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The Assessment of Forms and Bioavailability of Copper, Chromium, and Cadmium in Soils of Automobile Workshops using Sequential Extraction Procedure

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Abstract

The quantification the exact dimension of heavy metals pollution in soils requires more data than the total contents of metals in soils. The determination of different fractions (speciation) is necessary to understand the mobility and bio-availability of the metals in soils. This paper presents results of speciation of copper (Cu), chromium (Cr), and cadmium (Cd) in soils of ten automobile workshops in Sapele, Nigeria. Composite soils samples were taken from depth 0 – 60cm, and geochemical forms and total concentrations of the metals (Cu, Cr & Cd) in soils were determined by sequential extraction procedures and atomic absorption spectrometry. The total concentrations range of: 39.10 – 129.80mg/kgCu, 11.55 – 40.10mg/kgCr, and 3.15 – 6.28mg/kgCd obtained for the soils in the vicinities of the automobile workshops were distinctly higher than that of the control indicating enrichment of these metals in these soils. Speciation revealed that 20 – 33% Cu, 19 – 27% Cr and 25 – 45% Cd, were potentially mobile and bio-available.

Keywords: sequential extraction, bio-availability, heavy metals, soils, automobile workshops

1. Introduction

Metal can be toxic to plants and animals population at sufficiently high concentration. Generally, toxic metals cause enzymes inactivation, damage cells by acting as anti-metabolites or form precipitates or chelates with essential metabolites(Ademoroti, 1996; Igwe and Abia, 2006).The overall effects usually show up in form of: loss of ecosystem and agricultural productivity, diminished food chain quality, tainted water resources, economic loss, human and animal illness. Unlike organic contaminants, most heavy metals in soil environment do not undergo microbial or chemical degradation and therefore total concentrations and eco-toxicological effects persist for a long time after their introduction (Zhou and Haynes, 2010). Source of heavy metals pollution includes natural and anthropogenic activities. Anthropogenic sources include; mining, smelting, fossil fuel combustion, wastes disposal, and agricultural practices (He *et al.,* 2015). Automobile workshops activities is becoming a growing source of heavy metals pollution in most Nigerian cities because, the increasing inflow of used automobiles into Nigerian market has also resulted increase in automobile repairs and workshops activities in most Nigerian cities. Activities carried out in these workshops may include: servicing and overhauling of vehicles engines, electrical repairs and recharging of car batteries, welding, soldering and panel beating, painting, tire vulcanizing, open-air burning of condemned tires etc. During these activities, wastes (such as spent oils, metals scraps, used batteries, asbestos etc) are generated which contain among other pollutants heavy metals. A precise knowledge of the forms of heavy metals in soils (and not just their total concentrations) is required to define the extent of their negative impact on the ecosystem.

Total amount of heavy metals, though a useful index in quantification of the degree and extent of metal contaminations, it furnish little or no information on mobility and bioavailability of the metals in the soils. It is thus, limited in providing exact dimension of pollution. The use of total heavy metals alone, suggest that all forms of a given metals have an equal impact on the environment; thus, data on total contents of metals are quit insufficient to estimate the possible risk of remobilization of total metals under changing conditions and potential uptake of liberated metals by biota and as such the determination of different fractions (speciation) assume great importance (Sarka *et al.,* 2012). Metal fractionation (speciation) is a process of separating soils, sediments and soil component into operationally defined fractions in the assessment of contamination (Asagba *et al;* 2007). Metals may be distributed among many components of soil solids and may be associated with them in different ways and their mobility and availability in the soils is a function of their association (Rieuwerts *et al*., 1998; Kabata-Pendias and Pendias, 2001; Eggleton and Thomas, 2005). Water soluble and exchangeable forms are considered readily mobile and available to plants; while metals incorporated into crystallize lattices of clay appear relatively inactive. The other forms – precipitated as carbonate, occluded in Fe, Mn and Al oxides or complexed with organic matter could be considered relatively active or firmly bound depending upon the combination of physical and chemical properties of soil (Kabala and Singh 2001; Haung *et al*., 2007). The study of speciation is important in understanding how heavy metals are retained in different components hence, their mobility, solubility, bioavailability, and ultimate impacts of contaminants on the environment. The pH, soil texture (clay type and contents), organic matter, and Fe- Mn oxides have been found as important properties and components influencing the mobility and bioavailability of heavy metals in soils (Narwal and Singh, 1998;

Karsczewska *et al*., 1998; Rieuwerts *et al*., 1998; Sarkar *et al*., 2012).

