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FRACTIONATION OF HEAVY METALS IN SOIL FROM ACTIVE AUTOMOBILE WORKSHOPS IN BENIN CITY, NIGERIA

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Abstract
Heavy metals are potentially toxic to human life and the environment. Therefore, determining the chemical forms of metals in soil is essential for evaluating their mobility and bioavailability. This study investigated the speciation of selected heavy metals (Cd, Cr, Pb, Ni, and V) in soils around automobile repair workshops in Benin City, South-South Nigeria. Soil samples were collected from a depth of 0–15 cm using a soil auger. Control samples were obtained from a farmland at the Faculty of Agriculture, University of Benin. The modified BCR sequential extraction procedure was used to fractionate the soil samples into four operational groups: exchangeable/carbonate (B1), Fe-Mn oxide-bound (B2), organic-bound (B3), and residual (R) fractions. Metal concentrations in the extracts were determined using atomic absorption spectrometry (AAS). Cadmium, Cr, Ni, and V were predominantly found in the exchangeable/carbonate fraction, while Pb was primarily associated with the residual fraction. The total bioavailable metal content across zones followed the order: SW > NE > SE > NW. The average mobility factors for Cd, Cr, Pb, Ni, and V across all zones were 22.08%, 30.75%, 24.47%, 32.63%, and 32.88%, respectively.
***Keywords**: Soil, heavy metals, speciation, mobility, BCR sequential extraction, automobile workshops*

1.0 INTRODUCTION

Heavy metal pollution of the environment has become a serious ecological concern globally (Sobukola *et al.,* 2010; Abii & Okorie, 2011). In many developed and developing countries, rapid industrialization and the increasing demand for technological comfort, coupled with changing consumer tastes and fashion, have driven scientific and technological advancement (Ghobakhloo *et al.,* 2023). However, these developments have also negatively impacted the environment. The transformation of raw industrial materials into finished goods often generates harmful wastes, effluents, and toxic by-products. When discharged untreated, these toxic substances can interfere with ecosystem components and adversely affect human and other living organisms. Although heavy metals occur naturally in the environment, anthropogenic activities—particularly land use—can introduce elevated concentrations. The levels of metals in near-surface soils vary significantly across geographic regions due to differing physical and chemical processes (Stafilov *et al.,* 20242024). In recent years, considerable attention has been directed toward the chemical speciation of heavy metals in contaminated soils and sediments using sequential extraction techniques, as these methods provide valuable information on metal partitioning, mobility, bioavailability, and the strength of their association with different soil components (Yu, *et al.,* 2023). Although

sequential extraction procedures are relatively labor-intensive and time-consuming, they provide detailed information on the chemical partitioning, origin, mobility, bioavailability, physicochemical behavior, and potential environmental risks of trace metals in soils and sediments, making them indispensable tools for contamination assessment and remediation studies (Ali *et al.,* 2024). Metal migration in soil is influenced by the physicochemical characteristics of each metal and several environmental factors, including (i) soil type, (ii) total organic content, (iii) redox potential, and (iv) pH. While heavy metals are generally considered relatively immobile in most soils, their mobility in certain contaminated soils may exceed normal rates, posing significant risks to water quality (Bunzl *et al.,* 2001). Previous studies indicate that the metal constituents of surface soils directly influence metal movement, particularly in sandy soils (Cezary & Singh, 2001; Koptsik and Koptsik 2022; Yu *et al.,* 2023). The overall behavior of heavy metals in soil is largely governed by sorption and desorption reactions with soil constituents, especially clay components (Appel & Ma, 2002). Bioavailability depends on biological parameters and the physicochemical properties of metals, their ions, and compounds, which in turn are systematically described by the periodic table (VanLoon & Duffy, 2000).

