

Full Length Research Paper

Chemical fractionation of heavy metals in soils around the vicinity of automobile mechanic workshops in Kaduna Metropolis, Nigeria

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Accepted 23 December, 2010

The study of heavy metals in environmental niches is essential, especially with their potential toxicity to human life. Metal toxicity depends on chemical associations in soils. For this reason, determining the chemical form of a metal in soils is important to evaluate its mobility and bioavailability. In this manner sequential extraction was used to fractionate seven heavy metals (Cd, Cu, Ni, Zn, Cr, Fe and Pb) from ten contaminated soils into six operationally defined groups: water soluble, exchangeable, carbonate, Fe -Mn oxide, organic, and residual. The residual fraction was the most abundant pool for all the metals examined. A significant amount (2.00 to 73.47, 1.77 to 17.78, 9.76 to 58.54 and 1.71 to 54.11% respectively) of Cu, Cd, Cr and Pb was present in the potentially available fraction: non residual fraction. Contamination of Zn, Ni and Fe in these soils was not as severe as Cu, Cd, Cr and Pb. Overall, the order of contamination was Cu > Cr > Pb > Cd > Ni > Zn > Fe. The study indicated that the possible pollution of soils of this environment was as a result of activities carried out within these areas.

Key words: Fractionation, heavy metals, mechanic, workshops, Kaduna.

INTRODUCTION

The problem of soil and vegetation pollution due to toxic metals in spent oil is beginning to cause concern now in most major metropolitan cities (Vwioko et al., 2006). These toxic heavy metals entering the ecosystem may lead to geoaccumulation, bioaccumulation and biomagnification (Wong et al., 2002; Lokeshwari and Chandrappa, 2006). Spent oil soil pollution leads to the build-up of essential and non-essential elements in the soil and eventual translocation in plant tissues (Vwioko et al., 2006). Soil pollution by spent lubricating oil has been reported to cause growth retardation/reduction in plants and this has been attributed to the presence of heavy metals at toxic concentrations in the soil (Anoliefo and Vwioko, 1995).

Due to the ever-increasing population and industrialization, most environments are to some extent unnaturally

polluted. Nriagu (1978) reported that we may be experiencing a silent epidemic of environmental metal poisoning from the increasing amounts of metals released into the biosphere. Waste engine oil pollution is responsible for several environmental problems, including disruption of plant water relations, direct toxicity and indirect effects on plant metabolism (Racine, 1994). Edebiri and Nwanokwale (1981) found that metals present in spent lubricating oil are not necessarily the same as those present in unused lubricant. Heavy metals such as vanadium, lead, aluminum, nickel and iron which are low in unused engine oil gave higher concentrations in spent engine oil. Hall (2002) observed that heavy metals such as copper and zinc are essential for normal plant growth, elevated concentrations of both essential and non essential metals can result in growth inhibition and toxicity symptoms.

There are researches in the Southern part of Nigeria on oil pollution of soil and vegetation, but data is scarce on oil pollution in the Northern region of the country.

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Consequently, this work was initiated to study and evaluate soil and vegetation pollution due to heavy metals in spent lubricating oil in the vicinity of mechanic workshops in Kaduna metropolis of Northern Nigeria.

Kaduna was selected as the regional headquarters of Northern Nigeria in 1912 by the British colonial officials led by Lord Frederick Lugard. "Kaduna" is a Hausa word that means "crocodiles". This name was given to the town because of the presence of crocodiles in the river (River Kaduna) that now divides the town into two. The growth of Kaduna into an urban area was stimulated by its choice as an administrative centre and a garrison town by the colonialist because of its central location in the North and its now the capital city of Kaduna State. The development of industrial outfits and the growth of commercial activities led to an increased influx of people searching for jobs. By 1963, the population of Kaduna was less than 250,000 but the 1991 Census results put the population at 1,307,311. The population in 2001 was estimated to be 2,466,760 (Africa Atlases, 2002) while in 2008, it was estimated to be over 4,000,000.

MATERIALS AND METHODS

Kaduna lies at latitude 10°28'N and at longitude 7°25'E. It is located in the central area of what used to be called the Northern Region of Nigeria. The mean annual rainfall in the area ranges from 924.3 to 1,543.6 mm. Annual temperature varies between 29 to 38.6°C. Presently, Kaduna is the capital of Kaduna State which was created in 1987. The creation of states did not affect the growth of Kaduna as an administrative, industrial, a veritable commercial center and a functional urban area. Kaduna today ranks second only to Kano in Northern Nigeria in terms of population (about 4,000,000 residents), industrial and commercial activities.

Ten mechanic workshops: Old Artillery Barracks (OA), Inland Container (IC), Sabon Tasha (ST), Ungwan Boro (UB), Television (TV), Kurmi Mashi (KM), Badiko (BD), Ungwan Muazu (UM), Kakuri (KK) and Gonin Gora (GG): were selected based on availability of mechanic workshops and geographical location for soil and plant samplings from the study area (Kaduna) excluding control (Figure 1). Surface soil samples were collected from the immediate vicinity of the plant samples with the aid of a stainless spoon, washed with soap and rinsed with distilled water after each sampling (Awofolu, 2005). Twelve soil samples from each mechanic workshop (sampling location), were collected and mixed properly to give a composite sample mixture. Three control samples (A, B, and C) were collected to validate the heavy metal concentration in soil and plant in areas where no human activities such as those of auto mechanics have taken or are taking place.

