



British Journal of Applied Science & Technology
1(3): 94-115, 2011



SCIENCEDOMAIN *international*

www.sciencedomain.org

Geochemical Partitioning of Heavy Metals in Roadside Surface Soils of Different Grain Size along Major Roads in Kano Metropolis, Nigeria

O. J. Okunola^{1*}, A. Uzairu², C. E. Gimba² and J. A. Kagbu²

¹*National Research Institute for Chemical Technology,
P.M.B.1052, Basawa, Zaria, Nigeria.*

²*Department of Chemistry Ahmadu Bello University, Zaria, Nigeria*

Research Article

Received 25th January 2011
Accepted 5th February 2011
Online Ready 30th March 2011

ABSTRACT

This study evaluates the effect of grain size on levels of metal in roadside surface soils collected along high traffic roads in Kano Metropolis as a consequence of increase in automobile over the years. Composite surface soil samples were collected along ten different roads. Samples were analysed for soil physicochemical parameters, heavy metals (Cd, Cr, Ni, Pb, Cu and Zn) content. On an average a six sequential extraction of roadside surface soils showed that Cd, Cr, Ni, Pb, Cu and Zn are predominantly occur in the Fe-Mn oxide, residual, residual, carbonate bound, organic and residual fractions respectively. It was found that concentrations in the water soluble and exchangeable fractions were generally low for most of the studied metals. Considering the proportion of metals bound to the water soluble to the exchangeable and the carbonate bound fractions, the comparative mobility of metals showed the order; Ni > Cd > Pb > Cr > Cu > Zn. Highest mobility factor (MF) for all studied metals was obtained in 150µm samples with exception of Ni, Pb and Cu where highest percentage MF was obtained in 1400µm samples and 355µm for Zn. This could indicate other sources than fine particulate emission from vehicles responsible. With toxicity it appears that Cd, Cr, Ni, Pb and Cu pollution along the roadside is of concern.

Keywords: Roadside soil, Grain size, Metals, mobility, Kano;

* Corresponding author: E-mail: okunolaoj@gmail.com

1. INTRODUCTION

It has been reported that roads play a major role in stimulating social and economic progress of a society (Bai et al., 2008). However, roads construction has also resulted in heavy environmental pollution in many countries including Nigeria (Okunola et al., 2008), since road traffic is an important negative factor regarding air quality, noise and land consumption (Zechmeister et al., 2008). The contribution of vehicles and road transports to the global emission of atmospheric pollutant is regularly increasing (Viard et al., 2004). The road transports also induce the contamination of nearer soils by a pollutant transfer via the atmospheric fallouts (Nabuloa et al., 2006). Among the pollutant emitted during this process are heavy metal, which causes air, water and soil pollution in the vicinity of roads and highways. Among the metals are Pb, Cd, Cr, Ni, Zn and Cu that are associated with the mobile sources; since they are included in petrol, engines, tires, lubricant oil and galvanized parts of the vehicles (Saeedi et al., 2010).

Environmental and health effects of heavy metals in roadside soils depend on their mobility and bioavailability of the metals, which are a function of their partitioning with soils (Lee *et al.*, 2005). Hence, not only the determinant of metal concentrations but also the identification of binding sites and phase associations is essential for assessing environmental quality and human health in urban areas. Thus, to provide reliable information on the forms of association of heavy metals regarding their availability levels and hence potential mobility to food and water sources, a sequential extraction procedure has been largely relied upon to partition heavy metals, such that their chemical reactivity can be elucidated (Olajire *et al.*, 2003; Ogunfowokan *et al.*, 2009).

Just like other cities of the world, Kano metropolis developed over the years with a steady progress in industrialization, increase in population and traffic density (Ministry of Information, Kano State, 2005). From record, as at 1991 census, it had a population of 2,166,554 but currently estimated to be home to 2,376,372 people (TWG, 2010). With increased in population, economic activities increases leading to increase in road networks thereby accommodating more automobiles. Due to the rapid urbanization and large population, most people in Kano city live very close to busy roads (which is a very common phenomenon in Nigeria) where they can be exposed to metal pollution from various activities on the roads. Therefore, a detailed study of the levels and behaviour of metals in roadside soils is needed. Several studies have been carried out to assess total concentrations of metals in soils and roadside soils in Kano, among the studies no similar studies have been previously conducted to determine the chemical partitioning of metals in roadside soils. On the basis of the aforementioned information, the aims of this study were to carryout comprehensive investigation of the chemical speciation of Cd, Cr, Cu, Ni, Pb and Zn in roadside soils of Kano metropolis. These metals were chosen because of their known potential enrichment and toxicity due to anthropogenic activities, especially in urban environments (Lee *et al.*, 2005).

2. MATERIALS AND METHODS

2.1 SAMPLE COLLECTION AND PRE-TREATMENT

The criteria for selections of roads for the study were based foreknowledge of the relative traffic density on each roads and the desire to have each category of traffic density in different sections of the metropolis. Samples were collected from 10 roadside locations (1 - 10) and a control site (C) all over the Metropolis as shown in Figure 1. These sites were mainly located in residential and commercial areas of the metropolis.

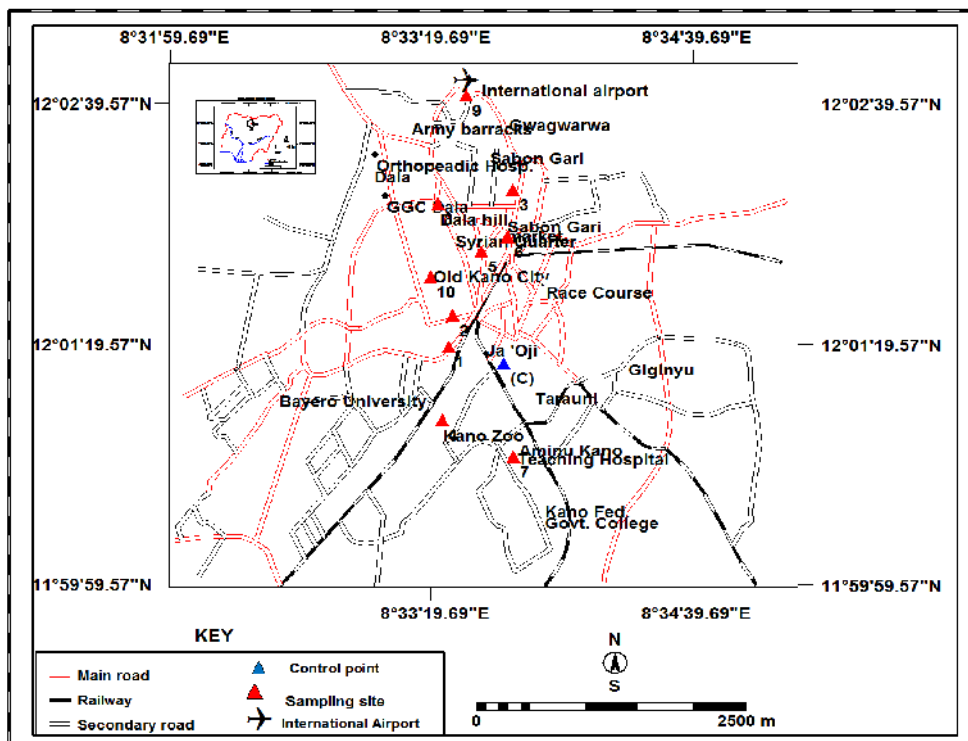


Fig 1. The sampling sites at Kano Metropolis

Source: Adapted and Modified from Google Map Data, 2010

Control samples were obtained from a small garden within a residential buildup area of farm center, which is not closer to any secondary or main road.

Approximately 20g of surface (0 – 5cm) roadside soils was collected from five sites at a distance of 10m apart from each side of the road within a given site with a stainless steel spoon, pooled and homogenized to form a representative sample for a given road (Onianwa, 2001). Samples were placed in polythene bags and air-dried in the laboratory for 3days. They were then passed through 1400µm, 355µm and 150µm sieve to achieve different grain sizes. Subsequently, chemical analyses were performed including both strong acid digestion and sequential extraction procedures. The samples for physicochemical analysis were removed from the representative sample before sieving.

2.2 QUALITY ASSURANCE

Glass wares, crucibles and plastic containers were washed with liquid soaps, rinsed with distilled water and soaked in 10% HNO₃ for 24hrs; cleaned with distilled – deionized water to prevent contamination (Adnan *et al.*, 2003). Thereafter, the apparatus were oven-dried for 12hrs at a temperature of 80°C. All reagents used were of analytical grade, and the instrument working calibration were made by diluting the commercial Scharlau Japan stock solution (1000ppm) standard with distilled-deionized water.

2.3 SOIL PHYSICOCHEMICAL

Soil pH, organic matter (OM), particle size distribution, electrical conductivity (EC) and cation exchangeable capacity (CEC) were determined to enable accurate assessment of elemental reservoirs, mobility, and bioavailability (Davidson *et al.*, 2004). Soil parameters viz., pH, EC, particle size distribution, CEC and OM were determined. All determination were done in triplicate using appropriate analytical procedures which are reported in methods of soil analysis (Sparks, 1996) as follows: soil pH and EC were measured with soil to water ratio 1:2 using Crison MicroPH 2000. The organic matter was determined using the Walkley and Black method Walkley and Black (1934). Particle size distribution was determined by the hydrometer method. Cation exchangeable capacity was determined using ammonium acetate.

2.4 DETERMINATION OF TOTAL METAL CONCENTRATION

Samples were digested for heavy metal analysis using the method of Ogunfowokan *et al.* (2009). For each sample, 1g of sample was digested in Teflon beakers with 30ml aqua-regia (HCl:HNO₃, 3:1) on a thermostatted hotplate 150^oC. After, about 2hrs of digestion, the Teflon beaker with its content was brought down from the hot-plate to simmer. Then, 5ml HF was added and digested for a further 30min. The Teflon beaker with the content was allowed to cool down to room temperature before the content was quantitatively transferred into 50ml volumetric flask and made up to the mark with distilled-deionized water. A blank determination was carried out using the procedure described above without the sample. The Cd, Cr, Cu, Ni, Pb and Zn were determined using Atomic Absorption Spectrophotometer (AAS) at the Kaduna State University, Kaduna, Nigeria.

2.5 SEQUENTIAL EXTRACTION OF HEAVY METALS FROM ROADSIDE SOIL

Chemical fractionation of heavy metal was done on soil using Finzgar *et al.* (2007) method. This method modified the conventional method developed by Tessier *et al.* (1979). The modified method determines fractionation of heavy metals into six (6) geochemical fractions as follows:

F I (fraction soluble in soil solution): 1g of air – dried soil sample (of a particular size fraction) was mix with 10ml of deionized water with continuous agitation for 1hr, centrifuge and supernant decanted and made up to 50ml with deionized water prior to analysis.

F II (Exchangeable Fraction): The residue from **F I** was leached at room temperature with 10ml of 1M MgNO₃ at pH 7.0 with continuous agitation for 1hr, centrifuge and supernatant decanted and made up to 50ml with deionized water prior to analysis. MgNO₃ displace ions electrostatically bound in the soil matrix.

F III (Acid Extractable – Carbonate bound Fraction): Residue from **F II** was leached at room temperature with 10ml of 1M NaOAc (pH 5 adjust with HOAc) with continuous agitation for 5hrs and centrifuge. The supernatant was decanted and made up to 50ml with deionized water prior to analysis. NaOAc solubilises carbonates (calcites, dolomite) and releases entrapped metals.