Although numerous studies have reported the total concentrations, spatial distribution, contamination status, and ecological or human health risks of heavy metals in soils from automobile repair workshops, only a few have investigated the chemical speciation of these metals using sequential extraction procedures (Chokor, 2017; Olusola 2018; Anegbe *et al* 2019). Total metal concentrations alone do not adequately reflect their environmental behavior because they provide little information on the mobility, bioavailability, and potential toxicity of individual metal fractions. Studies on heavy metal speciation in automobile workshop soils have been conducted in a few Nigerian cities such as Sapele and Oshogbo, but information for Benin City remains scarce. Furthermore, previous investigations in Benin City have largely focused on total metal concentrations, pollution indices, and health risk assessments without evaluating the distribution of metals among different geochemical fractions. Consequently, there is limited understanding of the forms in which these metals exist, their potential mobility under changing environmental conditions, and their long-term ecological risks. Therefore, this study aims to provide a comprehensive heavy metal speciation study for automobile repair workshop soils in Benin City using sequential extraction techniques, thereby providing valuable information on the origin, mobility, bioavailability, and environmental risk of heavy metals in these contaminated soils.

2.0 Materials and Methods

2.1 Study Area

Benin City is located between latitudes 6°06′ N and longitudes 5°30′ E and 5°45′ E, within the Benin lowlands—a geomorphic subunit sloping westward. The highest elevation, approximately 3,500 ft above sea level, occurs at the Ishan Plateau, about 70 km northeast of the city. Benin City is a rapidly growing transit town and the administrative capital of Edo State, with a population of 1,147,188 according to the 2006 census. Small-scale enterprises and artisan workshops are widespread across the city. Figure 1 shows a map indicating the 338

sampled automobile workshops. No waste management practices are employed at these workshops; wastes are indiscriminately discarded onto the soil.

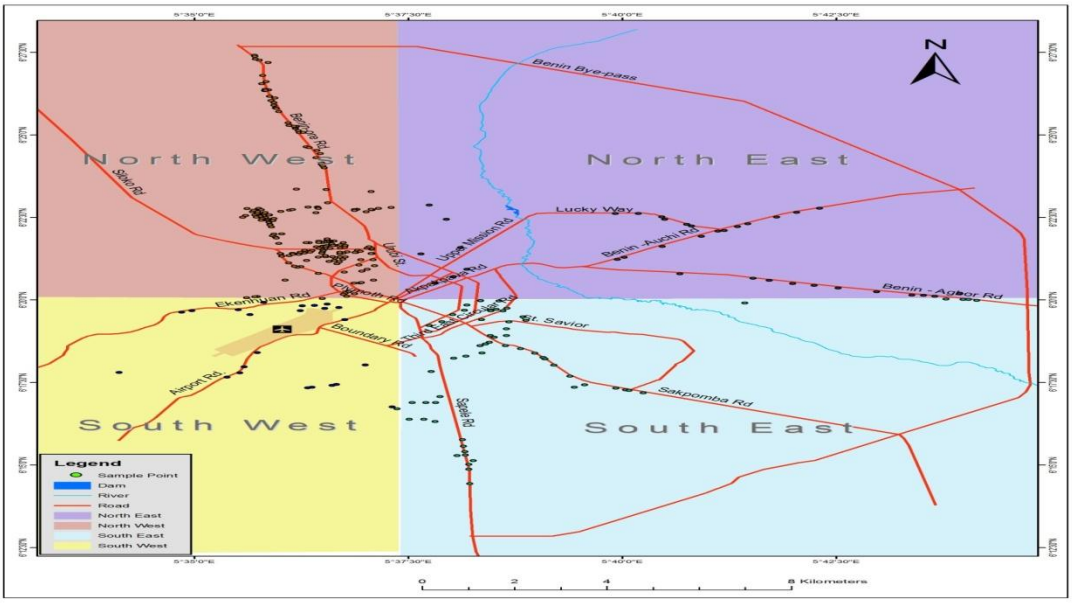

Fig. 1: Map with Three Hundred and Thirty-Eight Sampled Automobile Workshops.

