

**SEQUENTIAL EXTRACTION OF SELECTED HEAVY METALS IN THE SOILS OF ABUJA, NIGERIA***¹Ibrahim, R., ¹Dauda, M. S., ¹Igwemmar, N. C. and ²Abdu, B.¹Department of Chemistry, University of Abuja, Abuja²Department of Curriculum, Jigawa State College of Education, Gumel, Jigawa State.*Corresponding authors' email ibrahimrabi456@gmail.com Phone: +2348037842189**ABSTRACT**

Speciation of selected heavy metals in Abuja metropolitan soil samples was investigated using a sequential extraction analytical technique. Flame atomic absorption spectrometer was used for instrumental analysis. Metals were bound in six operational phases, in the sequential extraction method. Pb, Mn and Cd speciate more in exchangeable, As and Ni speciate more in bound to carbonate, Cu and Fe speciate more in bound to Fe-Mn oxide, Cr and Zn speciate more in organically bound while Al speciate more in residual in urban soil samples. In sub-urban samples, Pb and Cd speciate more in exchangeable and bound to Fe-Mn oxide, Cu speciate more in exchangeable, Al speciate more in bound to Fe-Mn oxide, Fe and Al speciate more in residual, Ni and As speciate more in bound to carbonate, Zn speciate more in organically bound and Cr speciate more in exchangeable and organically bound. Asokoro Forest (control) has most of the metals as non-residuals except Al and As which speciate more in residual phase. Sequence of ionic mobility in decreasing order for Abuja urban soils is as follows: Zn>Cu>Fe>Al>Mn>>As>Ni>Cr>Cd>Pb and in sub-urban soil samples is: Zn>Cu>Fe>Al>Mn>>Ni>As>Pb>Cd>Cr. From the results, it can be deduced that Zn is the ion with highest speciation. This portends danger to Abuja metropolis due to Zn phytotoxicity which hinders photosynthesis in plants, thereby increasing the amount of CO₂ giving rise to global warming. This requires that relevant authorities should enforce reduction of the activities that lead to abundance of Zn in Abuja soils.

Keywords: Abuja, Speciation, Sequential extraction, Mobility, Global Warming**INTRODUCTION**

Studies of environmental pollution in Africa indicate that toxic metal pollution has reached unprecedented level over the past decade and human exposure to toxic metals has become a major health risk on the continent and is the subject of increasing attention from national and international environmentalists according to Iordache *et al.*, (2022). Urbanization-driven soil sealing is one of the most pervasive mechanisms of degradation of fertile land around cities as observed by Di Feliciantino *et al.*, (2018). Urban soils are spatially and vertically diverse with a great variability along a gradient from nature-like to technical composed soils with high degree of artifacts having characteristics which are distinguished from non-urban soils as stated by Greinert, (2015).

Soils are also defined as large pools of carbon, nitrogen and other elements supporting plant growth and are located in the central position of urban ecological environment which are not only the sink of various pollutants but also the sources of various pollutants; so they are often used as important indicators of comprehensive environmental quality of urban centres as asserted by Li, (2017). Soils sustain biogeochemical cycles and serve as the foundations for maintaining ecosystem function and services of urban green spaces as observed by Mao *et al.*, (2014). Urban soils are also such types of soils which are excessively disturbed with high volume of anthropogenic activities such as housing, traffic, mining, commerce, manufacturing and agricultural practices which usually result in spatial heterogeneity according to Sager, (2020).

Historically, urban soils were ignored in soil studies but in the last decades, they have gained attention because of their importance for human health in the city environment according to Kumar and Hundel, (2016). Fast rising urbanisation, commercialization in urban centres and industrialisation has brought about the excessive amount of heavy metals and subsequent pollution of urban environment

by heavy metals and this has escalated their mobility and bioavailability in the anthropogenic urban soils as stated by Borrelli *et al.*, (2018). The current practice of urban planning does not pay proper attention to the quality of urban soils, to their multiple functions and to the supply of ecosystem services to the urban population as asserted by Calzolari *et al.*, (2020).

