SPECIATION, DISTRIBUTION AND BIOAVAILABILITY OF ESSENTIAL ELEMENTS IN WASTE IMPACTED SOILS WITHIN NIGER DELTA REGION OF NIGERIA

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Abstract
Top soil (0-15cm) samples were collected from six wastes impacted soils and a Control within Akwa Ibom State, Nigeria and assessed for the total contents, different forms and bioavailability of iron (Fe), copper (Cu), chromium (Cr) and zinc (Zn) in the area. Results obtained showed the following ranges (mg/kg) for total elements: 1052.10 – 1664.54 Fe; 1.165 – 9.862 Cu; 1.072 – 1.815 Cr and 29.411 – 51.412 Zn, the distribution of all the elements skewed to the right except Zn. These elements were also found to be below their minimum concentrations recommended by FAO/WHO, thus indicating their deficient status in the area. Speciation results revealed that all the essential elements examined existed mostly in the residual fraction thereby reducing their bioavailability in the study area. Bioavailability of these elements ranged as follows: 14.68 - 16.49% Fe; 8.75 – 21.18% Cu; 15.90 – 18.86% Cr and 17.26 – 19.43% Zn. These results show that copper was the most available element while iron was the least available. BCR speciation results also indicated mean percentage recovery of the elements as Fe (97%); Cu (97%); Cr (86%) and Zn (98%). A standard reference material (SRM 2710a Montana 1 soil) was also analyzed for these elements and results obtained were in agreement with the ones in literature thereby validating results and speciation techniques used in this study. Generally, this research has observed that plants yield and fertility may be seriously affected by the scarcity of these essential elements within the study area.

Keywords: Essential elements, Optimized BCR, speciation, Bioavailability, waste impacted soil and Montana 1soil.

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1. INTRODUCTION

Essential elements are soil nutrients necessary for plant growth which are needed in only very small quantities. They are sometimes referred to as minor elements or trace elements, but the use of micronutrient is encouraged by the American Society of Agronomy and the Soil Science Society of America. According to Stevovi *et al.* (2010) anthropogenic influence on the environment is reflected in the amount of macro- and microelements in soil and plants. A number of studies have shown that chromium is essential for plants and animal including human (Anderson, 2000; Wenk *et al*., 1995; Ott and Kivipelto, 1999; Subiyatno *et al*., 1996). Reports have also shown that iron, copper and zinc are essential elements for plant, animal and human (Nielsen, 1988; Eruvbetine, 2003, Lokeshappa *et al*., 2012, Atukorala and Waidyanatha, 1987). Rakkiyappan *et al.* (2002) reported that some micronutrients' deficiencies in soil is the major factor limiting plant yield. Micronutrients are inorganic substances present in all body tissues and fluids and their presence is necessary for the maintenance of certain physicochemical processes which are essential to life (Eruvbetine, 2003). Every form of living matter requires these inorganic elements or minerals for their normal life processes (Ozcan, 2003). Nevertheless, these essential elements can be toxic when present in excess within an organism (Kabata and Pendia, 1984; Pederson *et al.*, 2002). Minerals in soil are broadly classified into macro and micro elements. The macro elements include calcium, phosphorus, potassium, sodium and chlorine, while the micro-elements include iron, copper, cobalt, magnesium, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium and sulfur (Eruvbetine, 2003). Soil contamination by macro, micro and toxic elements from waste dumpsite has been a major concern due to their toxicity, threat to human life and the environment (Ma and Rao, 1997). Several research works have been conducted on soil contamination by both essential and non-essential elements from different anthropogenic sources including industrial and domestic wastes (Adeniyi and Okedeyi, 2004, Ebong, *et al.*,2008; Udosen *et al*., 2006; Ikem *et al*., 2003;), agricultural practice (Chlopecka *et al*., 1996; Ebong *et al*., 2007a), mining activity (Dudka *et al*., 1995; Kabala and Singh, 2001; Ramos *et al.*, 1994), automobile emissions (Arowolo *et al*., 2000; Ma and Rao 1997; Olajire and Ayodele, 1997). However, most of these works were based on total element evaluation thereby could not indicate the forms of the elements and quantity available for plant uptake. It has been identified that the particular behaviour of trace metals in the environment is determined mostly by their specific physicochemical fractionation and speciation, rather than by their total concentration (Tack and Verloo, 1995; Zaghloul *et al*., 2006).