Soil and plant (*Sida acuta* Brum. f commonly known as brown weed) samples were collected in April 2008 according to Chimuka et al. (2005) and Awofolu (2005) respectively. The plant and soil samples collected were pretreated and digested according to Awofolu (2005).

The pH and electrical conductivity of soil samples were measured with a soil: water ratio of 1:2 using pH and electrical conductivity meters (HANNA Model No 111991000) as described by Hendershot et al. (1993); organic carbon was determined by the method of Walkley and Black (1934); Cation Exchange Capacity (CEC) was determined by Hendershot et al. (1993); while particle size distribution was determined by the hydrometer method as described by Bougoucos (1951). Extractable sulphate (SO_4^{2-}) and

phosphate (PO_4^{3-}) were determined by methods described by Allen et al. (1974).

Sequential extraction was carried out on the principle of selective extraction, proposed by Tessier et al. (1979), with the following modifications: Water soluble was first of all extracted (Ma and Rao, 1997) and then, $\text{Mg}(\text{NO}_3)_2$ was used instead of MgCl_2 to extract exchangeable fraction because the chloride ion can complex metals (Shrivastava and Benerjee, 2004) and increase the solubility of several heavy metals within the soil. Also, the extraction of the oxidisable phase was undertaken after the extraction of the exchangeable phase. This method allows the destruction of organic matter, which entraps the mineral materials and then provides a better extraction of the following phases (Shrivastava and Banerjee, 2004). For the residual fraction, a combination of aqua regia/hydrofluoric acid ($\text{HCl}/\text{HNO}_3/\text{HF}$) was used (Shrivastava and Banerjee, 2004).

Quality control test was performed on soil and plant samples in order to validate the experimental procedures. This was done by spiking the pre-digested soil and plant samples with Multielement metal Standard Solution, MESS (0.5 mg l^{-1} of Cd and Cr and 5 mg l^{-1} for Cu, Fe, Ni, Pb and Zn) according to Awofolu (2005).

The validity of the extraction procedure and the precision and accuracy of the Atomic Absorption Spectrophotometer were tested by spiking experiment. The results of the 7 heavy metals present in the soil and plant samples as shown in Table 1 varied between 89.67 to 108.67 and 89.00 to 103.00 for the soil and plant respectively. The highest percentage recovery of 108.67 and 103.00 were recorded for Zn in soil and plant respectively while the lowest percentage recovery of 89.67 and 89.00 were recorded for Ni in soil and plant respectively. The pattern of recovery efficiency for both soil and plant were found to follow the decreasing orders; $\text{Zn} > \text{Cu} > \text{Fe} > \text{Cr} = \text{Pb} > \text{Cd} > \text{Ni}$ and $\text{Zn} > \text{Cr} = \text{Pb} > \text{Fe} > \text{Cu} > \text{Cd} > \text{Ni}$.

RESULTS AND DISCUSSION

Tables 2 and 3 show the results of the physico-chemical parameters of the surface soil of Kaduna in the study and control areas. The percentage of particle size distribution in Kaduna soil was in the range 22.0 to 34, 12.0 to 30.0 and 42.0 to 64% for clay, silt and sand respectively. Generally, the textural class of the soils was mainly loamy sand with a few (that is soil samples from Sabon Tasha, Badiko and Gonin Gora mechanic workshops) being loamy clay.

As shown in Table 2, soil pH varied from 7.00 to 8.00 and 7.30 to 7.60 for the study and control sites, respectively. This is consistent with the results of Maiz et al. (2000) and Osakwe and Otuya (2008). The soil pH serves as a useful index of availability of nutrients, the potency of toxic substances present in the soil and the physical properties of the soil. Several studies have shown that availability of heavy metals is pH dependent (Iwegbue et al., 2006; Gonzalez-Fernandez et al., 2008). Most of the pH values of the study areas did not indicate the tendency for availability of these metals and this could indicate low metal uptake by plants. Electrical Conductivity (EC) values ranged from 0.30 to $9.50 \mu\text{scm}^{-1}$ and 0.30 to $0.35 \mu\text{scm}^{-1}$ for study and control sites, respectively. Also, variation observed in electrical conductivity between sites could be due to the content of

