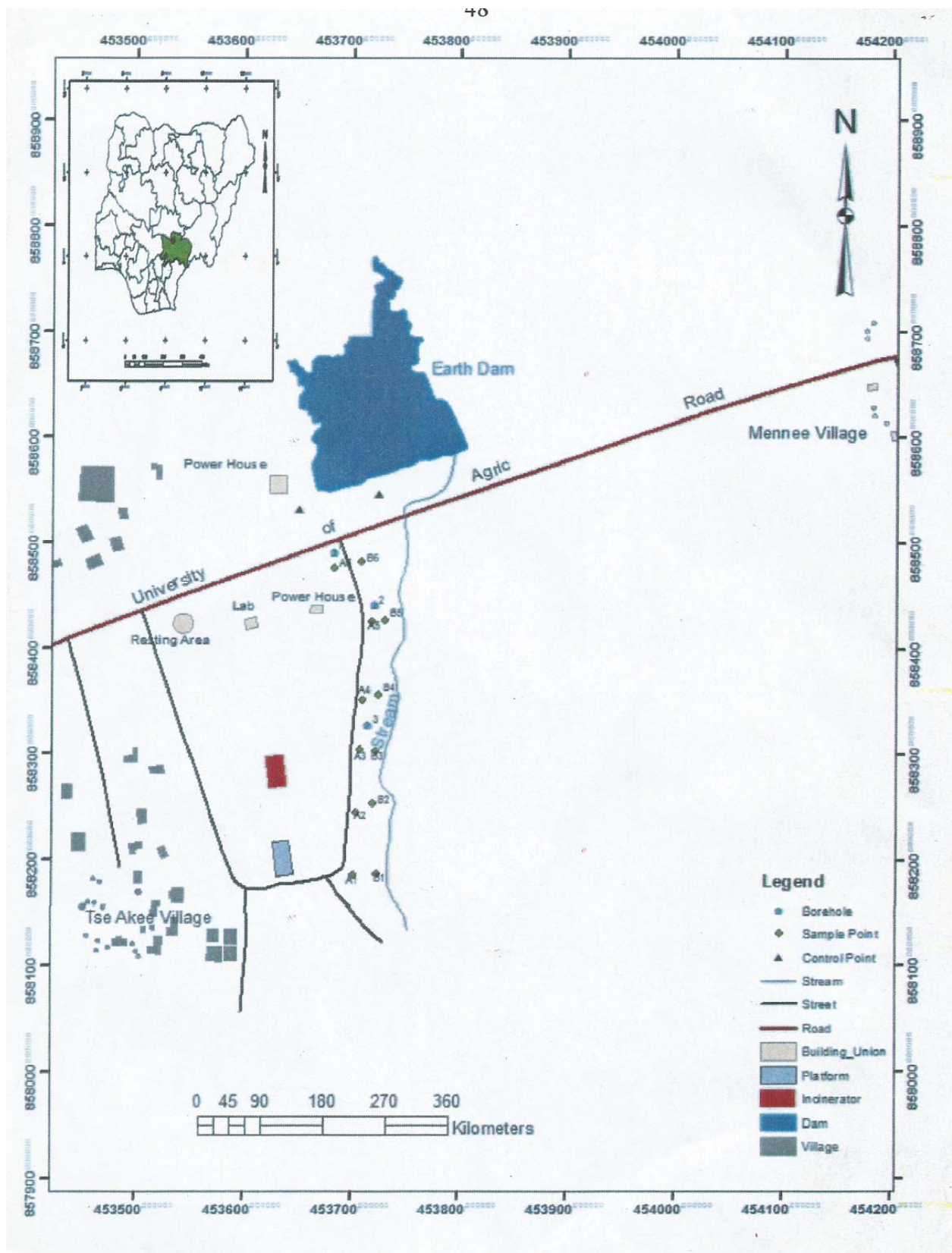


Figure 1: Map of Sampling Site showing the Dumpsite

Source: [14]

2.6 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 for three months. 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 plastic 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 leachates were 600 m upstream from the dumpsite as control sample. All the plastic containers that were used for collection of the leachate samples were washed and 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 in order to keep the pH of the sample low subsequently preventing precipitation of the metal [14, 15]. All samples collected were stored at 4°C during transportation to the laboratory.