The assessments of metals forms, especially using sequential extraction have largely involve surface soils (0-15cm) (He and Singh, 1995; Ma and Rao, 1997; Chlopecka *et al*., 1998; Ahumada *et al*., 1999; Oviasogie and Ndiokwere, 2008), studies of contaminated areas however; require that the whole soil profile including subsurface horizon be considered. Previous study on the speciation and potential bioavailability of metals at depth 0-60cm in soils of automobile workshops by Chokor (2017), investigated Zn, Mn and Pb in the soils. In this study however the focus is on Cu, Cr, and Cd in the soils. Thus the objectives of this study are to:

- examine the distribution and chemical fractions of Cu, Cr, and Cd, in the soil profile (depth: 0 – 60cm).
- evaluate the mobility and bioavailability of the metals and the degree of contamination in the different soils.
- investigate the relationship between soils' physicochemical properties and the chemical fractions of the heavy metals in the soils.

2. Methodology

2.1 Study area and site location

The study was conducted on soils from ten mechanic workshops sites located in Sapele, Nigeria. Viz: - Ogodo (N05°53.996'E005°40.290'), McPherson (N05°53.746'E005°40.129'), Reclamation (N05°53.384'E005°40.633'), Okpe Road (N05°53.384'E005°40.924), and Oleh (N05°53.204'E005°40.971'), Akintola (N05°53.421'E005°41.184), Ajogodo (N05°53.952'E005°41.779'), Gana-New Road (N05°54.701'E005°45.025'), Shell Road (N05°52.102'E005°41.632'), Okirigwre (N05°52.102'E005°42.528').

2.2. Sample Collection

Mechanic workshops in the metropolis were chosen with ages of establishment over seven years, obtained by personal communication with artisans working on these sites. No waste management practice is done on these workshops. Composite soil samples were collected at depths 0-60cm from ten (10) different mechanic workshops using standard soil (hand) auger. Sample of uncontaminated soil were obtained in similar manner from Ubeyiyi - a nearby virgin land (N05°52.847'E005°42.528') in the metropolis to serve as control. The collected samples were transferred into a black polythene bag, properly labeled and transported to the laboratory.

2.3. Preparation and analysis of Samples

The samples were air-dried for a period of two weeks in a well ventilated space. A good representative was obtained using quartering method. The dried representative soil samples were crushed in porcelain mortal and sieved through 2mm (10 mesh) stainless sieve prior to analysis. The physicochemical properties of the samples were determined according to the standard methods. Soil pH was determined in water according to the method of Folson *et al* (1981), Organic Carbon (by dichromate oxidation) as described by Nelson and Sommers (1982). Available phosphorus was estimated following the procedures described by Olsen and Sommers (1982), while the ammonium acetate method was used to determine the Cation Exchange Capacity (CEC) as specified by Nottidge *et al* (1995). The particle size distribution (PSD) analysis of soil was carried out by the hydrometer method with Sodium hexametaphosphate as dispersing agent (Gee and Or, 2002).

The procedure of Salbu *et al* (1998) was used to fractionate soil samples into six operationally defined fractions: reversibly physically sorbed as (F1) water extractable (water – soluble metals); (F2) extractable with 1M NH_4OAc at pH 7 (exchangeable); (F3) extractable with 1M NH_4OAc at pH 5 (specifically sorbed and carbonate bound); (F4) extractable with hydroxylamine (metals associated (sorbed or occluded) mainly on iron and manganese oxides); (F5) extractable with H_2O_2 in 1 M HNO_3 (strongly complexed by organic matter) and (F6) residual extracted with a mixture of HNO_3 and $HClO_4$ acid. Two grams of soil was weighed and placed in a 100ml polypropylene bottle. The following extractions were made sequentially (Salbu *et al*, 1998).