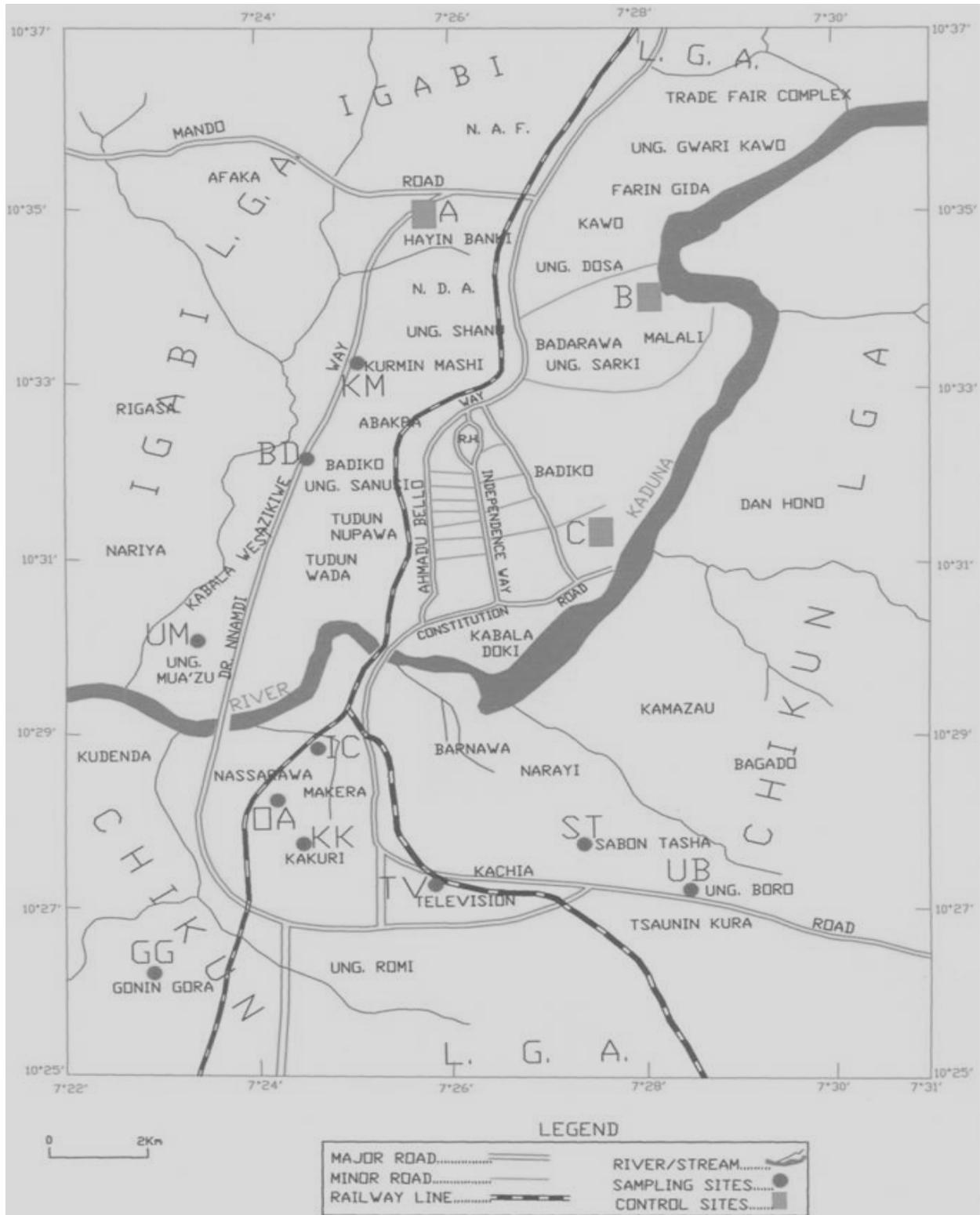


Figure 1. Kaduna Metropolis showing sampling sites. Source: Kaduna State Environmental Protection Authority

available soluble salts. The electrical conductivity values were higher than those obtained by Iwegbue et al. (2006) but much lower than Osakwe and Otuya (2008). The

percentage organic carbon content in the soil samples ranged between 25.90 (Inland Container) - 43.10% (Sabon Tasha) for the study soils and 13.20 to 16.40 for

Table 1. Percentage recovery of heavy metals in soil and plant samples.

Metals	Soil sample	Plant sample
Cd	90.67 ± 1.00	90.67 ± 1.20
Cr	93.00 ± 1.20	97.00 ± 2.00
Zn	108.67 ± 1.00	103.00 ± 2.10
Cu	98.00 ± 2.00	93.33 ± 3.00
Fe	93.33 ± 3.00	95.67 ± 4.00
Ni	89.67 ± 1.00	89.00 ± 1.00
Pb	93.00 ± 1.30	97.00 ± 2.50

Table 2. Physicochemical parameters of the soil in the study areas.

Site	Clay (%)	Silt (%)	Sand (%)	pH	EC (μScm^{-1})	OC (%)	CEC (Meq/100g of soil)	*Ext. PO_4^{3-} (mgkg ⁻¹)	*Ext. SO_4^{2-} (mgkg ⁻¹)
Old Artillery Barracks	24.00±0.00	12.00±0.00	64.00±0.00	7.00±0.21	0.30±0.01	27.50±0.02	19.20±0.40	55.00±1.20	12.00±0.30
Inland Container	22.00±0.00	14.00±0.00	64.00±0.10	8.00±0.34	0.75±0.01	25.90±0.10	18.70±0.40	45.00±1.00	16.00±0.10
Sabon Tasha	30.00±0.00	26.00±0.00	44.00±0.21	7.40±0.11	1.10±0.00	43.10±0.45	21.10±0.98	25.00±1.40	14.00±0.30
Ungwan Boro	26.00±0.00	20.00±0.00	54.00±0.00	7.50±0.01	0.40±0.01	30.30±0.30	15.20±0.65	22.00±1.00	11.00±0.33
Television	24.00±0.00	22.00±0.00	54.00±0.00	7.30±0.10	1.00±0.02	41.50±0.10	16.40±0.38	38.00±2.00	18.00±0.45
Kurmi Mashi	34.00±0.00	30.00±0.00	46.00±0.00	7.40±1.00	0.80±0.01	28.70±0.30	20.00±0.67	22.00±1.00	20.00±0.90
Badiko	32.00±0.00	28.00±0.00	40.00±0.00	7.40±0.00	0.85±0.00	40.70±0.11	23.10±0.10	30.00±2.00	16.00±0.14
Ungwan Muazu	26.00±1.00	22.00±0.00	52.00±0.00	7.00±0.13	9.50±0.00	38.30±0.10	20.20±0.39	30.00±1.00	18.00±0.20
Kakuri	24.00±0.00	20.00±0.00	56.00±0.00	7.50±0.00	0.75±0.23	31.90±0.01	17.30±0.37	28.00±1.00	22.00±0.56
Gonin Gora	30.00±0.00	28.00±0.00	42.00±0.00	7.40±0.00	0.50±0.10	35.90±0.50	15.20±0.20	25.00±1.00	22.00±0.50
Mean	27.20	22.20	51.60	7.39	1.60	34.38	18.64	32.00	16.90

*Ext. = Extractable.

