Determination of Heavy Metals in Dump Site at Katsina State

Muhammad Usman[1]& Abubakar Abdullahi Lema[2] & Mahmoud Dogara Abdulrahman[3]

[1]Biotechnology Department, Nigerian Defence Academy, Kaduna, Nigeria
[2]Department of Plant Science and Biotechnology, Faculty of Bioresources and Food Industry, Universiti Sultan Zainal Abidin (UniSZA), Besut Campus, 22200, Terengganu, Malaysia
[3]Department of Biology, Faculty of Education, Tishk International University, Erbil, Iraq.
Correspondence: Muhammad Usman, Nigerian Defence Academy, Kaduna, Nigeria.
Email: othmanmshitu@gmail.com

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Abstract: Heavy Metals are any metallic element that has a relatively high density and is toxic or poisonous at low concentration. Heavy Metals are general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3. Most of these metal ions can be released from industries, agriculture and individual household and are in simple cationic forms. This study aimed at determining some heavy metals contents in dump soil along Federal College Education (F.C.E.) Katsina. Three samples each were collected differently at the vicinity of the tannery and the surrounding tanneries, 10m away a nearby farms and nearby growing plants. Control samples was also collected far away from these areas for comparison. A distance between 5 to 10 m was maintained between each sampling point to study the metal distribution of the study area. Atomic Absorption Spectrophotometer (AAS) with air acetylene flame was used for the metal analysis. The results of the three samples studied obviously indicates that all the soil samples have Manganese concentration in the in the highest degree (A 3.83 mg/kg, B 3.652 mg/kg, C 6.602 mg/kg) while Co: 0.048 mg/kg, Cd: 0.028 mg/kg, Cd: 0.026 mg/kg) respectively indicates lowest concentration in the three samples. All of the soil samples contain high manganese concentrations and other heavy metals are present in negligible amounts. This means that manganese-containing waste is circulating in our environments at random. Contamination or soil pollution caused by high manganese concentrations in our environment is extremely dangerous since it puts domestic animals' and humans' health at risk.

Keywords: Heavy Metals, Dump Soil, Atomic Absorption Spectrophotometer (AAS)

1. Introduction

The term Heavy Metals refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentration (Duffus, 2002). Heavy Metals are general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 (Duruibe et al., 2007). Heavy Metals are also referred to those elements with a specific density at least five times the specific gravity of water, Heavy Metals include Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Iron (Fe) and Platinum group elements, Copper and Zinc are essential trace elements for living organisms at low concentration (<10mg/L). However, most of these metal ion (Cd, Cu, Zn, Hg, As, Ag, Cr and Fe) can be released from industries and are in simple cationic forms. The characteristics of heavy metals are described by (Duruibe et al., 2007).

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Heavy Metals cannot be degraded including bio treatment and are very toxic even at low concentration (1.0-10.0mg/L) (Abdulrahman et al., 2019). Heavy Metals are dangerous because they tend to bioaccumulations. Bioaccumulation processes implies an increase in the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment (Van et al., 2003). Compound accumulates in living things any time they are taken up and stored faster than they are broken down (Metabolized) excreted (Lema et al., 2022). World Health Organization (WHO) has established levels of metals in foods above which, they should not be consumed (Lema et al., 2022). For this reason, the levels of trace metals in our food should be of much importance and concern to us (Abdulrahman et al., 2019). Soil is a precious natural resource upon which economic activity like agriculture and existence of life depend (Abdulrahman, Hama, & Hamad, 2022). The properties and quality of soil can be adversely affected by the over-concentration of waste released from agriculture, industry, municipality and individual household (Abdulrahman, Hama, & Hamad, 2022). These wastes deteriorate the quality of soil and influence sustainable development. Today at global scale the magnitude of soil deterioration was significantly increased due to rapid rate of industrialization, exponential raise in population and urbanization which contributed for changes in the composition and quantity of waste generated. According to UNIDO (2011), the increment of waste load was leading to environmental pollution and degradation in many cities of the developing countries (Abdulrahman, Hama, & Hamad, 2022). It was estimated that in 2006 the total amount of municipal solid waste (MSW) generated globally reached 2.02 billion tones, representing a 7% annual increase since 2003 (Khandaker et al., 2020). The UNEP (2009), further estimated that between 2007 and 2011, global generation of municipal waste raised by 37.3%, equivalent to roughly 8% increase per year. In urban centres throughout African regions, less than half of the solid waste produced was collected, and 95 percent of that amount indiscriminately thrown away at various dumping sites on the periphery of urban centres (Lema et al., 2022). This study aimed at determining some heavy metals contents in dump soil along Federal College Education (F.C.E.) Katsina. It is expected that results obtained from the study will widen our knowledge on the environmental risks associated with solid waste dumps in terms of heavy metal toxicity and the suitability of such site for plant cultivation.

