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Speciation of Chromium and Nickel in Open-Air Automobile Mechanic Workshop Soils in Ngara, Nairobi, Kenya

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Abstract This study determined concentrations of Ni and Cr in the various fractions of soils obtained from open-air garages in Ngara, Nairobi, Kenya. Soil samples were collected twice from ten sampling sites at a depth of 0 to 10 cm. The modified Community Bureau of Reference (BCR) sequential extraction was used and metals analysed using a FAAS. The mean total concentration of Ni and Cr obtained was 487.96±12.58 mg/kg and 261.51±13.38 mg/kg respectively. The ranges in the soils were between 401.55±58.32 mg/kg to 584.31±46.34 mg/kg and 160.77±26.42 mg/kg to 361.72±78.16 mg/kg for Ni and Cr respectively. These results show that the levels are high when compared with maximum allowed limits. The percentage of Ni in the fractions followed the order exchangeable (29.09%)>oxidisable (26.93%)>residual (23.63%)> reducible (20.35%) while percentage of Cr followed the order exchangeable= residual (25.75%) > reducible (24.41%) >oxidisable (23.69%). The % of non-residual Ni and Cr was 76.37 and 74.25 respectively. The mobility factors for the heavy metals were 29.10% and 25.82% and ranged from 16.67% to 36.19% and 19.65% to 32.49% for Ni and Cr respectively. These shows that the concentration levels of the metals were not only high but substantial proportions were mobile and bioavailable. As expected from the high mobility factors obtained in the study, the concentration levels of the metals in nearby grass, water pools and run offs were found to be high. Pearson correlation of the exchangeable fraction with the total concentration showed a significantly positive correlation with Ni (r = 0.511) and Cr (r = 0.714). This indicates that high concentration levels of the metals in the soil infer increased amount of the metal in mobile fractions.

Keywords Speciation, Mobility, Bioavailability, Sequential Extraction, Heavy Metals, Soil

1. Introduction

It has been widely accepted that soil plays a key role in sustaining life in earth's ecosystems[1]. The very survival of mankind is tied on its productivity as a medium for plants to grow[2]. Soil consists of a heterogeneous media comprised of decomposed rock fragments, clay minerals, oxides of Fe, Al and Mn, organic materials, organo-metallic complexes and soil solutions[3]. However, soil is also a transmitter of many pollutants including potentially toxic metals into the atmosphere, biosphere and water resources[4]. Heavy metals in soil exist in several different forms and are associated with a range of other components[5]. The accumulation of metals in soil, particularly Pb, Cd, Cu, Ni, Cr and Zn is of concern [6, 7, 8, 9]. Heavy metals emanating from anthropogenic sources are more dangerous because of their instability and solubility leading to high bioavailability[10,11]. Their form can strongly influence their speciation and availability the plants[12]. They can also transform to other species and easily accumulate to toxic levels in the topsoil[13] because of their non-biodegradable nature[14]. At toxic levels they affect biogeochemical cycles and accumulate within living organisms and eventually make their way to humans through the food chain, where they can cause perturbation to biological reactions[15, 16, 17, 18].

Industrial advances and the many industrial and commercial uses of Ni, Cr and their compounds have led to their increased emission into ecosystems[19, 20, 21]. Although these metals are vital for the function of many organisms, they are toxic to living organisms[22, 23 ,24 ,25] at high levels. These metals are distributed uniformly through the soil profile and only accumulate at soil surfaces through deposition by industrial and agricultural activities. If left unchecked, these metals pose a major threat to soils in lands near towns, industrial areas, or even agricultural land receiving wastes such as sewage sludge[26]. Once in the soil, these metals can exist in several forms such as inorganic crystalline minerals, precipitates, complexes, adsorbed on organic or inorganic cations exchange surfaces, water soluble free-ion or chelated metal complexes in soil solution [27]. This necessitates identification of the chemical form or

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phases in which the metals exist in soils in order to estimate their biological availability, physico-chemical reactivity and mobilty in the environment and into the food chain[28].

