

Speciation of Some Trace Metals in Floodplain Soil of Eke-Mgbom, Afikpo, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author VIO designed the study and wrote the protocol. Author LOA performed the sampling and managed the analyses of the study. Author MNM managed the literature searches and wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Floodplain soil sediment at Eke-Mgbom, Afikpo, Nigeria, was sampled and subjected to chemical fractionation to reveal the geochemical forms in which some trace metals existed. The investigation was conducted to evaluate the bioavailability of these metals to receptor organisms. The speciation of iron, manganese, copper, zinc, nickel, lead, cadmium and chromium were estimated by the speciation method. The geochemical phases in which the metals partitioned followed the order: Oxidizable >> Exchangeable >> Carbonate > Residual > Reducible. This is an indication that most metals accumulated in humic matter. Percentage bioavailability ranged from 17.7%(Cr) to 52.6%(Cd) with an average value of 34.03%. Other trace metals, apart from copper and cadmium were undersaturated with respect to their availabilities to biota. Proper cleaning methods such as phytoremediation were suggested in order to minimize or keep these trace metals in stable forms in this rural agricultural soil.

Keywords: *Pollution; speciation; bioavailability; geochemical phases; water bodies; phytoremediation.*

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1. INTRODUCTION

The state of metal pollution has become a matter of growing international concern during the past three decades. The increasing population densities of people, human activities and environmental impact of site locations have affected the soil composition [1]. The levels of several trace metals, released into the soil by natural and anthropogenic sources have been noticed in different parts of the country [1,2]. Intense pollution of the soil has inevitably increased the levels of heavy metals in the soil [3].

The concentration levels of heavy metals in environment are continually changing due to man's activities. These have generated a lot of interest worldwide in pollution studies. Major natural sources of these metals are rock-weathering, releases from terrestrial and submarine sediments while anthropogenic sources include Industrial emissions, vehicular emissions, municipal wastes, agricultural wastes, etc [4]. Heavy toxic metals also entered into the environment through waste water from metal plating industries and industries of lead, Cd-Ni batteries, phosphate fertilizers, mining, pigments, electroplating, corrosion and other industrial wastes [5]. Heavy metals are produced in large amounts and discharged into the environment where they become toxic to plants and aquatic organisms and bio-concentrate within the organisms, sometimes to levels greater than that in the environment [6].

A number of trace metals are important for the development of living organisms but are known to be toxic and harmful at certain concentrations. For example, manganese serves as a cofactor of hydrolase, decarboxylase, and transferase enzymes but manganese poisoning has been linked to impaired motor skills and cognitive disorders at high concentration [7]. In a similar way, iron functions as haemoglobin in the transport of oxygen, but its accumulation has been related to some neurodegenerative disorders such as Alzheimer disease, Parkinson disease, type-1 neuro-degeneration with brain and host of others [8]. A large number of potentially harmful metals are known as pollutants but some have been implicated to several human's diseases [3]. Taking for instance, lead causes cancer, damage the brain and kidneys and ultimately death [9]. Also, cadmium causes kidney disease, lung damage, and fragile bones [10] and also linked with hypertension caused by kidney malfunction [11].

During transportation, trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena [6] which affect their behaviour and bioavailability. Trace metals are easily influenced by environmental factors such as surface runoff, groundwater, dissolution from sediment, deposition from the atmosphere and anthropogenic pollutants. Hence, trace metals may be sensitive indicators for monitoring changes in the environment [12].

Environmental (or ecological) risk is defined as "the potential for adverse effects on living organisms associated with pollution of the environment by effluents, emissions, wastes, or accidental chemical discharge; energy use; or the depletion of natural resources". It is a well known fact that the total concentration of a metal in the soil is not sufficient to predict the potential ecological risk that it represents [13]. Ecological risk is more connected to the bioavailability of the metal, which in turn, is related to the chemical form in which it is found in the soil [14]. Bioavailability is therefore, the fraction of the total element that is available to the receptor organism [15].