F IV (Reducible – Fe – Mn Oxides and Hydroxide Fraction): Residue from **F III** was leached with 20ml of 0.1M NH₂OH.HCl (pH adjusted with 25%v/v HOAc) at 96^oC for 6hrs with occasional agitation and centrifuge. The supernatant decanted and made up to 50ml with deionized water prior to analysis. NH₂OH.HCl reduces Fe and Mn oxides to soluble forms.

F V (Oxidizable – Organic Matter Bound Fraction): To the residue from **F IV**, 3ml of 0.02M HNO_3 and 30%v/v H_2O_2 was added. The mixture was heated to 85°C in a water bath for 3hrs. After cooling, 5ml of 1M NaOAc will then be use to extract with occasional agitation for 3hrs at 85°C . Mixture was centrifuge and supernatant made up to 50ml with deionized water prior to analysis. HNO_3 and H_2O_2 oxidize organic matter and solubilise sulphides. Oxidized organic matter releases complexed, adsorbed and chelated metals.

F VI (Residual and Inert Fraction): Residual from **F V** was digested with a mixture of 8ml of 5:1 mixture of HF and HClO_4 in acid digestion Teflon cup. Then mixture was dried ashed for 2hrs and evaporated to dryness. The residue was diluted to 50ml with deionized water prior to analysis.

After successive extraction, the sample was centrifuge at 3000rpm for 15mins. The supernatants was removed with pipette and filtered with Whatmann No 42 filter paper. The residue was washed with deionized water followed by vigorous hand shaking and then follows 15mins of centrifugation before next extraction. The volume of rinse water use was left at minimum to avoid excessive solubilization of solid materials. The process was carried out in triplicate for a particular sample. Appropriate reagent blanks were prepared and analyzed for each extraction type. All extracts were analyzed for the metals (Cd, Cr, Cu, Ni, Pb and Zn) by atomic absorption spectrophotometry.

Quality assurance test such as the spiking experiment is usually conducted to ascertain the accuracy of the analytical procedure in absence of reference standard. Table 3 shows the results of the spiking experiment conducted on soil samples. The percentage recoveries obtained for the metals under investigation (Cd, Cr, Ni, Pb, Cu, Zn) varied 90.4 – 103.2 for soil. The pattern of recovery for soils were found to follow the decreasing orders; Ni > Zn > Cr > Cu > Pb > Cd. High percentage recoveries obtained in these samples validate the experimental protocol.

Table 1. Percentage recovery of heavy metal ions in samples

Metal	Metal Recovery
Cd	90.40±0.50
Cr	96.10±1.20
Ni	103.20±0.90
Pb	93.20±0.56
Cu	93.40±1.00
Zn	101.20±1.00

3. RESULTS AND DISCUSSION

3.1 PHYSICOCHEMICAL PARAMETERS

Statistical analysis of roadside soils physico-chemical parameters, including the mean, standard deviation and student t-test analysis of means are summarized in Table 2. Multivariate correlation analysis between soil physicochemical parameters showed that some of the parameters were found to bear statistically significant correlation with each other indicating close association of the parameters. Significant positive correlation was obtained between: OM: EC ($p < 0.01$) and CEC: EC ($p < 0.05$). Significant negative correlations were also observed between particle size fractions and also between clay, silt and other parameters with few exceptions. As presented above, the roadside soils composition was dominated by sand. This is similar to Mohammed *et al.*

(2005), that soils closest to the road are usually dominated by sand fractions, constituting an average range 84 – 92%. According to Nyles and Ray (1999), soil with low clay content has usually high pollutant leaching potentials. It could therefore be deduced that underground water and farmland along the roadside could suffer from pollution.

Table 2. Physicochemical parameters of roadside soils

SITE	Particle size distribution corrected to 20°C (%)			pH	EC (dSm)	OM (%)	CEC (Cmol kg ⁻¹)
	CLAY	SILT	SAND				
1	6.67±0.58 ^a	22.33±0.58 ^a	71.33±0.58 ^a	6.60±0.10 ^c	1.30±0.10 ^c	1.47±0.01 ^d	5.10±0.10 ^f
2	4.67±0.58 ^b	4.67±0.58 ^b	90.67±0.58 ^b	7.07±0.15 ^e	1.10±0.10 ^{ab}	1.47±0.01 ^d	3.70±0.10 ^b
3	5.00±1.00 ^b	8.00±1.00 ^c	87.00±0.00 ^c	6.70±0.10 ^{cd}	1.00±0.10 ^a	2.14±0.01 ^e	3.80±0.10 ^b
4	3.00±1.00 ^c	8.00±1.00 ^c	89.00±0.00 ^d	7.00±0.10 ^e	1.00±0.10 ^a	0.99±0.01 ^a	4.30±0.10 ^d
5	5.00±1.00 ^b	4.00±1.00 ^b	91.00±2.00 ^b	6.20±0.10 ^a	3.00±0.00 ^d	5.79±0.02 ⁱ	5.60±0.00 ^g
6	5.00±1.00 ^b	4.00±0.00 ^b	91.00±1.00 ^b	6.50±0.10 ^{bc}	1.30±0.02 ^c	4.36±0.01 ^h	4.63±0.06 ^e
7	5.00±0.00 ^b	14.00±1.00 ^e	81.00±1.00 ^e	6.90±0.20 ^{de}	1.10±0.00 ^{ab}	1.40±0.02 ^c	5.60±0.10 ^g
8	7.00±1.00 ^a	8.00±0.00 ^c	85.00±1.00 ^f	6.90±0.00 ^{de}	1.40±0.02 ^c	2.66±0.01 ^g	4.00±0.00 ^c
9	5.00±0.00 ^b	8.00±0.00 ^c	87.00±0.00 ^c	6.40±0.00 ^b	1.10±0.10 ^{ab}	1.26±0.01 ^b	3.30±0.10 ^a
10	5.00±1.00 ^b	10.00±1.00 ^d	85.00±0.00 ^f	6.70±0.10 ^{cd}	1.15±0.01 ^b	2.18±0.01 ^f	5.80±0.00 ^h
**	10.00±1.00	10.00±1.00	80.00±1.00	8.30±0.40	1.18±0.03	2.51±0.92	3.61±0.48

Values are Mean±SD triplicate analysis of samples from each site.

Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$); ** Control

Also, Ericksson (1989) found that for a given total Cd concentration, Cd was more soluble and plant available in sandy soil than in clay soil. Which suggested that soil solution in this might be enriched with heavy metals, though might not be readily available as shown in seasonal decrease in % sand content.

Soil pH generally plays an important role in metal bioavailability, toxicity and leaching capability to the surrounding environment especially hot and dry seasons when the moisture content of soils are low. Hence heavy metals are most soluble and leached out in acidic pH (Okunola et al., 2007). From the results of pH, values were generally within pH 5.09 – 8.57 and 6.34 – 7.65 reported by Mohammed et al. (2005) and Yahaya et al. (2010) respectively. Most metals in the pH range 6.0 – 9.0 are not always in the free form (Porteus, 1985). The pH range of all the soil samples in the present study is slightly acidic to neutral implying that some metal ions may exist in the free form and hence could be leached into subsoil and subsequently into ground water. The implication according to Chimuka et al (2005) is that heavy metals in the roadside soil could remain for a long time exposed to plants and other organism that interact with them. In line with the trends in pH, Yaron (1995) states that a decrease in soil pH from 7.7 – 5.5 causes an increase in conductivity because many more ions, especially those of heavy metals go into solution. This is also supported by negative correlation observed between pH and EC in all the seasons.

The soil organic matter contain contain humic materials with highly complex functional groups, which have ability to complex metals thereby retaining them in the topsoil (Evans, 1989). The more organic matter is present in soil, the more functional groups available for complexation with the metals, hence, the more the retention. The organic matter of soils in the present study indicated high retention of metals, thereby making them unavailable for plant uptake. The value

of CEC obtained in this study is lower than range of 10.20 – 27.2Cmolkg⁻¹ reported in a similar study (Mohammed et al., 2005). The retention of metals by CEC or non-specific adsorption mechanisms is complex because it is dependent on various factors like pH, concentration of metal ion etc (Adie and Osibanjo, 2009). However, CEC of any soil is an important tool that could assist in explaining the retention capacity of many metals especially heavy metals in the soil. Metals bound by cation exchange mechanism are via electrostatic forces resulting in the formation of outer-sphere complexes. The ions in the solution are always in equilibrium with counter ions that balance the surface charge of the colloids. In general terms, the more the CEC of soil, the more the active sites available for cation exchange. The affinity of soil colloid surfaces for cations increases as the valency increases. For cations of the same valence, the adsorption strength is usually determined by the hydrated radius of the ions (Ji and Li, 1997). Cation exchange capacity normally ranges from 1.0 – 1000mmol_ckg⁻¹. It is least for sandy soils and most for clayey soils. The CEC of soils samples in the present study was low probably because of the sandy nature of the soils. The same trend was observed by Okunola et al. (2007), Adie and Osibanjo (2009) and Mashal et al. (2009).

3.2 TOTAL METAL CONTAMINATION OF ROADSIDE SOILS

The totals metal concentrations as shown in Tables 3, 4 & 5 describes that there was a distinct change in the contents of heavy metals among different grain size of roadside soils samples across the seasons. From the tables, the values obtained from the study area were generally higher than the control site, an indication of pollution of the roadside soils. The concentration of different heavy metals studied was in the following decreasing order across the seasons: Zn > Pb > Ni > Cu > Cr > Cd.

3.3 GEOCHEMICAL PARTITIONING OF METALS IN ROADSIDE SOILS

The sequential extraction procedure and analysis measures the mobility and availability of heavy metals in soils depending on how the metals are associated with the components of the soils. The mobility and availability of metals serves to predict the behaviour of heavy metals in the soils. The chemical fractionation pattern of Cd, Cr, Ni, Pb, Cu and Zn in the roadside soils of different grain sizes across the seasons is presented below. The results illustrated fractionation of metals which are graphed as leaching percentage, reflecting individual fraction removal relative to the sum of all fractions from any given sample as shown in Figs. 2 – 7a-c. Statistical analysis revealed significant differences in fractions of metals ($p < 0.05$) among the sites across the seasons. A satisfactory agreement was found between the total of metals obtained by single determination and the summed totals of the sequential extraction. For most samples, a recovery judged comparing the summed total with the independent total metal analysis falls within 95 – 105%, and is similar to other report (Chon *et al.*, 1998; Lee *et al.*, 2005). For all the studied metals across the seasons, high concentration were found in grain size 1400 μ m compare to 355 μ m and 150 μ m in FIV – FVI for all samples.

From the results as shown in Figs. 2 a-c, more than 50% of the total Cd in all the soils is associated with the non-residual fractions. FI – FIV indicated major carriers of Cd in all the sites across the seasons with some few exceptions in warm and dry season. This is similar to report by Oluwatosin *et al.* (2008). Among the non-residual, there was no clear distinction among the fractions as to which is dominant in all sites. The is evidence that the speciation pattern of Cd in the soils are variable with sampling sites which is similar to the research carried out in China (Yuan *et al.*, 2004).