F1: Sample was extracted with 20ml of deionized water for 1hr (20°C); F2: The residue from [F1] was extracted with 20ml of 1M NH_4OAc, pH.7 for 2hrs; F3: The residue from [F2] was extracted with 20ml of 1M NH_4OAc, pH 5 for 2hrs; F4: The residue from [F3] was extracted with 20ml of 0.04M $NH_2OH.HCl$ in 25% HOAc for 6hrs (water bath, 60° C); F5: The residue from [F4] was extracted with 15ml of 30% H_2O_2 at pH.2 (Adjusted with HNO_3) for 5hrs 30mins (water bath 80°C) after cooling 5ml of 3.2M NH_4OAc in 20% of HNO_3 was added; sample was shaken for 30 minutes and finally diluted to 20ml with water; F6: One gram of the residue [F5] after drying was digested in a conical flask with 5ml of HNO_3 and 1ml of $HClO_4$ acids on a hot plate for six hrs. After evaporation, 1ml of 2M HNO_3 was added and the residue after dissolution was diluted to 100ml.

All the solid phases (with exception of F6) were washed with 10ml of distilled water before the next extraction step. The washes were collected and analyzed with supernatant from the previous fraction. After each extraction, supernatant were separated by filtration (using Whatman No 1 Filter Paper). To verify the sum of sequential extractions the total concentration of Cu, Cr and Cd were determined after digestion with a mixture of

5ml of nitric and 1ml of perchloric acids. Atomic absorption spectrophotometer (Model 210 VGP) was then used to determine the concentration of heavy metals in the extract.

The analyses were carried out in triplicates and the results are expressed as mean and standard deviation from the mean (±). The mobility of the metal in soil was calculated as mobility factor (MF) (Salbu *et al;* 1998; Narwal *et al*, 1999) on the basis of the following equation:

$$MF = \frac{(F1 + F2 + F3)}{(F1 + F2 + F3 + F4 + F5 + F6)} \text{ X } 100$$

Since some metals forms (extracted in F3) are relatively less mobile (more strongly bound to the soil component than those extracted in F1 and F2, the above mentioned index describes the potential bioavailability/mobility (Salbu *et al*, 1998).

3. Results and Discussion

3.1 Physicochemical properties of the soils

The detail physicochemical properties of the soils have been discussed in earlier works by Chokor (2017). This presentation shows only the ranges and mean of the various parameters (Table 1). The soils were sandy-loam with moderately acidic character.

Table 1: The range and mean of some physicochemical properties of soil samples from the automobile Workshops and control (CT)

Parameter	Range	Mean	Control(CT)
pH	5.09 – 6.39	5.701 ±0.39	6.20 ±0.02
Clay(%)	1.40 – 10.40	6.80 ±3.04	10.40 ±1.00
Silt(%)	4.50 – 10.00	7.45 ±2.36	8.50 ±1.20
Sand(%)	80.10 – 93.10	85.75 ±4.84	81.10 ±3.00
TOC(%)	0.07 – 1.28	0.472 ±0.35	0.06 ±0.01
OM(%)	0.12 – 2 21	0.816 ±0.60	1.01 ±0.01
P(mg/kg)	7.02 – 101.55	52.446 ±30.97	28.94 ±7.40
Ca(mg/kg)	4.80 – 7.20	6.224 ±0.70	0.40 ±1.40
Mg(mg/kg)	3.92 – 5.52	4.484 ±0.47	5.32 ±0.60
Na(mg/kg)	0.24 – 0.48	0.335 ±0.07	0.30 ±0.10
K(mg/kg)	0.14 – 0.20	0.172 ±0.03	0.18 ±0.01
CEC(cmol/kg)	9.58 – 12.40	11.215 ±0.92	12.20 ±0.01

3.2 Geochemical forms of heavy metals in soil samples.

The geochemical forms, average total concentration of Cu, Cr, and Cd (mg/kg), percentage (%) recovery, as well as the % distribution of each forms and % bio-availabilities are presented in Tables 2 – 7. The overall recovery rates which is the sum of six fractions divided by the independent total concentration from the sequential extraction procedure, ranged from 91.57 to 99.58%. This indicates a high reliability in the sequential extraction procedures.