Nowadays, soil contamination attributed mainly to intense industrialisation, urbanisation and transport is becoming a global issue because metals are constantly spreading to the environment and pose a great threat to human health according to Rodrigo-Comino *et al.*, (2018). Many cities especially in Africa are becoming business as well as industrial hubs as developing economies and as such contaminations leading to pollution are becoming common eye sores in such areas as observed by Ronsivalle, (2020). The usage of construction materials, machineries and other equipments provides much waste from construction sites which affect not only the outlook of cities but also urban environment quality according to Jie and Nan, (2020).

Finally, the study of sub-urban areas has become an emerging theme in urban and regional research in recent decades as observed by Yang and Ye, (2020). The global drivers of sub-urban change include structural adjustment and the prevailing economic, socio-political conditions; producing land use changes in and around African cities as observed by Sroka *et al.*, (2019). Increasing level of heavy metals in soils has become a serious concern for human health as these can be transferred easily into human system through contaminated food chain according to Mettemicht *et al.*, (2019). Thus, increasing level of metals in their speciation in both urban and sub-urban soils is becoming an issue of serious concern to environment researchers in recent years, mainly due to growing population in urban centres and surrounding communities. Metal speciation also plays a major role in global warming which culminates in climate change. This

study intends to look into the contribution of metals in their speciation to global warming in Abuja Metropolis.

MATERIALS AND METHODS

Sampling Method

Grab sampling method was used to collect samples from 34 different sites from Abuja city and Asokoro Forest in Abuja metropolis. Samples were collected at soil depth of 15 cm using a plastic shovel. Samples were packed in a polythene bags for onward delivery to a laboratory at Centre for Genetic Engineering and Biotechnology, Federal University of Technology Minna, Niger State, Nigeria immediately.

Sample Area

Abuja metropolis is an area comprising of the city centre and its environs between the coordinates of Longitude 9.07°N and Latitude 7.40°E as observed by Orisakwe et al., (2017). Abuja is located in the North-Central Nigeria which serves as the capital of Nigeria and is blessed with abundant natural resources.

Sample Pretreatment

Collected samples were air dried for two weeks and grinded for uniformity and were sieved to obtain fine samples. The dried samples were taken to oven after the oven temperature was set at 65°C for 16 hours each. The oven dry method was employed to take care of any microbial activity that might have taken place during air drying in the laboratory as outlined by Mehlich, (1978).

Sequential Extraction

Six step sequential extraction procedure was used in this study to separate metals into; water soluble (F1), exchangeable (F2), bound to carbonates (F3), bound to metal oxide (reducible, F4), organically bound (F5) and residual phases (F6).
Water soluble fraction (F1): De-ionised water (about 30mL) was added to 1.0g of soil samples each in 100mL polypropylene centrifuge tubes with screw caps. The extraction was performed by shaking in a mechanical end-over-end shaker at a speed of 300 revolutions per minute (rpm) and at room temperature of 28°C for 5 hours and left over night. Solution was centrifuged at 3500 rpm for 10 minutes and the supernatant was filtered into a plastic container through Whatmann No. 1 filter paper and stored in a refrigerator at 3-4°C for instrumental analysis.

Exchangeable phase (F2): 50mL of 1molL⁻¹ MgCl₂ (pH 7) were added to the residue from f1 in 100mL polypropylene centrifuge tubes with screw caps and allowed to stand for 1 hour at room temperature. Centrifugation and filtration were performed according to the above operational phase.
Bound to carbonate phase (F3): Residue from F2 was extracted with 50mL of 1 molL⁻¹ C₂H₃NaO₂-CH₃COOH (pH 5) and allowed to stand for 5 hours at room temperature. Centrifugation and filtration were performed according to the above operational phase.
Bound to metal oxide fraction (F4): The residue from f3 was extracted with 50mL 0.04mol L⁻¹ C₂H₂O₄ in 25% (v/v) C₂H₇NO₂ and allowed to stand for 6 hours at 85°C in a water bath. Centrifugation and filtration were performed according to the above operational phase f3.

Organically bound phase (F5): The residue from f4 was extracted. About 4.5mL of 0.02molL⁻¹ HNO₃ and 7.2ml of 1.0 molL⁻¹ H₂O₂ was added and allowed to stand for 2 hours at 85°C in water bath. Finally, 8.8mL of 3.2molL⁻¹ C₂H₇NO₂ was added in 20% (v/v) HNO₃ and allowed to stand for 30 minutes at room temperature. Centrifugation and filtration were performed and filtrate kept 3-4°C, for instrumental analysis.

