

Examining toxic metals contamination, speciation and geochemistry of soil impacted by open disposal of waste cathode ray tubes in Nigeria

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Abstract. In this study, soil contamination by toxic metals released from cathode ray tubes (CRTs) openly discarded within the vicinities of artisans' workshops in Nigeria was assessed in order to ascertain the metal leaching potential of CRTs, mobility and bioavailability of the leached metals in soil. Furthermore, the ecological geochemistry of the impacted soils was carried out. Seventy soil samples were randomly collected from thirty five locations at depths 0 – 15 cm (top-soil) and 15 – 30 cm (sub-soil), respectively from two selected states each within five geographical regions of Nigeria. Environmentally available lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni) and copper (Cu) were extracted from dried and sieved soil samples using aqua regia solution and were analyzed using flame atomic absorption spectrometry (AAS). Additionally, the metals were also sequentially extracted into five fractions and their concentrations determined using AAS. Concentration of Pb ranged from 0.4 – 6510 mg/kg with all top-soils exceeding the Nigerian NESREA regulatory limit of 164 mg/kg while Cd, Cr, Ni and Cu levels were within their respective regulatory limits. Geoaccumulation index values indicated that approximately 83% of all top-soils represented strong to extreme contamination by Pb while sequential extraction showed that majority of the extracted Pb was in the Fe-Mn oxide, residual and exchangeable forms. The results generally suggest that CRT disposal areas are highly polluted with Pb with significant amounts in bioavailable phases. Thus, waste CRTs are required to be managed in an environmentally sound manner to forestall any probable harm to ecological functioning of such areas.

Keywords: cathode ray tube, leaching, toxic metals, geoaccumulation index, sequential extraction.

1. Introduction

The environment comprises the air, water, soil and biota. Maintaining the environment in a state as pristine as possible is a necessity owing to the importance of its components. However, urbanization, advances in technology, industrialization and modernization have resulted in an inevitable generation of wastes of various kinds at an alarming rate, which contribute to environmental contamination. One important waste stream that has attracted global attention in recent times is made up of substances generated from end-of-life (eol) Electrical and Electronic Equipment (EEE), simply called "e-waste". E-waste include a wide-range of EEE such as large household appliances (refrigerators, air conditioners, stereos and consumer electronics) and small household appliances (computers, monitors, televisions, etc.) [1]. This waste stream has been reported to be the fastest growing waste stream globally, at three times the rate of municipal solid waste [2].

One major component of the e-waste stream in Nigeria is the cathode ray tube (CRT) obtained mostly from discarded televisions and computer monitors. The presence of this category in the waste stream arises due to a transition from CRT-based devices to flat screen displays [3], transboundary movement of non-functional CRT devices into the country [4, 5] and decreased lifespan of used CRTs [6]. The major concern coming up

from its presence in the environment is its high metal content, especially lead. Considering the fact that waste CRTs are commonly disposed of inappropriately (mostly stockpiled in the open), rainfall can cause leaching of metals from the glass into top- and sub-soil, causing contamination of soil, surface waters (due to surface run offs) and crops planted around such vicinities. Metal concentrations in soil are of importance due to their non-biodegradability and bioaccumulative behavior, while their toxicities and bioavailabilities for plant uptake are dictated by their association with other soil components and the ability of the soil to release them [7].

Studies on toxic metal contamination in Nigerian soils due to leaching of several types of wastes abound with much emphasis on industrial areas, municipal dumpsites, e-waste recycling and burning sites, etc. [8 - 12]. However, there is paucity of data in literature on soil contamination due to metal leaching from discarded CRTs. The few cited studies in literature were concerned with metal leaching from CRT glass under simulated conditions where the glass was crushed into fine particles [13 - 15]. Therefore, this study was designed to evaluate contamination/ pollution status and chemical forms of metals in soil arising from open disposal of CRTs within artisans' workshops in Nigeria.

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2. Experimental

2.1. Study area

Nigeria is located on the west coast of Africa. It lies within latitude 9.082 and longitude 8.675. The climatic condition varies in most parts of the country; in the North, it is arid and in the South, there is an equatorial type of climate. It shares boundaries with the Republics of Cameroon in the East, Benin and Niger in the West, Niger and Chad in the North and the Gulf of Guinea in the South. It has a total area of 923,768 square kilometer, housing approximately 180 million people consisting of 374 ethnic groups with Hausa, Igbo and Yoruba constituting the major languages.