2.7 Sample Preparation and Analysis

The soil samples were air dried and were sieved with a 2 mm mesh size sieve. The glass electrode were used to determined 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 [16].

2.8 Digestion procedure for leachates samples

A volume of 5.0 mL of leachate sample were 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 concentrated nitric acid was 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 [17].

2.9 Digestion of soil samples

Exactly 1.0 g of soil samples which had been dried and sieved (2 mm) were 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 [18] were 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 were heated for 1 hour using a hot plate. The content was added continuously to enhance complete digestion and were 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 were repeated for all the soil samples for this study.

2.10 Mercury and Selenium Analysis by Cold Vapour Method and Hydride Generation

Using an AAS system with KBH_4 as carrier liquor and blank sample were connected into their respective sucking tubes. At the start of the hydride generator (connected to the main AAS), the solutions were automatically suck into the system where the hydride were produced and transmitted into the electric quartz absorption tube for detection. The concentrations were recorded in mg/L. The whistling of the hydride generator signals the completion of the hydride production and hence is ready for reading. After proper calibration with the standard ranging from 1-10 mg/L, the blank were replaced with sample to obtain the concentration of mercury and selenium [19].

2.11 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 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 deionised water whereas, blank B were 100 mL of

deionised water. The contaminate 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 HNO₃ + 9 mL HCl) which were heated for 1 hour and the content were 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 were 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 contaminates.

In addition to ensure accuracy the AAS equipment were calibrated using a known concentration of metals. These metals were run in the AAS equipment to determine the absorbance and concentration. Calibration curves were obtained by plotting concentration against absorbance for lead, cadmium, mercury, chromium and selenium and the following R² value of 0.9958, 0.994, 0.9937, 0.9989 and 0.9989 were obtained respectively

2.12 Data Analysis

The data were 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.

3 RESULT AND DISCUSSION

3.1 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 [20]
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 [21]. The concentration of Cd is below the permissible limit of 1.0 mg/L WHO [20], due to the reduction in the volume of the leachate for ultimate treatment. This result is in agreement with the result presented by [22].

