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Evaluation of Total Concentrations and Extractable Fractionations of Cd, Co and Ni in Soils from Dumpsites across Rivers State, Nigeria

***ODUAH, RN; AMAIBI, PM; KONNE, JL; BOISA, N**

Department of Chemistry, Rivers State University, Nkpolu-Oroworukwo, Port Harcourt, Nigeria

**Corresponding Author Email: oduahrita@gmail.com*
Co-Authors Email: oduahrita@gmail.com; atrik2k7@yahoo.com; konne.joshua@ust.edu.ng; talk2boisa@yahoo.com

ABSTRACT: The mobility of trace metals in soils strongly depends on the forms in which the metals are bound to major soil components. This study aims to determine the total concentrations and extractable fractionations of Cd, Co and Ni in soil samples collected from dumpsites across Rivers State, Nigeria. Solar Thermo Elemental Atomic Absorption Spectrometer model (SG 71906) was used after mixed acid digestion (HCl: HNO_3 in a ratio of 3:1 v/v) and modified BCR sequential extraction procedure. The concentration levels of Cd, Co and Ni in all the samples varied, with mean values of 13.48 ±11.85, 25.29 ± 17.62 and 20.52 ±15.66 mg/kg, respectively. Using the Community Bureau of Reference (BCR) sequential extraction procedure, the elements recoveries were within the acceptable range varying between 92.10% and 98.33% for Co and Cd, respectively. Data from the BCR extraction procedure revealed that the majority of Cd fraction was associated with residual fraction, Co fraction bound to the exchangeable fraction, while Ni was found to be associated with oxidisable fraction. These results suggest that the trace elements in the soil were highly mobile and bioavailable for plant uptake. Results from the findings particularly correlation analysis is indicative of the fact that some of the contaminants may have anthropogenic and natural origin. Hence, these contaminants could pose significant threat to human health and the environment.

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Dumpsite is a waste disposal land area in which the soil, underground and surface water as well as edible crops are potentially exposed to toxic chemicals including trace metals released into the environment. For example, trace metals (cadmium, cobalt and nickel) can leach from one point to another thereby posing severe threat to human health and the ecosystem ((McLaughlin *et al.*, 2000; Ling *et al.*, 2007). When the concentration of these toxic elements exceeds permissible limits it raises an environmental concern for further investigation. Total content of soil elements may be insufficient to assess the potential risks and mobility of the elements depending on their binding forms (Davutluoglu *et al.*, 2011; Nemati *et al.*, 2011). In the soil environment, trace metals occur in various geochemical forms commonly associated with their mobility and bioavailability (Rieuwerts, 2007; Romic *et al.*, 2001). These chemical forms can be bound to organic component, iron-manganese oxides, carbonates and the exchangeable fractions. The carbonate and exchangeable forms are considered as most bioavailable and water soluble. Whilst, the reducible form bound to the Fe-Mn oxides and the oxidisable form bound to soil organic matter are all bioavailable but the residual fraction strongly bound to the soil matrix is not available for plant uptake (Kabata-Pendias, 2004; Tessier *et al.*, 1979). Recently, a major focus is the use of selective sequential extraction to designate operationally defined fractions of trace elements in soil matrix (Rauret *et al.*, 1999). There is a growing concern on specific use of reagents in sequential extraction procedures. The traditionally Tessier method has been extensively studied to fractionate trace metals into five chemical forms in soils and sediments (Wang et al., 2022). This method suffered few drawbacks mainly due to the inability of some reagents to remove elements of interest from major mineral phases. It is thus necessary to adopt a more efficient method as an alternative approach since the previous method failed to identify targeted phases

**Corresponding Author Email: oduahrita@gmail.com*

and required a number of reagents for the extraction steps. The Community Bureau of Reference of the Commission of the European Communities (BCR) was developed by simplifying the sequential extraction process into three-stage protocol. The extraction scheme targets the chemical processes rather than the mineralogical phases present in the soil (Li et al., 2010). In BCR extraction method, there is availability of a certified reference material (CRM) to standardize and validate the method. An additional step (*aqua regia* digestion of residue from step 3) has been introduced for quality control purposes. This step (the residual fraction) is used to determine the element recoveries and effectiveness of the scheme.