The study area was categorized into five geographical regions and samples were collected from two selected states from each region. The regions and states in bracket were: South-South (SS - Delta and Bayelsa States), South-East (SE - Anambra and Abia States), South-West (SW - Lagos and Oyo States), North-Central (NC - Kogi and Abuja States) and North-West (NW - Kaduna and Kano States), respectively. The North-East region was not included in this study due to security concerns presently prevailing in that region. The selected States were considered because they are quite urbanized, and as a result, accessibility to artisans engaged in repair of ICT devices was easy. These artisans' workshops were

randomly distributed throughout the selected locations. Of particular interest were artisans engaged in the repair of CRT-based devices. There was no waste management practice for end-of-life CRT-based devices by these artisans as this waste category was normally seen stockpiled beside/ in front of the workshops. A map of the study area is shown in Fig. 1 while Plate 1 is a pictorial representation of some of the artisans' workshop indicating the discarded CRTs.



Figure 1. Map of study area, indicating sampling locations



Plate 1. Some of the sampled area

2.2. Soil sampling

From each State within each of the five regions studied, a control sample was collected and two to three composite samples were collected from the study areas by means of a soil corer at depths 0 – 15 cm (top-soil) and 15 – 30 cm (sub-soil), respectively. The number of samples collected for compositing was dictated by accessibility to the soils. About three (3) to five (5) samples were collected from within and at designated distances from the center of the disposal areas for compositing. Fourteen (14) composite samples (seven locations) were thus collected from each region comprising ten (10) from study areas and four (4) control samples. A total of 70 samples were collected from the five geographical regions.

About 0.5 kg of soil samples were separately collected from the top and sub-soils into well-labelled polythene bags. The soils were air-dried at ambient temperature in the laboratory for two weeks and were

sieved using a 2 mm mesh sieve. The 2 mm sieved soil samples were subsequently divided into two groups: the first group was for physicochemical parameters while the second group was for metals analyses. Samples for metal analyses were further size-reduced using agate mortar and pestle, sieved with 0.6 mm mesh sieve and stored in properly labelled polythene bags in a dry place until further preparation.

2.3. Physicochemical characteristics of the soil

2.3.1. Soil pH

The pH of the soil–water solution for each sample was measured using a pocket-sized digital pH meter (pHep®, Hanna Instrument, USA) which had earlier been calibrated with buffer solutions of pH 4 and 7 respectively. The soils' pH values were determined in soil: deionized water solution (ratio 1:5) according to Rayment and Higginson [16].

2.3.2. Total organic carbon

Total organic carbon was determined using the Walkley and Black [17] wet oxidation method.

2.4. Analysis of toxic metals

Wet digestion method using a mixture of nitric acid (69%, Fluka) and hydrochloric acid (37%, Sigma) was used for metals extraction. Exactly 1.00 g of each soil sample was placed in a beaker, followed by the addition of 9 mL HCl and 3 mL HNO₃ to form the digesting solution otherwise called aqua regia. This mixture was swirled to wet the sample, covered with a watch glass and allowed to stand overnight. The next day, the beaker was heated in the hood until the volume of acid mixture was reduced to about 5 mL. The digest was filtered using Whatman No. 1 filter paper and made up to 25 mL with 0.25 M HNO₃ [18].

Digested samples were analyzed for metals of environmental concern commonly used in CRT formulations, including lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu) and nickel (Ni) by Perkin Elmer AAnalyst 200 Atomic Absorption Spectrophotometer (Germany).

2.5. Quality assurance/ Quality control

Blanks were used to check method and reagent impurities. Analytical grade reagents were used for all analyses. All glassware and plastic ware were soaked in 5% HNO₃ overnight and rinsed with deionized water prior to use. Tools and work surfaces were carefully cleaned for each sample preparation during pulverization to avoid cross contamination. Samples were analyzed in duplicates to check for precision of the chosen method while blind samples were also sent for analysis to check the accuracy of the measuring instrument. Method validation was evaluated using the spiked recovery study. The spike recoveries for the various metals ranged from 92.6 to 104.3 %.

2.6. Assessment of soil contamination

2.6.1. Geo-accumulation index (I_{geo})

A common approach for approximating the enrichment of metals above background levels is to calculate the geoaccumulation index (I_{geo}) proposed by Müller [19]:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}$$

where:

- C_n is the measured concentration of element (n) in the enriched soil sample;
- B_n is the background concentration from the control area for element (n);
- 1.5 is a factor introduced to minimize the effect of possible variations in the background value (correction factor) due to lithological variations.