Table 3. Distribution of Cd & Cr (mgkg⁻¹) in various particle sizes in roadside soils from Kano Metropolis across the seasons

Site	Cool and Dry season			Hot and Dry season			Warm and Wet season			Warm and Dry season		
	Grain size			Grain size			Grain size			Grain size		
	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
Distribution of Cd (mgkg⁻¹) in various particle sizes												
1	1.13±0.01 ^a	2.76±0.04 ^b	3.74±0.01 ^b	1.42±8.90 ^a	3.23±0.19 ^b	4.77±0.16 ^b	0.88±0.01 ^a	2.15±0.04 ^b	2.91±0.06 ^b	1.25±0.01 ^a	2.50±0.01 ^b	3.25±0.02 ^b
2	1.23±0.02 ^a	4.10±0.07 ^d	4.50±0.07 ^c	1.91±0.01 ^a	4.37±0.09 ^c	5.49±0.36 ^c	0.97±0.01 ^a	3.30±0.07 ^c	3.65±0.25 ^c	2.00±0.08 ^b	3.00±0.01 ^c	3.50±0.04 ^c
3	1.21±0.01 ^a	2.00±0.00 ^a	2.11±0.06 ^a	1.45±0.01 ^a	2.45±0.04 ^a	2.77±0.16 ^a	0.92±0.01 ^a	1.55±0.04 ^a	1.63±0.26 ^a	1.25±0.00 ^a	2.00±0.07 ^a	2.00±0.07 ^a
4	3.32±0.01 ^d	6.80±0.07 ⁱ	8.92±0.01 ^g	4.16±0.11 ^a	6.75±0.18 ^e	10.59±0.29 ^f	2.56±0.01 ^c	5.27±0.02 ^e	7.16±0.24 ^g	3.75±0.73 ^d	4.25±0.01 ^e	6.75±0.04 ^g
5	3.40±0.07 ^e	6.10±0.00 ^g	7.80±0.14 ^f	3.78±0.16 ^a	6.85±0.11 ^e	10.48±0.37 ^f	2.77±0.16 ^c	5.06±0.04 ^e	6.48±0.37 ^f	3.00±0.06 ^{cd}	5.00±0.13 ^f	7.50±0.00 ^h
6	2.30±0.07 ^b	3.50±0.00 ^c	7.20±0.57 ^f	2.55±0.32 ^a	3.68±0.23 ^b	8.84±0.11 ^e	1.94±0.04 ^b	2.97±0.02 ^c	6.05±0.32 ^f	2.00±0.01 ^b	2.50±0.07 ^b	5.75±0.01 ^e
7	3.01±0.01 ^c	4.66±0.04 ^f	5.30±0.14 ^d	3.27±0.16 ^a	5.18±0.58 ^d	6.36±0.45 ^d	2.50±0.35 ^c	3.98±0.01 ^d	4.48±0.01 ^d	2.50±0.18 ^c	3.75±0.04 ^d	4.00±0.07 ^d
8	7.01±0.06 ^g	8.12±0.01 ^j	11.02±0.01 ⁱ	8.08±0.30 ^a	9.44±0.40 ^g	13.86±0.10 ^h	5.86±0.10 ^e	6.06±0.66 ^f	9.15±0.11 ⁱ	6.50±0.14 ^f	7.25±0.04 ^h	9.28±0.01 ^j
9	3.28±0.01 ^d	4.50±0.00 ^e	6.60±0.07 ^e	3.71±0.21 ^a	5.83±0.12 ^d	8.53±0.33 ^e	2.67±0.23 ^c	3.75±0.18 ^d	5.38±0.08 ^e	3.00±0.14 ^{cd}	5.00±0.14 ^f	5.90±0.07 ^f
10	4.35±0.04 ^f	6.30±0.07 ^h	9.85±0.04 ^h	5.39±0.43 ^a	7.84±0.11 ^f	12.76±0.17 ^g	3.54±0.33 ^d	5.24±0.18 ^e	8.16±0.11 ^h	4.75±0.04 ^e	6.50±0.28 ^g	9.08±0.06 ⁱ
**	0.07±0.00	0.09±0.00	0.21±0.01	0.07±0.00	0.15±0.00	0.23±0.00	0.21±0.01	0.75±0.01	0.90±0.02	0.50±0.02	0.95±0.02	1.51±0.01
Distribution of Cr (mgkg⁻¹) in various particle sizes												
1	2.50±0.00 ^a	16.30±0.14 ^b	18.52±0.01 ^a	2.46±0.38 ^a	20.07±0.30 ^b	23.54±0.04 ^a	1.97±0.02 ^a	12.93±0.05 ^b	14.76±0.17 ^a	1.63±0.05 ^a	16.00±0.07 ^b	15.50±0.07 ^a
2	22.60±0.07 ^f	24.10±0.64 ^d	39.53±0.33 ^g	26.27±0.16 ⁱ	28.95±0.04 ^e	52.89±0.08 ^f	17.09±0.64 ^f	18.30±0.42 ^d	32.17±0.59 ^f	21.58±0.01 ^h	23.30±0.14 ^g	36.35±0.04 ^c
3	13.02±0.01 ^{cd}	16.29±0.01 ^b	25.47±0.02 ^c	14.58±0.30 ^d	19.75±0.18 ^b	57.63±3.27 ^f	10.69±0.22 ^{cd}	13.39±0.28 ^b	21.38±0.44 ^c	11.30±0.07 ^d	15.75±0.04 ^b	58.00±0.35 ^d
4	13.27±0.01 ^d	26.46±0.25 ^e	29.20±0.57 ^e	11.52±0.34 ^c	29.19±0.22 ^e	43.30±0.00 ^e	10.47±1.08 ^d	21.29±0.21 ^e	23.44±0.40 ^d	6.25±0.04 ^c	21.00±0.71 ^e	34.00±0.42 ^c
5	10.92±0.06 ^b	14.42±0.13 ^a	24.55±0.32 ^c	9.50±0.35 ^b	13.95±0.04 ^a	33.39±0.01 ^c	9.00±0.71 ^b	12.08±0.06 ^a	20.76±0.17 ^c	5.00±0.07 ^b	8.03±0.05 ^a	24.00±0.49 ^b
6	18.44±0.40 ^e	22.64±0.18 ^c	26.15±0.60 ^d	21.01±0.01 ^f	27.49±0.36 ^d	29.25±0.32 ^b	14.54±0.33 ^e	17.68±0.23 ^c	20.59±0.29 ^c	17.00±0.07 ^f	22.25±0.04 ^f	16.75±0.18 ^a
7	11.70±0.14 ^{bc}	23.50±1.77 ^c	23.40±0.42 ^b	19.01±0.35 ^e	25.23±0.54 ^c	30.65±0.25 ^b	9.58±0.30 ^{bc}	18.89±0.08 ^d	18.89±0.08 ^b	20.50±0.07 ^g	17.75±0.04 ^c	22.00±0.35 ^b
8	21.37±0.16 ^f	28.61±0.36 ^f	103.26±0.18 ⁱ	21.94±0.04 ^g	31.00±0.71 ^f	136.77±0.16 ^h	16.77±0.16 ^f	84.04±0.33 ^h	84.04±0.68 ^h	15.75±0.07 ^e	21.75±0.00 ^{ef}	95.25±3.36 ^f
9	34.27±0.52 ^g	28.03±0.05 ^f	99.21±0.15 ^h	41.88±0.08 ^j	31.11±0.08 ^f	129.37±0.45 ^g	28.03±0.69 ^g	81.32±0.13 ^g	81.32±0.48 ^g	35.75±0.03 ⁱ	22.75±0.18 ^g	86.50±0.35 ^e
10	22.87±0.02 ^f	27.22±0.08 ^{ef}	35.52±0.34 ^f	23.55±0.32 ^h	28.05±0.67 ^{de}	39.13±0.62 ^d	17.97±0.02 ^f	27.92±0.06 ^e	27.92±0.06 ^e	17.00±0.00 ^f	18.55±22.13 ^d	0.32±0.01 ^b
**	ND	ND	ND	ND	0.01	0.01±0.00	ND	ND	ND	ND	ND	ND

Values are Mean±SD triplicate analysis of samples from each site.

Mean values in the same column followed by the same superscript letters are not significantly different (p > 0.05); ** Control

Table 4. Distribution of Ni & Pb (mgkg⁻¹) in various particle sizes in roadside soils from Kano Metropolis across the seasons