2.2 Soil Sampling and Preparation

A survey identified 507 active automobile workshops in Benin City. The city was divided into four zones: Northwest (NW), Northeast (NE), Southwest (SW), and Southeast (SE) to facilitate detailed examination of activities within each zone. Observations revealed that (i) typical workshops accommodate various artisans (mechanics, panel beaters, battery chargers, spray painters) and (ii) multiple semi-automobile workshops operate in clusters, each specializing in one or more vehicle brands or types. Based on workshop proximity, activities, and operational duration, soil samples were collected from 338 workshops. The number of samples analyzed was further reduced to 40 (NW), 15 (SE), and 10 each (NE and SW) based on workshop density. Topsoil samples were collected at the workshop epicenter (TS), 30 m from the epicenter (DTS), and from a control site (farmland at the University of Benin). Standard chain-of-custody protocols were followed during sample transport. Soil samples were air-dried, crushed in a porcelain mortar, and sieved through a 2 mm mesh; the <2 mm fraction was retained for analysis.

2.3 Fractionation of Heavy Metals

The modified BCR (European Community Bureau of Reference) sequential extraction procedure described by Golia et al. (2007) was used to fractionate metals into four operationally defined pools: exchangeable/carbonate (B1), reducible (Fe-Mn oxides, B2), organic-bound (B3), and residual (R). Extraction conditions are summarized in Table 1. Each extraction was performed on 1.0 g of pretreated soil (oven-dried at 105°C for 2 hours) using mechanical shaking (30 rpm). Detailed steps are provided below.

Table 1: BCR Sequential Extraction Scheme for Heavy Metal Speciation

Step	Soil phases	Extractant	Agitation time
B_1	Exchangeable	40mL of 0.11M CH_3COOH	16 hours at room temperature
B_2	Reducible	40ML of 0.5M $NH_2OH.HCl$ ($_pH$ 2)	16 hours at room temperature
B_3	Organic-bound	10mL 0f 8.8 H_2O_2 Cool + 50mL of 1M CH_3COONH_4 (pH 2)	16 hours at room temperature, then 1 hour at 85^oC 16 hours at room temperature
R	Residual	Aqua regia Digestion (21mL concentrated HCl + 7mL concentrated HNO_3)	180^oC

The extractions were performed by shaking 1.0g portion of the pre-treated soil sample oven dried at 105^oC for 2 hours in a mechanical shaker according to the steps described below:

Step 1 (B_1): 40 mL of solution 0.11 acetic acid solution was added to 1.0g of pretreated soil in a 100mL centrifuge tube and extracted by shaking (30rpm) for 16h at ambient temperature (overnight). No delay occurred between the addition of the extractant solution and the beginning of the shaking. The extract was separated from the soil residue by centrifugation, and decantation of the supernatant liquid into a polyethylene container. The container was stoppeered and stored at 4^oC prior to analysis. The residue was washed by adding 20mL of distilled water, shaking for 15 minutes and centrifuging. The cake obtained upon centrifugation was broken by using a vibrating rod prior to the next step.

Step 2 (B_2): 40mL of 0.5M hydroxylamine solution was added to the residue from step 1 in the centrifuge tube and extracted by shaking for 16 hours at ambient temperature (overnight). No delay occurred between the addition of the extractant solution and the beginning of the shaking. The extract was separated from the solid residue by centrifugation and decantation as in step 1. The extract was retained in a stoppered polyethylene tube as before, for analysis. The residue was washed by adding 20mL of distilled water, shaking for 15 minutes and centrifuging. The supernatant was decanted and discarded taking care to avoid discarding any solid residue. The residue was retained for step 3. The cake obtained upon centrifugation was broken by using a vibrating rod prior to the next step.

Step 3 (B_3): 10mL of 8.8M of hydrogen peroxide solution was added carefully, in small aliquots to avoid losses due to violent reaction to the residue in the centrifuge tube. The vessel was covered with a watch glass and digested at room temperature for 1 hour with occasional manual shaking. The digestion was continued for 1 hour at 85^oC and volumereduce to a few mL. Next, 50mL of 1.0M ammonium acetate solution were added to the cool moist residue and shaken for 16 hours at ambient temperature (overnight). No delay occurred between the addition of the extractant residue and the beginning of the shaking. The extract was separated from the solid residue by centrifugation and decantation in polyethylene tube as in step 1 and 2 stoppered and retained as before for AAS analysis.

