A Study on Single Extraction Technique of Some Selected Heavy Metals in the Soils of Abuja Metropolis, Nigeria

*Ibrahim, R.,¹ Dauda, M.S.,¹ Igwemmar, N.C.¹ and Obingwa, P. W.²

¹Department of Chemistry, University of Abuja, Abuja.
²Sheda Science and Technology Complex, Kwali, Abuja.

Email: ibrahimrabiu456@gmail.com

Abstract
Toxicity of metals in the soils has been a great environmental menace for decades. Toxicity of ions in Abuja soils at soil depth of 15cm was investigated using a single extraction analytical technique. Flame atomic absorption spectrometer was used for instrumental analysis. Single extraction ionic mobility sequence in urban soil samples is as follows: Zn>Cu>Fe>Al>Mn>>As>Ni>Pb>Cd>Cr. Mobility sequence in sub-urban soils is Zn>Cu>Fe>Al>Mn>>As>Ni>Pb>Cd>Cr and the sequence in Asokoro Forest soils (control) is Zn>Cu>Mn>Al>Fe>As>Ni>Cr>Cd>Pb. Zn ion has the highest mobility/bioavailability which indicates that Abuja metropolis could be sitting on Zn deposits. High mobility of Zn portends danger to plants and environment, as Zn toxicity hinders photosynthesis in plants thereby increasing the amount of CO₂ in the atmosphere which increases climate change subsequently. The study of metals toxicity in the environment will assist environmentalists and government policy makers in making decisions on how to tackle this menace. Abuja environment stakeholders should as a matter of urgency develop technical and legal frameworks to control the rise in metal build up in the metropolis.

Keywords: Abuja, Toxicity, Metals, Single extraction and Ions.

INTRODUCTION
Urban soils are soils of urban and environments intensively disturbed by human activity and that demonstrates a remarkably spatial heterogeneity (Dominique et al., 2021). Urban soils are essentially under strong human influence and also exerting a strong effect on human health, plants and soil organisms and on water infiltration (Pouyat et al., 2019). Atmospheric deposition reflected by high heavy metal concentration in urban dust is one of the main sources of heavy metal accumulation in urban soils (Jin et al., 2019).

The worst part about heavy metals is that once they build up in the body, they can cause irreversible damage and the effect of heavy metals can range from subtle symptoms to serious diseases (Griffin, 2020). Studies establishing close association between exposure to heavy metals and cancer epidemiology in sub-Saharan Africa are increasing (Kim et al., 2015). Several
health hazards have been associated with the consumption of high doses of heavy metals, and these hazards include but are not limited to: diarrhea, nausea, abdominal pain, nervous system disorder, kidney and diabetes diseases (Magaji and Mallo, 2020).

Soil is a fragile resource, since its health depends on physical conditions, environmental context, and the interlacing of inevitable natural processes (including extreme weather conditions: constant strong wind, heavy rain, floods, etc.), in relation to the intensity of human interventions, e.g. urbanization, industrialization, and local contamination (Cecchini et al., 2019). Soil is a dynamic, environmental matrix, assuring necessary support to any form of life on Earth and needing strict protection regulations (Brevik et al., 2015). Soil quality is intended as “the capacity of a soil to function, within land use and ecosystem boundaries, to sustain biological productivity, maintain environmental quality, and promote plant, animal, and human health (Salvati et al., 2018).

The concern over soil contamination by heavy metals started primarily from health risks, for instance Cu can cause health problems such as anemia, liver and kidney damage, stomach and intestinal irritation (Abdulrashid et al., 2017). According to World Health Organisation (WHO), long-term exposure to arsenic is mainly related to increased risks of skin cancer and some other cancers, as well as other skin lesions such as hyperkeratosis and pigmentation changes (WHO, 2018). Soil pollution assessment is common in recent times because of the wide range of health issues streaming from soil and plant relationship, soil and soil organism relationship, ecological degradation and environmental impact assessment issues (Tan et al., 2020).