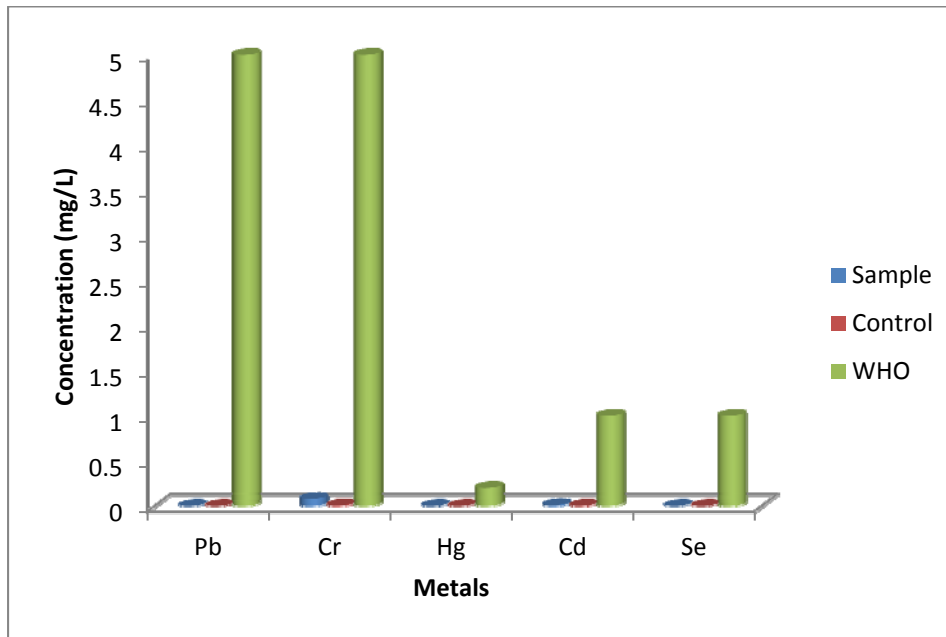


Figure 2: Variation of heavy metal concentration in different months

3.2 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 [23]. 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 [21]. The level was however found to be within the normal range in soils as reported by Radojevic and Bashkin [24] is as shown in Table 5. The values of Cr obtained in this study were lower than 900 – 2000 mg/kg reported by Adefemi and Awokunmi [25] 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 Olayiwola and Onwordi [26] 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 [14] 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. The values of chromium concentration obtained in this study were lower than $92.1 - 8.4$ mg/kg reported by Sapana *et al* [27] in the Assessment Of geo-accumulation index of heavy metal and source of contamination by multivariate factor analysis. This is as a result of less human activities capable of generating chromium in the environment [27]. Chromium +3 is less damaging to the health due to their absorption by the body (<1%), but Cr +6 is acutely poisonous and on contact with the skin, it triggers dermatitis, allergies and irritations, thus considered as carcinogenic to humans [28]. 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 [29]. As observed by Ghosh and Singh [30] 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 [31].

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 Ogunmodede *et al.* [32] 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 Musa *et al.* [14] 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 [33, 34].

The pollution of soil by Lead is very serious problems that have been given much attention by environment chemist since this metal is very toxic for humans and animals. This is due to the fact that lead is cumulative pollutant Dara [35] 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 foetuses and children [36, 37]. Lead toxicity also leads to anaemia both by mutilation of haemo-biosynthesis and increase of rate red blood cell destruction. In addition, Lead reduces sperm count, damages kidney, liver, blood vessels, nervous system and other tissues in human [27]. Lead production and operation facilities without waste-gas treatment system, battery production and scrap battery recovery facilities, thermal power plants, and iron–steel industries are the other sources

of Lead in the environment [27, 28]. 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 [25] 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 [38] 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 Musa *et al.* [14] 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. On the other hand, the mean concentration of cadmium in this study is lower than 28.32 mg/kg in Bioaccumulation level of Cadmium concentration in Wild population of Black-Headed Oriole *Oriolus Brachyrhynchus* (Swainson, 1837) from some selected locality in Benue State, Nigeria reported by Egwumah *et al.* [39] and this is as a result of the anthropogenic activities in the environment.

This difference in metal concentration could be accounted for due to location and nature of waste disposal. The half-life of cadmium in human body is between one and four decades [40]. During decomposition, the Cd component is leached into the surrounding soil and over time gets accumulated in the soil. Cadmium is considered to be a toxin in phosphate fertilizers Bhavani and Sujath, Lane and Cauty [41, 42] which is added to soil and food crops through normal farming practice [43]. 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 [44, 45]. The primary health risks of long term exposure are lung cancer and kidney damage, [37].

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 Ahmed *et al.* [46] in India. This current research work recorded a lower mercury concentration in soil compared to Hovart *et al.* [47], who reported mercury concentration of 289 mg/kg in contaminated soil in China. On the other hand, Hg concentration obtained in this disagrees with that of Musa *et al.* [14] 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.

Soil conditions in general are conducive for the formation of inorganic compounds such as mercury chloride (HgCl), mercury hydroxide (HgOH) and inorganic mercury (II) compounds, which are capable of forming complexes with organic anions [39]. This complex behaviour limits mobility of mercury in soil so that much of the mercury in soil so that much of the mercury in soil usually sticks to bulk organic matter and they are easily subjected to surface runoff during excessive rainfall because they are only attached to suspended soil or humus this finding is in agreement with the research work of [39]. 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 [27].

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 [27]. The value of selenium obtained in this study disagrees 0.038 – 0.037 mg/kg mean concentration

reported by Musa *et al.* [14] around CBN waste dumpsite Makurdi, Benue State Nigeria. In addition, higher selenium content in soil samples was also reported with a concentration range of 20–60 mg/kg in Enshi, China [48].

At the global scale, selenium is constantly recycled in the environment via the atmospheric, marine, and terrestrial systems. Estimates of selenium flux indicate that anthropogenic activity is a major source of selenium release in the cycle, whereas the marine system constitutes the main natural pathway [39]. 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 [49].