Residue (R): Aqua regia digestion was employed in the extraction of the residue

fraction. Next, 21mL of concentrated HCl and 7mL concentrated HNO_3 were added to the residue from step 3 and digested at 180°C overnight (in a fume chamber). The digest was kept for heavy metal assay (Wuana*et al*., 2013). The concentrations of Cd, Pb, Ni, V and Cr in every extract were measured by atomic absorption spectrophotometer.

3.0 Results and Discussion

The distribution of heavy metals as determined by sequential extraction does not necessarily reflect their association with discrete soil phases but rather is operationally defined by the methods of extraction. Tables 2, 3, 4 and 5 give the different average fractions of Cd, Cr, Pb, Ni and V is soil samples from the automobile workshops in the NW, NE, SW and SE zones of Benin City respectively. Extraction yields in each case expressed as a percentage of the sun of the three steps plus residual fraction, were calculated and presented in Figs. 2, 3, 4 and 5 respectively for the heavy metals in soil from automobile workshops in the NW, NE, SW and SE zones of Benin City respectively.

Table 2: Fractionation of Cd, Cr, Pb, Ni and V in Soil Samples from Automobile Workshops in NW Zone of Benin City (mg.kg^{-1} dry soil wt)

Fractions	Cd	Cr	Pb	Ni	V
B_1	2.01±0.56	13.42±3.75	7.09±2.23	7.93±1.66	8.99±1.95
B_2	0.99±0.31	8.93±2.50	4.60±1.83	5.05±1.25	6.42±1.65
B_3	1.54±0.43	11.08±3.12	5.08±3.12	5.36±1.26	6.63±1.33
Residual	1.50±0.39	13.23±3.81	10.18±3.08	8.46±1.93	8.28±2.07
Sum	6.06±1.58	46.67±12.07	26.96±7.89	26.81±4.86	30.32±5.48

The values are mean ± SD

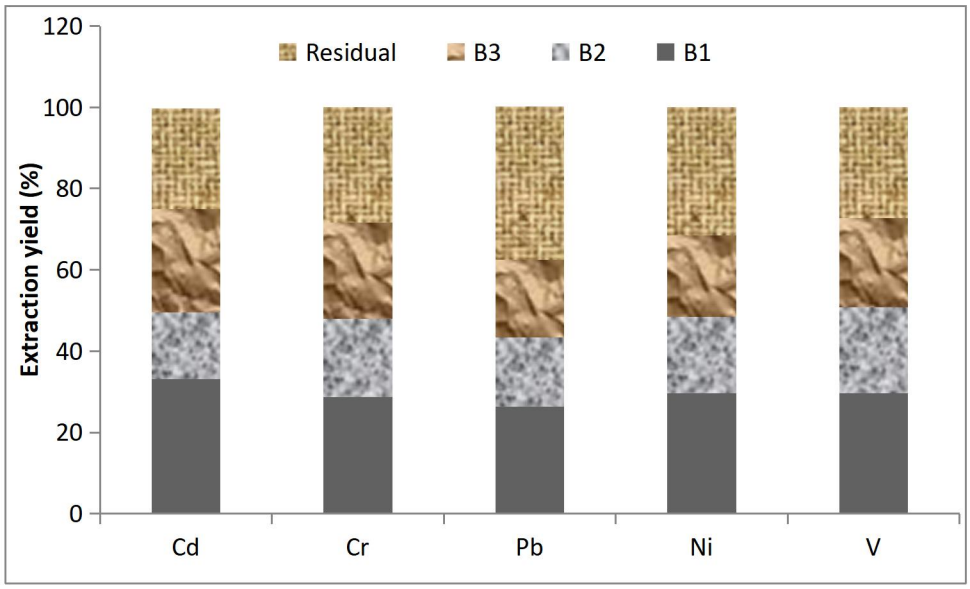

Fig. 2: Distribution Pattern of Cd, Cr, Pb, Ni and V in Soil Samples from automobile workshop in the NW zone of Benin City