Automobiles introduce a number of toxic metals into the environment[29]. The wear of auto tires, degradation of parts, greases, peeling paint and metals in auto-catalysts are sources of heavy metal pollution[30]. This has led to elevated levels of heavy metals in automobile mechanic garage soils[31, 32, 33]. This implies that water bodies (surface and groundwater) within and away from the automobile mechanic garages may equally be polluted with these metals due to continuous interactions between soil and water and the high dispersion rate[34]. The fate of the various heavy metals and metalloids in automobile mechanic garages is of great concern, because soil, water, and dust in these areas may contain higher than average abundances of these elements, which may cause the formation of the more bioavailable forms of these elements[35].

In Kenya, despite the large increase in unregulated open-air automobile garages, published data on heavy metal contamination in garage soils and urban areas is limited[36]. However studies elsewhere have shown that automobile mechanic garages and automobile scrap yards harbour substantial amounts of heavy metals[5,6,37,38]. Further, the few studies that have been done report total concentration of the heavy metals[36] present and not their form thus providing limited information about the potential toxic behaviour, mobility, bioavailability and environmental safety[39]. Therefore, it is necessary to determine the forms they exist and the concentration levels in each form. This will provide predictive insights on the bioavailability, mobility and fate of heavy metal contaminants[40,41]. The chemical form or species of the heavy metal is a crucial factor in assessing their impacts on the environment because it controls its bioavailability or mobility[42,43].

In recent years there has been increased interest in the studies on speciation or chemical forms of heavy metals in polluted soils and sediments using sequential extraction techniques because these provide knowledge on metal affinity to soil components and the strength with which they are bound to matrix[42]. The use of sequential extractions, although time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals[44,45]. Sequential extraction procedures selectively extract metals bound by specific soil fractions with minimal effects on the soil components. In practice, sequential fractionation schemes have been suggested to identify element distribution with operationally defined soil pools[46]. These chemical pools range from water soluble to recalcitrant forms immobilized in mineral lattices[46]. The modified BCR, four step sequential extraction method, has made it possible to harmonize the extraction schemes for the determination of extractable metals and can be used to enhance quality control of the whole analysis procedure, a key issue in interpreting this type of operational defined speciation[46].

The procedure consists of using four fractions which allow the identification of three distinct parts (or compartments) and a residual: The Fraction bound to carbonates (F1) comprises metals adsorbed on the surface of soil. It is the most accessible and represents the exchangeable fraction. Metals on this fraction are easily mobile and are assumed to be available. The decrease of pH leads them to migrate from the solid phase to water and plants[36]. This represents the water and acid soluble as well as exchangeable fraction and is extracted with 0.11 $molL^{-1}$ acetic acid[41]. The Fraction bound to iron and manganese oxides (F2) is sensitive to redox potential changes and represents the fraction that can be solubilized under reducible conditions. It represents the reducible fraction and extracted using a solution of 0.1 M $NH_2OH.HCl$ at pH 2. The fraction bound to organic matter (F3) is temporarily inaccessible and can only be solubilized under chemical oxidation. It represents the fraction combined with organic materials and is extracted using a solution of 1.0 M NH_4Ac after the sample has been digested with H_2O_2[47, 41]. The Residual fraction (F4) mainly contains metals built in the crystal lattice of minerals. In natural conditions, they are practically inaccessible for living organisms and can be considered as permanently immobile. This fraction is Extracted using aqua regia.

The aim of this study was to determine the concentration levels of Cr and Ni in the various chemical forms of soils of open-air automobile mechanic garage of Ngara, Nairobi, Kenya so as to assess their association, bioavailability and environmental contamination risk based on their chemical form. The need for this research arose because there are reports on speciation of heavy metals in soil of these garages despite their rapid increase due to a rapid increase in reconditioned automobile imports

2. Materials and Methods

2.1. Area of Study

The main focus of the study was Ngara area located within Nairobi city–Kenya. The area is a host to many open-air vehicle mechanic workshops. A section of the Nairobi River cuts across the study area from northwest to southeast.