According to Mench *et al*. (1994) assessing the mobility and availability of elements for plant are very important when evaluating the effect of soil contamination on plant minerals uptake and related phytotoxic effects. Studies have shown that the optimized BCR method of sequential extraction procedures is the most reliable method for examining the toxicity, mobility and fate of metals in soil (Mossop and Davidson, 2003; Quevauviller *et al*., 1996). The modified BCR methods of sequential extraction which operationally classifies metals into four (4) fractions namely: water soluble/carbonate bound/exchangeable fraction (Acid extractable phase), fraction bound to oxides of iron and manganese (reducible phase), fraction bound to organic matter/sulphide (Oxidisable phase) and fraction bound in crystalline soil lattice (Residual phase) was applied in this work.

This research work was carried out in waste impacted soils where the level of these elements may be high enough for sequential extraction, given that previous studies have confirmed higher levels of these elements at dumpsite soils (Udousoro *et al*., 2010; Ebong *et al*., 2008). This study aimed at identifying the distribution pattern, forms and bioavailability of essential elements at waste impacted soils within urban areas of Akwa Ibom State.

2. MATERIALS AND METHODS

2.1 Study Area

This research was carried out in some local government areas of Akwa Ibom State, Niger Delta region of Nigeria. Akwa Ibom State is located in the coastal south-south part of the country, lying between latitudes 4º 32! and 5º 33! North and longitudes 7º 25!   8º 25! East. This research work was done during dry season of the study area using top soil samples from urban waste dumpsites namely: Uyo (007. 56 E and 05.02 N); Abak (007.59 E and 04.59 N); Eket (007.55 E and 04.38 N); Onna (007.51 E and 04.37 N); Ikono (007.06 E and 05.06 N); Ikot Ekpene (007.42 E and 05.11N) (Fig. 1).

2.2 Sample collection, treatment and analysis

Surface soil samples were collected at six (6) urban waste dumpsite soils within Akwa Ibom State, Niger Delta region of Nigeria using soil auger according to the method of Aydinalp (2009) (See Fig. 1). Samples were collected from the different directions of each dumpsite and pooled together to form composite sample for that site (Anake *et al*., 2009). Soil samples were collected between the months of January and April 2011.

These samples were air dried for three (3) days and ground to pass through a 2mm mesh. Concentrations of total microelements (Fe, Cu, Cr and Zn) in the soils were determined using Unicam 939/959 atomic absorption spectrophotometer (AAS) after digestion with Aqua-regia (Ogunfuwokan *et al*., 2009).

The percentage of each fraction of the elements was obtained by dividing that fraction by the sum of all the fractions and multiplies by 100 % (Ajala and Onwukeme, 2012).