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: [23]

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: [24]

4 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.

REFERENCES

1. Bilal, M.; Rasheed, T.; Sosa-Hernández, J.E.; Raza, A.; Nabeel, F.; Iqbal, H.M.N. (2018). Biosorption: An Interplay between Marine Algae and Potentially Toxic Elements—A Review. *Marine Drugs*, 16, 65.
2. Herrera-Estrella, L.R.; Guevara-Garcia, A.A. (2009). Heavy metal adaptation. In *Encyclopedia of Life Sciences (ELS)*; John Wiley & Sons, Ltd.: Chichester, UK, pp. 1–9.
3. Tse, A. C. And Adamu C. I. (2012). Assessment Of Anthropogenic Influence On Quality Of Groundwater In Hand-Dug Wells In Parts Of Makurdi Metropolis, North Central Nigeria, *Ife Journal of Science*, **14** (1):123-135.
4. Odukoya, O.O., Bamgbose, O. and Arowolo, T.A. (2007). Heavy metals pollution from leachates in aquatic and terrestrial environment. *Journal of pure and applied science*. 467 – 472.
5. Lohe, R. N., Tyagi, B., Singh, V., Kumar Tyagi, P., Khanna, D. R., and Bhutiani, R. (2015). A comparative study for pollution tolerance index of some terrestrial plant species. *Global Journal of Environmental Science Management*, 1:315–324.
6. Ahmed, I.; Iqbal, H.M.N.; Dhama, K. (2017) .Enzyme-based biodegradation of hazardous pollutants—An overview. *Journal of Experimental Biology and Agricultural Science*, 5: 402–411.
7. Barrios-Estrada, C.; de Jesús Rostro-Alanis, M.; Muñoz-Gutiérrez, B.D.; Iqbal, H.M.N.; Kannan, S.; Parra-Saldívar, R. (2018). Emergent contaminants: Endocrine disruptors and their laccase-assisted degradation—A review. *Sci. Total Environ.*, 612: 1516–1531.
8. Bilal, M.; Rasheed, T.; Iqbal, H.M.N.; Hu, H.; Wang, W.; Zhang, X. (2018). Toxicological Assessment and UV/TiO₂-Based Induced Degradation Profile of Reactive Black 5 Dye. *Environ. Manag.* 61: 171–180.
9. Al-Raisi, S. A. H.; Sulaiman, H.; Suliman, F. E.; and Osman Abdallah, O. (2014) Assessment of Heavy Metals in leachate of an Unlined Landfill in the Sultanate of Oman *International Journal of Environmental Science and Development*, **5**(1): 1- 4.
10. Egwumah FA, Egwumah PO, Edet DI (2017) Paramount Roles of Wild Birds as Bioindicators of Contamination. *Int J Avian & Wildlife Biol* 2(6): 00041. DOI: 10.15406/ijawb.2017.02.00041
11. Esakku, S., Palanivela, K. and Kurian, J. (2003) Assessment of Heavy Metals in Municipal Solid Waste Dumpsite, Workshop on Sustainable Landfill Management, Chennai, India, 3–5 December, p 139-145.
12. Yurtsever, M. and Sengil, I.A. (2009) Biosorption of Pb (II) ions by modified quebracho tannin resin, *Journal of Hazard Material*, **163**(1): 58 – 64.
13. Pam, A. A., Sha’Ato, R. and Offem, J. O. (2013). Evaluation of heavy metals in soils around auto mechanic workshop clusters in Gboko and Makurdi, Central Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*, **5**(11): 298 – 306.
14. Musa, W. O., Eneji, I. S. and Wuana, R. (2016). Determination of heavy metal concentration in soil and groundwater around Central Bank of Nigeria waste dumpsite in Makurdi, Benue State Nigeria. *Canadian International Journal of Science and Technology*. www.tesse.org
15. Ogundiran, O.O and Afolabi, T.A. (2008). Assessment of the physicochemical parameters and heavy metals toxicity of leachates from municipal solid waste open dumpsite. *International Journal Environmental Science Technology*, **5** (2): 243-250.