2.2. Sampling and Sample Pre-treatment

Ten sampling points each 4m x 4m quadrants were chosen with reference to potential sources of the heavy metals. Each quadrant was subdivided into twenty cells (20cm by 20cm) denoting a sampling point. Soil samples from ten randomly selected cells of each quadrant were collected at depths of 0-10cm and mixed to obtain a representative composite sample. This was done twice in the rainy month of April ten days apart. The samples obtained were placed in separate labelled polyethylene bags and transported to the laboratory at room temperature on the same day. In the laboratory extraneous materials were removed, soil samples air-dried and homogenized by grinding. They were then oven-dried to a constant mass for 48 hours at 50^{o}C, cooled and sieved using size 600 µm mesh to remove large undesired particles sizes. The sieved soil samples were then ground to powder form using an agate mortar and pestle to particle sizes of nanometres range. The resultant powder was stored in clean labelled polyethylene bags in a desiccator until analysis[37].

2.3. Analysis

Heavy metals in the soil were extracted using the modified BCR chemical sequential extraction[40,41]. The exchangeable and acid soluble fractions (F1), was extracted by shaking about 1.0g soil sample in a 40mL solution of 0.11 M CH_3COOH for 16 hours at room temperature. The reducible fractions (F2), was extracted by shaking the residue from (F1) in a 40mL solution of 0.1 M $NH_2OH.HCl$ at pH 2 for 16 hours at room temperature. The residue from (F2) was treated twice with 8.8 $molL^{-1}$ hydrogen peroxide, evaporated to near dryness, 50 mL of ammonium acetate was added and the pH was adjusted to 2 using nitric acid and shaken overnight. The mixture was then centrifuged to separate (F3), the extract representing the oxidizable fraction. The residual fraction was extracted by digesting residue from (F3) using 20mL of aqua regia solution[40,41]. Similarly extract for total metal concentration (bulk soil analysis) was obtained by extracting about 1.0g of soil sample with about 20mL of aqua regia solution[40,41]. The concentration of metal in the various fractions was determined using a flame atomic absorption spectrophotometer (Model Buck Scientific 210 VGP). The levels of Cr and Ni obtained in the various fraction and bulk were used to calculate their concentrations in the fractions and bulk soil respectively.

The recovery of the sequential extraction was obtained as the sum of four fractions as percentage of the directly measured total, calculated as 100% sum of fractions/total metal[48]. All analysis were done triplicate and the three absorbance readings averaged. Quality checks were also performed on the instrument by checking the absorbance after every ten sample runs[49].

The pH and total organic carbon were measured using standard procedures[50]. Soil pH was measured by using a suspension of 1.0g of soil placed in 10mL of deionized water. For total organic carbon (T O C), 1.0 g of soil (dried at 105^oC for 1hr) was placed in a ceramic crucible, heated to 550^oC for 2 hours, cooled in a desiccator then weighed[51]. The soil organic matter (SOM) obtained was converted to total organic carbon (TOC) using a 1.9 correction factor [52,53,54]. The measurements were done in triplicates. All chemicals were of analytical grade and all plastic and glass wares for metal analysis were previously soaked in 10% nitric acid (HNO_3) (v/v), for 48 hours to remove all entrained metals, washed with detergents and rinsed with deionized water. All glassware were soaked in 10% HNO^3, washed before use, and rinsed with deionized water. The arithmetic means (AM) of the triplicate extraction results were calculated their standard deviations (Std) determined[55].

3. Results and Discussion

3.1. Total Heavy Metal Concentration

The total metal concentrations of Ni and Cr for the samples collected from the ten different sample locations at the study site are shown in table 1. Variations in total metal concentration are given in figure 1. The total Cr concentrations in the soils were found to range from 160.77±26.42mg/kg to 361.72±78.16mg/kg and its average mean in the ten sites was 261.51±13.38mg/kg. This concentration levels exceed the maximum allowed concentrations for Cr in soils set at 100mg/kg[56]. Total Ni concentration levels in the soils ranged from 401.55±58.32mg/kg-584.31±46.34mg/kg while the average mean in the ten sites was found to be 487.96±12.58mg/kg. These exceed the maximum allowed concentrations of 50mg/kg for Ni in soils[62]. This suggests Ni contamination from anthropogenic sources as compared to normal soil concentration levels range of 5 mg/kg to 50mg/kg[57]. This indicates that similar to literature reports, waste from automobile repair activities were contaminating the soils at the site[36,40].