Table 3. Physicochemical parameters of the soil in the control area.

Site	Clay (%)	Silt (%)	Sand (%)	pH	EC (μScm^{-1})	OC (%)	CEC (Meq/100 g of soil)	*Ext. PO_4^{3-} (mgkg ⁻¹)	*Ext. SO_4^{2-} (mgkg ⁻¹)
A	18.00±0.00	28.00±0.10	54.00±0.00	7.30±0.50	0.30±0.01	13.20±1.20	12.80±0.20	12.00±1.00	4.00±0.50
B	20.00±0.00	26.00±0.00	54.00±1.00	7.60±0.30	0.30±0.20	16.40±0.57	9.20±0.40	14.00±0.50	6.00±0.00
C	24.00±0.00	14.00±0.00	62.00±0.00	7.50±0.56	0.35±0.10	14.40±0.60	17.20±0.80	13.50±0.90	4.00±0.00
Mean	20.67	22.67	56.67	7.47	0.32	14.67	13.07	13.17	4.67

*Ext. = Extractable.

Table 4. Chemical fractionation of Cd (mgkg⁻¹) in surface soils of some selected mechanic workshops in the study areas.

Fractions	Sites									
	Old Artillery Barracks	Inland Container	Sabon Tasha	Ungwan Boro	Television	Kurmi Mashi	Badiko	Ungwan Muazu	Kakuri	Gonin Gora
Water soluble	0.00±0.00	1.85±0.10	1.85±0.20	1.85±0.01	3.70±0.02	0.00±0.00	1.85±0.00	3.70±0.01	1.85±0.00	1.85±0.16
% Water soluble	0.00	1.79	1.78	1.77	3.57	0.00	1.78	3.58	1.77	1.77
Exchangeable	7.41±0.01	7.41±0.34	7.41±0.15	7.41±0.24	9.26±0.44	7.41±0.21	7.41±0.11	9.26±0.02	7.41±0.10	7.41±0.13
% Exch.	7.17	7.16	7.11	7.08	8.92	7.21	7.11	8.96	7.08	7.08
CB	3.70±0.10	5.56±0.12	11.11±0.24	5.56±0.50	7.41±0.15	9.26±0.15	3.70±0.23	7.41±0.34	3.70±0.11	9.26±0.15
%CB	3.59	5.37	10.67	5.31	7.13	9.01	3.56	7.16	3.54	8.85
Fe-MnO	11.11±0.21	12.96±0.22	0.00±0.00	12.96±0.22	11.11±0.26	9.26±0.15	9.26±0.12	11.11±0.23	9.26±0.01	9.26±0.29
% Fe-MnO	10.76	12.54	0.00	12.39	10.70	9.01	8.89	10.75	8.85	8.85
Org. B	11.11±0.20	11.11±0.14	18.52±0.36	12.96±0.21	11.11±0.26	16.67±0.11	9.26±0.13	16.67±0.56	9.26±0.10	12.96±0.33
% Org. B	10.76	10.75	17.78	12.39	10.70	16.22	8.89	16.12	8.85	12.39
Residual	69.91±0.16	64.51±0.21	65.28±0.82	63.89±0.50	61.27±0.21	60.19±0.21	72.69±0.45	55.25±0.07	73.15±0.11	63.89±0.67
% Residual	67.71	62.39	62.67	61.06	58.99	58.56	69.78	53.43	69.91	61.06
Σ _T	103.24	103.40	104.17	104.63	103.86	102.78	104.17	103.40	104.63	104.63

the control soils. The high percentage organic carbon content in the study sites as compared to the control sites could be due to automechanic activities carried out within these sites, which release hydrocarbon waste. Hence, the relatively high total organic carbon content in samples could be due to the high organic content of used lubricants that were discharged at the sites (Akoto et al., 2008). The CEC of the sites varied between 15.20 (Ungwan Boro and Gonin Gora) to 23.10 mmolkg⁻¹ (Badiko) in study sites and 9.20 to 17.20 mmolkg⁻¹ in control sites. The CEC of soils is related to the nature and quality of clay and organic carbon contents. Hence, high percentage organic carbon from these sites could be responsible for the CEC. According to Awode et al. (2008), CEC of soil is more greatly influenced by organic matter than by the concentration of clays, hence CEC tends to be higher in the study sites than in the control sites. All study sites had

comparatively higher mean cation exchange capacity than the mean CEC of 8.14 mmolkg⁻¹ reported by Isirimah (1987).

In the study area, extractable sulphate content ranged from 11.00 to 22.00 mgkg⁻¹ while the sulphate in samples from the control area ranged between 4.00 to 6.00 mgkg⁻¹. Significant variation was observed between the sulphate level in the study and control areas. This could be due to the activities of battery chargers within the study area, an indication of soil contamination within this area. The level of extractable PO₄³⁻ in soil samples ranged from 22.00 – 55.00 mgkg⁻¹ in the study area while in the control area, the PO₄³⁻ ranged from 12.00 – 14.00 mgkg⁻¹. Similar to sulphate, phosphate level in the study area is very much greater than the level in the control area. For similar reasons, sulphate could be responsible for high phosphate within these sites. Extractable phosphates in the study area had a mean of 32.00

mg/kg which is similar to reports by Iwegbue et al. (2006).