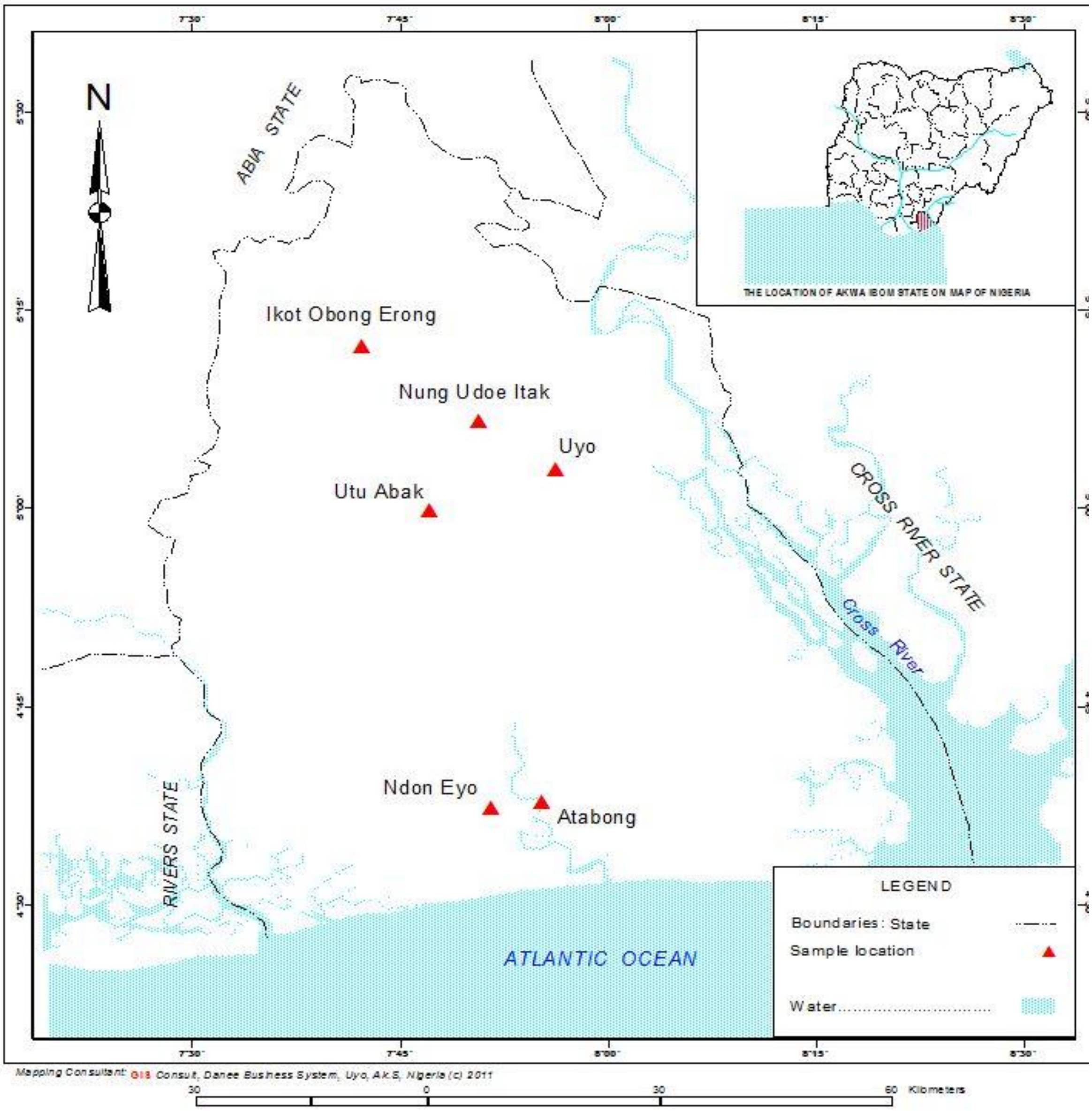

Fig 1 Map of Akwa Ibom State showing sample locations

Percentage bioavailability was calculated according the methods of Adaikpoh (2011) and Omuku *et al*. (2009) using F1/ F1 + F2 + F3 + F4 x 100.
Percentage recovery of each element was obtained by dividing the sum of the fractions of each element by the total concentration of the element and multiply by 100 (F1 + F2 + F3 + F4/Total metal x 100). Where F1 = Acid extractable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction and F4 = Residual fraction.

2.3 Sequential extraction procedures

The optimized BCR sequential extraction procedures described by Umoren *et al*. (2007) was applied for the separation of these elements in soil into acid extractable, reducible, oxidisable and residual fractions as shown below: (i) Acid extractable fraction: 40ml of acetic acid (CH_3COOH) was added to 1g of dry soil sample in a 50ml polypropylene tube. The mixture was shaken overnight (16h) in an end to end mechanical shaker at room temperature. The mixture was centrifuged at 3000rpm for 20mins to separate the extract from residue.