2.7. Statistical analysis

Data were expressed as mean \pm standard deviation. In order to confirm the relationship among soil properties (physicochemical properties and metal content), principal component analysis (PCA) was applied to the generated data sets for identifying groups of metals that

correlate, which can be considered as having a common source.

2.8. Metal speciation studies

Speciation analysis was conducted on soil samples which recorded metal levels above regulatory limits according to Tessier's five-step sequential extraction procedure [20]. This procedure was selected because it is well documented in literature to give detailed description of the available forms of metals in soils. The procedure was carried out with an initial weight of 1.00 g in 50 mL capacity centrifuge tubes.

3. Results and discussion

3.1. Physicochemical characteristics of soil

Summaries of the physicochemical characteristics of the studied soil samples are presented in Figs. 2 and 3, respectively. The average pH values (ranging from 6.44 – 9.75) show that the studied soils were predominantly alkaline except for SW soils, which were slightly acidic. All sub-soils except SE soils had higher pH values than top-soils (*i.e.* pH increased with depth) (Fig. 2). Similar pH trends have been previously reported for soils in various parts of Nigeria [9, 11, 21 - 23].

The percent TOC content in this study was found to range from 0.08 to 1.85% across all studied locations and depths. A decrease in the percent TOC from top to sub-soil was observed in all studied regions (Fig. 3). The results of this study are consistent with the findings of Iwegbue *et al.* [24], Wali *et al.* [25] and Ojuri *et al.* [26] where a drop in percent organic carbon with depth was observed. Soil organic matter and pH are among major factors that can influence availability and retention of metals. The pH range of all soils suggest low leachability of metals to sub-soils as most metals within this pH range are not free, rather, they exist either as precipitates or complexes. The TOC normally contains humid materials which have the ability to hold back metals at top-soils. The low TOC content implies low retentive capacity of the metals.

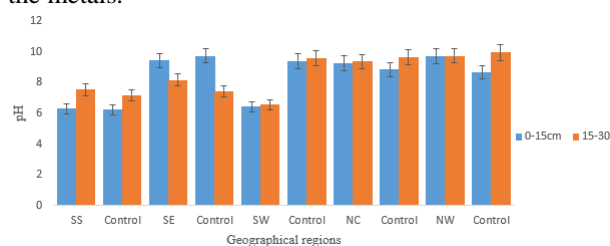


Figure 2. Comparison of the average pH values across the studied regions

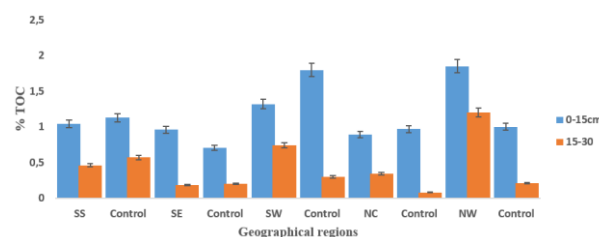


Figure 3. Comparison of the average percent total organic carbon across the studied regions

3.2. Toxic metal concentrations in soils

The average metal concentrations in soil samples obtained from CRT disposal and control areas on regional basis are displayed in Figs. 4 - 8. Lead levels in experimental soil samples were in the following ranges: 0.39 – 6510 mg/kg from South-South (SS), 18.9 – 1180 mg/kg from South-East (SE), 15.3 – 328 mg/kg from South-West (SW), 1.20 – 269 mg/kg from North-Central (NC) and 9.40 – 1250 mg/kg from North-West (NW), respectively. Control soil samples showed relatively low levels of Pb, ranging from 3.0 – 29.5 mg/kg across all locations and depths respectively. Of all the metals quantified, only Pb was detected at very high levels, which exceeded its regulatory limit set by the National Environmental Standards Regulations and Enforcement Agency, Nigeria [27].

Soil samples from SS showed a maximum concentration of 6510 mg/kg. Many factors could be responsible for this. The CRTs from this region were found discarded without their plastic casings. Furthermore, this region experiences acid rain as a result of petroleum exploration activities. Acid rain has a tendency of influencing higher leachability of metals from the CRT glass. This is demonstrated from the lowest acidic pH indicated in soils from SS. The results presented in Fig. 4 reveal that all top-soils had higher mean Pb concentration compared with the sub-soils in all studied regions and hence, top soils were better indicators of metallic burdens [28]. The high Pb levels reported in this study are similar to the findings of Bridgen *et al.* [29] where CRTs were broken and openly discarded.