The residual fraction including the sum of the other three steps are compared to the soil total content (pseudo-total content) of elements. However, the performance of this method is still limited to certain soil properties. Although, a number of researchers have attempted to adapt this method to different reference materials, soil types and sediments but more work is needed (Rauret *et al.,* 1999).

Hence, there is a need for further study of selected trace elements (cadmium, cobalt and nickel) found in soils mainly across dumpsites in Rivers State, Nigeria. The objective of this study therefore is to evaluate total concentrations and extractable fractionations of Cd, Co and Ni in soils collected from dumpsites across Rivers State, Nigeria.

MATERIALS AND METHODS

Apparatus and reagents: All of the chemicals used including acetic acid, hydroxylamine chloride, nitric acid, hydrogen peroxide, hydrochloric acid and Ammonium acetate were of high analytical grade and were obtained from Med-Lab Scientific Enterprises, Port Harcourt, Rivers State. For the purposes of quality control, certified reference material (BCR 143R) was purchased (the European Commission of Joint Research Centre) and analysed along with the soil samples to determine trace metal content using flame atomic absorption spectrometer (Solar Thermo Elemental Atomic Absorption Spectrometer model SG 71906).

*Study area and sampling**:*** Soil samples used in this study were collected from dumpsites located in Rivers State, Nigeria. A total of 50 samples were taken randomly from selected locations around historic and currently used dumpsites. The sampling locations were chosen to assess the potential sources of soil contamination. The study area under investigation covers 20 different sites between the coordinate of 4^{o} 45' N and 6^{0} 50' E as shown in Figure 1.

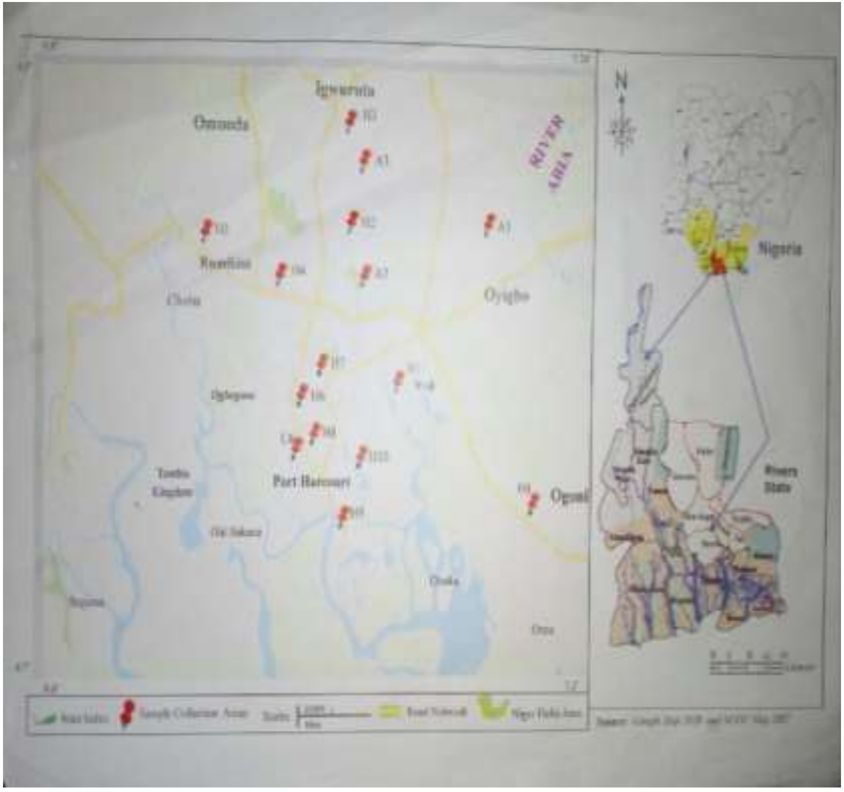


Fig.1: Map of Rivers State showing sampling locations
Source: Research Field Survey, ODUAH, R.N. 2018.