Apart from the health hazards of metals to humans and animals, they also could cause phytotoxicity in plants. Zn phytotoxicity for instance, includes the disruption of photosynthesis in plants which could increase the amount of CO₂ in the atmosphere. This study intends to emphasize on this issue in order to contribute to the natural solution to climate change.

MATERIALS AND METHODS

Sampling Method
Grab sampling method was used at 34 sampling points in Abuja metropolis to collect soil samples, which were selected from several locations in the metropolis in mid-July of the year of collection. Abuja soils were classified into urban, sub-urban and Asokoro forest soils (control) in this work. Soils were dug at depths of 15 cm using a plastic shovel and collected in polythene bags. Collected samples were taken immediately to a laboratory immediately for air drying.

Sample Area
Abuja metropolis is an area comprising of Abuja city and its environs between the coordinates of Longitude 9.07°N and Latitude 7.40°E (Orisakwe et al., 2017). Asokoro forest is which is part of Abuja metropolis, is considered to be an unexploited land which is not used for farming or any significant anthropological activities as of the time of carrying out this work.

Sample Preparation
Samples were pretreated for clean up before analysis. They were first air dried at room temperature in the laboratory for 2 weeks after collection and sieved with 100mm mesh one after the other to get a uniform mass. The dried samples were taken to oven after the oven
temperature was set at 65°C for 16 hours each according to Mehlich, (1978). The oven dry method was employed to take care of any microbial activity that might have taken place during the 2 weeks of air drying in the laboratory.

**Single Extraction**

This extraction method shows a relatively fast, cheap and simple way to assess mobility of trace elements in contaminated soils. Putting into consideration, the objectives of the extraction methods, water, less concentrated salts solutions or even stronger reagents like Ethylene diamine tetra acetic acid (EDTA) as Ammonium EDTA are used according to Oliveira, (2012).

Fractions are operationally defined by means used to separate them and the mobile fraction is equivalent to available fraction which shows potential availability of trace elements in soil. Reagents used in this extraction method were of analytical grade which included; \( \text{CH}_3\text{COOH}, \text{NH}_3 \) and EDTA. 0.05mol/L ammonium-EDTA extraction solution was prepared as an ammonium salt solution by adding in a fume cupboard 146.12 ±0.05mL of ammonium-EDTA free acid to 800±20 mL distilled water and by partially dissolving and stirring in 130±5mL of concentrated ammonia solution until all the EDTA was dissolved. The obtained solution was filtered (with20µm filter paper) and diluted with water to 9.0±0.5L. The pH was adjusted to 7.0±0.05 by addition of a few drops of HCl. Finally the solution was diluted with distilled water to 10±0.1L, well mixed and then stored in a stoppered polythene bottle. 0.43mol/L \( \text{CH}_3\text{COOH} \) extracting solution was prepared by adding 250±2mL of distilled glacial \( \text{CH}_3\text{COOH} \) in a fume cupboard to about 5L of distilled water to 10mL volume, well mixed and then stored in a stoppered polythene container. 20mL of a 0.05mol/L ammonium-EDTA solution was added to 2.00g of soil sample. The suspension was shaken for 1 h in a reciprocal shaker. Centrifugation at 3500 revolution per minute for 10 minutes was carried out. Solution was decanted and filtered; the supernatant was kept in a 50mL polythene bottle for instrumental analysis according to Cappuyns, (2012).

Note: After measuring the pH, the \( \text{CH}_3\text{COOH} \) extracts were added to the pH< 2. The EDTA extracts were not acidified prior to analysis to prevent precipitation of EDTA with concentrated HNO\(_3\) to bring the salts at very low pH according to Oliveira, (2012).

**RESULTS AND DISCUSSION**

Results of single extractions of ions in both urban and sub-urban soils with Asokoro Forest soil as control are as outlined in the following tables.