Site	Cool and Dry season			Hot and Dry season			Warm and Wet season			Warm and Dry season		
	Grain size			Grain size			Grain size			Grain size		
	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
Distribution of Cd (mgkg⁻¹) in various particle sizes												
1	224.78±0.16 ⁱ	279.75±0.18 ⁱ	331.75±0.18 ^j	263.30±0.07 ^h	340.43±0.40 ^j	450.87±0.09 ^j	184.61±0.28 ^h	233.65±0.25 ^h	272.63±0.45 ^j	221.50±0.35 ^e	274.00±0.71 ^h	330.00±1.41 ⁱ
2	27.34±0.01 ^a	37.32±0.48 ^a	52.92±0.06 ^c	35.15±0.60 ^b	42.30±0.49 ^a	71.81±0.13 ^b	21.46±0.38 ^a	29.36±0.45 ^a	42.90±0.00 ^b	32.00±0.71 ^{ab}	31.75±0.04 ^a	52.00±2.12 ^b
3	35.58±0.01 ^d	46.81±0.13 ^e	60.78±0.16 ^d	40.60±0.28 ^d	54.14±0.61 ^d	80.34±0.47 ^c	28.97±0.02 ^d	38.14±0.25 ^d	50.39±0.43 ^c	33.00±0.35 ^{ab}	41.50±0.35 ^c	57.50±0.35 ^c
4	34.95±0.04 ^d	39.20±0.57 ^b	50.72±0.20 ^b	37.62±0.27 ^c	43.69±0.22 ^b	66.67±0.23 ^a	28.85±0.11 ^d	32.22±0.16 ^b	41.53±0.33 ^b	28.50±0.35 ^a	32.00±0.71 ^a	47.00±0.71 ^a
5	31.95±0.04 ^c	47.30±0.49 ^e	65.40±0.28 ^e	38.13±0.62 ^c	61.10±0.64 ^g	90.39±0.43 ^d	26.13±0.62 ^c	38.59±0.29 ^d	53.01±0.70 ^d	32.25±0.53 ^{ab}	51.75±0.18 ^e	66.75±0.18 ^d
6	28.20±0.57 ^b	41.45±0.39 ^c	48.45±0.25 ^a	33.65±0.25 ^a	57.56±0.31 ^e	79.63±0.26 ^c	22.91±0.06 ^b	233.84±0.11 ^h	39.64±0.25 ^a	28.25±0.53 ^a	51.75±0.18 ^e	67.75±0.18 ^d
7	42.60±0.28 ^f	93.52±0.34 ^g	220.53±0.33 ^h	50.25±0.18 ^e	116.95±0.04 ^h	308.98±0.01 ^h	34.48±0.37 ^e	75.02±0.69 ^f	184.36±1.16 ^g	42.25±0.53 ^{bc}	96.75±0.18 ^f	232.00±0.71 ^h
8	45.96±0.03 ^g	150.65±0.25 ^h	228.00±0.35 ⁱ	55.01±0.70 ^f	171.09±0.64 ⁱ	303.29±0.50 ^g	37.37±0.45 ^f	122.36±0.45 ^g	187.03±0.69 ^h	46.25±0.18 ^c	126.50±0.35 ^g	216.25±2.65 ^g
9	37.78±0.16 ^e	42.96±0.03 ^d	135.46±0.38 ^g	41.15±0.60 ^d	49.08±0.65 ^c	184.77±0.16 ^f	28.89±0.08 ^d	35.14±0.10 ^c	105.36±1.16 ^f	31.75±14.32 ^{bc}	36.75±0.18 ^b	134.50±0.35 ^f
10	71.10±0.64 ^h	52.05±0.67 ^f	92.80±0.14 ^f	82.61±0.28 ^g	58.99±0.71 ^f	120.28±1.22 ^e	61.02±0.69 ^g	42.52±0.34 ^e	75.64±0.25 ^e	67.25±0.18 ^d	44.00±0.71 ^d	86.75±0.18 ^e
**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Distribution of Cr (mgkg⁻¹) in various particle sizes												
1	55.73±1.74 ^b	61.86±0.10 ^e	93.46±0.38 ^a	60.68±0.93 ^e	82.91±0.06 ^e	133.42±0.41 ^a	45.72±0.20 ^f	50.38±0.27 ^e	76.22±0.55 ^a	45.75±0.18 ^f	71.50±0.35 ^e	98.75±0.18 ^a
2	11.61±0.28 ^a	21.81±0.13 ^a	121.40±0.42 ^f	10.39±0.43 ^a	19.78±0.16 ^a	166.99±0.01 ^d	9.33±0.47 ^a	17.60±0.28 ^a	94.92±0.06 ^d	6.05±0.67 ^a	10.78±0.16 ^a	122.48±0.37 ^{bc}
3	30.04±0.03 ^{ab}	53.08±0.01 ^c	143.24±0.18 ^g	33.62±0.27 ^c	75.60±0.28 ^d	188.09±0.64 ^e	22.97±0.02 ^c	42.63±0.26 ^c	112.95±0.04 ^f	26.50±0.35 ^c	69.50±0.35 ^d	130.00±0.71 ^c
4	20.90±0.07 ^{ab}	52.89±0.08 ^c	176.78±0.16 ⁱ	21.70±0.21 ^b	59.33±0.47 ^c	233.51±0.35 ^h	17.17±0.59 ^b	43.28±0.20 ^c	141.65±0.25 ^h	16.00±0.71 ^b	44.00±0.71 ^c	166.50±0.35 ^d
5	80.51±0.35 ^{ab}	115.19±0.71 ⁱ	896.18±0.58 ^j	91.35±0.46 ^g	150.47±1.08 ⁱ	1174.22±0.55 ⁱ	65.56±0.31 ^h	93.04±0.03 ^j	711.13±0.62 ^j	73.25±0.53 ^h	130.00±0.71 ⁱ	866.00±13.44 ^f
6	31.75±0.18 ^{ab}	27.90±0.07 ^b	108.66±0.24 ^b	34.02±0.69 ^c	31.94±0.04 ^b	156.54±1.03 ^b	25.23±0.54 ^d	22.27±0.19 ^b	86.14±0.61 ^b	25.75±0.18 ^c	24.50±0.35 ^b	121.25±0.53 ^{bc}
7	126.12±0.08 ^{ab}	107.63±0.26 ^h	117.64±0.25 ^e	98.37±0.45 ^h	139.88±0.08 ^f	214.79±0.15 ^f	100.99±0.71 ^j	81.94±0.04 ^g	90.29±0.50 ^c	41.00±0.71 ^e	120.00±1.41 ^g	197.50±0.35 ^e
8	47.76±0.17 ^{ab}	56.31±0.49 ^d	115.02±0.27 ^c	48.19±0.93 ^d	111.22±0.55 ^f	213.52±0.34 ^f	38.06±0.66 ^e	44.80±0.14 ^d	90.50±0.35 ^c	33.50±0.35 ^d	125.75±0.53 ⁱ	199.00±0.00 ^e
9	64.63±0.26 ^{ab}	80.37±0.45 ^f	116.17±0.02 ^d	74.73±0.19 ^f	94.21±0.56 ^c	160.46±0.38 ^c	53.10±0.64 ^g	64.98±0.01 ^f	96.87±0.09 ^e	62.25±0.53 ^g	73.75±0.18 ^f	119.25±0.18 ^b
10	86.50±0.35 ^{ab}	106.20±0.57 ^g	145.05±0.67 ^h	106.52±0.34 ⁱ	141.08±0.65 ^g	219.03±0.69 ^g	71.13±0.09 ⁱ	86.10±0.07 ^h	117.10±0.64 ^g	93.00±0.71 ⁱ	123.25±0.53 ^h	174.75±0.18 ^d
**	20.11±0.60	20.00±0.62	32.50±2.02	21.11±0.60	22.00±0.83	30.50±0.60	2.00±0.83	3.56±0.60	5.56±2.02	20.88±2.11	22.30±0.40	32.20±2.93

Values are Mean±SD triplicate analysis of samples from each site.

Mean values in the same column followed by the same superscript letters are not significantly different (p > 0.05); ** Control

Table 5. Distribution of Cu & Zn (mgkg⁻¹) in various particle sizes in roadside soils from Kano Metropolis across the seasons

Site	Cool and Dry season			Hot and Dry season			Warm and Wet season			Warm and Dry season		
	Grain size			Grain size			Grain size			Grain size		
	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
Distribution of Cd (mgkg⁻¹) in various particle sizes												
1	9.90±0.07g	13.31±0.49e	19.64±0.25a	12.45±0.04g	10.53±0.33d	26.02±0.01a	8.02±0.69ab	10.62±0.27e	16.06±0.31a	11.08±0.06cd	3.75±0.00b	18.25±0.53a
2	4.55±0.32e	7.19±0.01d	36.36±0.45e	4.84±0.11c	7.42±0.41c	50.43±0.30d	3.74±0.40b	5.84±0.11d	29.56±0.31e	3.53±0.05abc	4.75±0.00c	38.48±0.06g
3	3.62±0.06d	16.02±0.06f	32.98±0.01d	3.06±0.31b	21.53±0.33e	44.01±0.01c	2.86±0.10ab	13.19±0.57f	26.92±0.06d	1.53±0.23bcd	19.18±0.13e	32.83±0.12e
4	11.06±0.10h	29.51±0.35i	155.50±0.35i	11.65±0.25f	35.32±0.48h	203.73±0.90h	9.33±0.33ab	24.31±0.22i	127.27±0.52i	8.53±1.36abcd	28.43±0.05g	154.53±0.33j
5	0.50±0.07a	4.68±0.23b	49.37±0.45f	6.58±0.30d	23.14±0.10f	55.72±0.20e	0.38±0.08a	3.89±0.08b	40.67±0.23f	10.75±0.04cd	33.55±0.04i	34.08±0.01f
6	3.31±0.06c	6.56±0.31c	54.78±0.86g	1.94±0.04a	6.86±0.10b	72.09±0.64f	2.61±0.06ab	5.26±0.18c	45.20±0.57g	0.00±0.00a	4.53±0.05c	52.75±0.04h
7	16.75±0.04i	22.70±0.21h	104.50±0.35h	18.59±0.29h	29.89±0.08g	133.27±1.22g	13.62±0.27ab	18.30±0.42h	85.14±0.61h	14.80±0.00d	26.20±0.07f	94.78±0.16i
8	3.58±0.06cd	19.30±0.28g	27.38±0.44b	2.86±0.10b	29.60±0.28g	37.42±0.41b	2.98±0.01ab	15.89±0.08j	22.35±0.46b	1.25±0.01ab	29.25±0.53h	28.75±0.18d
9	8.06±0.04f	19.00±0.00g	27.50±0.35b	8.39±0.22e	22.04±0.03e	37.17±0.12b	6.33±0.05ab	15.40±0.42g	22.09±0.06b	6.03±0.01abc	17.00±0.00d	27.53±0.33c
10	2.82±0.13b	3.20±0.28a	28.75±0.18c	1.68±0.23a	2.29±0.15a	37.88±0.08b	2.24±0.03ab	2.57±0.30a	23.24±0.54c	0.00±0.00a	0.53±0.01a	26.25±0.53b
**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Distribution of Cr (mgkg⁻¹) in various particle sizes												
1	798.94±10.30h	1043.62±0.56h	331.28±0.81b	507.36±0.28i	282.52±0.53b	331.28±6.47b	651.09±0.05i	846.45±0.30g	258.44±0.38b	447.45±0.39e	585.20±3.39d	782.00±0.71b
2	483.15±1.06d	703.00±0.64c	1896.00±0.68h	317.64±0.38e	1389.09±0.76h	1896.00±0.68h	393.17±0.17e	572.68±0.78c	1543.16±0.25h	470.75±0.18g	548.50±0.35c	947.50±0.35d
3	447.24±1.71c	743.11±0.59e	290.50±3.53a	303.85±0.31c	267.09±0.77a	290.50±3.53a	365.11±0.59d	603.39±0.74e	219.14±0.42a	602.73±0.19i	811.00±0.00i	998.75±0.18e
4	74.72±1.27g	1001.69±0.06g	1727.24±1.84g	483.12±0.53h	1277.41±0.60g	1727.24±1.84g	609.47±0.19h	809.82±1.22f	1395.08±3.64g	593.50±4.60h	689.50±0.35g	1170.25±0.53g
5	493.96±0.28e	754.45±0.39f	1336.09±0.74f	322.84±0.42g	983.59±1.42f	1336.09±2.16f	397.48±0.13f	600.82±1.23d	1059.00±1.36f	462.75±0.18f	617.50±0.35e	847.25±0.53c
6	388.41±4.12b	680.21±0.60b	1128.80±0.70d	257.70±0.68b	879.10±0.68e	1128.80±1.41d	340.94±0.38b	547.41±0.62b	894.67±0.21d	429.00±0.71d	723.75±1.24h	1405.75±0.18i
7	445.34±2.43c	544.61±1.30a	948.71±1.30c	315.51±0.57d	786.25±0.35c	948.71±2.01c	358.65±2.43c	439.59±1.48a	767.21±1.33c	819.25±0.53j	1242.25±0.18j	1801.00±0.71j
8	871.54±3.25i	1534.40±0.69i	3269.98±0.13j	537.34±0.36j	2284.86±0.93j	3269.98±0.13j	692.26±0.25j	1232.72±1.23i	2634.90±0.68j	270.75±0.88c	629.75±0.18f	1035.00±0.71f
9	52.24±0.37a	1547.96±0.26j	2409.37±0.92i	45.71±1.99a	1755.01±6.99i	2409.37±0.92i	40.88±0.13a	1226.26±0.23h	1905.28±1.49i	245.75±0.18b	427.75±1.59b	1212.00±0.71h
10	516.15±0.30f	708.02±1.94d	1198.17±0.91e	319.05±2.45f	861.17±5.81d	1198.17±1.22e	417.92±0.56g	1905.28±0.08j	968.04±0.40e	170.00±0.00a	256.00±0.71a	381.25±0.53a
**	30.03±1.40	30.00±0.17	48.20±3.40	32.00±5.20	34.12±0.20	56.10±2.10	22.00±0.20	20.00±0.30	30.20±0.90	37.00±2.30	38.14±1.40	64.14±0.68

Values are Mean±SD triplicate analysis of samples from each site.