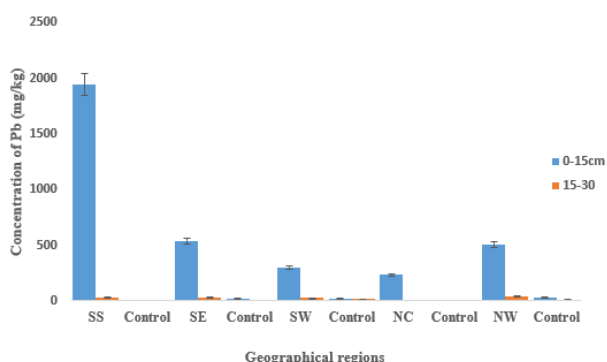


Figure 4. Comparison of average Pb levels in soil across studied regions and depths

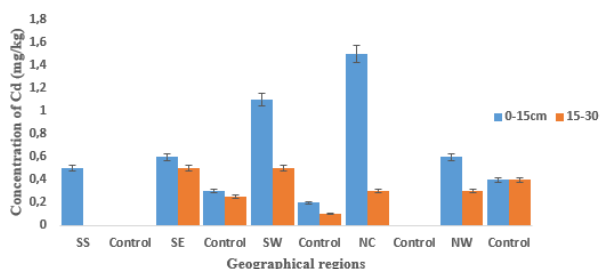


Figure 5. Comparison of average Cd levels in soil across studied regions and depths

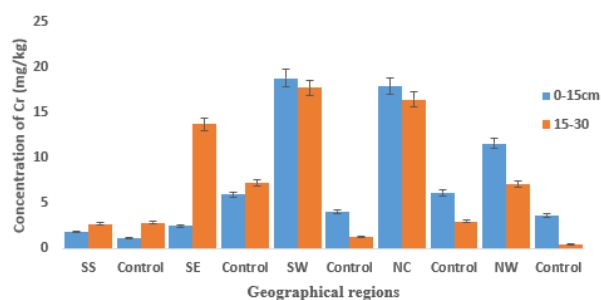


Figure 6. Comparison of average Cr levels in soil across studied regions and depths.

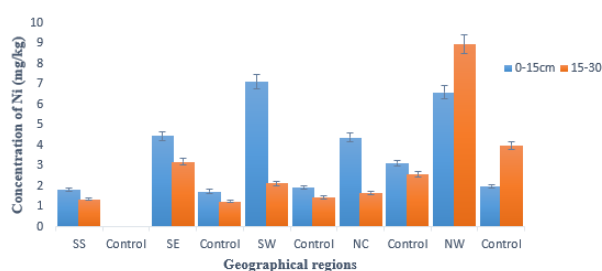


Figure 7. Comparison of average Ni levels in soil across studied regions and depths.

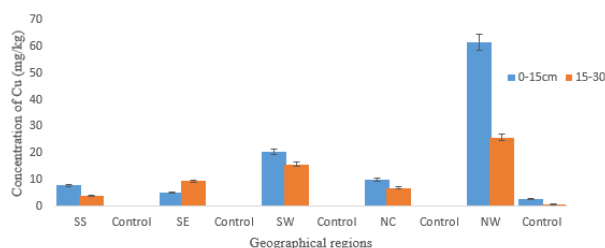


Figure 8. Comparison of average Cu levels in soil across studied regions and depths

Cadmium concentration in control soil samples ranged from ND – 0.04 mg/kg while for experimental soil samples it ranged as follows: ND – 0.55 mg/kg from SS, ND – 1.50 mg/kg from SE, 0.50 – 2.00 mg/kg from SW, ND – 1.50 mg/kg from NW and ND – 1.75 mg/kg from NW respectively. Like Pb, Figs. 5, 6, 7 and 8 indicate that the top-soils generally had higher average Cd, Cr (except SS and SE soils), Ni (except NC soils) and Cu (except SS and SE soils) levels in all studied locations. However, these metals were all within their respective NESREA [27] regulatory limits in soil, suggesting that the metal concentrations in soils within the premises of CRT disposal were not posing any significant hazard to human health and the environment. However, a little elevation in metal levels across the regions of the studied areas compared with the control is a sign that there was a form of some leaching of the metals from CRT glass.