<p>| Table 1. Mean Total Single Extraction Results in Urban, Sub-urban and Asokoro Forest |</p>
<table>
<thead>
<tr>
<th>Sampling Zones</th>
<th>Pb (µmole/L)</th>
<th>Cd (µmole/L)</th>
<th>Fe (µmole/L)</th>
<th>Ni (µmole/L)</th>
<th>Zn (µmole/L)</th>
<th>Al (µmole/L)</th>
<th>Mn (µmole/L)</th>
<th>Cu (µmole/L)</th>
<th>Cr (µmole/L)</th>
<th>As (µmole/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Urban Soils</strong></td>
<td></td>
<td></td>
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<tr>
<td>15cm</td>
<td>0.24±0.01</td>
<td>0.34±0.01</td>
<td>33.66±0.01</td>
<td>3.80±0.01</td>
<td>136.21±0.21</td>
<td>20.12±0.21</td>
<td>18.73±0.00</td>
<td>89.12±0.03</td>
<td>0.81±0.01</td>
<td>73.73±0.00</td>
</tr>
<tr>
<td><strong>Sub-Urban Soils</strong></td>
<td>0.27±0.01</td>
<td>0.14±0.01</td>
<td>17.44±0.57</td>
<td>1.13±0.01</td>
<td>91.52±0.02</td>
<td>14.63±0.01</td>
<td>13.31±0.01</td>
<td>86.95±0.01</td>
<td>0.09±0.01</td>
<td>4.82±0.00</td>
</tr>
<tr>
<td><strong>Asokoro Forest (Control)</strong></td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td>0.28±0.00</td>
<td>0.02±0.00</td>
<td>2.49±0.01</td>
<td>0.31±0.01</td>
<td>0.31±0.01</td>
<td>1.73±0.01</td>
<td>0.08±0.01</td>
<td>0.16±0.01</td>
</tr>
</tbody>
</table>

Fractions of ions in single extraction Ions mobility in Abuja urban soils in the decreasing order: Zn>Cu>Fe>Al>Mn>>As>Ni>Cr>Cd>Pb
Ions mobility in sub-urban soils in decreasing order: Zn>Cu>Fe>Al>Mn>>As>Ni>Pb>Cd>Cr
Ions mobility in Asokoro forest soils (control) in decreasing order:
Zn>Cu>Mn>Al>Fe>As>Ni>>Cr>Cd>Pb

Total mean fraction of Pb ions extracted from urban soils is 0.225±0.007, which is lower than that of sub-urban soils which is 0.27±0.008. Moderate amount of Pb ions concentration for both urban and sub urban soils could be due to efficient extraction of Pb ions in NH₄-EDTA as it forms Pb-EDTA complexes; this conforms to the findings of Nair and Varghese, (2020). Total mean fraction of Cd ions in urban soils is 0.335±0.007 while that of sub-urban soils is 0.135±0.007. Low concentration of Cd ions from reaction with NH₄-EDTA could be due to buffering effect of soil-solid phase, as this does not affect Cd ion absorption as it forms Cd-EDTA complex; this is in conformity with the findings of Custos et al., (2014). Moreover, the total mean fraction of Fe ions is 33.66±0.014 in urban soils which is higher than that of of sub urban soils which is 17.44±0.565. High total mean fraction of Fe ions in NH₄-EDTA extraction could be due to efficient extraction ability of EDTA for Fe ion in solid phase as it forms Fe-EDTA complex; this conforms to the findings of Chiumiento et al., (2015). Total mean fraction of Ni ions in urban soils is 3.80±0.007 which is lower than that of of sub urban soils which is 17.44±0.565. High total mean fraction of Ni ions could be due to efficient extraction of Ni ion by NH₄-EDTA agent in soil samples especially when pH is considered as a factor here, as Ni complexes with EDTA to form Ni-EDTA; this conforms to the findings of Zhu et al., (2018).