Mean values in the same column followed by the same superscript letters are not significantly different (p > 0.05); ** Control

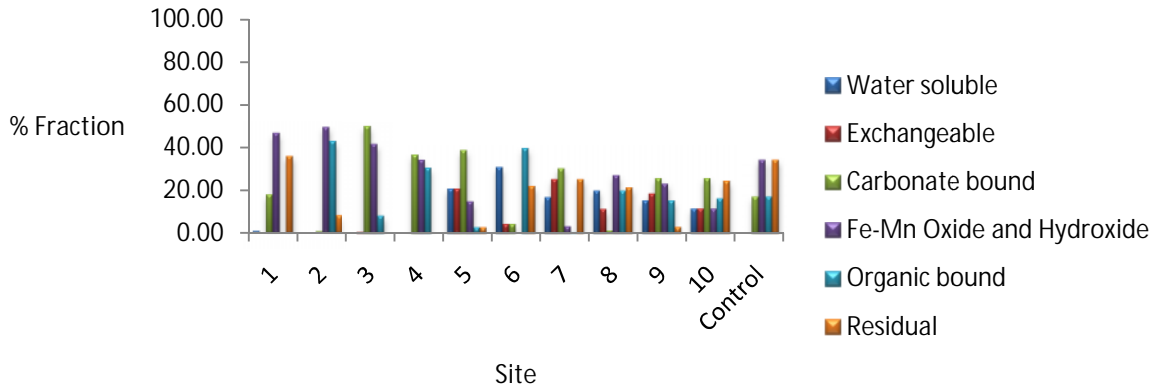


Fig 2a. Cd Percentage in each operationally fraction of roadside soils (particle size 1400µm)

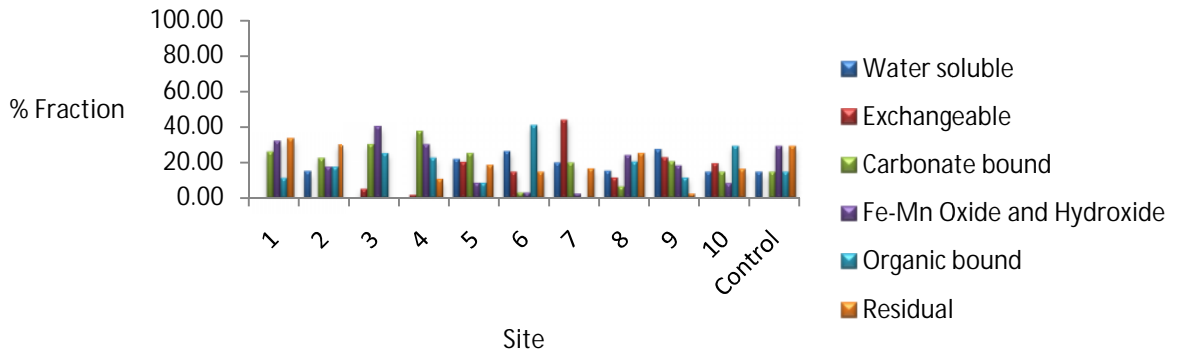


Fig 2b. Cd Percentage in each operationally fraction of roadside soils (particle size 355µm)

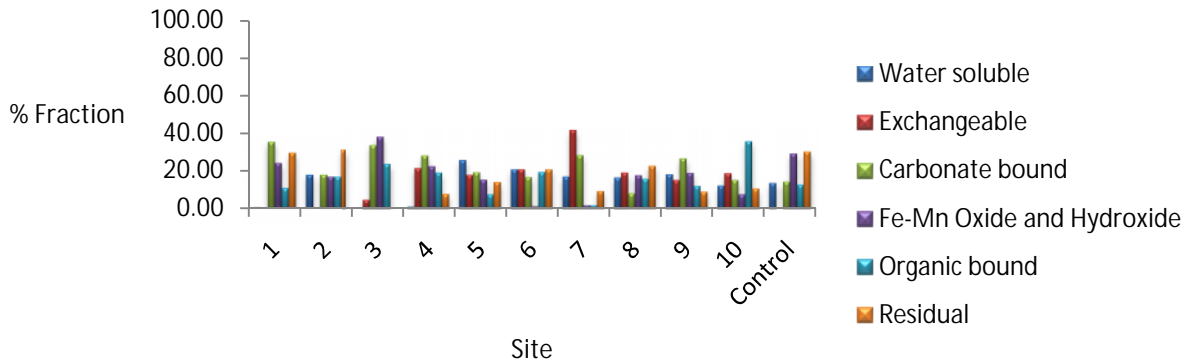


Fig 2c. Cd Percentage in each operationally fraction of roadside soils (particle size 150µm)

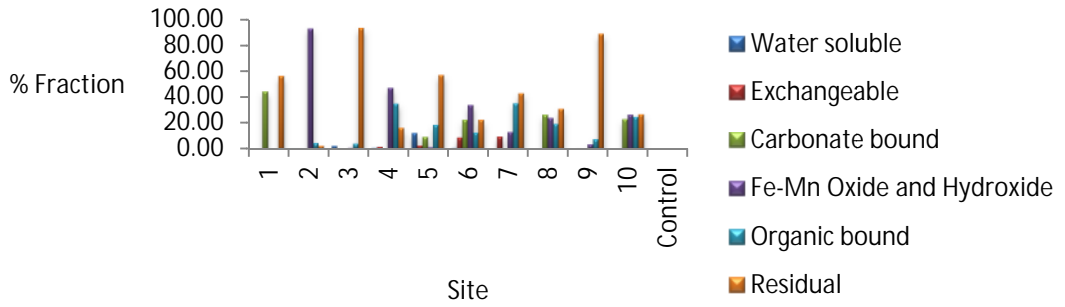


Fig 3a. Cr Percentage in each operationally fraction of roadside soils (particle size 1400µm)

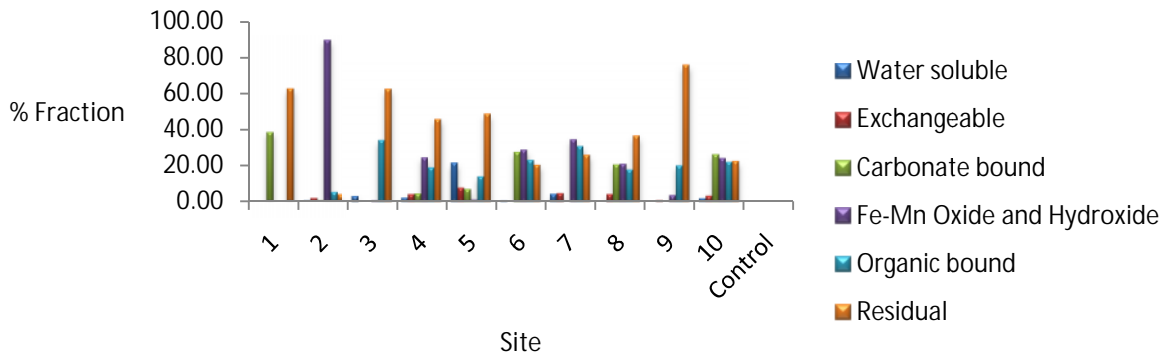


Fig 3b. Cr Percentage in each operationally fraction of roadside soils (particle size 355µm)

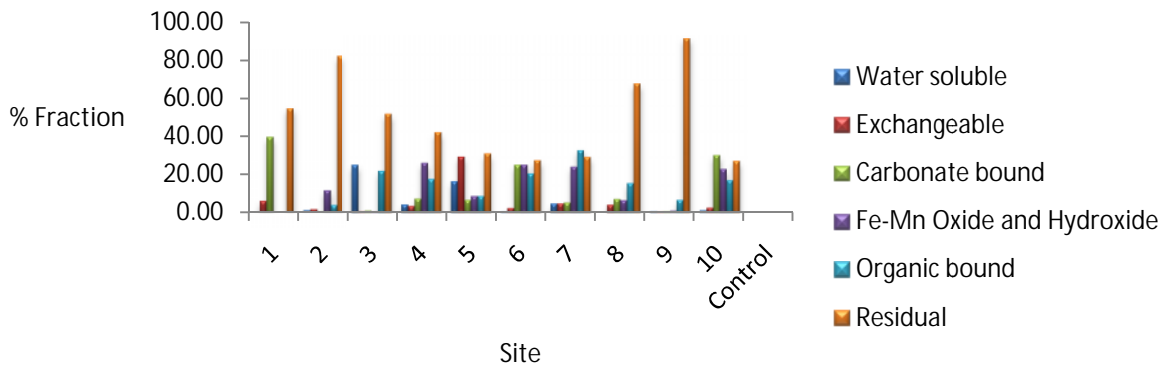


Fig 3c. Cr Percentage in each operationally fraction of roadside soils (particle size Percentage 150µm)

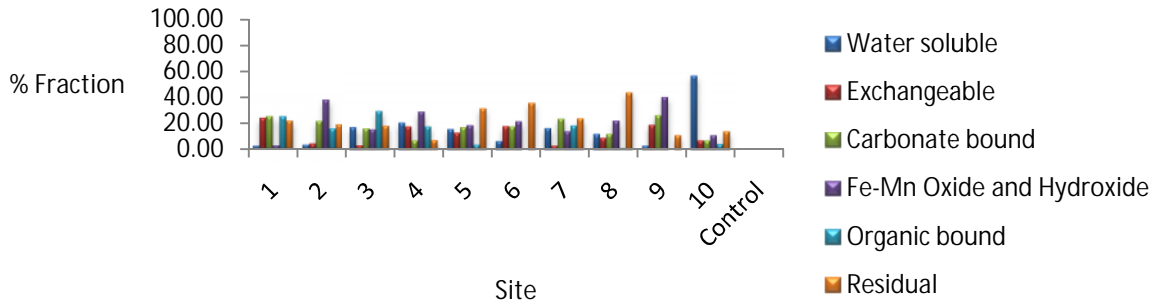


Fig. 4a. Ni Percentage in each operationally fraction of roadside soils (particle size 1400µm)

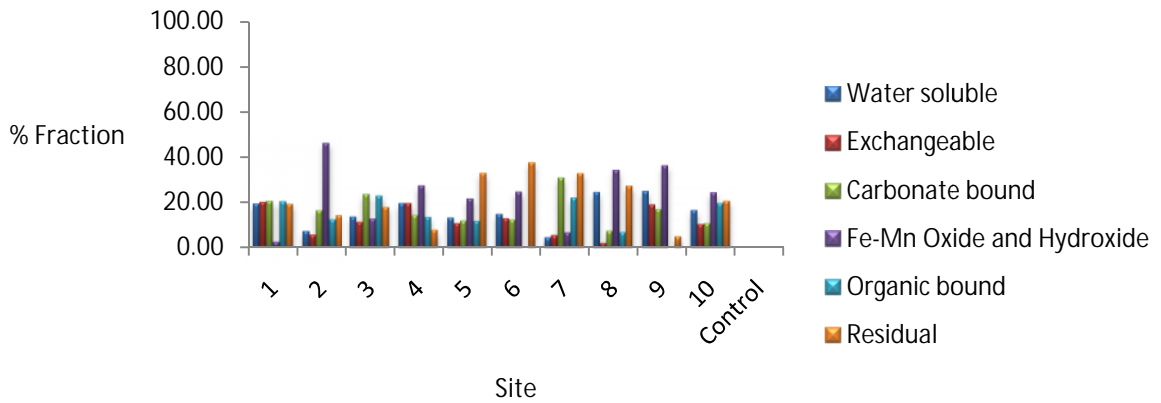


Fig. 4b. Ni Percentage in each operationally fraction of roadside soils (particle size 355µm)