The mobility and availability of heavy metals in soils depend on how the metals are associated with the components of the soil, and the measure of the mobility and availability of metals serves to predict the behavior of heavy metals in the soil. The metals are bound to the solid component of the soil through phases such as water soluble, exchangeable, carbonate, oxides and hydroxides, and organics. The selective sequential extraction of heavy metals provides detailed insight on how the metals are associated with the components of the soil. Tables 4 to 10 present total and sequentially fractionated metal (Cd, Cr, Zn, Cu, Fe, Ni and Pb) concentrations in soil, and the heavy metal percentage for each fraction calculated for Kaduna soil.

Analysis of variance between heavy metals across sites revealed significant differences ($p <$

Table 5. Chemical fractionation of Cr (mgkg⁻¹) in surface soils of some selected mechanic workshops in the study areas.

Fractions	Sites									
	Old Artillery Barracks	Inland Container	Sabon Tasha	Ungwan Boro	Television	Kurmi Mashi	Badiko	Ungwan Muazu	Kakuri	Gonin Gora
Water soluble	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
% Water soluble	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Exchangeable	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
% Exch.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CB	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.12
%CB	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe-MnO	9.76±0.23	9.76±0.11	0.00±0.00	0.00±0.00	19.51±0.34	0.00±0.00	9.76±0.34	9.76±0.00	9.76±0.23	9.76±0.34
% Fe-MnO	15.69	12.31	0.00	0.00	26.23	0.00	13.56	14.37	14.04	11.94
Org. B	0.00±0.00	29.27±0.34	29.27±1.20	58.54±0.23	39.02±0.22	29.27±0.67	29.27±0.56	39.02±0.45	29.27±0.45	29.27±0.98
% Org. B	0.00	36.92	33.80	78.69	52.46	39.34	40.68	57.49	42.11	35.82
Residual	52.44±0.34	40.24±0.19	57.32±0.45	15.85±0.11	15.85±0.12	45.12±0.45	32.93±0.67	19.11±0.78	30.49±0.22	42.68±0.34
% Residual	84.31	50.77	66.20	21.31	21.31	60.66	45.76	28.14	43.86	52.24
Σ _T	62.20	79.27	86.59	74.39	74.39	74.39	71.95	67.89	69.51	81.71

Table 6. Chemical fractionation of Zn (mgkg⁻¹) in surface soils of some selected mechanic workshops in the study areas.

Fractions	Sites									
	Old Artillery Barracks	Inland Container	Sabon Tasha	Ungwan Boro	Television	Kurmi Mashi	Badiko	Ungwan Muazu	Kakuri	Gonin Gora
Water soluble	7.50±0.023	12.50±0.34	0.00±0.00	2.50±0.01	7.50±0.23	0.00±0.00	2.50±0.00	12.50±0.01	7.50±0.01	7.50±0.10
% Water soluble	1.39	2.07	0.00	0.43	1.129	0.00	0.41	1.343	1.23	1.09
Exchangeable	25.00±0.45	50.00±0.01	22.50±0.34	10.00±0.19	20.00±0.56	32.50±0.67	20.00±0.120	27.50±0.20	22.50±0.10	25.00±1.20
% Exch.	4.62	8.28	1.919	1.70	3.011	4.88	3.31	2.954	3.70	3.65
CB	142.50±0.56	172.50±1.56	250.00±2.10	115.00±2.00	225.00±0.33	142.50±1.00	150.00±2.10	250.00±2.00	137.50±2.00	225.00±1.33
%CB	26.33	28.57	21.322	19.59	33.877	21.39	24.84	26.858	22.62	32.85
Fe-MnO	42.50±0.78	35.00±0.38	47.50±0.67	42.50±0.30	40.00±0.20	40.00±1.11	35.00±0.20	50.00±0.00	40.00±1.00	40.00±0.10
% Fe-MnO	7.85	5.80	4.051	7.24	6.023	6.00	5.80	5.372	6.58	5.84
Org. B	87.50±0.37	140.00±5.10	145.00±1.00	100.00±1.00	180.00±2.10	117.50±1.20	125.00±3.00	145.00±0.10	115.00±1.00	150.00±1.00
% Org. B	16.17	23.19	12.367	17.03	27.102	17.64	20.70	15.577	18.92	21.90
Residual	236.25±0.23	193.75±0.90	707.50±1.00	317.08±1.00	191.67±1.00	333.75±0.99	271.25±1.90	445.83±1.20	285.42±1.00	237.50±1.00
% Residual	43.65	32.09	60.341	54.01	28.858	50.09	44.93	46.95	46.95	34.67
Σ _T	541.25	603.75	1172.500	587.08	664.167	666.25	603.75	930.833	607.92	685.00

Table 7. Chemical fractionation of Cu (mgkg⁻¹) in surface soils of some selected mechanic workshops in the study areas.