During soil erosion, materials are settled at floodplain which collects the load of sediments carried by the runoff around a particular area and afterward, distribute the deposited

materials into water bodies nearby. Most studies of trace metals in the soil focused on the total metal concentrations. The fact that total concentrations of metals should be used as a yardstick to determine the potential health risk of these metal pollutants in the environment implies that the bulk metal concentration is available to the biota. This assertion has been refuted by many authors [13,16,17,18]. It is evidence that the speciation of trace metal pollutants with the various sediment phases determines their specific impact on the environment. Also, the type of the phase specific bonding of the trace metals in contaminated natural sediments specifies suitable methods of their potential cleaning and utilization [19].

The solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents and each metal quantified separately. The use of sequential extraction furnishes detailed information about the origin, mode of occurrence, biological and phytochemical availability, mobilization and transport of trace metals [11]. Apart from Horowitz [13] used in this study, other notable speciation techniques had been documented [2,11,20].

This preliminary study is to examine the speciation of these trace metals in the anoxic environment with a view to evaluating possibilities of their physical and physicochemical treatments. The choice of this sediment site lies on the fact that, it remains the collection point of all flood water in Afikpo, Nigeria, as all flood water end at this point before entering the river bodies. There is therefore, need to assess the impact of trace metals in this agricultural and densely populated area to assess bioavailability and health consequences as well as cleaning and utilization techniques. This research is pertinent since there has not been any information documented concerning the partitioning and bioavailability of trace metals in floodplain sediment near Ndibe beach River despite the economic importance of this river to the people of this fast growing community. Hence, there is a need to establish the geochemical forms in which these trace metals exist in the sediment via sequential extraction since the chemical forms of inorganic components in soils and sediments determine their availability to biota and their geochemical interactions [21].

2. MATERIALS AND METHODS

2.1 Study Area

Afikpo is situated between 5°53'N 7°56'E coordinates. It has an estimated population of 672,000 in 2005. The town has a boundary with cross river by a river in which fishing and transportation activities are taking place. The topography of the area is basically sloppy and undulating rugged sedimentary terrain. The area experiences an average farming and commercial activities. The large population of automobile attracts mechanic workshop and automobile dumpsites. Due to rapid urbanization of the area and poor disposal of solid wastes, whenever it rains, materials transported by erosion are settled at floodplain before finally finding their ways into nearby water bodies.

2.2 Sample Collection and Preparation

Floodplain soil sediment was collected at Eke-Mgbom market road, Afikpo, Nigeria. The sample was collected with plastic spoon. Composite sampling technique was adopted in taking representative sample. The sample was air-dried and homogenized by using 90 mesh size sieve and stored in polythene bag at 4°C prior to leaching.

2.3 Sequential Extraction Procedure

The method of Horowitz [13] as modified in our previous works [22,23] was used for the sequential extraction of the trace metals investigated. The procedure is summarized in Table 1 below:

Table 1. Procedure used for trace metal speciation of the sediment sample

Fraction	Trace Metal Speciation	Extraction Reagent / Condition
1	Adsorbed and Exchanged	1M magnesium chloride, pH 7, 1hr
2	Bound to Carbonate	1M sodium acetate, pH 5, 1hr
3	Bound to Iron & Manganese	0.2M ammonium oxalate + 0.2M oxalic acid, 1hr
4	Bound to Organic Matter	0.1M sodium hydroxide, 1hr
5	Residual	Conc. hydrofluoric and hydrochloric acids, 5hrs

2.4 Chemical Analysis

All the supernatant solutions from stages (I) to (IV) and the residual digest (v) were analyzed for the following trace elements: iron, manganese, copper, zinc, lead, nickel cadmium, and chromium using Perkin Elmer Atomic Absorption Spectrophotometer (model 403).