The results in Table 1 show that the lowest concentration values for Ni and Cr concentration were 401.55±58.32mg/kg and 160.77±26.42mg/kg respectively at site 7 and 1 while the highest values were 584.31±46.34mg/kg for Ni and 361.72±78.16 for Cr at site 9. Even the lowest Ni and Cr concentrations were above the tolerable limit value of 50mg/kg and 100mg/kg respectively[62]. The low Ni and Cr values obtained for some soil sites compared to other may be due to the lesser impact of anthropogenic sources of pollution in the locations. Similar findings by other investigators have reported drastic decrease in metal concentration away from the source point[58,59]. The decreasing tendency with distance indicates the accumulation of metals by the anthropogenic activities within the locations[64,65].

The contamination indexes (pollution index-Pi) of the heavy metals in the soil samples were obtained by dividing the total concentration obtained by MAL as the background[62,60]. The pollution indexes were 2.62 and 9.76 for Cr and Ni respectively. Traditionally the data obtained from calculation of the contamination index is grouped into four grades ranging from unpolluted to very highly polluted as follows: 0 to 0.99 (uncontaminated), 1.0 to 1.19 (moderately to highly contaminated), 1.2 to 1.99 (highly contaminated), 2.0 to 3.5 (very highly contaminated)[39,66]. The pollution levels of these metals are expressed in terms of the pollution indexes in Table 1 indicate that the study site is highly by all the heavy metals studied. It can therefore be inferred from the results that the area is heavily polluted by Cr and Ni which are known to be dangerous to human health at elevated levels[13].

Table 1. Total mean concentration and pollution index of Cr and Ni at the ten sampling sites

Site	Cr (Mean±SE) mg/kg	Pollution index (PI)**	Ni (Mean±SE) mg/kg	Pollution index (PI)**
1	160.77±26.42	1.61	427.08±1.70	8.54
2	238.47±33.64	2.38	413.64±3.61	8.27
3	278.66±37.22	2.79	584.31±46.34	11.70
4	229.09±28.21	2.29	467.40±36.10	9.35
5	246.51±37.22	2.47	510.40±45.71	10.20
6	262.59±53.95	2.63	549.37±10.29	11.00
7	274.64±34.19	2.75	401.55±58.32	8.03
8	277.32±28.21	2.78	464.71±38.54	9.29
9	361.72±78.16	3.62	582.97±6.25	11.70
10	285.36±8.99	2.85	478.15±4.66	9.56
p-value	0.150	-	<0.001	-
Min	160.77±26.42	1.61	401.55±58.32	8.03
Max	361.72±78.16	3.62	584.31±46.34	11.70
Mean	261.51±13.38	2.62	487.96±12.58	9.76
MAC*	100mg/kg	-	50mg/kg	-