Fractions	Sites									
	Old Artillery Barracks	Inland Container	Sabon Tasha	Ungwan Boro	Television	Kurmi Mashi	Badiko	Ungwan Muazu	Kakuri	Gonin Gora
Water soluble	2.00±0.00	0.00±0.00	2.00±0.10	0.00±0.00	2.00±0.00	2.00±0.19	0.00±0.00	2.00±0.45	0.00±0.00	2.00±0.56
% Water soluble	12.25	0.00	8.70	0.00	2.00	3.46	0.00	2.45	0.00	2.00
Exchangeable	0.00±0.00	0.00±0.00	0.00±0.00	4.00±0.16	2.00±0.00	2.00±0.34	0.00±0.00	2.00±0.00	0.00±0.00	2.00±0.78
% Exch.	0.00	0.00	0.00	13.71	2.00	3.46	0.00	2.45	0.00	2.00
CB	6.00±0.10	14.00±0.45	10.00±0.20	12.00±0.56	72.00±1.00	10.00±0.67	14.00±0.23	60.00±0.45	14.00±1.00	14.00±0.23
%CB	36.74	38.89	43.48	41.14	72.00	17.29	42.42	73.47	36.84	13.98
Fe-MnO	0.00±0.00	0.00±0.00	0.00±0.00	2.00±0.77	2.00±0.00	2.00±0.77	0.00±0.00	2.00±0.10	0.00±0.00	2.00±0.00
% Fe-MnO	0.00	0.00	0.00	6.86	2.00	3.46	0.00	2.45	0.00	2.00
Org. B	2.00±0.34	2.00±0.20	2.00±0.40	2.00±0.11	2.00±0.00	2.00±0.26	2.00±0.67	2.00±0.10	2.00±0.11	2.00±0.01
% Org. B	12.25	5.56	8.70	6.86	2.00	3.46	6.06	2.45	5.26	2.00
Residual	6.33±0.50	20.00±0.30	9.00±0.27	9.17±0.00	20.00±1.00	39.83±0.87	17.00±0.56	13.67±0.30	22.00±0.45	78.17±0.90
% Residual	38.77	55.56	39.13	31.43	20.00	68.88	51.52	16.74	57.89	78.04
Σ _T	16.33	36.00	23.00	29.17	100.00	57.83	33.00	81.67	38.00	100.17

Table 8. Chemical fractionation of Fe (mgkg⁻¹) in surface soils of some selected mechanic workshops in the study areas.

Fractions	Sites									
	Old Artillery Barracks	Inland Container	Sabon Tasha	Ungwan Boro	Television	Kurmi Mashi	Badiko	Ungwan Muazu	Kakuri	Gonin Gora
Water soluble	14.71±0.56	17.65±0.10	14.71±0.10	14.71±0.20	14.71±0.13	11.76±0.87	14.71±0.10	17.65±0.00	14.71±0.00	17.65±0.11
% water soluble	3.28	3.64	3.02	3.08	3.06	2.46	3.08	3.64	3.13	3.64
Exchangeable	29.41±0.01	11.76±0.34	17.65±0.10	11.76±0.10	20.59±0.56	14.71±0.33	17.65±0.30	29.41±0.10	14.71±0.00	14.71±0.21
% Exch.	6.56	2.42	3.62	2.46	4.29	3.08	3.69	6.06	3.13	3.03
CB	23.53±0.00	20.59±0.45	26.47±0.34	35.29±0.22	29.41±0.56	20.59±0.29	23.53±0.10	29.41±0.10	32.35±0.10	29.41±0.10
%CB	5.25	4.24	5.43	7.38	6.12	4.31	4.92	6.06	6.88	6.06
Fe-MnO	29.41±0.34	14.71±0.10	14.71±0.44	17.65±0.11	14.71±0.89	17.65±0.33	17.65±0.34	20.59±0.30	14.71±0.10	20.59±0.11
% Fe-MnO	6.56	3.03	3.02	3.69	3.06	3.69	3.69	4.24	3.13	4.24
Org. B	14.71±0.20	26.47±0.20	11.76±0.56	17.65±0.34	17.65±0.20	14.71±0.67	17.65±0.20	20.59±0.10	17.65±0.30	17.65±0.20
% Org. B	3.28	5.45	2.41	3.69	3.67	3.08	3.69	4.24	3.75	3.64
Residual	336.76±0.11	394.12±1.90	402.45±1.00	380.88±1.11	383.33±1.67	398.53±5.10	386.76±1.30	367.65±1.89	376.47±2.10	385.29±1.90
% Residual	75.08	81.21	82.51	79.69	79.80	83.38	80.92	75.76	80.00	79.39
Σ _T	448.53	485.29	487.75	477.94	480.39	477.94	477.94	485.29	470.59	485.29

Table 9. Chemical fractionation of Ni (mgkg⁻¹) in surface soils of some selected mechanic workshops in the study areas.