3. RESULTS AND DISCUSSION

3.1 Results

The results of sequential extraction of some selected trace metals from floodplain soil sediment in Afikpo, Ebonyi State, Nigeria is presented in the table and percentage occurrence of each metal in the fractions are shown in Figs. 1 to 8 below:

The exchangeable and carbonate fractions captured the most reactive and presumably the most mobile and bioavailable fractions [24]. On that basis, % bioavailability is calculated thus:

$$\left(\frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times \frac{100}{1} \right) \%$$

Where

- F₁ = Metal content bound to exchangeable fraction
- F₂ = Metal content bound to carbonate fraction
- F₃ = Metal content bound to iron and manganese oxides
- F₄ = Metal content bound to organic matter
- F₅ = Residual fraction.

3.2 Discussion

The results of distribution patterns of the trace metals investigated in the floodplain soil sediment based on their geochemical fractions are presented in the Table 2 and expressed as percentage in Figs 1-8. The most noticeable concentration of Iron (7.5mg/kg) was found

in oxidizable fraction widely followed by carbonate bounded phase (2.5mg/kg) while exchangeable, reducible and residual fractions had 1.5mg/kg each (Table 2). The % occurrence of iron in organic form (51.72%) signifies that in this type of sediment, iron has medium liability and with time, decomposition and/or oxidation of organic matter may make it to be available. Organic form of iron can be introduced into the soil through formation of complexes with organic ligands and can be taken up by plants [25]. This result was consistent with those of other researchers [12, 25, 26]. The % bioavailability of iron was 27.6 (Table 2), which implies that the occurrence of this trace metal in the study area was very low. Exchangeable iron (10.34%) was found to represent a minor percentage of the fractions (Fig. 1). This was evidenced with the results conducted earlier [11,22,23].

Table 2. Results of speciation of some trace metals in the flood plain soil sediment of Eke-Mgbom, Afikpo, Nigeria

Fraction	Fe	Mn	Cu	Zn	Pb	Ni	Cd	Cr	Total	Mean	% Fraction
Exchangeable	1.5	0.2	3.7	6.2	32.5	3.5	6.0	1.4	55.0	6.88	22.72
Carbonate	2.5	6.2	4.0	8.9	3.4	0.5	4.0	0.8	30.3	3.79	12.52
Reducible	1.5	0.0	3.5	11.8	0.5	0.5	3.0	2.3	23.1	2.89	9.54
Oxidizable	7.5	16.4	1.2	2.5	66.6	5.4	5.0	2.8	107.4	13.43	44.36
Residual	1.5	0.0	3.2	11.6	1.6	2.3	1.0	5.1	26.3	3.29	10.86
Total Fraction	14.5	22.8	15.6	41.0	104.6	12.2	19.0	12.4	242.1		
Mean Fraction	2.90	4.56	3.12	8.20	20.92	2.44	3.80	2.48			
Bioavailability	4.0	6.4	7.7	15.1	35.9	4.0	10.0	2.2			
% Bioavailability	27.6	21.0	49.4	36.8	34.3	32.8	52.6	17.7		34.03	