Table. 1: Reagents used for the modified BCR-SES procedure

Stage	Reagent	Fraction	Targeted phase
1	0.11 mol/L acetic acid solution	Exchangeable	Water soluble, exchangeable cations and carbonates
2	0.5 mol/L hydroxylammonium chloride at pH 1.5 (with HNO_3)	Reducible	Iron and manganese oxides
3	H_2O_2 (85 °C) then followed by 1.0 mol/L ammonium acetate at pH 2	Oxidisable	Sulphides and organic matter
4	*Aqua regia*	Residual	Crystalline silicates

N/B: Stage 4 (Aqua regia) was not officially part of the BCR-SES procedure.

Preparation of soil samples: Soil samples were collected from dumpsites, a control sample was taken from 100 m away from the dumpsite location. Samples were air dried and passed through 2 mm mesh sieve prior to further analyses. A Soil-water ratio of 1:2.5 (w/v) suspension was prepared to determine soil pH using a pH meter. To determine soil electrical conductivity (EC), a soil suspension was subjected to mechanical shaker for 1 h at 15 rpm and filtered to collect the supernatant. The supernatant was analysed using a conductivity meter probe. The amount of phosphorus in the soil was measured according to the method described previously by Bray and Kurtz No. 1 method (Olsen and Sommers, 1982). For determination of soil organic carbon, 1 g of each sample was accurately weighed into a 500 mL Erlenmeyer flask, then 10 mL $K_2Cr_2O_7$ (1 M) and 20 mL of concentrated H_2SO_4 was added as described by the modified Walkley and Black method (Nelson and Sommers, 1982). For soil particle size analysis, the detailed procedure as presented elsewhere (Bouyoucos, 1951) was adopted. Nitrogen content in each of the samples was determined by kjeldahl digestion method following the procedure described by US EPA (2001).

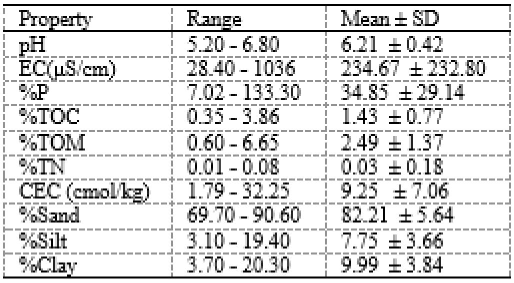
Soil digestion procedure: Soil samples were treated with *aqua regia* (HCl: HNO_3 in a ratio of 3:1 v/v) followed by microwave assisted digestion. To prepare the soil extract prior to FAAS analysis, each soil sample (0.5 g) was accurately weighed (in triplicate) into a Teflon vessel pre-cleaned with 10% HNO_3 solution. Then, 13 mL of *aqua regia* was added to the sample in a fume hood (USEPA, 1996). For analysis of the samples, aliquots of the soil extracts, blanks and calibration solutions were prepared prior to determination of the total concentration of the elements. All elemental concentrations were reported as mg/kg, dry weight.

Modified BCR sequential extraction procedure: A sequential extraction approach developed by the Community Bureau of Reference (BCR) was adopted due to the availability of the chemical reagents. A total of 10 sub-samples (< 2 mm fraction) were subjected to different chemical regents according to the modified BCR-SES protocol (Rauret et al., 1999). A certified reference material (BCR 143R) was applied to evaluate the method. This was done by analysis of the CRM along with the test samples using the same procedure. The reagents used in each stage of the extraction to release trace metals associated with the targeted mineral phase are presented in Table 1: The summary of BCR method performed in this study was adopted from Rauret et al. (1999). *Statistical analysis:* The data sets from the results obtained were suggested to statistical analysis using the Minitab statistical package version 18. The analyses performed include: descriptive statistics and Pearson correlation.

RESULTS AND DISCUSSION

Characterization of soil: Physicochemical properties of the soil samples including pH, SOM, CEC and soil texture were performed according to standard methods. Results obtained from the analyses are shown in Table 2. The soil pH varied from 5.20 to 6.80 with a mean value of 6.21. Electrical conductivity of the soil was between 28.40 and 1036 µS/cm while the SOM varied between 0.60 and 6.65%. Particle size distribution indicated sand, silt and clay content ranging from 69.70-90.60%, 3.10 – 19.40% and 3.70 – 20.30%, respectively.