2. Materials and Methods

2.1 Study Area

Katsina is one of Nigeria's states, and it can be found in the country's northwest. After being split off from Kaduna State in 1987, Katsina became its own state. Katsina State currently has common borders with the states of Kaduna, Zamfara, Kano, and Jigawa. The Nigerian city of Daura is known as the "Home of Hospitality" and as one of the country's "ancient seats of Islamic culture and learning," alongside the state capital. The study area is located dump soil along Federal College of Education (FCE) katsina state, Nigeria. On the latitude 120 56’4” N and longitude 70 36’14” E.

2.2 Soil Location

Soil samples were collected from the location indicated at the depth of not more than 10 cm using plastic scoops. Three samples each were collected at the vicinity of the tannery, surrounding tanneries, 10m away, a nearby farm and nearby growing plant (Abdulrahman, Hama, & Hamad, 2022). Control samples far away from this area were also collected for comparison. A distance between 5 to 10 m was maintained between each sampling point to study the metal distribution of the study area. Samples were placed in polyethylene bags, sealed and transported to laboratory.

2.3 Sample Collection

All the soil samples collected were air dried and grounded, using pestle and mortar, to ensure homogeneity. The samples were sieved through 2mm mesh sieve and then placed in a clean plastic bag and sealed, a representative of the sample was further crushed for the digestion process.

2.4 Preparation for Analysis

All glassware and plastic containers were washed with detergent, 20% nitric acid and then rinsed with tap water and finally with distilled water. The concentrations of the following heavy metals are considered (Cd, Cr, Cu, Ni, Fe, Mn, Pb and Zn) in the digested samples (Abdulrahman et al., 2020).

2.5 Sample Digestion

About 0.2 g of the prepared soil sample were accurately weighed into platinum crucible. The soil sample was then heated on a hot plate in a mixture of 6.0 mL conc. HCl and 1.0 mL HF. After cooling the mixture, follows the addition of 5.0 mL HF and 1.0 mL conc. HCl. Heated on a sand bath at a temperature of 200 - 230 ºC until the acid evaporates to dryness. After cooling, 6.0 mL of 1.0 M HCl were poured and heated for 10 min (Abdulrahman et al. 2020). The resulting solution were filtered and made up to 25.0 mL mark in a volumetric flask. Triplicate digestions of each sample together with a blank were carried out. Blank samples were prepared from only reagents without sample to check for background contamination by the reagents used

2.6 Wet Ashing

Ten grams of each sample was air-dried in circulating air to a constant weight and passed through a 2mm sieve. Twenty grams of the sieved soil samples were weighed, ground to powder and digested in 5ml mixture of concentrated Nitric acid (HNO3) and perchloric acid (HClO4) at 105◦C for 1hr. The digest was allowed to cool and then filtered through Whatman Filter Paper No. 42 and diluted up to 25ml with double-distilled water. The digest was allowed to cool and filtered using a 0.45mm Millipore filter kit.

2.7 Plant Sampling

The plant sample were removed from the farm and washed under a stream of water and then washed with distilled water. The collected plants were air-dried, placed in a dehydrator for 2-3 days and then dried by oven dried for four hours at 100ºC. The dried samples were powdered and stored in polyethylene bags. 1gm of the powdered plant were weighed in separate digestion flasks and digested by adding HNO3 and H2O2 in the ratio of 6:2 respectively. The digestion on hot plate at 120ºC for 2 hour or continued till a clean solution as obtained after filtering with Whatman No. 42 filter paper (Abdulrahman et al. 2020).

2.8 Calibration Curve

The calibration curves were prepared from standards by dissolving appropriate amounts of the metal salts in purified nitric acid, diluting with deionized water and storing as stock solutions in a quartz flask.

2.9 Sample Analysis

Atomic Absorption Spectrophotometer (AAS) with air acetylene flame were used for the metal analysis. The recovery and reproducibility of the method were checked by spiking and homogenizing already analyzed samples with varying amounts of standard solutions.

2.10 Statistical Analysis

Descriptive statistics and analysis of variance (ANOVA) were calculated using Microsoft - Excel 2013. ANOVA was used for the mean comparison of metal concentrations of the sampling locations. Pearson Product Moment Correlation was used in determining the associations among the metals considered. All test was carried out at $p< 0.05$ and 0.01 significance level

3. Results

Results of Heavy metals concentrations obtained from three dumpsites are designated as (A, B, and C). From the (Table 1-3), Manganese (Mn) shows the highest concentration among the heavy metals studied with (3.652 mg/kg) dry weight, while cobalt (Co) shows the lowest concentration with (0.048 mg/kg) dry weight. The concentration of Fe, Co, and Zn did not exceed the Dutch intervention values of 0.809, 0.049, and 0.844 mg/kg dry weight respectively, only Mn has its value exceeding the Dutch intervention value of 2.94 mg/kg dry weight. On the other hand, the concentration of chromium and cadmium were below the Dutch intervention limits. However, Table 2 shows the mean concentration of the B soil sample. The mean concentration of heavy metals in soil sample B ranged from 0.028 mg/kg to 3.83 mg/kg dry weight.