Note: Concentrations of the metals are in mg/kg

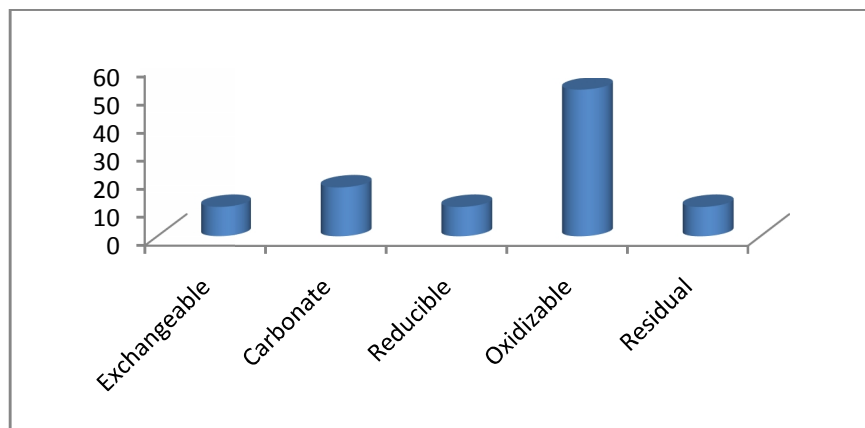


Fig. 1. % occurrence of Fe in the fractions

Just like iron, manganese also partitioned greatly in organically complexed phase (16.4mg/kg) (Table 2). Manganese was not accumulated in reducible and residual geochemical phases. A very high % of manganese (77%) in organic form is expected due to the strong complex it tends to form with humic matter [15]. Similar result had been documented [12]. Carbonate bounded manganese gave a percentage occurrence of 27.19% (Fig. 2). This result was in agreement with those of Iwegbue [27] and Abeh et al. [28]. The metal had a % bioavailability of 21.0 (Table 2), this value in this type of sediment was at its tolerable level.

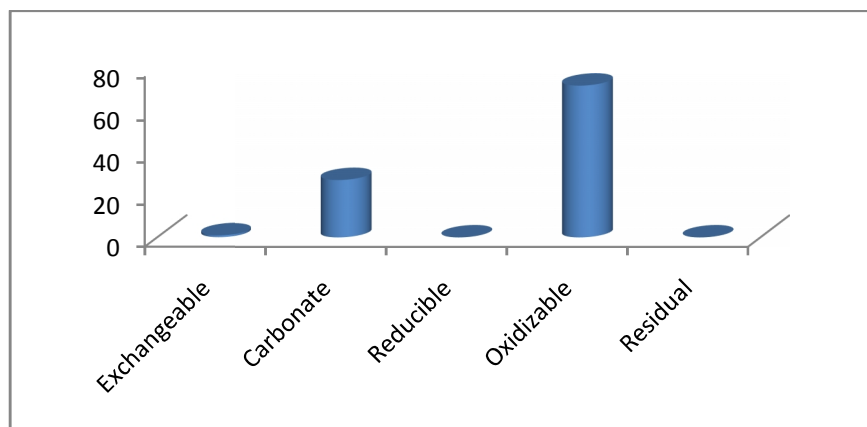


Fig. 2. % occurrence of Mn in the fractions

The % bioavailability of copper in this study was slightly below average (49.4%). This implies that copper is becoming more available. It is a known fact that copper and some trace metals like manganese, iron and zinc are essential to maintain the body metabolism [14], however, they can become toxic when they exceed the threshold limit [1]. Exchangeable copper was found to be 3.70mg/kg (23.72%) (Table 2 & Fig. 3). Metals partitioned here are likely affected by sorption-desorption processes [10,11]. The highest accumulation of copper was associated with carbonate fraction (Fig. 3). Metals in this form and exchangeable phase are believed to be highly soluble, mobile and easily released into solution; hence bioavailability to biota is inevitable [29].

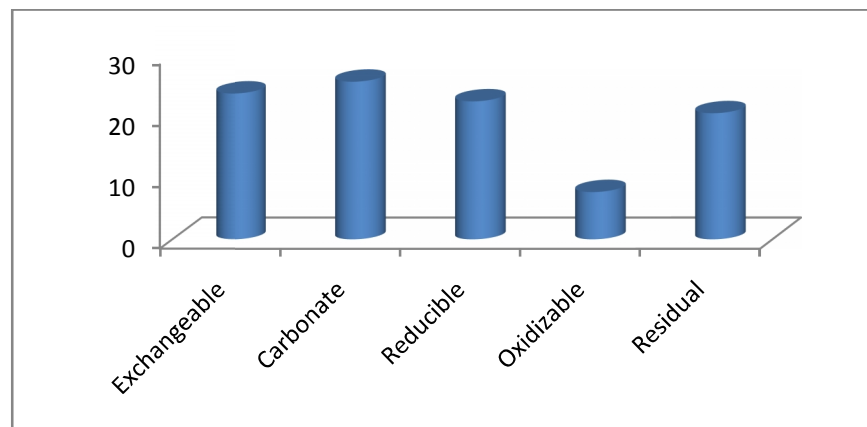


Fig. 3. % occurrence of Cu in the fractions

Zinc had % bioavailability of 36.8 (Table 2); at this level, zinc could not pose any threat to the environment. The metal content for the Fe-Mn oxides phase was relatively high (Fig. 4). This result was similar to finding of Adaikpoh [12]. Metals in this fraction exist as cement between soil particles. The metal fraction occluded in this form are known to be less soluble under oxidizing conditions but are more soluble under reducing environment with variation in redox conditions [18]. Therefore, metals in this form are thermodynamically unstable under anoxic