*62 **total concentration/MAL

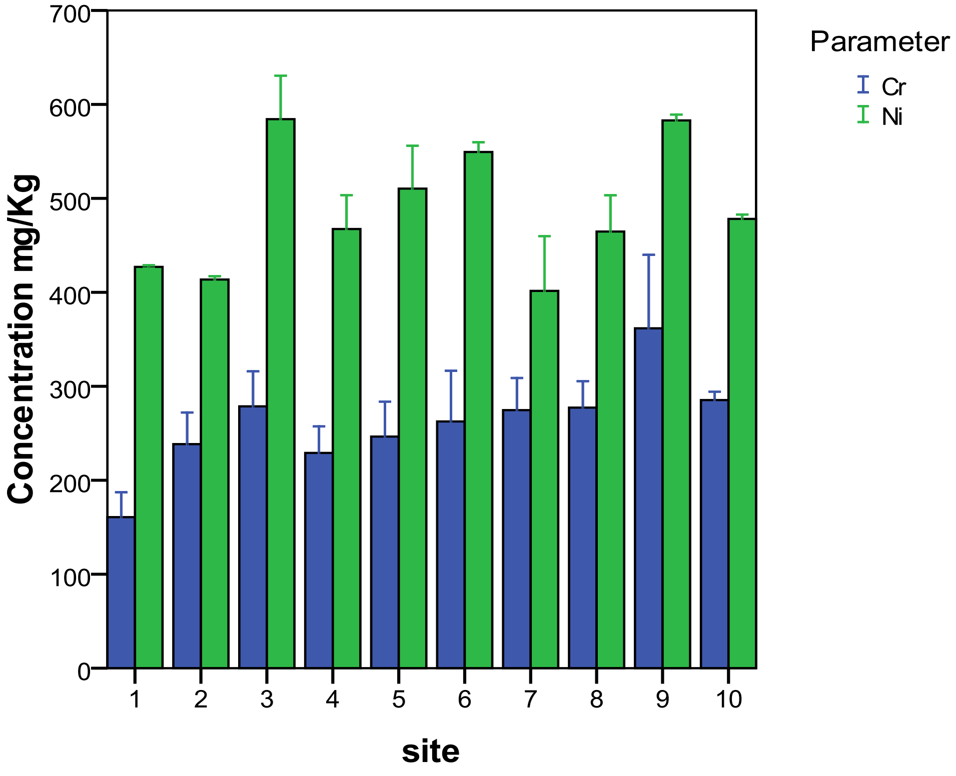

Figure 1. Variations in the total concentration of Cr and Ni at the ten sampling sites

3.2. Fractionation of Heavy Metals

The average concentrations of Cr and Ni in the four fractions at the ten sites are presented on table 2. The results indicate that the soil samples collected from the various sites varied in both the mean concentrations and distribution of the metals in the exchangeable, reducible, oxidisable and residual fractions. Average mean concentrations of Cr and Ni in the four fractions show that the highest concentration was found in the exchangeable fraction as represented in figure 2. Chromium fractionation follows the order: exchangeable > residual > reducible >oxidisable at mean values of 71.81±3.92mg/kg, 71.81±4.02mg/kg, 68.06±3.68 mg/kg and 66.43±4.10mg/kg respectively.

For Ni, the concentrations in the fractions follow the order: exchangeable >oxidisable> residual >reducible at mean values of 140.43±12.22mg/kg, 129.98±9.85mg/kg, 114.09± 4.43mg/kg and 98.24±5.73mg/kg respectively.

The percentage proportion of Cr in the exchangeable fractions was 25.82% of the total while that of Ni was 29.10% of the total. These moderately high levels of the studied heavy metals in the exchangeable fraction indicate that they are highly available for plants[4]. The relatively high proportion of Cr and Ni in the mobile fractions and the high mobility index is a further indication that metals are of anthropogenic origin[61,62]. The percentage proportions in the reducible fractions were 24.41% for Cr and 20.35% for Ni. Metals in the reducible fraction can easily go into solution when a soil is subjected to reducing conditions because of the high susceptibility of Mn oxide to reduction followed by Mn release into the soil pore water[63,4]. Studies have shown that high proportion of heavy metal association with oxide phases is an indication of anthropogenic pollution[4].

About 26.93% of Ni and 23.69% of Cr were found in the oxidizable fraction. The moderately high percentage of the oxidizable (organic bound) fraction indicates the strong ability of the heavy metal to form complexes with organic matter thereby reducing its mobility and phytotoxicity[4,67]. The residual fractions contained about 26.00% of Cr and 23.86% of Ni. This fraction is a relatively stable and weakly available fraction and reflects the native metal concentration in soil which has little or no environmental significance. Although this latter assumption might be questionable, studies have shown that the removal of metals from the residual fraction requires the use of aggressive extracting solutions[64,65].

Table 2. Average concentrations of Cr and Ni in the four fractions at the ten sampling sites

Fraction	Cr (Mean± SE*)	% Cr **	Ni (Mean± SE*)	% Ni **
Exchangeable	71.81±3.92a	25.75	140.43±12.22b	29.09
Reducible	68.06±3.68a	24.41	98.24±5.73a	20.35
Oxidisable	66.43±4.10a	23.69	129.98±9.85ab	26.93
Residual	71.81±4.02a	25.75	114.09±4.43ab	23.63
Pseudo total	278.83±3.93	-	482.74±8.06	-

*values followed by different letters within the same column are significantly different ($p<0.05$ at $\alpha = 0.05$). % ** obtained by mean concentration of fraction/pseudo total