The total concentrations of Cu (mg/kg) (Table 2) in automobile workshops soils ranged from 39.10 to 129.80mg/kg. These values are much higher than 5.30mg/kg recorded for the control. The order of fractions in the soils was: residual > organically complexed </> Fe- Mn oxide > carbonate bound > exchangeable > water soluble. The dominance of Cu in the residual fraction has been reported by other workers (Chlopecka *et al*, 1998; Asagba *et al*, 2007). The high levels of Cu in this fraction may be due to presence of acid resistant mineral and organic materials. Also, because the soil samples are mainly sandy, the metals may have co-precipitated with various silicate species consequent to their adsorption into the mineral lattice (Manceau *et al*, 1996; Asagba *et al*, 2007).

Table 2: Geochemical forms of Cu (mg/kg) in soil samples of the automobile workshops and control (CT)

SAMPLES	RESULTS ±SD								
	F1	F2	F3	F4	F5	F6	SUM[a]	TOTAL[b]	% RECOVERY[R]
OG	1.60	2.90	4.70	7.90	11.20	12.60	40.90	42.55	96.12
	±0.40	±0.45	±0.50	±0.50	±0.70	±0.50	±0.90	±1.50	
MP	1.10	2.60	3.80	5.90	9.70	14.70	37.80	39.10	96.68
	±0.00	±0.45	±0.30	±0.50	±1.05	±1.00	±1.00	±2.10	
RC	3.33	6.10	9.90	13.40	15.20	28.20	76.10	78.40	97.07
	±0.50	±0.90	±1.50	±1.08	±3.90	±0.90	±3.10	±2.30	
OP	9.80	12.80	16.20	20.40	26.00	37.90	123.10	129.80	94.84
	±1.45	±1.50	±1.80	±3.55	±4.50	±3.70	±3.30	±2.70	
OL	7.40	9.70	12.30	16.10	19.90	26.90	92.30	96.30	95.85
	±1.10	±2.05	±1.70	±1.90	±2.00	±0.55	±2.70	±1.90	
AK	3.30	6.70	9.60	12.50	7.40	20.90	60.40	63.30	95.42
	±0.45	±0.00	±0.50	±0.70	±0.55	±2.50	±1.90	±3.20	
AJ	3.70	5.90	9.30	11.20	7.60	19.10	56.80	61.90	91.76
	±0.20	±0.50	±0.50	±1.05	±1.00	±1.50	±1.10	±3.10	
GN	2.80	5.40	8.80	13.70	8.20	13.00	51.90	55.80	93.01
	±0.50	±0.55	±1.50	±2.90	±1.90	±1.80	±2.30	±2.90	
SR	3.20	7.80	9.90	16.90	12.40	22.40	72.60	73.40	98.91
	±0.50	±0.70	±2.50	±4.50	±1.60	±2.30	±3.80	±1.10	
OK	2.70	4.90	5.80	8.70	6.80	12.30	41.20	44.10	93.42
	±0.35	±0.00	±0.50	±0.55	±1.40	±1.10	±0.85	±2.30	
CT	0.15	0.25	0.52	1.22	1.40	1.58	5.12	5.30	96.60
	±0.05	±0.00	±0.00	±0.20	±0.10	±0.05	±0.25	±1.00	

OG = Ogodo, MP = McPherson, RC = Reclamation, OP = Okpe Rd, OL = Oleh, AK = Akintola, AJ = Ajogodo, GN = Gana-New Rd, SR = Shell Rd, OK = Okirigwre, CT = Control

The values are mean ± S.D

a = The sum of metal concentration in the six fractions

b = The independent total concentration of metals

R = (a/b) x 100

F1 = Water soluble fraction; F2 = Exchangeable fraction; F3 = Carbonate fraction

F4 = Fe-Mn Oxide fraction; F5 = Organic fraction; F6 = Residual fraction

Table 3: Distribution of Cu (%) in soil samples of the automobile workshops and control (CT).