Fractions	Sites									
	Old Artillery Barracks	Inland Container	Sabon Tasha	Ungwan Boro	Television	Kurmi Mashi	Badiko	Ungwan Muazu	Kakuri	Gonin Gora
Water soluble	26.67±0.10	26.67±0.76	26.67±0.11	20.00±0.20	20.00±0.30	20.00±0.90	26.67±0.10	26.67±0.12	20.00±0.00	26.67±0.00
% Water soluble	13.01	12.28	12.60	9.84	9.68	9.52	12.70	12.70	9.52	12.73
Exchangeable	20.00±0.30	13.33±0.30	20.00±0.00	6.67±0.34	13.33±0.20	13.33±0.78	13.33±0.50	20.00±0.34	13.33±0.43	13.33±0.12
% Exch.	9.76	6.14	9.45	3.28	6.45	6.35	6.35	9.52	6.35	6.37
CB	20.00±0.30	13.33±0.11	20.00±0.10	13.33±0.67	6.67±0.56	6.67±0.28	20.00±0.10	20.00±0.56	13.33±0.10	13.33±0.12
%CB	9.76	6.14	9.45	6.56	3.23	3.17	9.52	9.52	6.35	6.37
Fe-MnO	33.33±0.10	26.67±0.21	26.67±0.23	33.33±0.78	33.33±0.78	26.67±0.89	26.67±0.00	33.33±0.89	33.33±0.00	33.33±0.00
% Fe-MnO	16.26	12.28	12.60	16.39	16.13	12.70	12.70	15.87	15.87	15.92
Org. B	40.00±0.11	26.67±0.20	26.67±0.20	26.67±0.98	40.00±0.20	33.33±0.87	26.67±0.00	33.33±0.44	33.33±0.20	33.33±0.00
% Org. B	19.51	12.28	12.60	13.11	19.35	15.87	12.70	15.87	15.87	15.92
Residual	65.00±0.45	110.56±1.00	91.67±0.00	103.33±1.90	93.33±0.57	110.00±1.00	96.67±1.90	76.67±0.10	96.67±0.56	89.44±0.87
% Residual	31.71	50.90	43.31	50.82	45.16	52.38	46.03	36.51	46.03	42.71
Σ _T	205.00	217.22	211.67	203.33	206.67	210.00	210.00	210.00	210.00	209.44

Table 10. Chemical fractionation of Pb (mgkg⁻¹) in surface soils of some selected mechanic workshops in the study areas.

Fractions	Sites									
	Old Artillery Barracks	Inland Container	Sabon Tasha	Ungwan Boro	Television	Kurmi Mashi	Badiko	Ungwan Muazu	Kakuri	Gonin Gora
Water soluble	18.80±0.20	19.64±0.45	20.00±0.20	22.00±0.12	16.80±0.56	17.60±0.00	16.00±0.18	21.20±0.10	20.40±0.10	18.00±0.50
% Water soluble	2.63	2.85	3.05	3.80	2.76	2.59	2.40	3.40	2.96	2.56
Exchangeable	12.40±0.10	10.44±0.34	12.40±0.30	12.00±0.56	10.40±0.20	12.00±0.10	10.00±0.65	10.00±0.00	10.40±0.19	13.20±0.10
% Exch.	1.74	1.52	1.89	2.07	1.71	1.77	1.50	1.60	1.51	1.87
CB	172.00±1.20	173.20±2.10	194.40±1.20	213.20±1.29	184.80±2.11	208.00±0.80	178.00±1.50	163.60±8.10	173.60±0.70	200.00±2.00
%CB	24.10	25.17	29.63	36.80	30.38	30.62	26.67	26.24	25.18	28.40
Fe-MnO	15.20±0.10	15.60±0.19	17.20±0.20	15.60±0.45	16.40±0.50	16.80±0.22	15.20±0.20	17.20±0.30	15.60±1.00	17.60±0.20
% Fe-MnO	2.13	2.27	2.62	2.69	2.70	2.47	2.28	2.76	2.26	2.50
Org. B	324.40±1.20	302.00±2.10	304.40±3.00	302.40±2.00	329.20±1.00	303.60±1.99	304.00±1.00	308.80±1.10	326.00±2.13	296.00±1.20
% Org. B	45.46	43.89	46.40	52.20	54.11	44.69	45.55	49.52	47.28	42.04
Residual	170.83±1.00	167.19±1.80	107.63±1.12	14.10±0.30	50.77±0.40	121.30±0.90	144.23±0.50	102.73±1.00	143.53±1.50	159.37±1.11
% Residual	23.94	24.30	16.41	2.43	8.34	17.86	21.61	16.48	20.82	22.63
Σ _T	713.63	688.07	656.03	579.30	608.37	679.30	667.43	623.53	689.53	704.17

Table 11. Correlation matrix among physicochemical parameters and heavy metals in surface soils of mechanic workshops in Kaduna.

Parameter	Clay	Silt	Sand	pH	EC	OC	CEC	Ext. P	Ext. SO ₄ ²⁻	Cd	Cr	Zn	Cu	Fe	Ni	Pb
Cd	-0.054	0.162	-0.307	0.186	-0.266	0.352	-0.436	-0.426	0.075	1						
Cr	0.314	0.450	-0.461	0.557	-0.271	0.328	-0.098	-0.461	0.113	0.315	1					
Zn	0.655*	0.759*	-0.663*	0.332	-0.214	0.096	-0.138	-0.655*	0.653*	0.157	0.654*	1				
Cu	0.035	0.286	-0.324	0.129	-0.095	0.225	-0.564	-0.199	0.561	0.515	0.378	0.554	1			
Fe	0.267	0.540	-0.503	0.422	0.284	0.462	-0.005	-0.601	0.302	0.211	0.764*	0.559	0.367	1		
Ni	0.002	0.050	-0.013	0.615	0.105	-0.045	0.380	0.048	0.348	-0.225	0.460	0.344	0.060	0.514	1	
Pb	0.109	-0.089	0.066	0.091	-0.314	-0.357	0.219	0.364	0.349	-0.208	-0.059	0.266	0.156	-0.373	0.410	1

*. Correlation is significant at the 0.05 level (2-tailed). Ext.= Extractable.

0.05). A correlation matrix for heavy metals in the soil of the different sites was calculated to see if some metals were interrelated with each other and the results are presented in Table 11. Negative correlation was especially found between the metals in the study areas, Cd: Ni and Pb; Pb: Cr; and Pb: Cd, though not significant ($p > 0.05$).