(ii) Reducible fraction: 40ml of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) containing 2.5ml 2M HNO_3 (pH ≈ 1.5), was added to residue from step 1 residue, shaken for 16 h at 22 ± 5°C. the mixture was centrifuged as in step 1.
(iii) Oxidisable fraction: The residue from step two (2) was treated twice with 10ml of hydrogen peroxide (H_2O_2) and allowed to digest for one (1) hour with intermittent manual mixing.
The mixture was evaporated to dryness, then 50ml of 1mole/dm^{3}ammonium acetate (NH_4OAc). Adjusted to pH = 2 with 2M HNO_3 was added shaken for 16h at 22 ± 5°C and centrifuged to separate the extract from residue.
(iv) Residual fraction: to the residue from step three (3), 20ml of aqua- regia solution which was made up of 10ml (1:1) tri-oxonitrate (v) acid (HNO_3) and 25ml of (1:4) HCl was added and digested on a hot plate.

3. RESULTS AND DISCUSSION

Results for the distribution of total iron, copper, chromium and zinc are shown in Table 1; Tables 2-7 give results for the speciation and percentage bioavailability of the elements while Table 8 shows results for validation of the BCR speciation method used.

Table 1 Statistical presentation of total concentration of micronutrients in dumpsite soils between January and April, 2011

	Fe	Cu	Cr	Zn
MIN	1052.10	1.165	1.072	29.441
MAX	1664.54	9.862	1.815	51.412
MEAN	1295.33	5.714	1.329	41.951
MEDIAN	1295.64	5.531	1.279	42.774
SD	164.47	2.995	0.223	5.982
SKEW	0.52	0.01	1.13	–0.43
KURT	0.49	–1.37	0.28	–0.22

3.1 Total concentration of micronutrients

Concentrations of total iron recorded ranged between 1052.10 and 1664.54mg/kg with a mean concentration of 1295.33±164.47mg/kg. The mean concentration recorded in this study is higher than 843.23mg/kg reported at waste contaminated soils in Ngaoundere, Cameroon by Adjia *et al*. (2008). Concentrations of total iron obtained skewed to the right signifying that, Fe relatively recorded few high values. The positive kurtosis obtained furthermore corroborated the peaked distribution exhibited by the element
Copper recorded total concentration ranging from 1.165 to 9.862mg/kg and a mean concentration of 5.714±2.995mg/kg. The range of copper reported in this study is higher than 0.165 – 5.419mg/l recorded in dumpsite soils within Abeokuta, Nigeria by Okeyode and Rufai (2011). Results obtained for Cu in Table 1 show that, its distribution skewed to the right as shown by the positive value of skewness (0.01). Although, kurtosis indicated a negative value of -1.37, it also confirmed a flat distribution pattern of Cu in the study area.
Results in Table 1 also indicate that chromium recorded a range of 1.072 – 1.815 mg/kg and a mean concentration of 1.329±0.223mg/kg. This mean concentration is higher than 0.020mg/kg reported in dumpsite soils within Makurdi Benue State, Nigeria by Luter *et al*. (2011). The distribution of Cr skewed to the right thus most of the values including median lied to the left of the mean. In other words, Cr recorded relatively few high values as confirmed by the positive value of kurtosis obtained.
The distribution of total Zn ranged between 29.411 and 51.412mg/kg in the area studied. Zinc also indicated a mean concentration of 41.951±5.982mg/kg however; this is lower than 954.91mg/kg reported for waste contaminated soils in China by Jie *et al*. (2009). Concentrations of total Zn recorded skewed to the left thus, the bulk of values including median lied to the right of the mean. The negative kurtosis recorded also confirmed a flat distribution with relatively few low values for zinc.Generally, results obtained for total trace elements in this study have shown that despite (i) their requirements for plants and human growth (ii) their anthropogenic supply at dumpsites, their concentrations at waste impacted soils were below their recommended levels (mgkg^{-1}) (100) Cr; (300) Zn; (50,000) Fe and (100) Cu by FAO (2001).

Table 2: Sum concentration (mg/kg) of trace metal fractions in Uyo dumpsite soils.

Metal	F I	%	F II	%	F III	%	F IV	%	Total	% Bio
Fe	873.49	14.86	1448.30	24.63	1137.67	19.35	2420.83	41.17	5880.29	14.86
Cu	4.736	14.98	8.683	27.47	5.773	18.26	12.422	39.29	31.614	14.98
Cr	0.875	16.89	0.861	16.62	1.020	19.69	2.425	46.81	5.181	16.89
Zn	36.986	19.42	48.837	25.64	29.626	15.56	74.995	39.38	190.444	19.42

Table 3: Mean concentration (mg/kg) of trace metal fractions in Abak dumpsite soils.