Samples	F1	F2	F3	F4	F5	F6	% Bioavailability
OG	4	7	12	19	27	31	23
MP	3	7	10	15	26	39	20
RC	4	8	13	18	20	37	25
OP	8	10	13	17	21	31	31
OL	8	11	13	17	22	29	32
AK	5	11	16	21	12	35	32
AJ	7	10	16	20	13	34	33
GN	5	11	17	26	16	25	33
SR	4	11	14	23	17	31	29
OK	7	12	14	21	16	30	33
CT	3	5	11	24	28	31	19

OG = Ogodo, MP = McPherson, RC = Reclamation, OP = Okpe Rd, OL = Oleh, AK = Akintola, AJ = Ajogodo, GN = Gana-New Rd, SR = Shell Rd, OK = Okirigwre, CT = Control

The large proportion of Cu in the organic and Fe-Mn oxides fractions agrees with many studies that have shown that Cu forms strong specific (covalent) bonds with electron-rich functional groups in organic matter (Balasoiu *et al*., 2001; Basta *et al*., 2005), and that iron and manganese oxides are involved in the sequestration of heavy metals in soil matrix (Nacghtegaal and Sparks, 2004; Asagba *et al*, 2007). The concentrations of Cu in water-soluble and exchangeable fraction (Table 3) range from 3 to 8 and 7 to 12% of the total Cu respectively. 20 to 33% Cu were potentially bio-available in the contaminated soils. The control sample recorded 19% potential bioavailability with carbonate bound fraction being the most abundant of the three (F1, F2 & F3) fractions.

The geochemical forms of Cr (mg/Kg) as well as its percent (%) distribution in the soils samples are as shown in Tables 4 and 5.

Table 4: Geochemical form of Cr (mg/kg) in samples of the automobile workshops and control

SAMPLES	RESULTS ±SD								
	F1	F2	F3	F4	F5	F6	SUM^a	TOTAL^b	% RECOVERY^R
OG	1.80 ±0.40	2.96 ±0.40	3.80 ±0.20	5.65 ±0.50	8.44 ±0.55	14.40 ±1.00	37.05 ±0.60	39.20 ±1.50	94.52
MP	1.40 ±0.45	2.45 ±0.50	4.30 ±0.60	6.70 ±1.00	8.20 ±0.00	13.89 ±2.10	36.94 ±1.90	38.20 ±2.00	96.70
RC	2.00 ±0.45	2.70 ±0.20	4.30 ±0.50	5.80 ±0.50	9.20 ±0.70	13.90 ±2.40	37.90 ±2.10	40.10 ±1.90	94.51
OP	1.40 ±0.25	1.60 ±0.15	2.30 ±0.20	3.70 ±0.50	4.90 ±0.50	6.30 ±0.50	20.20 ±0.45	21.90 ±1.75	92.24
OL	0.50 ±0.00	0.80 ±0.10	1.40 ±0.10	1.85 ±0.25	2.20 ±0.30	4.13 ±0.50	10.88 ±1.00	11.55 ±1.70	94.20
AK	0.80 ±0.05	1.10 ±0.20	1.55 ±0.10	2.05 ±0.45	2.40 ±0.55	5.70 ±0.65	13.60 ±0.78	14.35 ±1.30	94.77
AJ	2.30 ±0.45	2.70 ±0.05	4.30 ±0.00	7.40 ±0.00	9.70 ±0.50	11.00 ±1.50	37.40 ±1.70	38.74 ±2.90	96.54
GN	1.60 ±0.40	2.40 ±0.32	3.70 ±0.34	5.30 ±0.50	7.90 ±0.60	9.90 ±1.00	30.80 ±1.00	32.10 ±3.10	95.95
SR	0.60 ±0.05	1.10 ±0.15	1.40 ±0.40	2.20 ±0.00	4.70 ±0.10	5.40 ±0.50	15.40 ±0.50	16.40 ±1.30	93.90
OK	0.40 ±0.02	0.90 ±0.05	1.10 ±0.05	1.80 ±0.25	3.00 ±0.45	5.70 ±0.00	12.90 ±0.40	13.80 ±1.70	93.48
CT	<0.04	0.04 ±0.00	<0.04	<0.04	<0.04	0.07 ±0.00	0.11 ±0.00	0.12 ±0.05	91.67