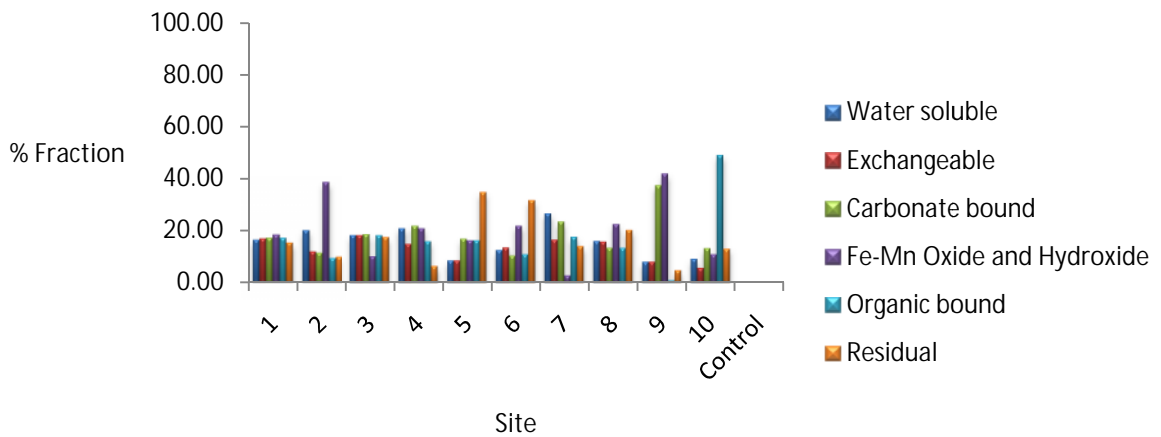


Fig. 4c. Ni Percentage in each operationally fraction of roadside soils (particle size 150µm)

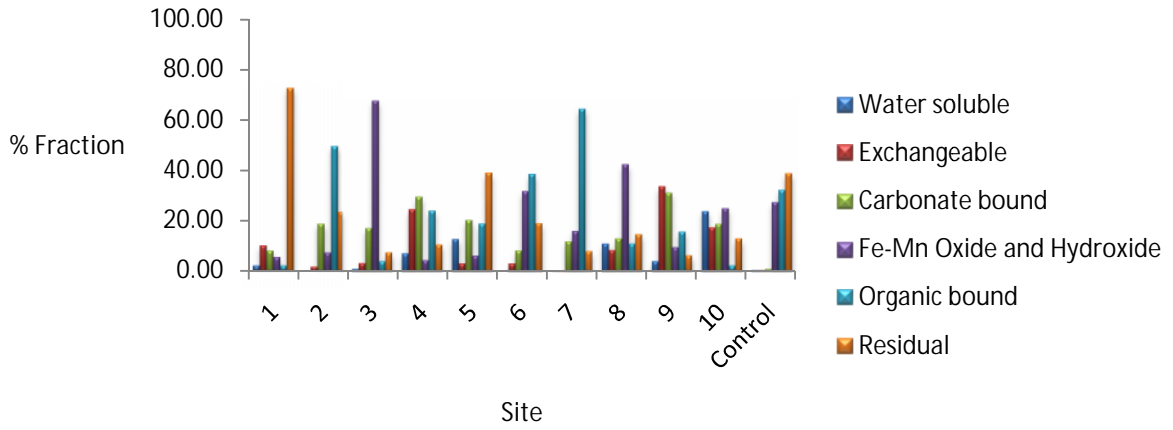


Fig. 5a. Pb Percentage in each operationally fraction of roadside soils (particle size 1400µm)

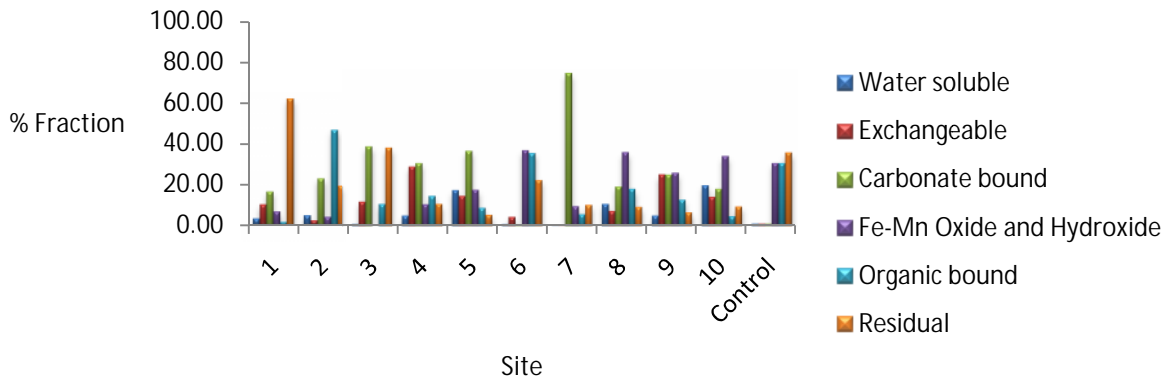


Fig. 5b. Pb Percentage in each operationally fraction of roadside soils (particle size 355µm)

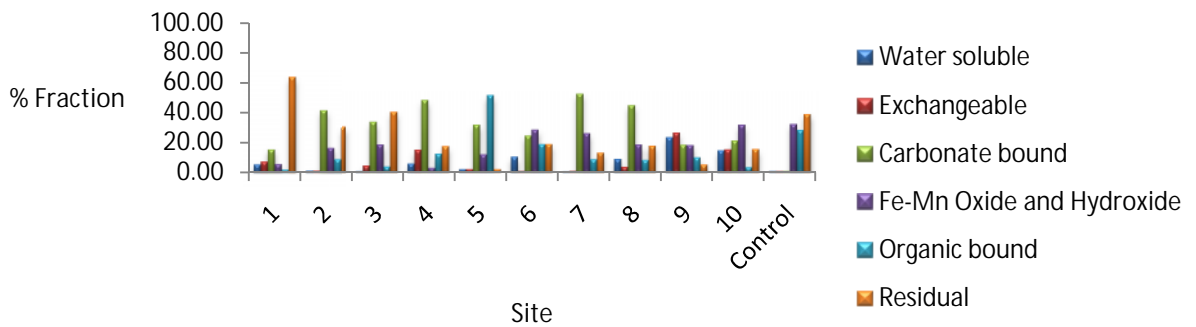


Fig. 5c. Pb Percentage in each operationally fraction of roadside soils (particle size 150µm)

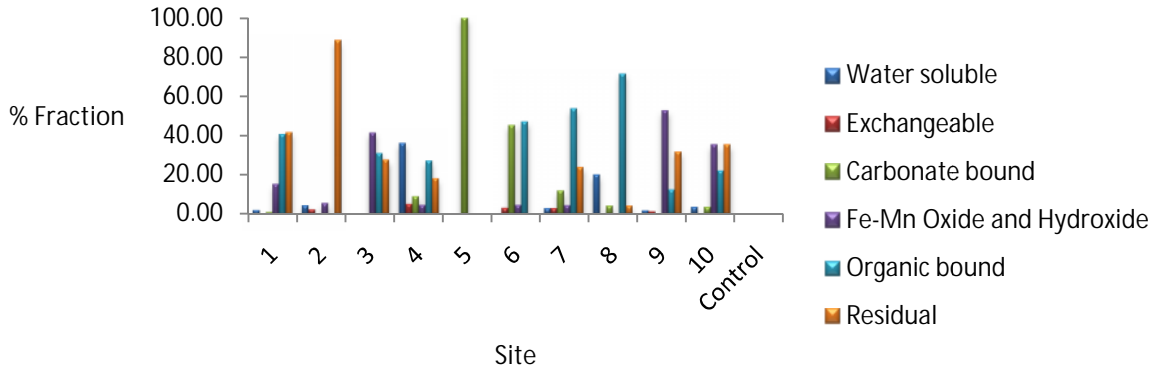


Fig. 6a. Cu Percentage in each operationally fraction of roadside soils (particle size 1400µm)

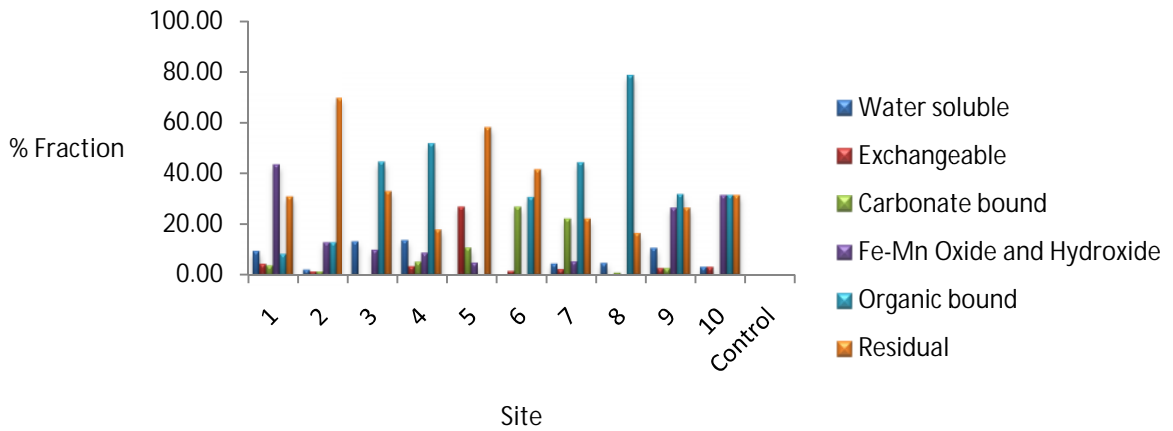


Fig. 6b. Cu Percentage in each operationally fraction of roadside soils (particle size 355µm)

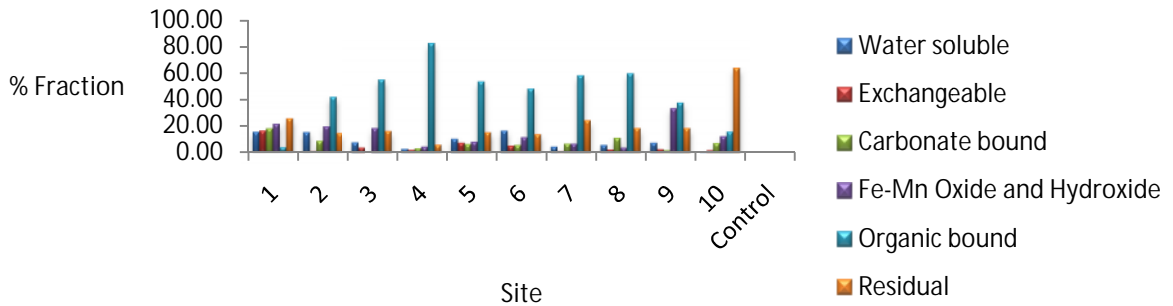


Fig. 6c. Cu Percentage in each operationally fraction of roadside soils (particle size 150µm)

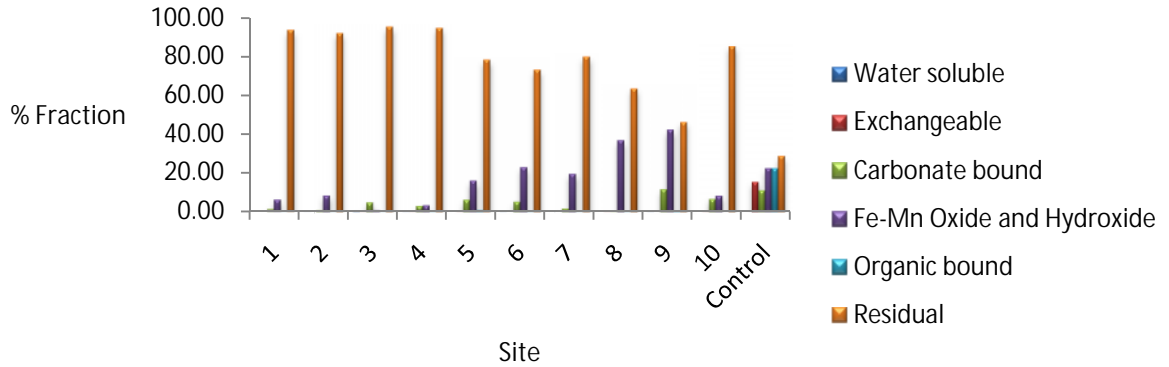


Fig. 7a. Zn Percentage in each operationally fraction of roadside soils (particle size 1400µm)