Residual phase (F6): The residue from f5 above was evaporated to dryness. A 0.25g subsample was taken and this was analyzed by tri-acid digestion with 3mL of 1 molL⁻¹ HNO₃, 2mL of 2molL⁻¹ of HCl and 1 mL of 8.8 molL⁻¹ (40%) H₂O₂ solutions each in platinum crucibles. After acids have been digested and evaporated, 40mL of 7M HNO₃ was added and wormed on a sand bath and filtered into 50mL labeled plastic containers and filled to volumes with the 0.25M HNO₃ solution. The digested residual samples were stored in the refrigerator at 3-4°C for instrumental analysis. Note: Total metal content of the original soil samples was similarly determined earlier using 0.25g of soil samples, as all outlined by Qayyum et al., (2016).

RESULTS AND DISCUSSION

Result of sequential extractions of metals in the urban and sub-urban soils of Abuja Metropolis is presented below in tables 1 and 2 below. Pb, Cd, Mn and Cr have the highest mobility in exchangeable phase; Fe and Cu have the highest mobility in bound to Fe-Mn oxide, Ni and As had the highest mobility in bound to carbonate, Al and Zn had the highest mobility in organically bound phase

Table 1: Sequential Extraction in the Soils of Abuja Urban Soil Samples (ppm)

Ions Extractions	Pb	Cd	Fe	Ni	Zn	Al	Mn	Cu	Cr	As
Water Soluble	0.001	0.03	5.61	0.24	23.99	2.82	2.46	20.80	0.02	1.24
Exchangeable	0.19	0.15	4.24	0.43	26.52	2.89	4.76	20.77	0.05	1.00
Bound to Carbonate	0.005	0.04	4.98	1.46	30.15	2.70	4.29	17.16	0.02	1.73
Bound to Fe-Mn oxide	0.004	0.032	6.41	1.05	19.90	3.56	3.59	24.16	0.02	0.74
Organically bound	0.009	0.08	6.26	0.63	33.47	4.22	3.62	1.33	0.07	1.00
Residual	0.03	0.008	6.17	0.004	2.20	3.94	0.04	4.92	0.004	1.44
Total	0.24	0.34	33.67	3.81	136.23	20.13	18.76	89.14	0.81	7.15
Control	0.04	0.05	6.05	0.83	51.48	4.84	3.98	33.35	0.04	1.58

Control = Asokoro Forest

Ion Mobility in Abuja urban soils in decreasing order:

Zn>Cu>Fe>Al>Mn>>As>Ni>Cr>Cd>Pb

Ion Mobility in Asokoro Forest soils in decreasing order:

Zn>Cu>Fe>Al>Mn>As>Ni>Cd>Cr>Pb

Zn ion had the highest extraction efficiency in the following phase:

Organically Bound.

Cu ion had the highest extraction efficiency in the following phase

Bound to Fe-Mn oxide.

Table 2: Sequential Extraction of Ions in Abuja Sub-Urban Soil Samples (ppm)

Ions Extractions	Pb	Cd	Fe	Ni	Zn	Al	Mn	Cu	Cr	As
Water Soluble	0.002	0.01	3.33	0.18	10.94	2.45	2.45	9.11	0.01	0.64
Exchangeable	0.12	0.04	2.11	0.08	22.79	2.06	3.14	22.09	0.03	0.60
Bound to Carbonate	0.002	0.02	3.18	0.59	32.43	1.78	2.18	16.45	0.01	1.08
Bound to Fe-Mn oxide	0.12	0.04	3.56	0.44	12.13	2.92	2.38	18.06	0.01	0.94
Organically bound	0.05	0.03	1.16	0.43	30.93	2.12	2.01	16.06	0.03	0.73
Residual	0.0003	0.002	4.14	0.003	2.31	3.33	1.15	5.23	0.002	0.84
Total	0.29	0.14	17.48	1.14	91.53	14.66	13.31	86.97	0.09	4.83
Control	0.04	0.05	6.05	0.83	51.48	4.84	3.98	33.35	0.04	1.58

Ion Mobility in sub-urban soils in decreasing order:

Zn>Cu>>Fe>Al>Mn>>Ni>As>Pb>Cd>Cr

Zn ion had the highest extraction efficiency in the following phase:

Organically bound

Cu had the highest extraction efficiency in the following phase:

Exchangeable.