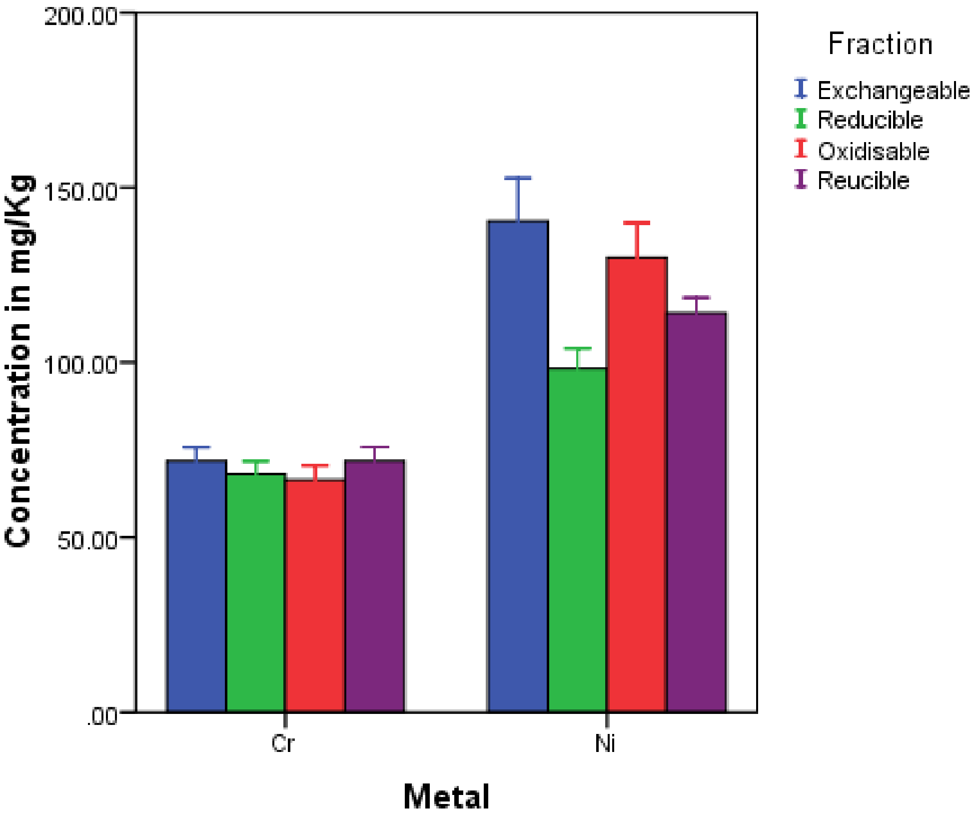

Figure 2. Variations in the average concentration of Cr and Ni in the four fractions at the ten sampling sites

The percentage proportions of Cr and Ni in the various fractions were found to differ in the ten sampling sites as shown in figures 3 and 4. Site 4, 5 and 10 had a higher proportion of Cr in the exchangeable form while Site 1, 3 and 10 and a higher proportion of the Ni in the exchangeable form. The relative availability and consequently the comparative mobility of the studied metals followed the order 29.09% for Ni and25.75% for Cr. Evaluating the metal speciation at the sampling sites reveals that non-residual fractions had considerably high values of up to 74.25% and 76.37% at all sites for Cr and Ni respectively.