Metal	F I	%	F II	%	F III	%	F IV	%	Total	% Bio
Fe	905.30	16.49	1435.41	26.14	1105.12	20.13	2045.37	37.25	5491.20	16.49
Cu	5.812	21.18	8.071	29.41	5.181	18.88	8.381	30.54	27.445	21.18
Cr	0.830	16.18	0.846	16.49	0.962	18.75	2.493	48.59	5.131	16.18
Zn	34.493	19.14	49.973	27.73	27.808	15.43	67.924	37.69	180.198	19.14

Table 4: Mean concentration (mg/kg) of trace metal fractions and their % bioavailability in Eket dumpsite soils.

Metal	F I	%	F II	%	F III	%	F IV	%	Total	% Bio
Fe	844.54	15.95	1436.21	27.12	1044.65	19.73	1969.90	37.20	5295.30	15.95
Cu	4.567	15.43	8.596	29.04	5.618	18.98	10.823	36.56	29.604	15.43
Cr	0.750	15.90	0.771	16.35	0.767	16.26	2.428	51.48	4.716	15.90
Zn	31.678	19.43	45.745	28.05	23.565	14.45	62.076	38.07	163.064	19.43

Table 5: Mean concentration (mg/kg) of trace metal fractions in Onna dumpsite soils.

Metal	F I	%	F II	%	F III	%	F IV	%	Total	% Bio
Fe	718.65	14.68	1357.76	27.74	991.25	20.25	1827.47	37.33	4895.13	14.68
Cu	4.016	15.78	7.520	29.56	4.817	18.93	9.090	35.73	25.443	15.78
Cr	0.906	18.86	0.901	18.76	1.000	20.82	1.997	41.57	4.804	18.86
Zn	31.819	19.38	46.017	28.03	24.487	14.92	61.840	37.67	164.163	19.38

Table 6: Mean concentration (mg/kg) of trace metal fractions in Ikono dumpsite soils.

Metal	F I	%	F II	%	F III	%	F IV	%	Total	% Bio
Fe	665.91	14.91	1331.20	29.81	851.32	19.06	1617.27	36.22	4465.70	14.91
Cu	1.839	14.60	3.449	27.38	2.105	16.71	5.202	41.30	12.595	14.60
Cr	0.695	17.38	0.627	15.68	0.644	16.10	2.033	50.84	3.999	17.38
Zn	24.523	17.26	35.15	24.73	17.743	12.49	64.697	45.52	142.113	17.26

It was also noticed that, all the elements recorded their highest concentrations at Uyo dumpsite soil while their lowest concentrations except that of zinc were obtained at Ikot Ekpene dumpsite soil. This maybe attributed to the large size, old age, its location within metropolis and high volume of wastes at Uyo dumpsite (Ebong *et al*., 2007b).

3.2 Sequential extraction of trace elements

The elements were extracted sequentially using the optimized BCR procedures into the four (4) operational fractions namely:(i) Acid Extractable (Aex) which comprises water soluble, exchangeable and carbonate bound fractions (ii) Reducible (Red) (Fraction bound to oxides of iron and manganese (iii) Oxidizable (Ox) (Fraction bound to organic matter and sulphide) and (iv) Residual (Res) (Fraction occluded in the silicate matrix of soil).

Results obtained for speciation of the elements in Tables 2-7 indicate that iron occurred mainly in the residual fraction and it varied between 36.22% and 41.17% at the different locations studied. Iron bound to oxides of iron and manganese (reducible fraction) varied between 24.63% and 29.81% while iron bound to organic matter/sulphide ranged between 19.06% and 20.25% The lowest level of iron was found in the acid extractable fraction with a range of 14.68% — 16.49%. These results signify that iron may not be readily available in the study area since the quantity in acid extractable fraction is relatively low. Similar results were reported by Shivakumar *et al.* (2012) in soils of industrial area in Mysore city, India. However, more iron could be released under oxidizing and reducing conditions of the soil into acid extractable fraction since a higher proportion of the element exist in the mobilizable phase. Generally, the distribution of iron in the different fractions followed the trend: Res > Red > Ox > Aex.