Sequential extraction in six phases was carried out. In water soluble phase, extractant was de-ionised water. Metals react with water in this phase to produce oxides and hydroxides compounds, it is considered to be a mobile phase as products are accessible to plants easily. Pb ion fractions are 0.001 in urban soil samples. Less concentration could be due to the formation of the layer of lead oxide (PbO) on the metallic surface of Pb ion the layer makes it not to react with deionized water properly: this was in conformity with the findings of Escudero *et al.*, (2013).

Exchangeable phase had primary extractant as MgCl₂. MgCl₂ reacts with most metals to form simple and complex salts. Pb ion fractions in this phase are 0.19. Moderate concentration of Pb ion in MgCl₂ solution could be due to the formation of a precipitate of PbCl₂: this was in conformity with the findings of Wang *et al.*, (2016). Bound to carbonate phase had primary extractant as sodium acetate (Na(COOH)₂), while the secondary extractant was acetic acid (COOH)₂. This phase is considered to be mobile for metal absorption in the soil and has the highest concentration of ion fractions than other phases; this conforms to the findings of Alvarez *et al.*, (2014). Pb ion fractions in urban samples were 0.005. Low concentration of Pb ions could be due to the formation of Pb(COOH)₂ precipitate: this was not in conformity with the findings of Karwowska, (2020).

Bound to Fe-Mn oxide had primary extractant as oxalic acid while the secondary was acetic acid. The primary organic extractant was used in place of a primary inorganic extractant NH₂OH.HCl due to environmental considerations. The extractants here produce metal acetates and oxalates with the metals. Pb ion fractions in urban soil samples were 0.004, lower than fractions in sub-urban samples which are 0.12. Low concentration of Pb ion could be due to low concentration of Pb in Abuja soils. Pb ion was immobilized by reacting with oxalic acid to give organometallic of PbC₂O₄, as attested to by Jiang *et al.*, (2012).

Cd ion fractions in urban samples were 0.032, lower than fractions in sub-urban samples which were 0.04. Relatively low concentration of Cd ion in samples could be due to oxalic acid reducing Pb ion content: this conformed to the findings of Li *et al.*, (2022). In organically bound, primary extractants included HNO₃ and H₂O₂, while secondary extractant was ammonium acetate {NH₄(COOH₂)}. Pb ion fractions in urban samples were 0.009, lower than in sub-urban samples which were 0.05. Very low concentration of Pb ion could be due to combined digestion of HNO₃/H₂O₂ which does not affect increase in Pb ion even though Pb oxalate was formed with NH₄(COOH₂): this conformed to the findings of Castro-

Gonzalez *et al.*, (2022). Cd ion fractions in urban samples were 0.08, lower than in sub-urban samples which were 0.03. Low concentration of Cd ion could be due to low reactivity of Cd with extractants; this was in conformity with the findings of Wang *et al.*, (2016), who observed that modification of H₂O₂ in Cd binding is further explored by adding HNO₃.

Fe ion fractions in urban samples were 6.26, higher than fractions in sub-urban samples which were 1.16. High concentration of Fe ion could be due to effective leaching ability of the combination of HNO₃/H₂O₂ on metals, thus, Fe (II)/Fe (III) compounds could have been formed as Fe ion was immobilized: this conformed to the findings of Nakayama and Wagatsuma, (2021), who observed that HNO₃/H₂O₂ bring about rapid decomposition of metals.