Total mean fraction of Zn ions in urban soils is 136.21±0.021 which is higher than that of of sub urban soils of 91.515±0.021. High total mean fraction of Zn ions in reaction with NH₄-EDTA could be due to strong affinity of EDTA to Zn ion as a chelating agent as it readily forms Zn-EDTA complex: this is in conformity with the findings of Hosseinpur and Motaghian, (2014). But Zn phytotoxicity disrupts plant photosynthesis which increases the amount of CO₂ in the atmosphere according to the findings of Vassilev et al., (2011) who concluded that “excess Zn triggers disturbances in the waters relations which affect photosynthesis, namely stomatal conductance and therefore plant growth”. Total mean fraction of Al ions in urban soils is 20.115±0.021 which is higher than that of of sub urban soils which is 17.63±0.021. High total mean fraction of Al ions in reaction could be due to efficient absorption of Al ion by EDTA, as it forms Al-EDTA complex: this conforms to the findings of Zhao et al., (2018). Mn ions have a total mean total fraction of 18.73±0.042 which is higher than that of of sub urban soils with a value of 13.305±0.007. Moderate concentration of Mn ions in reaction with NH₄-EDTA could be due to easier leaching of Mn ion by NH₄-EDTA from soil samples to form Mn-EDTA complex: this conforms to the findings of Zhang et al., (2018). Cu ions have a total mean fraction of 89.12±0.028 which is higher than that of of sub urban soils which is 86.95±0.028. Very high concentration of Cu ion could be due to NH₄-EDTA as an extracting and chelating agent ability to remove Cu ions efficiently from soil samples to form Cu-EDTA complex: this conforms to the findings of Cappuyns, (2012).

Cr ions have a total mean fraction of 0.825±0.007 in urban soil samples which is higher than that of sub urban soils which is 0.085±0.007. Low mean concentration of Cr ions from reaction with NH₄-EDTA could be due to forms, oxidation states of Cr ion and soil properties: this conforms to the findings of Lesniewska et al., (2017). Total mean fraction of As ions in urban soil samples is 7.125±0.001 which is higher than that of sub-urban soil samples which is 4.815±0.02. Moderate concentration of As ions in samples could be due to less affinity of EDTA to As ion to form As-EDTA complex: this conforms to the findings of Gonzaga et al., (2012). Therefore, based on the above results, it could be observed that Zn ions have the highest mobility in Abuja soil samples extraction. Heavy metals phytotoxicity, like Zn phytotoxicity can be detrimental to the environment as it disrupts the process of photosynthesis in plants.
This phenomenon can increase the amount of CO2 in the atmosphere (CO2 being a raw material for photosynthesis in plants). Large amount of CO2 in the atmosphere will increase global warming which will give rise to climate change in Abuja Metropolis.

**CONCLUSION**

Metal mobility in urban soil samples is found in the decreasing order; Zn>Cu>Fe>Al>Mn>>As>Ni>Cr>Pb. Mobility in sub-urban soil samples is; Zn>Cu>Fe>Al>Mn>>As>Ni>Pb>Cd>Cr. Mobility in Asokoro forest soils samples is Zn>Cu>Mn>Al>Fe>As>Ni>Cr>Pb. Metal mobility in both urban and sub-urban soils in single extraction was found to be higher than in Asokoro Forest soil samples, indicating higher anthropogenic activities in Abuja urban and suburban areas than in Asokoro Forest. Zn and Cu were discovered to be the metals with the highest mobility in single extraction. Pb, Cd, Ni, Zn, Al, Mn, Cu and Cr have concentration within regulatory authorities’ limits. Fe and As have no available standard from regulatory authorities. Metals under study (Pb, Cd, Fe, Ni, Zn, Al, Mn, Cu, Cr and As) were found to be within the limits of regulatory authorities. Zn phytotoxicity disrupts plant photosynthesis among other things, which increases the amount of CO2 in the atmosphere thereby increasing global warming and by implication, Abuja Metropolis is in danger of the consequences of rapid climate change. Regulatory authorities should give more attention to periodic environmental risk assessment of Abuja soils in order to checkmate the rising metal build up in the metropolis.

Stakeholders should endeavor to contain the high amount of Zn in Abuja soils in order to protect plants from its toxicity which can increase climate change in Abuja and its environs. Public enlightenment should be employed to promote advocacy for the control of metals in the environment. Periodic environmental risk assessment should be conducted across urban and sub-urban centers in Abuja metropolis. Policy makers should as matter of urgency, formulate policies geared towards safeguarding green zones in particular and Abuja ecosystem in general. A further study should be carried out on all the metals obtainable in soils in order to have a further understanding of metals mobility/bioavailability in Abuja soil

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