It can be seen from the results given in Table 2 and shown in Fig. 2 that the exchangeable/carbonate bound metal pool in the soil from automobile workshops in the NW zone of Benin City is about the same order of magnitude but varying somewhat in the same

order Cr > V > N ≥ Pb> Cd corresponding to the trend of the pseudo-total levels of the metals in the soil samples the residual metal pool is frequently regarded as the pre-industrial, background level of the heavy metals in soil. The residual metal pool in soil samples from automobile workshops in the NW zone of Benin City varied in the order Cr >Pb> Ni ≥ V > Cd. The reducible metal pools in the soil were Cr 8.93±2.50 $mg.kg^{-1}$, V 6.42±1.65 $mg.kg^{-1}$, Ni 5.05±1.25$mg.kg^{-1}$, Pb 4.60±1.83$mg.kg^{-1}$ and Cd 0.99±0.31$mg.kg^{-1}$ suggesting that subject to the redox flux in these levels of heavy metal may become available and increase the potential for deleterious impact on the environment. Unlike the pattern of heavy metal fraction in soils from open dumpsites in which preponderant amounts of heavy metals (As, Cr, and Cu) were Fe-Mn oxides bound and reducible (Ataikiru and Okieimen, 2014) larger proportions of heavy metals: Cd 25.41%; Cr 23.74%, V 20.87%, Ni 19.19% and Pb 19.09% in this study were found organic matter and/or sulphide bound.

Similar trends in the results of chemical fractionation of the heavy metals in soils from automobile workshops in the NE zone of Benin City were observed (Table 27 and Fig.19).

Table 3: Fractionation of Cd, Cr, Pb, Ni and V in soil samples in automobile workshops from NE zone of Benin City ($mg.kg^{-1}$ dry soil wt)

Fractions	Cd	Cr	Pb	Ni	V
B_1	1.69±0.64	14.91±1.55	5.62±1.37	8.81±1.37	10.98±2.37
B_2	1.52±0.22	8.09±1.82	4.24±1.24	5.84±0.49	5.08±1.29
B_3	1.55±0.46	11.51±1.52	4.79±1.09	4.87±1.32	7.26±1.82
Residual	1.85±0.58	8.82±1.77	11.41±1.48	6.62±1.58	6.53±1.67
Sum	6.61±2.01	43.34±1.51	26.05±1.74	26.13±1.52	29.82±1.68

As with the soils from the automobile workshops in the NW zone of Benin City, heavy metals in the exchangeable/carbonate bound fraction were the highest: Cd 1.69±0.64 (225.57%) Cr 14.91±0.55 (34.40%); Pb 5.62±1.37 (21.57%) Ni 8.81±1.37 (33.72%) and V 10.98±2.37 (36.82%) metal pool in the soils from automobile workshops in the NE zone of Benin City. The levels of organic matter/sulphide bound metal were higher than the reducible, Fe-Mn oxides bound metal pool. The residual metal pool represented between 20% and about 44% of the sum of heavy metals in the soil in the mechanical workshops in the NE zone of Benin City.

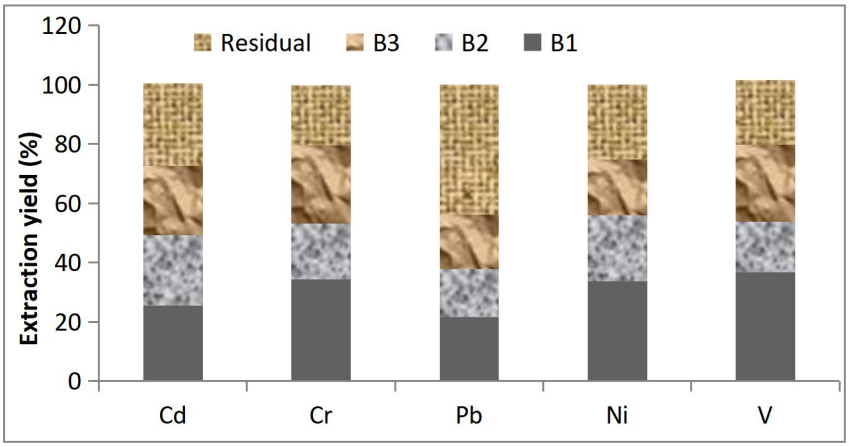

Fig. 3: Distribution pattern of Cd, Cr, Pb, Ni and V in soil samples from automobile workshops in the NE zone of Benin City