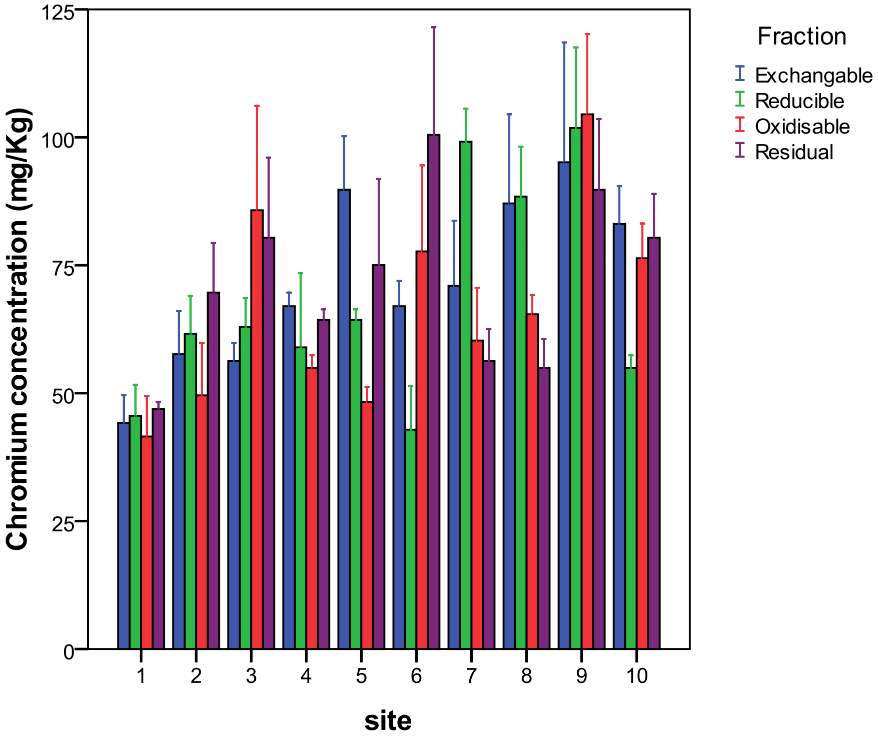

Figure 3. Variations in the concentrations of Cr in the four fractions at the ten sites

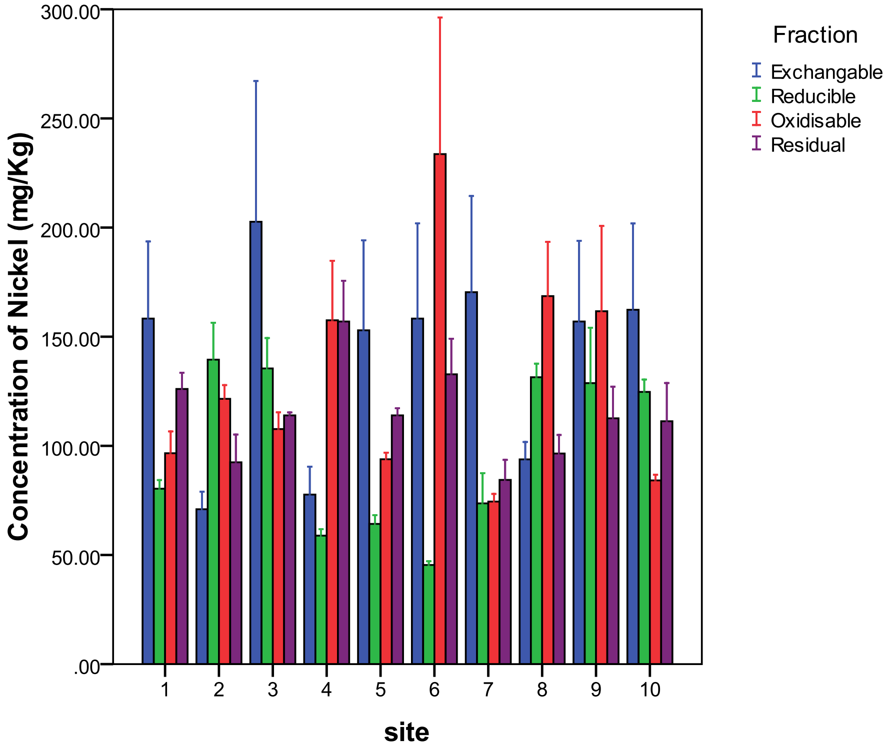

Figure 4. Variations in the concentration of Ni in the four fractions at the ten sites

Element availability is very important when assessing the effect of soil contamination on plant metal uptake and related phytotoxic effects[67,66]. The exchangeable amount as a percentage of the total metal content in this study was moderately high at values of 29.10% Ni and 25.82% Cr. This indicates a moderately high availability of the metals. Studies have shown that heavy metals are potentially available for plant uptake, if the bioavailability percentage is above 10%[67,71].