This study revealed that, copper also existed mainly in the residual fraction with a range of 39.29% — 44.15%; this is in agreement with the results recorded by Kim and Kim (2010) in soil of shooting range in Gyeonggi province in Korea and Karathanasis and Pils (2005) in soils of Cincinnati, Kentucky, USA. Copper bound to oxides of iron and manganese (reducible fraction) ranged between 27.38 and 32.37%, the range of copper in acid extractable fraction is 8.75% — 21.18%. The lowest copper concentration was in the fraction bound to organic matter which varied between 14.73 and 18.98% (Table 2-7). Results obtained for speciation of copper followed the order: Res > Red > Aex > Ox.

Speciation analysis of soil samples from the different waste dumpsites indicated that, chromium existed mainly in the inert phase (residual fraction) with a range of 41.57% — 51.48% (Tables 2-7). This is similar to reports by Osakwe (2012) in soils of Onitshia, Anambra State, Nigeria. Oxidizable fraction which followed the residual fraction ranged between 16.10 and 21.29%. Ranges obtained for acid extractable and reducible fractions are 15.90% — 18.86% and 15.68% — 18.81% respectively. These results show that chromium existed mostly in the immobilizable fractions, thus its toxicity may be insignificant within the area due to its low concentration in the readily available/mobile fraction. Trend recorded for the different fractions of chromium followed the order: Res > Ox > Aex > Red.

Results in Tables 2-7 show that zinc too occurred principally in the fraction bound in soil matrix (residual fraction) and ranged from 37.67% to 45.52%. This is in agreement with the findings by Jie *et al.* (2009) in soils of Hunan province of China and Itanna *et al.* (2008) in soils of Kera and Kolfe farms in Addis Ababa, Ethiopia. The next fraction was that bound to carbonate/exchangeable (reducible) with a range of 24.16% — 28.05%. Acid extractable fraction showed a low range of 17.26% — 19.43%, while the lowest fraction of Zn occurred in the fraction bound to organic matter/sulphide which ranged from 11.92% to 15.56%. The order for the distribution of zinc in the four different fractions is similar to that of copper which is Res > Red > Aex > Ox.

Table 7 Mean concentration (mg/kg) of trace metal fractions in Ikot Ekpene dumpsite soils.

Metal	F I	%	F II	%	F III	%	FIV	%	Total	% Bio
Fe	635.30	14.78	1204.62	28.03	822.76	19.14	1635.24	38.05	4297.92	14.78
Cu	0.562	8.75	2.079	32.37	0.946	14.73	2.835	44.15	6.422	8.75
Cr	0.678	17.50	0.729	18.81	0.825	21.29	1.643	42.40	3.875	17.50
Zn	27.744	18.85	35.549	24.16	17.545	11.92	66.324	45.07	147.162	18.85

Table 8 Summary of measured and certified reference trace metal concentrations in SRM 2710a (Montana soil 1)

Element	Certified value ± SD	Measured mean value ± SD	Recovery (%)
Cr	CNA	CNA	CNA
Cu (mg/kg)	3420 ± 50	3230 ± 46.7	94
Fe (%)	4.32 ± 0.08	3.58 ± 0.04	83
Zn (mg/kg)	4180 ± 20	3921 ± 23.82	94

Source: Gaithersburg *et al*. (2003), CNA = Certified value not available.