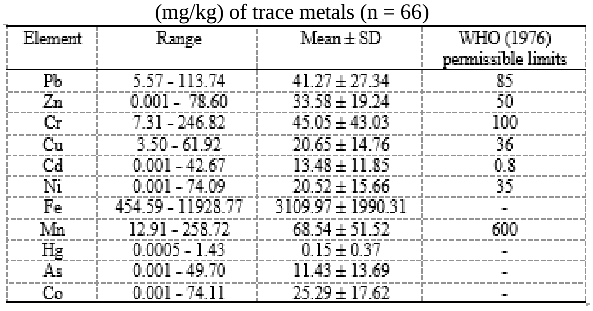
Table 2: Descriptive statistics of physicochemical properties of soil samples (n = 66)



Property	Range	Mean ± SD
pH	5.20 - 6.80	6.21 ± 0.42
EC(µS/cm)	28.40 - 1036	234.67 ± 232.80
%P	7.02 - 133.30	34.85 ± 29.14
%TOC	0.35 - 3.86	1.43 ± 0.77
%TOM	0.60 - 6.65	2.49 ± 1.37
%TN	0.01 - 0.08	0.03 ± 0.18
CEC (cmol/kg)	1.79 - 32.25	9.25 ± 7.06
%Sand	69.70 - 90.60	82.21 ± 5.64
%Silt	3.10 - 19.40	7.75 ± 3.66
%Clay	3.70 - 20.30	9.99 ± 3.84

Pseudo-total concentration of trace metals: The mean values of the trace metals were 41.27, 33.58, 45.05, 20.65, 13.48, 20.52, 11.43 and 25.29 mg/kg for Pb, Zn, Cr, Cu, Cd, Ni, As and Co, respectively. Cr soil content appeared to be highest in all the samples, although, the concentrations of the elements were low with As having the lowest value (Table 3).

Table 3: Statistical summary of pseudo-total concentration (mg/kg) of trace metals (n = 66)



Element	Range	Mean ± SD	WHO (1976) permissible limits
Pb	5.57 - 113.74	41.27 ± 27.34	85
Zn	0.001 - 78.60	33.58 ± 19.24	50
Cr	7.31 - 246.82	45.05 ± 43.03	100
Cu	3.50 - 61.92	20.65 ± 14.76	36
Cd	0.001 - 42.67	13.48 ± 11.85	0.8
Ni	0.001 - 74.09	20.52 ± 15.66	35
Fe	454.59 - 11928.77	3109.97 ± 1990.31	-
Mn	12.91 - 258.72	68.54 ± 51.52	600
Hg	0.0005 - 1.43	0.15 ± 0.37	-
As	0.001 - 49.70	11.43 ± 13.69	-
Co	0.001 - 74.11	25.29 ± 17.62	-

Table 4: Pearson Correlation Matrix for dumpsite soil samples

	Clay	*Silt*	*Sand*	*OC*	*CEC*	*pH*	*Pb*	*Zn*	*Cr*	*Cu*	*Cd*	*Ni*	*Fe*	*Mn*	*Hg*	*As*	*Co*
Clay	1																
Silt	-0.453	1															
Sand	**-0.799**	-0.169	1														
OC	**-0.774**	**0.627**	0.399	1													
CEC	**-0.736**	**0.774**	0.296	**0.829**	1												
pH	-0.403	0.0448	0.409	0.169	0.127	1											
Pb	0.412	-0.005	-0.462	-0.020	0.099	-0.102	1										
Zn	-0.162	**-0.639**	0.579	0.005	-0.284	0.554	-0.056	1									
Cr	-0.175	-0.495	0.511	-0.066	-0.310	0.467	-0.496	**0.734**	1								
Cu	-0.315	-0.108	0.384	0.293	0.120	**0.638**	-0.0178	**0.708**	**0.628**	1							
Cd	0.573	0.038	**-0.690**	-0.053	-0.066	-0.173	0.600	-0.078	-0.089	0.217	1						
Ni	-0.360	-0.35	**0.655**	-0.183	-0.151	0.504	**-0.635**	0.438	0.496	0.171	**-0.663**	1					
Fe	0.184	-0.368	-0.015	0.186	-0.137	0.241	0.452	**0.614**	0.260	0.533	0.534	-0.128	1				
Mn	-0.151	-0.244	0.324	0.110	0.183	**0.640**	0.419	0.588	0.223	0.568	0.144	0.319	**0.610**	1			
Hg	0.172	-0.403	0.099	-0.260	-0.219	-0.466	-0.184	-0.007	0.401	-0.089	0.046	-0.071	-0.193	-0.269	1		
As	-0.532	0.173	0.459	0.490	0.585	0.534	0.197	0.394	0.114	**0.707**	0.054	0.231	0.388	**0.781**	-0.316	1	
Co	0.539	-0.169	-0.492	-0.209	-0.128	-0.230	0.414	-0.021	0.171	0.240	**0.867**	-0.469	0.367	0.149	0.485	0.039	1