Chemical fraction content in the from automobile workshops in the SW zone of Benin City are given in Table 29 and shown in Fig. 20. The predominant metal fractions in the soils from automobile workshops in the SW zone of Benin City were the exchangeable/carbonate metal pool and the residual metal pool which accounted for between 24 and 36% and 23 and 46% of the sum of the heavy metals in the soils.It is well accepted that the exchangeable metal fraction occurs as free hydrated ion or as complexes with organic and inorganic ligands. This fraction represents the most labile/mobile metal pool in soils.The carbonate bound metal fraction occurs in precipitated and co-precipitated forms that have been implicated in immobilizing a large proportion of heavy metals by providing adsorbing nucleating surfaces and by buffering soil pH (Dudley *et* residual fraction may represent the amount in the parent rock and may only be released under harsh acid treatment conditions, and is least, if at all, mobile metal pool in the soil. The organic matter/sulphide metal pool: Cd 1.34±0.25mg.kg^{-1}; Cr 11.96±3.24mg.kg^{-1}; Pb 4.27±0.71mg.kg^{-1}; Ni 4.27±0.97mg.kg^{-1} and V 4.27±0.97mg.kg^{-1} were found to be somewhat higher than the corresponding values for reducible, Fe-Mn oxide bound metal pools. Metals associated with organic matter and/or sulphides are determined after oxidation of sample and include complexed and adsorbed metals. Heavy metals interact with organic matter through various mechanisms which affect bioavailability. This trend was observed for the fractionation of the heavy metals in soils from the NW and NE zones of Benin City.

Table 4: Fractionation of Cd, Cr, Pb, Ni and V in soils from automobile workshops in SW of Benin City (mg.kg^{-1} dry soil wt)

Fractions	Cd	Cr	Pb	Ni	V
B_1	1.64±0.21	16.25±3.24	5.85±1.42	8.48±0.89	10.92±3.37
B_2	1.31±0.25	9.27±2.91	3.31±0.75	5.83±1.06	5.08±1.64
B_3	1.34±0.25	11.96±3.24	4.27±0.71	4.27±0.97	7.11±1.84
Residual	1.54±0.23	13.53±3.87	11.10±2.46	5.85±1.20	6.83±1.71
Sum	5.83±0.85	51.01±11.83	24.53±4.66	24.43±3.33	29.99±7.73

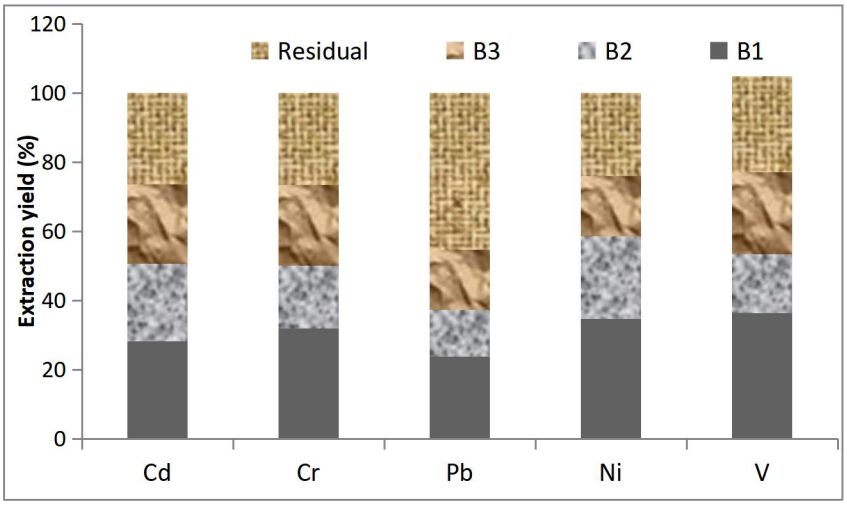

Fig. 4: Distribution pattern of Cd, Cr, Pb, Ni and V in soil samples from automobile workshops in the SW zone of Benin City

The fractionatior ɪil samples from soils from automobile workshops from the SE automobile workshop in the other (NW, NE zone of Benin City (Table 30 and Fig. 21) and SW) zones of Benin City.