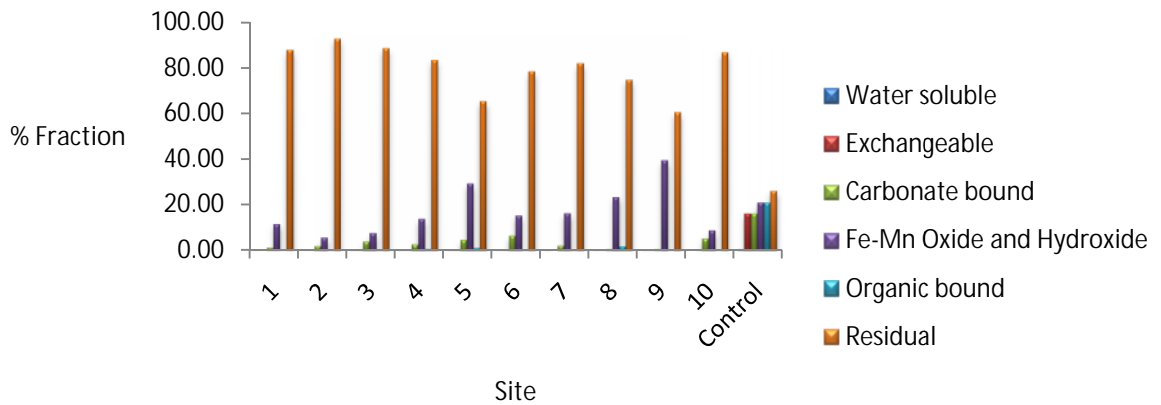


Fig. 7b. Zn Percentage in each operationally fraction of roadside soils (particle size 355µm)

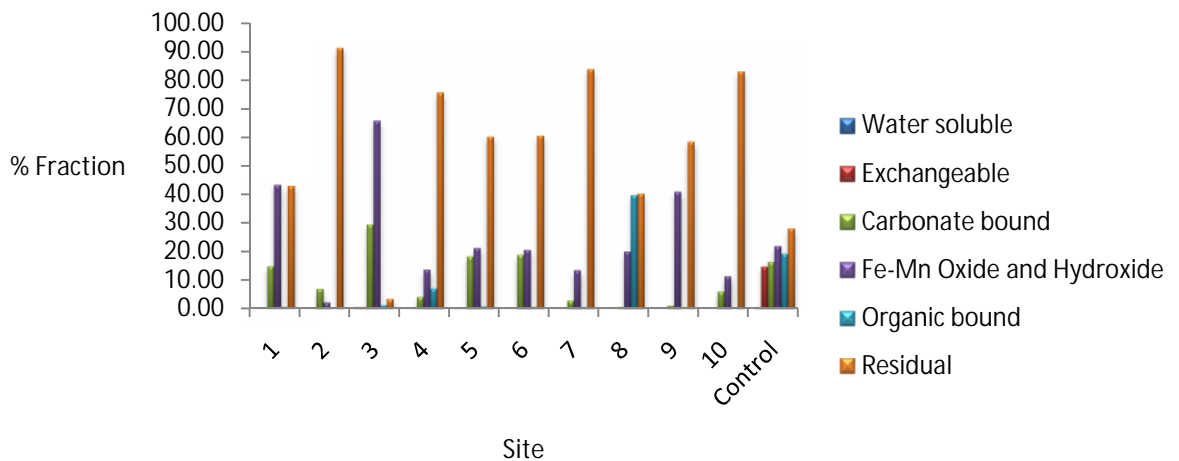


Fig. 7c. Zn Percentage in each operationally fraction of roadside soils (particle size 150µm)

However, the sequence of extraction follows the order of decreasing solubility of the geochemical forms of the metals, thus water soluble and exchangeable fractions indicate the forms most available for plant uptake (Ma and Rao, 1997; Onianwa, 2001). By this standard, > 20% in the soils was presently available to the environment. The high level of exchangeable and carbonate fraction is similar with the value reported for upland soils in south-western Nigeria (Olajire et al., 2003). It was also observed that the distribution of Cd in various chemical fractions is independent of the total content in these soils. Cd was present in all geochemical fractions.

The results of speciation of Cr in Figs. 3a-c shows that Cr was primarily bound to residual fraction (FVI) accounting on average > 50% of the total Cr, with the organic and Fe-Mn oxide (FV and FIV respectively) containing the majority of the remaining fractions. The results in the roadside soils are comparable to those reports from Seoul, Republic of Korea (Lee et al., 2005) and Ibadan Nigeria (Onianwa, 2001). This result is probably due to preferential incorporation of Cr into the silicate lattice. Also, the high level of Cr in the organic bound fraction may be attributed to the ease of complexation and peptisation products formed between the metal and natural organic matter like humic and fulvic acids (Ogunfowokan et al., 2009). The high level of Cr in the Fe-Mn oxide fraction was probably due to the high association or retention ability of the mineral crystal structure, such as with resistant sulphides. Generally, the high percentage of Cr in the residual fraction, indicate that the risk of Cr leaching is comparatively small and suggesting that Cr is of minor importance especially with large grain particle size during the warm and dry season and with respect to ecotoxicity. Although toxicity due to Cr seems high especially at Site 5 across the seasons and Site 3 in cool and dry seasons. This could indicate a possible pollution due to Cr to other environmental niches within the site. This is because, metals released from roadside soils can be flushed through drain networks into drainages, thereby contaminating underground water nearby and most important the rivers flowing across Kano Metropolis.

Ni was found in all the fractions, irrespective of the total Ni concentration in all the studied roadside soils. Ni as observed from the results (Figs. 4a-c) was identified as potentially the most bioavailable metal as it had the highest percentage > 50% with grain size 1400 μ m in all seasons. The majority of Ni is partitioned in the carbonate, Fe-Mn oxide, organic and residual fractions while the proportion of Ni in the exchangeable fraction is low. High percentages of Ni in the residual fraction have also been reported by Sutherland et al. (2005), Banerjee (2003) and Lee et al. (2005).

Since Pb concentration in roadside soils was higher than the control soils (Figs 5a-c), we assume that most of it is of anthropogenic origin. The non-residual fraction act as a predominant sink for anthropogenic Pb accounting for about 55% of total Pb except in Site 1 (63.29 – 87.98%) where residual fraction dominate. These results indicate that water soluble, exchangeable, carbonate, Fe-Mn oxide and organic fractions contain most of the Pb in roadside soils in Kano metropolis. Pb in the residual fraction varied widely from 0.00 – 87.98%. Such variability of the Pb partitioning may be a function of different levels of anthropogenic contamination along the roadside (Sutherland and Tack, 2000; Norrström and Jacks, 1998). As shown in the results, the reducible Pb is more abundant than the other non-residual fractions of Pb in some sites. The fact that Pb can form stable complexes with Fe-Mn oxide (Ramos et al., 1994) may be the reason for this. The reducible Pb predominating in the non-residual fractions in this study have been reported by many researchers (Li et al., 2001; Ip et al., 2007; Gao et al., 2008).

The chemical association of Cu is dominated by the oxidizable (FV) fraction (0.0 – 95.56%) as shown in Figs. 6a-c which is similar to other studies on roadside soils (Wang et al. 1998; Banerjee, 2003; Charlesworth et al., 2003). This likely indicates the effectiveness of organic matter as a scavenger of Cu in roadside soils. Also, a number of studies on speciation of Cu have show that Cu are mainly associated with the oxidizable phase, occurring as organically complexed metal species (Pardo et al., 1993; Fytianos and Laurantou, 2004). This is because Cu shows high affinity with humic substances, which are a fraction of natural organic matter chemically active in complexing such metals (Pempkowiak et al., 1999). The role of water soluble (FI) fraction is not significant although significant in Site 4 (35.19 – 38.59%) for grain size 1400µm.

Zn partitioning is dominated by the residual (FVI) fraction followed by reducible (FIV) fraction then carbonate fraction (FIII) as shown in Figs. 7a-c, indicating that these three fractions are of major importance as the Zn carriers in the roadside soils of Kano Metropolis. This is in agreement with previous finding for roadside soils (Banerjee, 2003; Lee et al., 2005) and urban cities soils in south-western Nigeria (Oluwatosin et al., 2008). Highest percentage residual fraction decreases as the grain size of the soils increases from 1400 - 150 µm. The greater percentage of Zn in the residual fraction probably reflects the greater tendency for Zn to become unavailable once it was in soils. Similar Zn results were reported for contaminated soil (Ma and Rao, 1997). Among the non residual fractions, Fe-Mn oxide fraction contained the greatest among the fraction with few exceptions in some sites. This may be partially due to the high stability constants of Zn oxides. Several other workers have also found Zn to be associated with Fe-Mn oxide (Kuo et al., 1983; Ramos et al., 1994; Ma and Rao, 1997; Gao et al., 2008). The percentages content of the water soluble, exchangeable and organic fractions in these soils at average are relatively low. Although a large percentage of the total Zn was in the residual fraction in these soils, the amount of Zn present in the non-residual fractions were also appreciable from the standpoint of potential Zn mobility and bioavailability. Generally, Zn was present in all geochemical fractions, irrespective of the total Zn fractions.

3.4 MOBILITY OF METALS IN ROADSIDE SOILS

Mobility of metals in soil may be assessed on the basis of absolute and relative content of fractions weakly bound to soil components. Since some of the metal fraction (FIII) are strongly bound to the soil components (relatively less mobile) than those extracted in FI and FII, hence, the relative index of metal mobility was calculated as a mobility factor (MF) according to Yusuf (2007) and Kabala and Singh (2001) on the basis of the following equation:

$$MF = \frac{FI + FII + FIII \times 100}{FI + FII + FIII + FIV + FV + FVI}$$

The mobility factor of Cd, Cr, Ni, Pb, Cu and Zn in roadside soil samples. The mobility factor showed variations especially across the sites: 0.81 – 86.79% for Cd, 0.58 – 52.10% for Cr, 27.80 – 70.60% for Ni, 5.48 – 68.43% for Pb, 0.00 – 100.00% for Cu, and 0.00 – 18.85% for Zn. Highest MF for all studied metals were obtained in 150µm samples with exception of Ni, Pb and Cu where highest percentage MF was obtained in 1400µm samples and 355µm for Zn. This indicates that particle size concentration distribution across the particle size does not show any marked trend. Thus the proportion of metals appears not uniformly distributed in different particle size, which could be due to other sources other fine particle emission form vehicles.

Percentage MF apart from reflecting levels of water soluble, exchangeable and carbonate bound of these metals, high MF values, an indication of lability and biological availability of heavy metals (Ahumada *et al.*, 1999; Kabala and Singh, 2001; Yusuf, 2007), showed the extent of the vulnerability of living things generally to heavy metals (Ogunfowokan *et al.*, 2009). From this study, it is evident that the inhabitants of sites 1, 5, 6, 7 and 9 have the highest vulnerability to Cd, Cr, Ni, Pb, Cu and Zn exposure, while those living around sites 2, 3, 4, 8 and 10 have low vulnerability compare to others. The low MF value for some metals in this study could be an index of the high stability of these metals in the sample (Ogunfowokan *et al.*, 2009). Generally, the results of the present study, suggest that the high mobility and bioavailability of these metals followed the profile below: Cd > Pb > Ni > Cu > Cr > Zn, this is also in agreement with other study (Yusuf, 2007).