conditions and could increase mobility with increased toxicity [10,11,12,15]. The next important fraction of zinc is residual (28.29%). This means that this inactive form is fixed in the crystal lattice and can only be available after the decomposition of the crystals. The next noticeable content of zinc was associated with carbonate fraction (21.17%). It is a known fact that zinc is scavaged by non-dentriral carbonate metals, organic matter and oxide minerals, and it is less mobile [30]. Therefore, the possibility of its release into food chain is reduced.

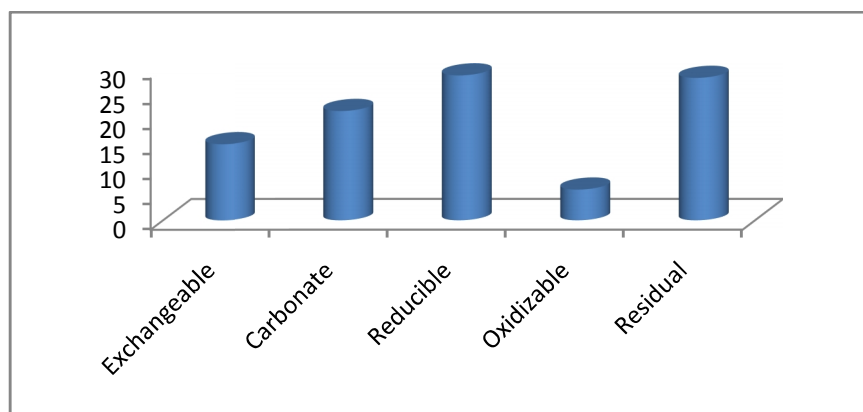


Fig. 4. % occurrence of Zn in the fractions

Lead partitioned predominantly in oxidizable fraction (66.6mg/kg). This value was on high side knowing fully the perilous nature of lead in organic form [31]. The high distribution of lead in organically bounded fraction (Fig. 5) is expected due to the strong complexes it tends to form with humic minerals [15]. Exchangeable form of lead was the next important fraction with a value of 32.5mg/kg (Table 2). Metals in this phase are soluble and easily release into biota. The accumulation of lead in this fraction call for concern because lead is one of the metals (just like cadmium) that constitutes the widest possible health risk to humans through the plant uptake dietary route [12]. The percentage bioavailability was calculated to be 34.3%. The observed trend of lead in the fractions is in order: Reducible < Residual < Carbonate << Exchangeable << oxidizable.

Nickel accumulated mostly in humic material (44.26%) widely followed by exchangeable fraction (28.69%) while carbonate and reducible (4.10%) forms partitioned least (Fig. 6). The high organically bounded nickel (like manganese and lead) is due to the strong complexes it tends to form with humic materials [12]. Low level of nickel (0.5mg/kg) (Table 2) in this geochemical phase was in agreement with other findings [27, 32, 33]. It has been suggested that the levels of nickel in this phase depends on how much manganese oxide is absorbed in soil because Ni^{2+} can substitute for surface manganese in mixed valence manganese oxides [32]. The significant percentage of nickel associated with exchangeable phase was in line with a previous report [32]. This is an indication that some amount of nickel is potentially available for plants' uptake in this sediment. High proportion of organically bounded nickel (44.26%) and absolutely low concentration (0.5mg/kg) in reducible fraction had also been documented [27]. The % bioavailability of nickel in this site was determined to be 32.8. This was in consonant with the finding of Omuku et al. [34] who reported nickel to have 35.88% average bioavailability of three sites studied.