The values are mean ± S.D
a = The sum of metal concentration in the six fractions
b = The independent total concentration of metals
R = (a/b) x 100
F1 = Water soluble fraction; F2 = Exchangeable fraction; F3 = Carbonate fraction
F4 = Fe-Mn Oxide fraction; F5 = Organic fraction; F6 = Residual fraction

Table 5: Distribution of Cr (%) in soil samples of the automobile workshops and control

Samples	F1	F2	F3	F4	F5	F6	% Bioavailability
OG	5	8	10	15	23	39	23
MP	4	7	12	18	22	37	23
RC	5	7	12	15	24	37	24
OP	7	8	12	18	24	31	27
OL	5	7	13	17	20	38	25
AK	6	8	11	15	18	42	25
AJ	6	7	12	20	26	29	25
GN	5	8	12	17	26	32	25
SR	4	7	9	14	31	35	20
OK	3	7	9	14	23	44	19
CT	0	36	0	0	0	64	36

The total Cr concentration ranged between 11.55mg/kg (sample OL) and 40.10mg/kg (sample RC). The total Cr concentration in the control (CT) was 0.12mg/kg. Values of 39.20, 38.74, and 38.20mg/kg were recorded for OG, AJ and MP respectively. The average concentration of Cr in the different fractions of soils analyzed shown in table 4, have more Cr in the residual fractions (4.13 - 14.40mg/kg). The order of fractions was: residual > organically bound > Fe-Mn-oxides > carbonates bound > exchangeable > water-soluble. The predominance of Cr in residual fraction of contaminated soils has been reported by other investigators (Ryan et al., 2002; Iwegbue et al., 2009; Osakwe, 2013). The percentage sum of the weakly bound fractions (F1+F2+F3) which reflects the potential bio-availability of the metals ranged between 19% (sample OK) and 27% (sample OP). Samples AJ, AK, and GN, all have percentage bioavailability of 25% (table 5). Rai *et al* (1987) reported that Cr(III) forms hydroxyl complexes in natural water including Cr(OH)$_2^+$, Cr(OH)$^{2+}$, Cr(OH)$_3^0$, and Cr(OH)$_4^-$, that can be readily adsorbed by soils. Griffin and Shimp (1978), in a study of the relative mobility of metals in soil at pH 5, reported Cr(III) to be the least mobile. The relative mobility of Cr(III) found in this study tended to agree with these researchers. Bioavailability of weakly bound heavy metals can be altered by change in pH, organic matter content and redox status of the contaminated soils (Karczewska *et al*, 1998; Sarkar et al., 2012).

Table 6: Geochemical forms of Cd (mg/kg) in soil samples of the auto-mobile workshops and control (CT)

SAMPLES	RESULTS ±SD								
	F1	F2	F3	F4	F5	F6	SUM[a]	TOTAL[b]	% RECOVERY[R]
OG	0.20 ±0.00	0.70 ±0.15	1.20 ±0.23	0.57 ±0.00	1.30 ±0.00	0.70 ±0.10	4.67 ±0.25	5.10 ±0.45	91.57
MP	0.35 ±0.00	0.55 ±0.07	0.95 ±0.08	0.45 ±0.02	0.80 ±0.07	1.35 ±0.20	4.45 ±0.30	4.70 ±0.35	94.68
RC	0.30 ±0.00	0.55 ±0.03	1.35 ±0.17	0.65 ±0.10	1.45 ±0.30	0.68 ±0.00	4.98 ±0.23	5.40 ±0.50	92.22
OP	0.15 ±0.00	0.45 ±0.03	0.90 ±0.07	0.51 ±0.00	1.05 ±0.22	0.83 ±0.23	3.89 ±0.20	4.15 ±0.25	93.73
OL	0.15 ±0.03	0.35 ±0.02	0.70 ±0.00	0.55 ±0.05	1.52 ±0.03	0.95 ±0.07	4.22 ±0.30	4.55 ±0.38	92.75
AK	0.20 ±0.04	0.40 ±0.00	0.55 ±0.07	0.95 ±0.07	1.65 ±0.30	0.95 ±0.18	4.70 ±0.28	4.72 ±0.20	99.58
AJ	0.35 ±0.03	0.55 ±0.07	0.65 ±0.05	0.55 ±0.05	1.30 ±0.23	1.05 ±0.00	4.45 ±0.25	4.70 ±0.30	94.68
GN	0.45 ±0.05	0.90 ±0.15	1.05 ±0.00	0.80 ±0.23	1.30 ±0.25	1.60 ±0.20	6.10 ±0.28	6.28 ±0.15	97.13
SR	0.20 ±0.00	0.35 ±0.00	0.50 ±0.00	0.30 ±0.00	1.00 ±0.00	0.70 ±0.00	3.05 ±0.00	3.15 ±0.25	96.83
OK	0.35 ±0.03	0.55 ±0.05	0.65 ±0.10	0.45 ±0.05	0.80 ±0.03	1.25 ±0.23	4.05 ±0.20	4.25 ±0.30	95.29
CT	ND	ND	ND	ND	ND	ND	ND	<0.01	