3.3. Assessment of toxic metals contamination in soil

3.3.1. Geoaccumulation index (Igeo)

Geoaccumulation index (Igeo) values are displayed in Table 1. The Igeo for Pb in top-soils for all studied locations ranged from 2.4 to 8.2 (approximately 83%, representing strong to extreme contamination by Pb) and from -5.7 to 2.6 for sub-soils, indicating uncontamination to moderate contamination by Pb. From Igeo analysis, about 23% of all top-soils analyzed were designated as being extremely contaminated. The mean Igeo for all

sub-soils was less than 1, implying a relative absence of Pb leaching down the soil profile. The Igeo of Cd ranged from -3.9 – 2.7, indicating uncontamination to moderate contamination by Cd. With the exception of SW soils which showed a mean Igeo value of 1.3, all other soils determined had mean Igeo values less than 1, suggesting uncontamination of these soils by Cd. The Igeo values for

Cr and Ni for all studied soils across all depths were less than 0, absolutely specifying no contamination. The Igeo values for Cu showed that about 8% of the total sample population had values greater than 0 but less than 2. Soils from these regions also recorded high Igeo values for Pb and Cd, suggesting a probable common source of the metals.

Table 1. Range of geoaccumulation index (mean in parenthesis) of metals studied

Location	Depth (cm)	Geoaccumulation index range				
		Pb	Cd	Cr	Ni	Cu
South	0 – 15	2.2 – 9.4 (3.0)	-1.6 – 0.4 (0.8)	-7.9 – -5.1 (-6.5)	-6.1 – -5.9 (6.0)	-5.8 – 1.9 (-3.7)
South	15 – 30	-3.4 – 3.7 (0.6)	-0.3 – 0.4 (-0.03)	-6.8 – 0 (-3.6)	-7.0 – -6.0 (-6.5)	-5.5 – -3.4 (-4.4)
South	0 – 15	1.8 – 5.2 (3.5)	-5.5 – 0 (-3.5)	-10.2 – 0 (-5.3)	-5.4 – -3.4 (-4.7)	-7.6 – -2.4 (-4.9)
East	15 – 30	1.3 – 2.6 (2.1)	0 – 0.4 (0.08)	-3.6 – 0 (-1.7)	-6.5 – -2.6 (-4.8)	-4.5 – 0.5 (-2.5)
South	0 – 15	3.4 – 3.6 (3.5)	-0.5 – 1.4 (0.3)	-3.6 – 0 (-2.5)	-5.7 – 0 (-3.8)	-2.7 – 0 (-1.6)
West	15 – 30	2.1 – 3.0 (2.9)	-0.3 – 2.1 (0.6)	-3.7 – -2.7 (-3.4)	-5.7 – -4.7 (-5.9)	-3.1 – 1.7 (-2.3)
North	0 – 15	3.7 – 4.9 (4.3)	-1.6 – 1.0 (-0.1)	-3.3 – 0 (-2.1)	-6.3 – 0 (-3.9)	-2.9 – 0 (-1.9)
Central	15 – 30	-4.2 – -1.64 (-2.3)	-0.3 – 1.3 (0.2)	-3.5 – 0 (-2.2)	-6.9 – 0 (-4.3)	-4 – 0 (-2.4)
North	0 – 15	2.5 – 4.7 (3.1)	0 – 1.5 (0.3)	-5.6 – 0 (-3.9)	-5.6 – 0 (-3.2)	-4.3 – 1.2 (-1.8)
West	15 – 30	1.2 – 5 (2.6)	-0.3 – 0.7 (0.4)	-5.3 – -3.3 (-4.6)	-6.6 – 0 (-3.3)	-4 – 0.3 (-1.9)

3.4. Correlation studies

3.4.1. Principal Component Analysis (PCA)

Results of PCA application for all sites and depths are presented in Figs. 9 and 10 respectively. At depth 0-15 cm, three factors were obtained accounting for 65.2% of the total variance. Factor 1 was dominated by TOC, Cd, Cr and Ni, accounting for 27.7% of the total variance. This factor showed that metal complexation to organic matter was the predominant way of metals retention in soil [30, 31]. Factor 2 accounted for 24.1 % of the total variance and was dominated by EC and Pb, indicating that Pb had association with soil electrical conductivity. The open disposal of CRTs and the subsequent leaching of Pb from the leaded CRT glass was considered the main contributor to its presence in these soils as indicated by its very high concentration. Bipolarity of factor with higher loading of pH was observed. Factor 3 was dominated by high loading of Cu and accounted for 13 % of the total variance. This factor suggested that Cu in some regions could have been present in the soil from other sources entirely different from those of other metals.