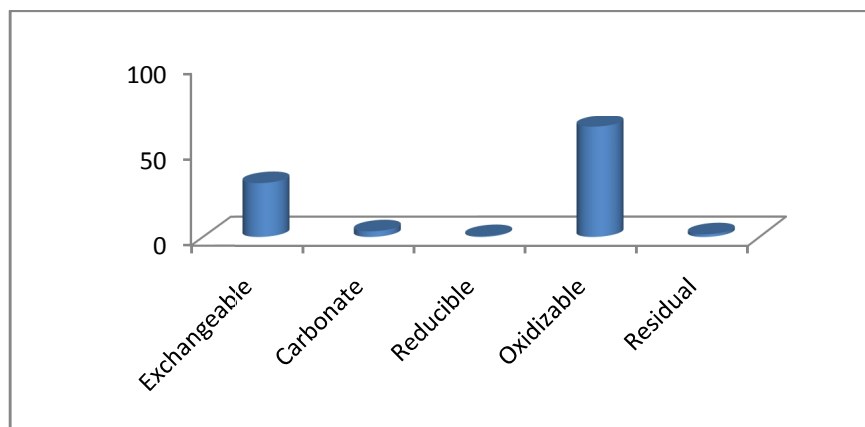


Fig. 5. % occurrence of Pb in the fractions

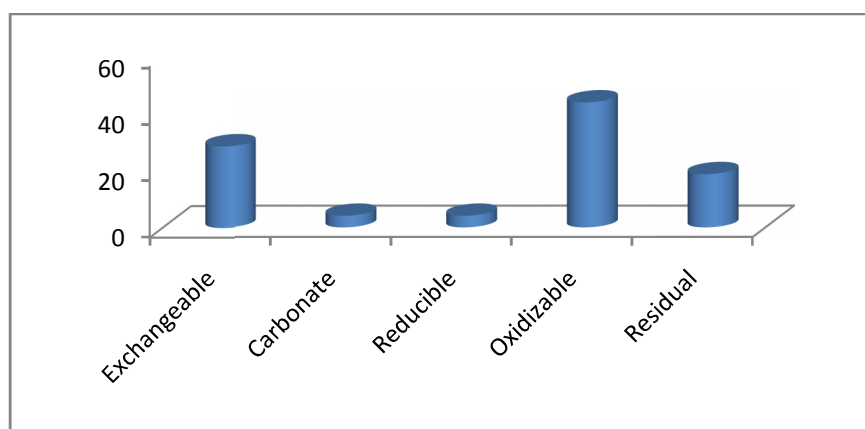


Fig. 6. % occurrence of Ni in the fractions

The 52.6% bioavailability of cadmium in this study area revealed the gradual pollution by this metal, taking into account the toxic nature of this metal even at low concentration [31]. The most prominent occurrence of cadmium was in exchangeable phase (Fig. 7). Organically complexed cadmium was the next significant fraction. The high level of cadmium in carbonate bounded fraction (21.05%) cum exchangeable phase (31.58%), (which are known to be major contributors to mobility and bioavailability) connotes that, it is bioavailable. Similar reports of cadmium in these phases had been documented [12,23]. Cadmium like mercury exhibits a profound capacity of combining with thiol group (-SH) to form a stable complex. Cadmium and mercury however compete with and displace zinc with a number of zinc-containing metalloenzymes by irreversibly bonding to the active site, thereby destroying normal metabolism [31]. The inactive form of cadmium had least value of 1.0mg/kg (Table 2). The low value was also reported in our previous study [23].