Table 7: Distribution of Cd (%) in soil samples of the automobile workshops and control (CT)

Samples	F1	F2	F3	F4	F5	F6	% Bioavailability
OG	4	15	26	12	28	15	45
MP	8	13	21	10	18	30	42
RC	6	11	27	13	29	14	44
OP	4	11	23	14	27	21	38
OL	4	8	17	13	36	22	29
AK	4	9	12	20	35	20	25
AJ	8	12	15	12	29	24	35
GN	8	15	17	13	21	26	40
SR	7	11	16	10	33	23	34
OK	9	13	16	11	20	31	38
CT	0	0	0	0	0	0	0

The speciation results in Tables 6 and 7, show that Cd is largely concentrated in the organically complexed fraction of the contaminated soils (18 to 36%); thus evidencing the influence of soil organic matter upon cadmium adsorption. The dominance of organically complexed fraction of Cd over the residual form has been reported by other investigators (Krishnamurti *et al.*, 1995). Experimental data on 16 surface soils of Saskatchewan with wide variation in physico-chemical properties indicated the predominance of cadmium in the form of metal-organic complex-bond, accounting for 31 – 55% of the total Cd present in the soils. The levels of Cd in the residual fraction of the soils were next to those in the organic fraction. The levels ranged between 14% (sample RC) and 31% (sample OK). The concentration of exchangeable Cd was significantly higher (9 to 15% of total Cd) than that in water-soluble (4 to 9% of total Cd) fraction of the soils. The dominant fraction among the weakly bound fractions was that extracted with NH_4OAc at pH 5.0 (carbonates bound fraction). This fraction accounted for 12 to 27% of total Cd. The percentage sum of the weakly bound fractions of Cd (F1+F2+F3) was highest in sample OG, (45% of total Cd). This was followed by sample RC and MP with 44% and 42% potential bio-availabilities respectively. Sample GN had 40% bioavailability, while both samples OP and OK had 38% potential bioavailability. The lowest percent Cd potential bio-availability was 29% (sample OL). The total concentration of Cd in the soils ranged between 3.15mg/kg (sample SR) and 6.27mg/kg (sample GN). Cadmium was undetected in the control samples. The detection limit for Cd was 0.01mg/kg.

3.3 Statistical analysis

The analytical results were compiled to form a multi-element data base using excel as statistical software. Pearson's correlation coefficients and P-values were calculated for all possible variable pairs (Tables 8 - 9). Mobility index of metals in soil very significantly correlated with total content of metals. This implies overloading of the geochemical system in the contaminated soils were anthropogenically added metals remained weakly bound to soil constituents (Ramos *et al*., 1994). Significant positive correlations were present between sand fractions and Cu fractions, clay fractions and Cr fractions, clay and total Cr content, clay fractions and F1, F2, F3 fractions of Cd , clay fraction and total Cd content, Organic matter with F4 and F5 fractions of Cd. Negative correlations were found for clay fraction and F1, F2, F3, F4 fractions of Cu, silt fraction and F1, F2, F3, F4 fractions of Cu, clay and total Cu, silt and total Cu, CEC and F3, F4, F6 fractions of Cu, sand fraction and fractions of Cr, sand fraction and total Cr content, sand fraction with F1, F2, F3 fractions Cd, CEC and F5 fraction of Cd.