At 15-30 cm depth, three factors were also obtained accounting for 70.2% of the total variance. Factor 1 accounted for 40.2 % of the total variance, and was dominated by TOC, Pb and Ni. This factor indicated that complexation to organic matter was the prevailing way of retention of Pb and Ni in soils at this depth [30]. Factor 2 accounted for 15.4 % of the total variance and was dominated by Cd and Cu. Copper had higher loading of 0.866, which might be explained by the chalcophilic characters of these metals *i.e.* they form sulfides which are poorly soluble minerals *e.g.* Cu_2S , CuS and CdS [31]. Copper forms stronger organic complexes than other bivalent transition metals and therefore, soil rich in organic matter can retain more copper [32]. Factor 3

accounted for 14.5 % of the total variance and was dominated by Cr, suggesting that this metal could come from sources different from those of other metals. Bipolarity of factor with a high negative loading for pH was also observed.

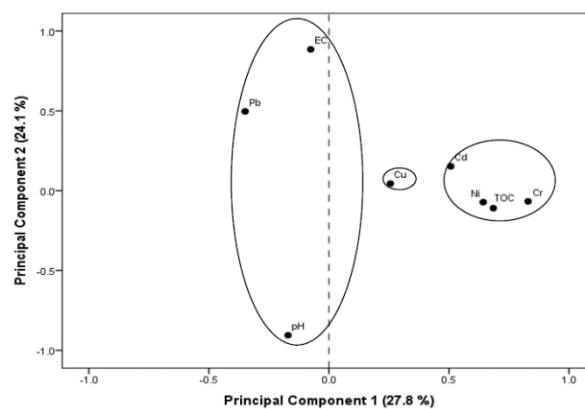


Figure 9. The loading plot of PCA of physicochemical parameters and metals from the study area at depth 0-15 cm

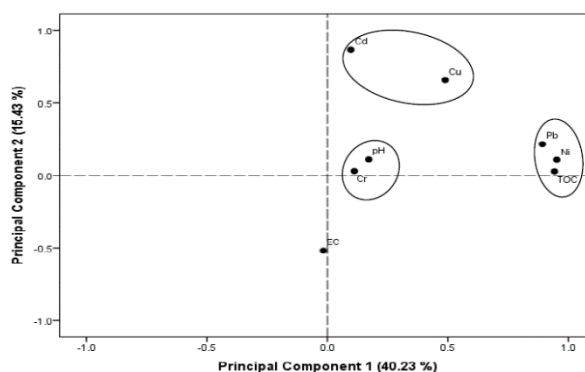


Figure 10. The loading plot of PCA of physicochemical parameters from the study area at depth 15-30 cm.

3.5. Lead speciation in soil

Soil samples with metal concentration greater than their respective regulatory limit was speciated using the five-step sequential extraction procedure developed by Tessier *et al.* [20] to assess the bioavailability potential of the metal. In this study, only Pb concentration exceeded its Nigerian regulatory limit in soil. The concentrations of other metals (Cd, Cr, Ni and Cu) studied were within accepted limits. The speciation of these metals was not necessary. The percentage of Pb in each speciated fraction relative to the total concentration of Pb is displayed in Fig. 11. Lead was found in all fractions, and the speciation of Pb in these soils followed the order – SS: Fe-Mn oxides > Exchangeable > Carbonate > Residual > Organic; SE: Residual > Carbonate > Fe-Mn oxide > Organic > Exchangeable; SW: Fe-Mn oxide > Exchangeable > Residual > Organic > Carbonate; NC: Fe-Mn oxide > Residual > Organic > Exchangeable > Carbonate, and NW: Organic > Residual > Fe-Mn oxide > Carbonate > Exchangeable.