Organically bound phase had primary extractants as nitric acid (HNO₃) and hydrogen peroxide (H₂O₂), while secondary extractant was NH₄(COOH₂). Pb ion fractions in urban samples are 0.009, lower than in sub-urban samples which were 0.05. Very low concentration of Pb ion could be due to combined digestion of HNO₃/H₂O₂ which does not affect increase in Pb ion even though Pb oxalate was formed with NH₄(COOH₂): this conformed to the findings of Castro-Gonzalez *et al.*, (2022). Cd ion fractions in urban samples which were 0.08 lower than in sub-urban samples which were 0.03. Low concentration of Cd ion could be due to low reactivity with extractants; this was in conformity with the findings of Wang *et al.*, (2016), who observed that modification of H₂O₂ in Cd binding is further explored by adding HNO₃.

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Zn ion fractions in urban samples were 33.47, higher than fractions in sub-urban samples which were 30.93. Very high concentration of Zn ion in this phase could be due to rapid decomposition of Zn ion by HNO₃/H₂O₂; this conformed to the findings of Karas and Frankowski, (2018). Zn was observed to be high here and excess Zn in soils, causes phytotoxicity in plants. Zn phytotoxicity is detrimental to Abuja environment, as it retards the rate of photosynthesis in plants, thereby increasing 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.

Residual phase had primary extractants as HNO₃ and HCl, while secondary extractant was H₂O₂. Ions of metals got immobilized by the extractants to form metal chlorides, nitrates and oxides. Though soluble compounds were formed but can become occluded in lattices of organic matter. Due to this process, the complexes formed in this phase are hardly accessible to plants when discharged to soil. Pb ion fractions in urban soil samples were 0.03, higher than fractions of 0.0003 in sub-urban samples. Low concentration of Pb ions could be due to low availability of Pb ion in Abuja soils: this did not conform to the findings of Li *et al.*, (2016), who observed that Pb ion is higher in residual and Fe-Mn oxide fractions in sequential reaction.

Cd ion fractions in urban samples were 0.008, higher than fractions of sub-urban samples of 0.002. Low concentration of Cd ion could be due to immobilization of Cd ion to form nitrates, chlorides and oxide compounds on reaction with the extractants: this did not conform to the findings of Benhacem and Harrache, (2021), who observed high level of Cd ion in residual phase. Fe ions Fractions in urban samples were 6.17, higher than fractions in sub-urban fractions which were 4.14. Relative high fractions could be due to high reactivity of Fe ions in the samples: this did not conform to the findings of Attakhiru and Okiemen, (2021), who observed that the metals under study were found mostly in bound to Fe-Mn oxide phase.

Ni ion fractions in urban samples were 0.004 lower than fractions in sub-urban samples which were 0.003. Very low concentration of Ni ions could be due to low formation Ni compounds with extractants: this conformed to the findings of Pakula *et al.*, (2012). Zn ion fractions in urban samples were 2.20 lower than fractions in sub-urban samples which were 2.31. Low concentration of Zn ion in samples could be due to low formation of Zn nitrates, chlorides and oxides with the extractants: this was not in conformity with the findings of Husnain *et al.*, (2016). Al ion fractions in urban samples were 3.94, higher than fractions obtained in sub-urban samples which are 3.33. High concentration could be due to high availability of Al in Abuja soils: this was in conformity with the findings of Rodgers *et al.*, (2015).

CONCLUSION

Sequential extraction analytical technique showed highest extraction in bound to carbonate phase in urban soils. Ion mobility in urban soils in decreasing order is as follows: Zn>Cu>Fe>Al>Mn>>As>Ni>Cr>Cd>Pb. Sequential extraction in sub-urban soils showed highest extraction in bound to carbonate phase too. Ion mobility in sub-urban soils in decreasing order is as follows: Zn>Cu>Fe>Al>Mn>>Ni>As>Pb>Cd>Cr. Sequential extraction in Asokoro soil showed highest extraction phase was bound to carbonate and its ionic mobility sequence is as follows: Zn>Cu>Fe>Al>Mn>As>Ni>Cd>Cr>Pb. From the results, Zn ion was observed to have the highest mobility in urban, sub-urban and Asokoro Forest, signifying that Abuja Metropolis could be sitting on Zn deposits. This phenomenon portends danger to the environment as Zn phytotoxicity hinders photosynthesis which increases CO₂ in the environment thereby increasing global warming resulting in climate change. This requires that relevant authorities should enforce reduction of the activities that lead to abundance of azan in Abuja soils.

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