4. CONCLUSION

The heavy metal concentration of roadside samples from Kano Metropolis varied to a great extent by the difference of the sampling sites and metal type. On average the percentage of heavy metal retained by each fraction in the roadside soil was different according to metal type, the group of Cr, Ni and Zn were retained predominantly by the residual fraction, while Cd is highest in the Fe-Mn oxide fraction, Pb in the carbonate bound fraction, and Cu in the organic fraction. It was found that concentrations in the water soluble and exchangeable fractions were generally low for most of the studied metals.

Considering the proportion of metals bound to the water soluble to the exchangeable and the carbonate bound fractions, the comparative mobility of metals in this order; Ni > Cd > Pb > Cr > Cu > Zn. Highest MF for all studied metals was obtained in 150 μ m samples with exception of Ni, Pb and Cu where highest percentage MF was obtained in 1400 μ m samples and 355 μ m for Zn. As potential changes of redox state and pH may remobilize the metals bound to carbonate, Fe-Mn oxide and organic matter, and may release and flush them through drain networks into streams (Lee *et al.*, 2005). This could indicate other sources than fine particulate emission from vehicles responsible. With toxicity it appears that Cd, Cr, Ni, Pb and Cu pollution along the roadside is of concern.

ACKNOWLEDGMENTS

We appreciate the effort of Mal. Muazu and Mrs Khadijat both of Kaduna State University Kaduna for assistance given on sample analysis. Mr Ilu of Soil Science Department, Ahmadu Bello University, Zaria, Nigeria is also acknowledged for his assistance in soil analysis and remaining part of sample analysis. You are wonderful and hope to keep up our collaboration in the future.

REFERENCES

- Adie, G. U. and Osibanjo, O. (2009). Assessment of soil-pollution by slag from an automobile battery manufacturing plant in Nigeria. *Afr. J. Environ. Sci. Technol.*, 3(9), 239 – 250.
- Adnan, M., Feras, A. and Qasem, J. (2003). Determination of cadmium and lead in different cigarette brands in Jordan. *Acta Chim Slov.*, 50, 375 – 381.

- Ahumada, I., Mendoza, J., Ascar, L. (1999). Sequential extraction of heavy metals in soils irrigated with wastewater. *Commun. Soil Sci. Plant Anal.*, 30, 1507 – 1519.
- Bai, J. Cui, B., Wang, Q., Gao, H., Ding, Q. (2008). Assessment of heavy metal contamination of roadside soils in southeast China. *Stoch. Environ. Res. Risk Assess.*, doi.10.1007/s00477-008-0219-5.
- Banerjee, A. D. K. (2003). Heavy metal levels and solid phase speciation in street dusts of Delhi, India. *Environ. Pollut.*, 123, 95–105, doi:10.1016/s0269-7491(02)00337-8.
- Charlesworth, S., Everett, M., McCarthy, R., Ordonez, A. and De Miguel, E. (2003). A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. *Environ. Int.*, 29, 563 – 573.
- Chimuka, L. Mugwedi, R. Moboladisoro, B. H. and Odiyo, O. J. (2005). Metals in environmental media: A study of trace and platinum group metals in Thohoyandou, South Africa. *Water SA*, 31(4), 581 – 588.
- Chon, H.-T., Ahn, J.-S., Jung, M. C. (2008). Seasonal variations and chemical forms of heavy metals in soils and dusts from the satellite cities of Seoul, Korea. *Environ. Geochem. Health*, 20, 77-86.
- Davidson, C. M., Thomas, R. P., Mcvey, S. E., Perala, R., Littlejohn, D. and Ure, A. M. (1994). Evaluation of sequential extraction procedure for the speciation of heavy metal in sediments. *Analytica Chimica Acta*, 291, 277 – 286.
- Ericksson, J. E. (1989). The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to the soil. *Water, Air and Soil Pollution*, 48, 317 – 335.
- Evans, L. J. (1989). Chemistry of metal retention by soils. *Environ. Sci. Tech.*, 23(9), 1046 – 1056.
- Finžgar, N. Tlusto, P. and Leštan, D. (2007). Relationship of soil properties to fractionation, bioavailability and mobility of lead and zinc in soil. *Plant Soil Environ.*, 5, 225 – 238.
- Fytianos, K and Lourantou, A. (2004). Speciation of elements in sediment samples collected at Lakes Volvi and Koronia, N. Greece. *Environment International*, 30, 11 – 17.
- Gao, X., Chen, S., Long, A. (2008). Chemical speciation of 12 metals in surface sediments from the northern South China Sea under natural grain size. *Baseline/Marine Pollut. Bull.*, 56, 770 – 797.
- Ip, C. C. M., Li, X. D., Zhang, G., Wai, O. W. H., Li, Y. S. (2007). Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *Environ. Pollut.*, 147, 311 – 323.
- Kabala C.I., Singh B. R. (2001). Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *J. Environ. Qual.*, 30, 485 – 492.
- Kuo, S., Heilman, P. E., Baker, A. S. (1983). Distribution and forms of copper, zinc, cadmium, iron and manganese in soils near a copper smelter. *Soil Sci.* 135, 101 – 109.
- Lee, P. K., Yu, Y. H., Yun, S. T. and Mayer, B. (2005). Metal contamination and solid phase partitioning of metals in urban roadside sediments. *Chemosphere*, 60, 672–689.
- Li, X., Shen, Z., Wai, O. W. H., Li, Y. S. (2001). Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. *Marine Pollut. Bull.*, 42, 215 – 223.
- Ma, Q. L. and Rao, N. G. (1997). Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *J. Environ. Qual.*, 26, 259 – 264.
- Mashal, K., Al-Qinna, M. and Yahya, A. (2009). Spatial distribution and environmental implication of lead and zinc in urban soils and street dust samples in Al-Hashimeyeh municipality. *Jordan J. Mech. Indust. Engg.*, 3(2), 141 – 150.
- Mohammed, S., Nkobobi, M., Georges-Ivo, E., Ekosse, O. T., Julius, A. (2005). Soil heavy metal concentration patterns at two speed zones along the Gaborone-Tlokweng

- Border post highway, Southeast Botswana. *J. Appl. Sci. Environ. Manage.*, 10(2), 135 – 143.
- Nabuloa, G., Oryem-Origa, H., Diamond, M. (2006). Assessment of lead, cadmium and zinc contamination of roadside soils, surface films and vegetable in Kampala city, Uganda. *Environ. Res.* 101, 42 – 52.
- Norrström, A. C. and Jack, G. (1998). Concentration and fractionation of heavy metals in roadside soils receiving de-icing salts. *Sci. Total Environ.*, 218, 161 – 174.
- Ogunfowokan, A. O., Oyekunle, J. A. O., Durosinmi, L. M., Akinjokun, A. I. and Gabriel, O. D. (2009). Speciation study of lead and manganese in roadside dusts from major roads in Ile-Ife, South Western Nigeria. *Chemistry and Ecology*, 25(6), 405 – 415.
- Okunola, O. J., Uzairu, A. and Ndukwe, G. (2007). Levels of trace metals in soil and vegetation along major and minor roads in metropolitan city of Kaduna, Nigeria. *Afr. J. Biotechnol.*, 6(14), 1703 – 1709.
- Okunola, O. J., Uzairu, A., Ndukwe, G. I. and Adewusi, S. G. (2008). Assessment of Cd and Zn in roadside surface soils and vegetations along some roads of Kaduna metropolis, Nigeria. *Res. J. Environ. Sci.*, 2(4), 266 – 274.
- Olajire, A. A., Ayodele, E.T., Oyediran, G.O. and Oluyemi, E. A. (2003). Levels and speciation of heavy metals in soils of industrial Southern Nigeria, *Envir. Monit. Assess.*, 85, 135–155.
- Oluwatosin, G. A., Adeyolanu, O. D., Dauda, T. O., Akinbola, G. E. (2008). Levels of geochemical fractions of Cd, Pb and Zn in valley bottom soils of some urban cities in Southwestern Nigeria. *Afr. J. Biotechnol.*, 7(19), 3455 – 3465.
- Onianwa, P. C. (2001). Roadside topsoil concentrations of lead and other heavy metals in Ibadan, Nigeria. *Soil and Sediment Contamination*, 10(6), 577 – 591.
- Pardo, R., Barrado, E., Castrillejo, Y., Velasco, M. A., Vega, M. (1993). Study of the contents and speciation of heavy metals in river sediments by factor analysis. *Analytical Letters*, 26, 1719 – 1739.
- Pempkowiak, J., Sikora, A., Biernacka, E. (1999). Speciation of heavy metals in marine sediments vs their bioaccumulation by mussels. *Chemosphere*, 39, 313 – 321.
- Porteus, A. (2005). Hazardous waste management handbook, Butterworths and Co Publishers, UK.
- Ramos, L., Hernandez, L. M., Gonzalez, M. J. (1994). Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National Park. *J. Environ. Qual.*, 23, 50 – 57.
- Saeedi, M., Hosseinzadeh, M., Jamshidi, A., Pajooheshfar, S. P. (2009). Assessment of heavy metals contamination and leaching characteristics in highway side soils, Iran. *Environ. Monit. Assess.* 151, 231 – 241.
- Sparks, D. L. (1996). *Methods of soil analysis. Part 3: Chemical Methods*. 2nd ed. Maidson: SSSA.
- Sutherland, R. A. and Tack, F. M. G. (2000). Metal phase association in soils from an urban watershed, Honolulu, Hawaii. *Sci Total Environ.*, 256, 103 – 113.
- Tessier, A., Campbell, P. G. C., Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51, 844 – 851.
- TWG (2010). Current population figures for cities, towns and administrative divisions of the world. <http://www.world-gazetter.com/home.htm> accessed 10th November, 2010.
- Vaird, B., Pihan, F., Promeyrat, S., Pihan, J. C. (2004). Integrated assessment of heavy metal (Pb, Zn and Cd) highway pollution: bioaccumulation in soil, Graminaceae and land snails. *Chemosphere*, 55, 1349 – 1359.
- Walkley, A and Black, I. A. (1934). An Examination of the Detjare method for determining soil organic matter and a proposed modification of the chronic acid titration. *Soil Sci.*, 37, 29 – 36.

- Wang, W. H., Wong, M. H., Leharne, S., Fisher, B. (1998). Fractionation and biotoxicity of heavy metals in urban dusts collected from Hong Kong and London. *Environ. Geochem. Health*, 20, 195 – 198.
- Yahaya, M. I., Ezech, G. C., Musa, Y. F. and Mohammed, S. Y. (2010). Analysis of heavy metals concentration in roadsides soil in Yauri, Nigeria. *Afr. J. Pure Appl. Chem.*, 4(3), 022 – 030.
- Yaron, B. (1995). Retention of pollutants on and within the soil solid phase. *Soil Pollution. Processes and Dynamics*. Verlag Berlin.
- Yuan, C., Shi, J. He, B., Liu, J., Lung, L., Jiang, G. (2004). Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environ. Int.*, 30, 769 – 783.
- Yusuf, K. A. (2007). Sequential extraction of Pb, Cu, Cd and Zn in soils near Ojota waste site. *J. Agron.*, 6(2), 331 – 337.
- Zechmeister, H.G., Hohenwallner, D., Hanus-Ilmar, A. (2005). Estimation of element deposition derived from road traffic sources by using mosses. *Environ. Pollut.*, 138, 238 – 249.

© 2011 Okunola et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/2.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.