Table 8: Coefficient of relations between heavy metal content and mobility index in soils

	Cu	Cr	Cd
Mobilty index	0.9707**	0.9876**	0.7764**

**significant at the %1 level, *significant at the %5 level

Table 9: Coefficient of relations between heavy metal fractions (dependent variable) and clay, silt, sand, organic matter, cation exchange capacity (independent variables) in soils samples.

		F1	F2	F3	F4	F5	F6	Mt
Cu	Clay	-0.5496*	-0.6557*	-0.5671*	-0.5435*	-0.3128	-0.4754	-0.5132*
	Silt	-0.7057**	-0.6771**	-0.7136**	-0.6096*	-0.4055	-0.4648	-0.6111*
	Sand	0.6898*	0.7425**	0.7046**	0.6391*	0.3945	0.5256*	0.6207*
	OM	0.1323	0.1672	0.2172	0.1262	-0.0834	0.1063	0.1040
	CEC	-0.3183	-0.4970	-0.5808*	-0.5932*	-0.2190	-0.5336*	-0.4680
Cr	Clay	0.6693*	0.8229**	0.7923**	0.7701**	0.8532**	0.8423**	0.8419**
	Silt	0.0941	0.3181	0.2403	0.2132	0.3585	0.5221	0.3728
	Sand	-0.4667	-0.6726*	-0.6153*	-0.5881*	-0.7113**	-0.7842**	-0.7111**
	OM	-0.2788	-0.3593	-0.3523	-0.4466	-0.5040	-0.3449	-0.4114
	CEC	0.1977	0.3691	0.3187	0.4012	0.3704	0.4142	0.3847
Cd	Clay	0.6697*	0.7553**	0.7128**	-0.1648	-0.2923	0.2382	0.5293
	Silt	0.2437	0.1585	0.3197	-0.4164	-0.4365	-0.2030	-0.1030
	Sand	-0.5399*	-0.5522*	-0.6042*	0.3068	0.3967	-0.0507	-0.2825
	OM	-0.1285	-0.0716	-0.0923	0.8471**	0.6203*	0.0791	0.3233
	CEC	0.4077	0.4828	0.2353	-0.4899	-0.7042**	0.3697	0.0688

**significant at the %1 level, *significant at the %5 level
F1 = Water soluble fraction; F2 = Exchangeable fraction; F3 = Carbonate fraction,F4 = Fe-Mn Oxide fraction;
F5 = Organic fraction; F6 = Residual fraction, Mt = Total metal content.

4. Conclusion

The determination of forms of metals in soils of automobile workshops was necessary to ascertain the mobile and bio-available fractions of heavy metals in the soils; as it serves as key factor in risk assessment analysis. The results of sequential chemical fractionations of soils in the vicinities of automobile workshops reveal that the distributions among geochemical forms were usually a function of: the metal, its total content, and soil texture. In all soils samples analyzed (for Cu, Cr, & Cd), the last three fractions (residual, organically complexed, and Fe-Mn-oxides bond), were predominant, with the residual taking the lead except for cadmium were the organically complexed fractions were most dominant. The potentially mobile and bio-available fractions for the three metals in the soils were generally less than 45% with Cd being the most mobile (25 – 45%) of the metals. The general order of percentage bio-availability of metals in soil was: Cd > Cu > Cr. The percentage potential bio-availability/mobility of Cu and Cr in the soil taken into considerations their total concentrations and their essentialities does not constitutes treat to environment. However, the high concentration of Cd, its non-essentiality and high toxic nature couple with its high mobility in the soils, requires attention. Also, as a result of possible accumulation of metals in soils, measures such proper enlightenment campaign should be carried out to alert all stake-holder on the danger inherent in indiscriminate dumping. Also laws and regulations on waste management in automobile workshops should be enacted to forestall the effects of heavy metals' related problems on the environment, particularly ground water.

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