Correlation between total concentrations and soil properties: The relationship between total concentration of trace metals and the soil properties was investigated by calculating the Pearson correlation coefficient as shown in Table 4. Pearson correlation result indicated that a strong association exists between CEC and OC (R = 0.829) which may be due to an enriched organic surface fraction of the soil. The influence of this association has been observed in the positive correlation between Cd and Pb, Cr and Zn, Cr and Fe, As and Cu, Co and Mn bound fraction. However, six elements including Cd, Pb, Cr, Zn, As and Cu reflect the anthropogenic activities on the study sites (Lv et al., 2015; Agbaire and Akporhonor, 2014; Kedir *et al.,* 2017). In this study, the results showed that Cd was strongly associated with Co (R = 0.867), therefore, increase in Cd increases the Co content in the soil. From the correlation matrix, Cd and Ni have a strong negative association (R = - 0.663) suggesting the both elements may influence each other. A similar association exists between Cr/Zn and As/Cu found in the soil. Although, the present of Fe and Mn bound trace elements may be found in the soil, such associations could be commonly attributed to natural sources from the soil profile (Table 4). The association of Zn/Fe and As/Mn may likely be due to the presence of natural minerals found in the soil. Earlier reports confirmed that anthropogenic activities may be the cause of a strong correlation between Cd, Cr, As and Pb, Zn, Cu, respectively (Li *et al*; 2010; Lv *et al;* 2015). At low soil pH, permanently charged sites are created to adsorb soil trace elements for ion exchange reactions. The interaction of trace elements forms complexes on a mineral surface (Rieuwerts *et al.,* 1998). The results from the correlation analysis suggest that trace elements interact with each other and could be relatively mobile along the soil profiles (Jena *et al;* 2013; Kedir *et al;* 2017).

Fractionation of Cd, Co and Ni using sequential extraction: A mass balance approached was applied by considering the sum of four fractions (including the residual fraction) and compared to the pseudo-total concentration of the elements studied as presented in Table 5. Results of the recoveries for the elements of interest ranged from 17.60%, 92.10%, and 98.33% for Ni, Co, and Cd, respectively. These values except for Ni were all within the accepted limit. It was observed that Cd remained less extractable as illustrated in Figure 2. This result supports the findings of Rinklebe and Shaheen (2014). The elements differed considerably in terms of the extractable amount from various fractions of the BCR extraction.

Table 5: Validation of BCR method for chemical speciation study

Trace metal	Certified total (BCR 143R)	Measured total (mg/kg) (n = 3)	Mass recovery (%)
Ni	296.00 ± 4.0	52.03 ± 1.28	17.60
Co	12.30 ± 0.30	11.33 ± 2.35	92.10
Cd	72.00 ± 1.80	70.80 ± 1.17	98.33

The distribution of Cd in different fractions showed that Cd was dominant in the residual fraction (Figure 2). These results imply that Cd found in the soil may not be mobile and bioavailable for plant uptake.