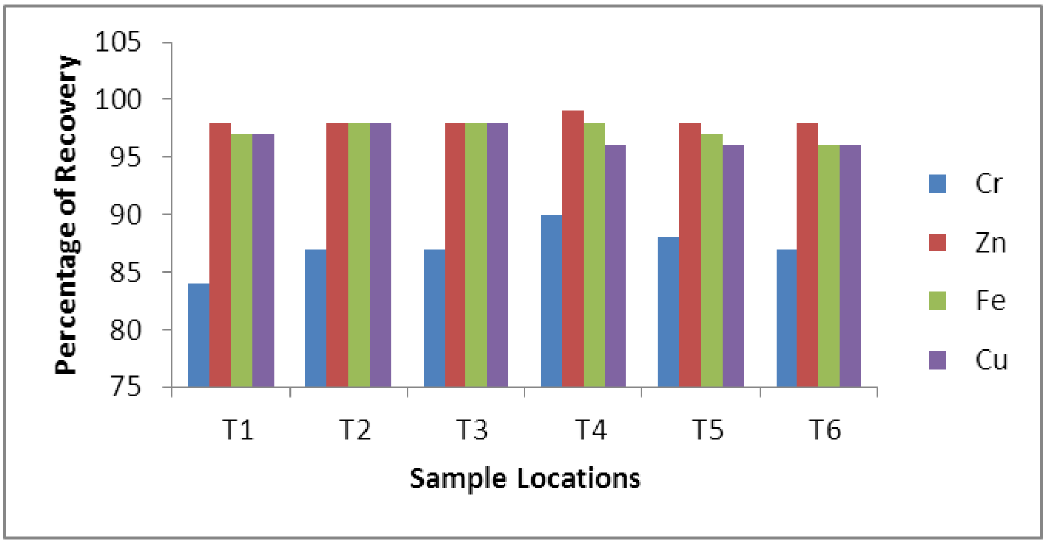

Fig. 2. Percentage Recovery of the elements from dumpsite soils

It is evident from these results that zinc existed mostly in the mobilizable fractions thus reducing and oxidizing conditions of the soil may elevate the mobile phase of the element. Consequently, since these elements are essential for proper plants and animal growth supplementary sources may be sought for and applied in soil within the area.

3.3. Percentage bioavailability of microelements in waste dumpsite soils

The percentage of microelements readily available for plant uptake is referred to as their bioavailability (Brezonik *et al*., 1991). Results in Tables 2-7 give the percentage bioavailability of each micro element at each waste dumpsite soil studied. These results show that, the percentage bioavailability of iron ranged between 14.68% and 16.49%. The highest % bioavailability of iron was recorded in Abak dumpsite soil while the lowest was in Uyo dumpsite soil. Bioavailability of copper in the study area ranged between 8.75% in Ikot Ekpene dumpsite soil and 21.18% in Abak dumpsite soil. A range of 15.90% —18.86% was obtained for chromium bioavailability potentials in dumpsite soils studied, Eket dumpsite soil recorded the lowest % bioavailability while Onna dumpsite soil showed the bioavailability potential of chromium. Zinc recorded the highest bioavailability potential (19.43%) at Eket dumpsite soil while its lowest bioavailability rate (17.26%) was found at Ikono dumpsite soil. Trend for the general results followed the order: copper > zinc > chromium > iron, showing that zinc was more available than other elements while copper was the least available element. These findings have confirmed that, the bioavailability of an element in soil is not solely dependent upon its total concentration as opined by Peijnenburg *et al*. (2000). Consequently, this study has shown that the proportion of these elements available for plant uptake was very low and this may affect plant yield. This maybe attributed to the existence of these elements mainly in the residual fraction which is almost inert to soil dynamics.

3.4. Validation of optimized BCR sequential extraction procedures used and results obtained

Standard reference material SRM 2710a (Montana 1 soil) from National Institute of Standards and Technology, USA was used as the standard material for the validation of sequential extraction method employed and results obtained from soil samples collected. Iron, copper, chromium and zinc were extracted sequentially based on the Optimized BCR sequential extraction procedures were applied for the extraction of iron, copper, chromium and zinc in SRM 2710a soil. On comparing results obtained to the results in literature (certified results), the values obtained in this study were in excellent agreement with the certified concentrations of these elements (Table 8). Results in Fig. 2 show the percentage recovery of elements using the modified BCR procedures and results recorded indicate the mean percentage recovery of the elements as Fe(97%); Cu(97%); Cr(86%) and Zn(98%) indicating high level of accuracy and precision in the analytical techniques used and validity of results obtained.

4. CONCLUSION

It could be inferred from this study that, the existence of these essential elements mainly in residual phase greatly affected their availability for plant uptake. Thus improved plant and animal yield maybe achieved by the application of artificial sources of these elements to soils within the study area.

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