Table 1: Mean concentration of heavy metals in soil sample A

Heavy Metals	Concentration
Zn	0.310
Fe	0.187
Cr	0.599
Cu	0.273
Mn	3.652
Ni	0.221
Co	0.048
Cd	0.130

Table 2: Mean concentration of heavy metals in soil sample B soil

Heavy Metals	Concentration
Zn	0.383
Fe	1.164
Cr	0.175
Cu	0.193
Mn	3.830
Ni	0.342
Co	0.041
Cd	0.028

Table 3: Mean concentration of heavy metals in soil sample C

Heavy Metals	Concentration
Zn	0.810
Fe	0.513
Cr	0.167
Cu	0.293
Mn	6.602
Ni	0.216
Co	0.301
Cd	0.026

Manganese (Mn) also shows the highest concentration among the heavy metals studied (3.83 mg/kg) dry weight while cadmium (Cd) shows the lowest concentration (0.028 mg/kg) dry weight. Iron and cobalt concentrations, have exceeded the Dutch intervention values of 0.809mg/kg, and 0.049mg/ kg dry weight respectively. Mn also has its value exceeding the Dutch intervention value of 2.94 mg/kg dry weight. On the other hand, the concentration of chromium and cadmium were below the Dutch intervention limits. On the other hand, Table 3 shows the mean concentration of the C soil sample. The mean concentration of heavy metals in soil sample C ranged from 0.026 mg/kg to 6.602 mg/kg dry weight. Manganese (Mn) still shows the highest concentration among the heavy metals studied (6.602 mg/kg) dry weight while cadmium (Cd) shows the lowest concentration (0.026 mg/kg) dry weight. The concentration of Fe and Cd have exceeded the Dutch intervention limit of 0.809mg/kg dry weight, but Zn did not exceed the Dutch intervention values of 0.844 mg/kg dry weight respectively. On the other hand, Mn concentration also has its value exceeding the Dutch intervention value of 2.94 mg/kg dry weight.

4. Discussions and Conclusion

4.1 Discussion

Research into heavy metals in soil, which is universally recognized as one of the most important sinks for trace elements originating from a wide range of human activities, has received considerable attention in recent decades (Capitelli et al., 2002). The behavior and fate of heavy metals in soil can vary greatly from one entry route to another, both in terms of their source and species. Commercial fertilizers, liming materials, agrochemicals, sewage sludges and other soil amendment materials, irrigation waters, and atmospheric deposition from industrial, urban, and road emissions are the primary sources of heavy metals in soil (Capitelli et al., 2002). Since heavy metals can significantly

alter an ecosystem's health, they are often cited as a major contributor to environmental pollution (Tüzen, 2003). Heavy metal pollution caused by human activity is on the rise. Soil heavy metals accumulate from air and industry pollution, affecting the local ecosystem (Lema et al. 2022). Heavy metal concentrations in soil samples are a useful indicator of environmental pollution (Mahmoud & Abba, 2021). The levels of copper, nickel, zinc, iron, manganese, cadmium, and chromium were selected as representative trace metals because they provide a reliable index of environmental health. Consuming excessive amounts of even essential metals can have harmful effects ((Jumare, Mahmoud, & Amlabu, 2022). The mean values of metal contents in each fraction for Cu, Ni, Zn, Fe, Mn, Cr and Cd in samples collected from dumpsite at different depth levels have exceeded the Dutch intervention values of 0.809mg/kg, and 0.049mg/ kg dry weight respectively. The dump site has high levels of toxic metals, as reported by the Food Agricultural Organisation and the World Health Organisation. Among all the metals estimated, Manganese (Mn) shows the highest concentration, while Cobalt (CO) shows the lowest concentration. There is a difference in absolute metal fractions of these samples with depth variation. The concentration of Chromium and Cadmium were below the dutch intervention limit. In general, the total metal content increased with increasing depth level. Contamination or soil pollution due to manganese concentration within our environment is very hazardous as it's inclined to high health risk and life span of domestic animals and human being at large. This study yielded similar findings in that human exposure to heavy metals occurs through three routs i.e inhalation, ingestion and skin absorption (Abdulrahman et al., 2020; Lema et al., 2022). A correlation exists between the types of activities taking place at dumping grounds and the heavy metal content of the waste produced there. Although the exact mechanism for heavy metal accumulation is not well understood, it appears to be linked to a chelation reaction involving sulfhydryl groups found in proteins, particularly methionine.

4.2 Conclusion

After the successful analysis on the selected dumpsite soils, the content of the selected heavy metals was assessed. From the result obtained, it is obvious that there are highly significant concentrations of manganese, chromium, copper and iron in all the soil samples of the dumpsites. Other heavy metals showed their concentrations at minimal levels. Conclusively, from the entire samples studied, it is obvious that all the soil samples have Manganese concentration in the in the highest degree and other heavy metals in their respective trace quantities. This signifies that manganese containing refuse are in random circulation within our environments. Contamination or soil pollution due to manganese concentration within our environment is very hazardous as it is inclined to high health risk and life span of domestic animals and human beings at large.

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