16. Warmate, A.G., Ideriah, T.J., Tamunobereton, I.T., Udonam Inyang, U.E., and Ibaraye T. (2011) "Concentrations of heavy metals in soil and water receiving used engine oil in Port Harcourt, Nigeria" *Journal of Ecology and The Natural Environment* **3**(2), 54-57.
17. Aziz, S. Q., Aziz, H. A., Yusuf M. S. and Bashir, M.J.K. (2010). Leachate characterization in semi-aerobic and anaerobic sanitary landfills: A comparative study, *Journal of Environmental Management*, 91: 2608 – 2614
18. Adedosu, H.O. Adewuyi, G.O. and Adie G.U. (2013). Assessment of Heavy Metals in Soil, Leachate and Underground Water Samples Collected from the Vicinity of Olusosun Landfill in Ojota, Lagos, Nigeria. *Transnational Journal of Science and Technology*, **3**(6):1-14.
19. Aaron Hineman, (2011). Determination of As, Se and Hg in Waters by Hydride Generation/Cold Vapor Atomic Absorption Spectroscopy. https://www.perkinelmer.com/.../APP_PinAAcle-ToxicMetalsinWaterbyHG-CVAA.pdf
20. WHO (World Health Organization). (1991). Revision of the WHO Guidelines for Water Quality Report of the First Review Group Meeting on Inorganics, (Netherlands) World Health Organization Geneva WHO/PEP/91.18.
21. Kaana, A. (2013). Evaluation of heavy metals in waste dumpsite. *International Journal of Modern Chemistry*, **1**(1): 28-35.
22. Adewuyi, G.O. and Opasina, M.A. (2010). Physicochemical and heavy metals assessments of leachates from a perin abandoned dumpsite in Ibadan city, Nigeria. *E-Journal of Chemistry* **7**(4):1278-1283.
23. European Commission Director General Environment, (ECDGE) (2010). Heavy metals and organic compound from waste used as organic fertilizer, PP. 73 – 74
24. Radojevic, M. and Bashkin, V. N. (2006). *Practical environmental analysis*. Cambridge City.
25. Adefemi, O.S., and Awokunmi, E.E (2009). The impact of municipal solid waste disposal in Ado Ekiti metropolis, Ekiti State, Nigeria. *African Journal Environmental Science and Technology*, **3**(8): 186-189.
26. Olayiwola, O. A and Onwordi C. T. (2015). "Environmental Fate of Heavy Metals in Soil of Ido-Osun Waste Dump Site, Osogbo, Osun, Nigeria." *American Journal of Environmental Protection*, **3**(10):1-4.
27. Sapana, G., Vinod, J., Natalija, M., Veronika, K. and J S Solanki, J.S. (2014). Assessment of Geo-Accumulation Index of Heavy Metal and Source of Contamination by Multivariate Factor Analysis. *International Journal of Hazardous Material* **2**(2): 18-22.
28. Anhwange, B.A. and Kaana, A. (2012). Evaluation of heavy metals in waste dumpsite. *International Journal of Modern Chemistry*, **1**(1): 28-35
29. Wyszowska J. (2002). Soil Contamination by Chromium and its Enzymatic Activity and Yielding. *Polish Journal Environmental Studies*, **11**(1): 79-84.
30. Ghosh, M., and Singh, S.P. (2005). Comparative Uptake and Phytoextraction Study of Soil Induced Chromium by Accumulator and High Biomass weed Species. *Applied Ecological Environmental Research*, **3**(2):67 - 79. <http://www.ecology.kee.hu>
31. Reyes-Gutiérrez, L.R, Romero-Guzmán, E.T, Cabral-Prieto, A. and Rodríguez- Castillo R. (2007). Characterization of Chromium in Contaminated Soil Studied by SEM, EDS, XRD and Mössbauer Spectroscopy. *Journal of Mineral Material Characterization Engineering*, **7**(1): 59-70.
32. Ogunmodede O.T, Ajayi O.O, Amoo I.A , and Adewole, E. (2013). Characterization of Dumpsite Soil: Case Study of Ado – Ekiti and Ijoro Ekiti Nigeria *IOSR Journal Of Environmental Science, Toxicology And Food Technology (IOSR-JESTFT) e-ISSN: 2319-2402, p- ISSN: 2319-2399*. **3**(6) :43-50 www.iosrjournals.Org.
33. Agyarko, K., Darteh, E. and Berlinger, B. (2010) "Metal levels in some refuse dump soils and plants in Ghana," *Plant Soil Environment*, **56** (5): 244-251.