Table 5: Fractionation of Cd, Cr, Pb, Ni and V in soils from automobile workshops in SE of Benin City (mg.kg^{-1} dry soil wt)

Fractions	**Cd**	**Cr**	**Pb**	**Ni**	**V**
B_1	1.66±0.44	10.58±4.14	6.41±1.57	7.36±2.17	7.89±2.89
B_2	0.87±0.29	8.45±3.66	4.92±1.23	3.79±0.97	6.18±2.57
B_3	1.34±0.52	9.21±3.94	4.96±0.97	4.74±1.55	6.59±2.07
Residual	1.44±0.59	9.54±3.96	8.21±2.27	6.76±1.55	6.88±2.12
Sum	5.31±0.58	37.79±14.91	24.49±5.54	22.65±5.32	27.55±8.85

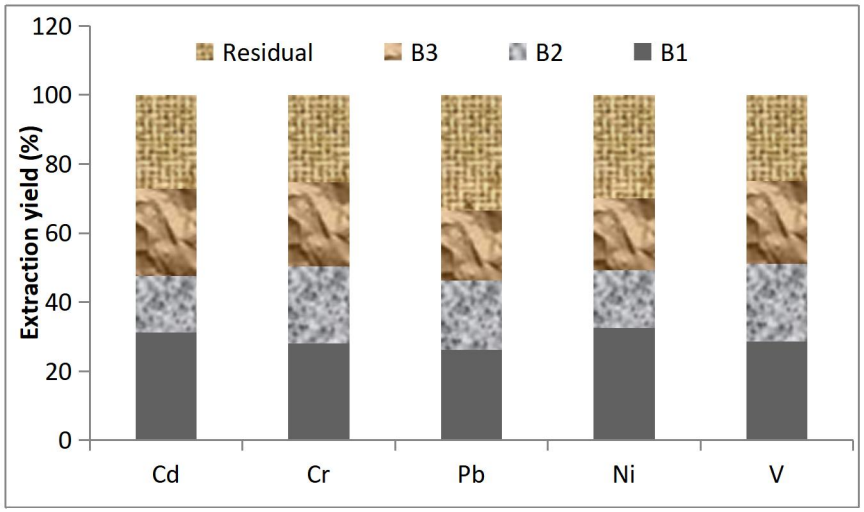

Fig. 5: Distribution pattern of Cd, Cr, Pb, Ni and V in soil samples from automobile workshops in the SE zone of Benin City.

In summary, Lead was mainly found in the residual fraction (R)in its fractions in all zones. This is similar to the results obtained by Anegbe and Okuo (2013). The metal may have co-precipitated with various silicate species as a result of their adsorption into the mineral

lattice because of the sandy nature of the soil (Manceau*et al.*, 2006). Cadmium was least associated with the reducible (Fe-Mn oxides bound) metal fraction in all zones among its fractions. This fraction includes chemically bonded and co-precipitated metals. Iron and manganese oxides have been implicated in sequestering heavy metals in the environment (Nacghtegaal and Sparks, 2004). Chromium was mostly associated with the exchangeable/carbonate fraction (B1) in all zones when compared with other fractions.

3.1 Bioavailability

Contaminant mobility in soil is increasingly being used as key indicators of potential risk to environmental receptors. The operationally defined mobile metal pool obtained from sequential extraction procedure as stated previously referred to as mobility factor. The mobile Cr, Cr, Pb, Ni and V in the soils from automobile workshops in the NW, NE, SW and SE zones of Benin City are given in Table 6.

Table 6: Mobile metal pools in soil samples from automobile workshops in the NW, NE, SW and SE zones of Benin City

Heavy metals	**Mobile metal fractions (mg.kg^{-1} dry soil wt)/locations**			
	NW	**NE**	**SW**	**SE**
Cd	2.01±0.50	1.69±0.64	1.64±0.21	1.66±0.44
Cr	13.42±3.75	14.91±1.55	16.25±3.24	10.578±4.14
Pb	7.09±2.23	5.62±1.37	5.85±1.42	6.41±1.57
Ni	7.93±1.66	8.81±1.37	8.48±0.89	7.36±2.17
V	8.99±1.95	10.98±2.32	10.92±3.37	7.89±2.89
∑	31.44±10.15	42.01±7.16	43.14±9.13	33.90±11.21