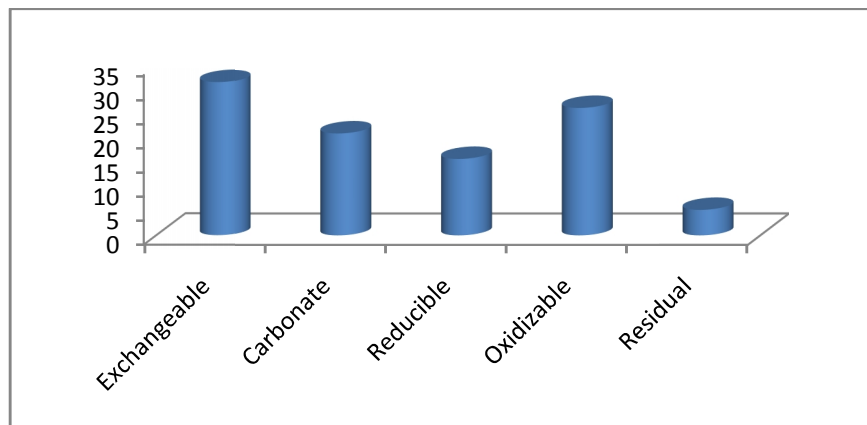


Fig. 7. % occurrence of Cd in the fractions

In Fig. 8, residual form of chromium was predominant (41.13%). High level of chromium (5.1mg/kg) (Table 2) was implicated in this phase. The result compared favourably with those of other researchers [27,32,34]. This fraction is taken as a guide to the degree of metal pollution of sediments, in that, the greater the percentage of the metal present, the lower the degree of pollution of the area under study [35]. It is evidenced that residual solid holds trace metals within crystal matrix and are likelihood associated within silicate mineral [10,32]. Therefore, metals in this phase are not expected to be released into solution over a reasonable time span under the conditions normally encountered in nature [10,11,20,31,32], hence, they are not available to biota. Organic form of chromium partitioned next to residual phase with 22.58% occurrence. This result was consistent with that of other researchers [25, 32,36]. The concentration of chromium in exchangeable fraction was 1.4mg/kg (Table 2). The result of this investigation was slightly higher when compared with the findings of metal speciation reported by Osakwe [32] who reported average chromium in contaminated soils to be 0.98mg/kg. The low level of carbonated bounded chromium (6.45%) corroborated previous result [12], where it was reported to be between 4.82 - 9.42%. The % bioavailability of 17.7 (Table 2) of chromium in this sediment was at its minimal. The value was lower when compare to another report [34].

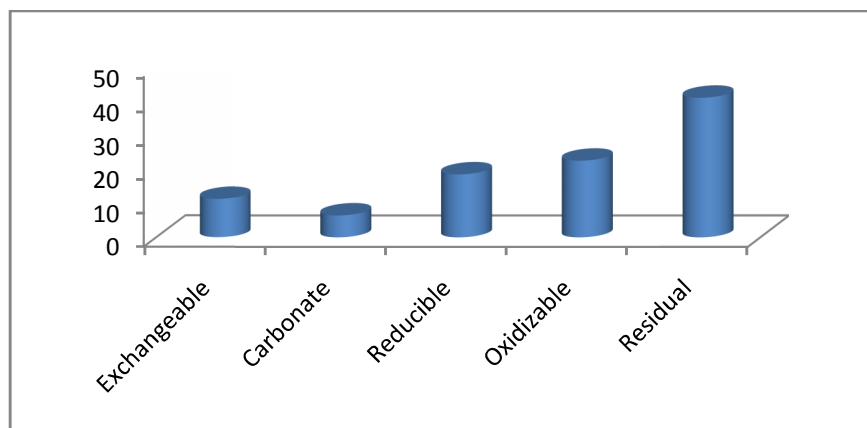


Fig. 8. % occurrence of Cr in the fractions

4. CONCLUSION

The metals investigated were under-saturated with respect to the minerals which could potentially control the metal solubility and liability, hence, their availabilities. Apart from cadmium and copper, trace metals studied were mainly in stable forms and bioavailabilities were extremely low. This signifies that they do not pose immediate environmental threats. The relative predominance of organically complexed metals (except copper and zinc) in this study should be monitored, owing to the fact that decomposition of humic materials may bring about the release of these trace metals into the food chain.

Despite the sharp increase of unleaded fuel utilization, followed by rapid decline of lead levels in the atmosphere, its content (104.6mg/kg) (Table 2) in this area still remain alarming, with a consequence associated risk via the soil-hand-mouth pathway. In accordance to the results of this investigation, it is pertinent that protective measurements (such as proper waste management, phytoremediation) should be embarked upon as soon as possible to prevent metal pollution of this ecosystem in the nearest future.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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