Lead was fractionated predominantly in the Fe-Mn oxides bound fraction in soils from SS, SW and NC, and midway in soils from SE and NW respectively. The percentage of Pb in the Fe-Mn oxide fraction ranged from 2.16 to 70.7 % with an average of 37.6% across all studied regions. The high amount of metals in the Fe-Mn fraction of soils was reported to be influenced by high amounts of Fe-Mn minerals in soil [33]. A greater amount of Pb in the Fe-Mn oxide fraction could also be as a result of the formation of stable complexes, since these minerals are excellent scavengers for trace metals [34]. High amounts of Pb in this fraction can thus limit its mobility and bioavailability [35]. This fraction however, is thermodynamically unstable and can be sensitive to reducing conditions and environmental changes (*e.g.* changes in soil pH and organic matter), and such changes can lead to redistribution of metals in the available forms [36].

In the residual fraction, Pb was partitioned predominantly in soils from SE and NW respectively. It ranged from 0.6 to 62.6%, with an average value of 25.2%. The high amounts of Pb in this fraction indicate little or no serious threat of the metal to human and the surrounding environment, considering the fact that metals in this fraction are not readily environmentally available [37].

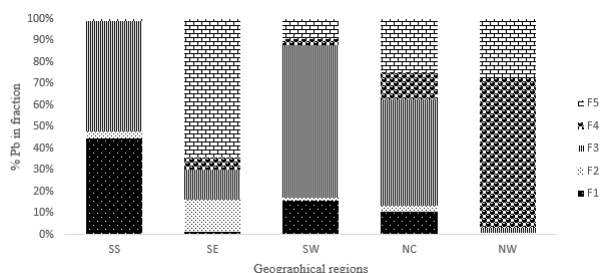


Figure 11. Percentage of Pb in the various geochemical fractions as a function of total Pb content in soils (F1 - Exchangeable, F2 - Carbonate bound, F3 - Fe-Mn bound, F4 - Organic bound, F5 - Residual)

The exchangeable form of Pb ranged from 0.44 to 46 % with an average of 14.8%. This form is next to the Fe-Mn oxide form in SS and SW soils and least in NW

soils. Metals in this fraction are in ionic forms; hence, they have a high mobility, can be easily drained by water and are easily released into biota [38]. The strong association of Pb with this fraction in soils from SS and SW calls for concern as Pb is one of the metals that constitutes the widest possible health risk to humans through plant uptake dietary route [39, 40] and direct ingestion of soil particles, especially by children via hand-to-mouth activities.

The percentage of Pb in the carbonate fraction ranged from 0.64 to 14.1 % with an average of 4.02 %. Like the exchangeable fraction, this fraction is also extractable and can accumulate in plants [38]. It is however, observed to be least in soils from SW and NC, and midway in SS and NW soils. The percentage of Pb in the organic fraction ranged from 0.07 to 72.7 % with an average of 18.7 %. Lead in this fraction was observed to be highest in NW soils and low in SS, SW and NW soils. The high and low distributions of Pb within the organic fraction could be attributed to the corresponding percent total organic carbon recorded in these soils [11, 40, 41].

The overall difference in Pb distribution among the five fractions is a function of the prevailing soil chemical environment [42]. For instance, the prevailing chemical environment in NW soils was high organic matter, which gave rise to a greater distribution of Pb in such soils relative to soils with low organic matter while metals associated with Fe-Mn oxide fractions can be released under reducing conditions.

5. Conclusions

Environmental assessment of soils from CRT disposed areas revealed that:

- Elemental analysis showed significantly high levels of Pb in top-soils of all studied regions, indicating that Pb leaching from discarded CRTs under the action of natural precipitation occurred. The significantly low Pb levels in sub-soils compared with top-soils suggested a relative absence of leaching down the soil profile. Similarly, the Pb levels in all top-soils were significantly higher than the control and regulatory limit set by NESREA. However, the concentrations of Cd, Cr, Ni and Cu were relatively low and within their respective Nigerian regulatory limits.
- Geoaccumulation index showed very strong contamination of top-soils with Pb.
- The results of elemental analyses and pollution indices summarized above point to the fact that Pb metal was the major concern arising from open disposal of CRT glass with less environmental impact from the other studied metals.
- Sequential extraction results indicated that Pb was readily bioavailable for surface and ground water as well as biota uptake in SS, SW, NC and NW soils but was of moderate bioavailability in SE soils.
- The results generally suggest that soils within the vicinity of CRT disposal areas are highly affected by Pb leachability from the CRTs and the presence of bioavailable Pb in the studied soils confers toxic characteristic on the soils. Waste CRTs are thus required to be managed in an environmentally sound

manner to forestall any probable harm to ecological functioning of such areas and to prevent the release of environmentally unstable occluded metals into the available forms.

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