The distribution pattern of the mobile and potentially bioavailable heavy metal pools in soils in automobile workshops in Benin City is shown in Fig. 22 and suggests that the potential for soils in automobile workshops to deleteriously impact the environment is of the order SW zone > NE zone > SE zone > NW zone when compared with the average total levels of heavy metals in the soils from automobile workshops given in Table 19 (Section 4.4.1), these results (Table 31) indicate that a large proportion of the heavy metals are sequestered, bound to the soil matrix and therefore may be unavailable to be of imminient environmental and public health concern.

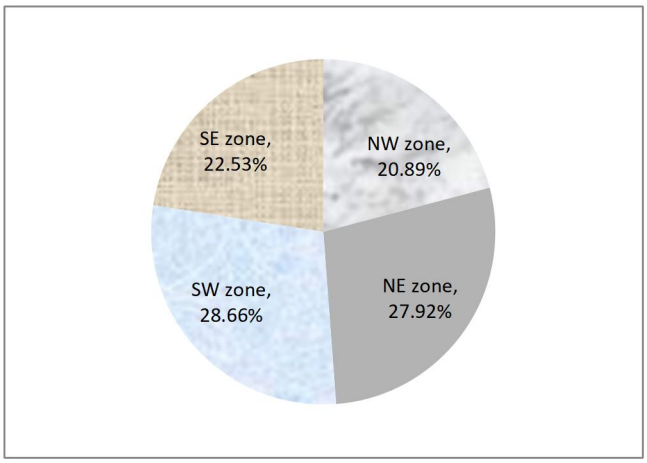

Fig. 6: Distribution pattern of mobile metal pools in soils from automobile workshops in different zones of Benin City

3.2 Mobility Factor (M_F)

The relative indices of metal mobility were calculated as the mobility factor (MF) (Kabala and Singh, 2001), on the basis of the following equation

$$M_F = \left(\frac{B1}{B1+B2+B3+R}\right) X\ 100 \qquad \text{-------(1)}$$

The mobility factor described the potential mobility of metals, as some metals are more strongly bound to the soil component than some. High M_F values have been reported as symptoms of relatively high liability and biological availability of heavy metals in soil. Mobility factor values observed in all the different sites indicate that the metals will be available for plant uptake in all the soil profile.

Table 7: Mobility Factors (%) of Cd, Cr, Pb, Ni and V in the Soil Samples

Heavy metals	Mobile Factors (%)				
	NW	NE	SW	SE	Average
Cd	33.2	25.57	28.13	31.26	22.08
Cr	28.76	34.40	31.86	27.99	30.75
Pb	26.30	21.57	23.85	26.17	24.47
Ni	29.58	33.72	34.71	32.49	32.63
V	29.65	36.82	36.41	28.64	32.88
Average	29.50	30.42	30.99	29.31	

The results obtained from table 5 above showed Pb had the lowest mobility in all the zones except in NW zone where Cd had the lowest mobility. V had the highest mobility in all the zones except in SE zone where Ni had the highest mobility. Considering the average mobility of all metals analyzed in each zone, it was observed that NW and SW showed the lowest and highest mobility respectively. According to Wong *et al*. (2007), high mobility of metals in acidic sandy loam is due to low pH, low clay and low organic matter contents. This means that soil sample with low pH, low percentage of clay and low organic matter content retains fewer metals. Thus, more metals would be released into the soil solution.

4.0 Conclusion

Heavy metal contamination in soils from automobile workshops in Benin City poses potential environmental and public health risks. Although total metal content provides a measure of contamination intensity, speciation analysis offers critical insight into metal behavior and bioavailability. Cadmium, Cr, Ni, and V were predominantly found in the exchangeable/carbonate fraction—the most labile and bioavailable form—while Pb was primarily in the residual fraction. Mobility factors indicate that these metals are sufficiently mobile to be taken up by plants growing near the workshops, potentially leading to biomagnification along the food chain. Regular monitoring and remediation strategies are recommended for these sites.

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