A positive correlation between Cd and Co also indicated that both elements may be similar in terms of its mobility in the soil. In the exchangeable fraction, the lowest Cd extractable amount (3%) was observed, which implies that the contaminant cannot be leached outside the dumpsites. In contrast, Cd was found to be relatively mobile in tropical soils conducted by previous studies (Mbila *et al.*, 2001; Madyiwa *et al.*, 2002). In the residual fraction, the highest amount of Cd (82%) was obtained due to strong interaction within the mineral phase. A relatively high Co content (51%) extracted from the soils was found in the exchangeable fraction (Figure 3). Exchangeable fraction is an acid soluble fraction of the metal that can be readily leached across the soil. Trace metals released in this fraction are loosely adsorbed on different solid-phases in soil. The results indicate that Co released in the reducible fraction was next to the exchangeable fraction.

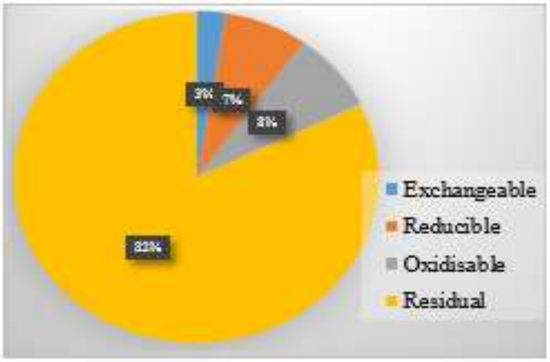


Fig 2: Percentage Concentration of Cadmium in Different Geochemical Fractions

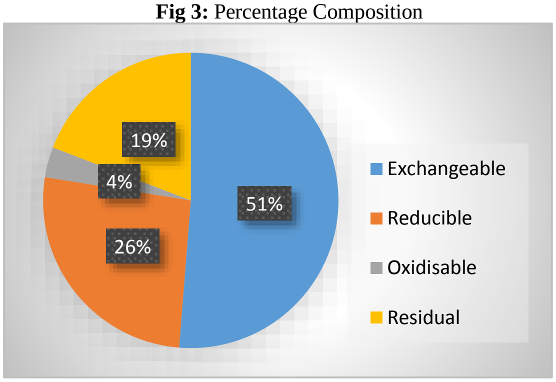


Fig 3: Percentage Composition of Cobalt in Different Geochemical Fractions

The amount of Co found in each fraction decreases as follows: exchangeable > reducible > residual > oxidisable fraction. In the reducible fraction, the Co species may have been typically bound to Fe and Mn oxides as solid-phases present in the soil. This result is in line with previously conducted study on industrially contaminated soil samples (Van Herreweghe *et al.*, 2002). Figure 4 showed that high proportion of Ni (76%) was extracted in oxidisable fraction compared to other fractions. The oxidisable fraction is mostly associated with organic matter and sulphur contents in the soil environment The results showed decrease in amount of Ni released from the extraction scheme in the following order: oxidisable > residual > reducible> exchangeable. The amount of Ni (8%) in the exchangeable fraction appeared to be smaller than in other fractions, similar to results reported previously for agricultural field samples by Sungur *et al*. (2015). The highest Ni content found in oxidisable fraction indicated that Ni can be possibly transferred into the food chain through plant uptake. (Tokalioglu *et al.*, 2003). Mobility of trace metals in soil is influenced by soil pH, organic matter content and solid minerals in which the conditions may vary depending on the metal species.

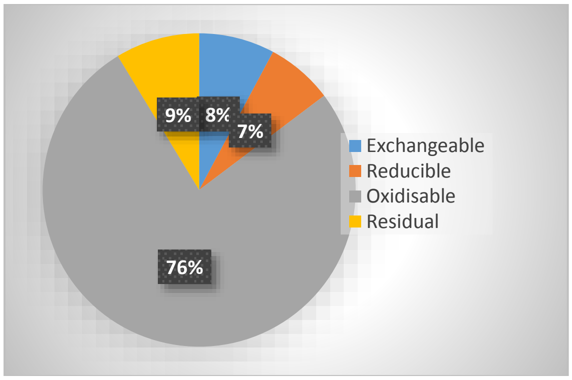


Fig 4: Percentage Composition of Nickel in Different Geochemical Fractions

Conclusion: The soil samples from the dumpsites yielded varying results for Cd, Co and Ni in each of the solid-phase fractions. The soil Ni contents were found in the following fractions: oxidisable > residual > reducible> exchangeable. The highest Ni content in the oxidisable fraction suggests that this element may be available for plant uptake.

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