34. Okeyode, I. C. and Rufai, A. A. (2011). "Determination of elemental composition of soil samples from some selected dumpsites in Abeokuta, Ogun State, Nigeria using atomic absorption Spectrophotometer," *International Journal of Basic and Applied Sciences*, 11: 55-70.
35. Dara, S.S (1993): A text book of environmental chemistry and pollution control. S. Chand and company Ltd. 1st edition. Ram Nagar, New Delhi 110055.
36. Lenntech, B. V. (2012). Water treatment solutions. Rotterdamseweg 402 M 2629 HH Delft, Netherland. <http://www.lenntech.com/periodic/water/iron/ironandwater.htm#ixzz2lhhMVLrO>. Retrieved 25/11/2013.
37. Wuana, R., and Okieimen, F. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. ISRN Ecology. Vol 2011.
38. Luter, L., Akaahan, T. J and Simon A. J. (2011). Heavy Metals in Soils of auto- mechanic shops and refuse dumpsites in Makurdi Nigeria *Applied Science Environmental Management*, **15** (1) 207 – 210.
39. Egwumah, F.A., Egwumah, P. O. and Tyowua, B.T. (2017) Evaluation of Black-Headed Oriole *Oriolus brachyrhynchus* (Swainson, 1837) as Bioindicator of Arsenic Contamination Using Atomic Absorption Spectrometry (AAS). *Journal of Agriculture and Ecology Research International* 12(3): 1-9.
40. Rezende, H. C., Nascentes, C. C. and Coelho, N.M. (2011) Cloud point extraction for determination of cadmium in soft drinks by thermospray flame furnace atomic absorption spectrometry, *Microchemical Journal*. 2011; **97**(2):118-121,
41. Bhavani P, Sujath B (2014) Impact of Toxic Metals Leading to Environmental Pollution National Seminar on Impact of Toxic Metals, Minerals and Solvents leading to Environmental Pollution. *Journal of Chemical and Pharmaceutical Sciences* (3): 70-72.
42. Lane EA, Canty MJ (2017) Overview Appendix 7: Cadmium exposure in cattle: a review
43. Martelli A, Rousselet E, Dycke C, Bouron A, Moulis JM (2006) Cd toxicity in animal cells by interference with essential metals. *Biochimie* 88(11): 1807-1814
44. Jarup, L. (2003). Toxicity of heavy metals and sources in the environment. *British Medical Bulletin* 68: 167 – 182.
45. Ebong, G.A., Akpan, M.M. and Mkpene, V.N (2008). Heavy metal content of municipal and rural dumpsite soils and rate of accumulation by *Carica papaya* and *Talinum triangulare* in Uyo Nigeria. *E-Journal of Chemistry*, 5(2): 281-290.
46. Ahmed, Q., Khan, D. and Ali, Q.M. (2014). Heavy metals (Fe, Mn, Pb, Cd, and Cr) concentrations in muscles, liver, kidneys and gills of torpedo scad [*Megalaspis cordyla* (Linnaeus 1758)] from Karachi waters. *International Journal of Biological Biotechnology*, **11**(4): 517-524.
47. Hovart, M., Nolde, N., Fajon, V., Jereb, V. and Logar, M. (2003). Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. *Science Total Environment* **304**(1- 3): 231- 256
48. Courtman, C., Ryssen, J.B.J. and Oelofse, A. (2012). Selenium concentration of maize grain in South Africa and possible factors influencing the concentration. *South African Journal of Animal Science*, 42 (5): 454- 458.
49. Reilly, C. (2006). Selenium in food and health, 2nd edition. Springer Science + Business Media, LLC. New York, USA.