However, others showed significant ($p < 0.05$) positive correlation between Cr: Zn and Fe. Also, Table 11 shows the correlation between heavy metals in soils and the soil physico-chemical parameters revealed significant ($p < 0.05$) positive correlation between Zn: clay silt and extractable SO₄²⁻ and Cu: extractable SO₄²⁻. Hence, positive correlation between metal concentration and physico-chemical parameters could imply a significant effect on the amount of heavy metals in the soil, since the mobility and bioavailability of metals present in soils depend on physico-chemical properties of both the metal and the soil (McEldowney et al., 1993).

The distribution pattern of metals in the six geo-chemical phases of the soil showed differences in the study sites. As shown in the results, the highest percentage of metals was found in the residual fractions while the water soluble fraction had the least percentage. However, the chemical

partitioning trends were found to be different for each metal. Majority of the metals were found to be concentrated in the residual fraction with the exception of Pb. The highest percentage fractions obtained by the sequential extraction procedure shows the following metal distribution pattern:

Cd: Residual > Organic > Fe-MnO > Exchangeable > Carbonate > Water Soluble
 Cr: Residual > Organic > Fe-MnO > Exchangeable = Carbonate = Water Soluble
 Zn: Residual > Carbonate > Organic > Fe-MnO > Exchangeable > Water Soluble
 Cu: Residual > Carbonate > Organic > Water Soluble > Exchangeable > Fe-MnO
 Fe: Residual > Carbonate > Exchangeable > Fe-MnO > Organic > Water Soluble
 Ni: Residual > Fe-MnO > Organic > Water Soluble > Carbonate = Exchangeable
 Pb: Organic > Carbonate > Residual > Water Soluble > Fe-MnO > Exchangeable.

As observed from the results, the highest percentage fraction of 69.91 and 44.50 were associated with the residual fraction for Cd in Kakuri. This situation is however different from Tessier et al. (1979), where insignificant amounts

of Cd are associated with Fe-MnO fraction, whereas in the other fractions, Cd concentrations were below the limit of detection. Association of Cd to the residual fraction does not generally constitute an environmental risk. This is due to the stable nature of the compound and the fact that the metals are bonded firmly within a mineral lattice that restricts the bioavailability of this metal (Coetzee, 1993; Abu-Kukati, 2001).

The distribution of Cr, Zn, Cu, Fe, Ni and Pb were similarly dominated by residual and organic fractions. The variations across these fractions between the study areas could be due to different anthropogenic sources of these metals. For Cr, the highest value of 83.31% was associated with residual and organic fractions in Old Artillery. There is no water soluble, exchangeable and carbonate fractions of Cr noticeable in all the sites; this was also similar to Venkateswaran et al. (2007) where no Cr was detected in the first three fractions.

According to Venkateswaran et al. (2007), the leaching of Cr to the environment from these samples may not occur readily Cr(VI) is a highly toxic metal that has been linked to cancer in humans following prolonged inhalation, and is toxic to plants at relatively low concentrations

(USEPA, 1998).

The predominant form of Zn (60.34% in Sabon Tasha) was in the residual and carbonate fractions, followed by organic and Fe-MnO fractions. There was no significant variation in absolute mobile fractions (water soluble exchangeable and carbonate bound fraction). Higher concentrations of Zn in Fe-MnO fraction can be attributed to diffusion mechanism (Backes et al., 1995). This metal can be released into the environment under extremely reducible conditions (Venkateswaran et al., 2007).

Also, the predominant form of Cu available in the entire fractions was residual fractions. The mobile fraction of Cu contributed over 40%; the high percentage of Cu in the organic fraction was due to higher stability constant of Cu complexes with organic matter (Venkateswaran et al., 2007). Infact, the highest value of 87.69 of Cu was found in the residual fraction, indicating that it is mainly of lithogenic origin (Xuelu et al., 2008). This coincided with the researches carried out on soils in China (Liu et al., 2003; Yuan et al., 2004).

Though Fe is not a toxic heavy metal because it serves as a micronutrient, it was also analysed in the present study and the results discussed since it was the predominant metal available in all sites. The highest value of 76.47% was available in the residual fractions in the studied soil. Since the Fe concentration was very high in the residual fraction, it could be converted to reducible fraction by plant roots (Otte et al., 1995).

Fe-MnO, residual and organic bound fractions were the predominant forms of Ni in all the samples. About 15 - 33.33% was in the exchangeable and carbonate fractions which can cause environmental toxicity during mobility (Karbassi and Shankar, 2005). Similar to this study, Behnar and Catherine (2006) showed that Ni in soil was concentrated in residual fractions. Pb in the soil was found mainly in the organic and residual fractions and then in carbonate and exchangeable forms in all the sites with few exceptions. In a smaller amount, it was bound to water soluble and Fe-MnO fractions. A similar distribution of Pb forms among fractions was reported for the fluvial deposits by Sobczynski and Siepak (2001).

Conclusion

The distribution pattern of metals in the six geochemical phases of the soil showed differences in metal content across the sites. The highest percentages of metals were found in the residual fractions while the water soluble fraction had the least percentages.

However, in most soils, a significant percentage of the total metals were associated with the no residual fractions. The metal fraction associated with the residual fraction can only be mobilized as a result of weathering and as such, this is only associated with long-term effects. Generally, the study indicated possible soil pollution in this environment by activities carried out within these areas.

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