3.3. Mobility, Mobility Factor, (MF) and Recovery

The relative index of metal mobility was calculated as the mobility factor, MF[70,67,68] and the results obtained showed that Cr ranged from 19.65 % to 32.49% with a mean of 25.82% while Ni ranged from 16.67 % to 42.18% with a mean of 29.10% as represented in figure 3 and 4. The order in the average mobility of the metals was Ni>Cr at 29.10 and 25.82 respectively as shown in table 3. A high MF value for heavy metals in soil has been interpreted as evidence of relatively high labiality and biological availability[69]. The relatively high mobility factor observed for Ni and Cr is in agreement with the high percentage of exchangeable fraction of these metals recorded from the chemical fractionation results. Metals associated with Fe-Mn oxides (reducible fraction) have a medium mobility and that may change under reducing conditions to cause a release the metals[70]. Metals associated with organic matter (oxidizable fraction) have medium to low mobility[75].

Table 3. Average mobility and recovery of Cr and Ni in the ten sampling sites

Description	Cr %*	Ni %*
% non-residual**	74.25	76.37
% residual*	25.75	23.63
Potential mobility %***	25.82	29.10
Total(mg/kg)	261.51±13.38	487.96±12.58
Pseudo total(mg/kg)	278.83±3.93	482.74±8.06
% recovery****	106.35	98.93

*F4 x 100/ pseudototal, ** (F1+F2+F3) x 100/ pseudototal and ***F1 x100/pseudototal, ****= pseudototal x 100/ total concentration

The pseudo total concentration of the sequential extraction calculated as a sum of four fractions was found to be 278.83±3.93mg/kg for Cr and 482.74±8.06mg/kg for Ni, The recovery total concentration of the sequential extraction was calculated as a percentage of calculated pseudo total concentration divided by the directly measured total concentration and found to range from 98.93% to 106.35% as shown in table 3[71,54]. This recovery range shows that the results of obtained from single digestion with aqua regia were in good agreement with those of the sequential extraction procedure[72].

3.4. Soil Physicochemical Properties (pH and Total Organic Carbon -TOC)

The soils studied were oily and greasy and their pH ranged from 8.5 to 9.17 as shown in Table 4. These pH values were higher than the values reported by other workers[73,74,75]. Alkalinity observed in soils is common to reduced (anaerobic) soils[76,77,78]. Heavy metals are mostly soluble and available at low pH[79]. There was significant variation in the values of the T.O.C obtained for the samples analysed. The T.O.C values ranged from 13.51 to 18.95%.

Table 4. pH and total organic carbon (T.O.C) in the ten sampling sites

Site	pH (Mean±SE)	% T.O.C (Mean±SE)
1	8.50±0.18	18.42±0.19e
2	8.50±0.18	18.95±0.19e
3	8.50±0.18	15.79±0.19d
4	8.50±0.18	13.68±0.19a
5	8.50±0.18	14.74±0.19b
6	8.50±0.18	15.26±0.19bc
7	8.50±0.18	15.09±0.29bc
8	8.50±0.18	16.32±0.19d
9	8.50±0.18	13.68±0.19a
10	9.17±0.18	13.51±0.22a
p-value	0.330	<0.001

3.5. Interrelationships among the Fractions, pH and TOC

A correlation coefficient was calculated in order to determine the relationship between the Cr and Ni fractions and their total concentrations as shown in table 5. From the results, a strong positive correlation of Cr was found between the exchangeable fraction and the reducible fraction. A positive correlation of Cr was also found between the exchangeable and the oxidisable fraction. In addition a positive correlation of Cr was observed between the exchangeable and residual fractions. Further a strong positive correlation was observed for all metals between the exchangeable and the total metal concentrations.

A strong positive correlation was also obtained between the reducible and residual fractions and the total concentration for Cr while a strong positive correlation of Cr was also obtained between the oxidizable and the exchangeable, reducible and residual fractions. A positive correlation was obtained for both the metals between the oxidizable the total concentrations. Further a positive correlation was obtained for Cr between the residual and the exchangeable and reducible fractions. Levels of Cr in the residual fraction correlated positively with those in the oxidizable fraction. A strong positive correlation was obtained for all the metals between the residual fraction and their total concentrations. Further a significant positive correlation of the metal levels in all the fractions with their total concentration except for the reducible fraction in Ni was obtained indicating that the heavy metal concentrations in the fractions were dependent on the total concentration of the heavy metal in the soil. The positive correlation of the total concentration of Cr and Ni with their levels in the fractions also suggests overloading of the geochemical system by contamination from anthropogenic sources.

Table 5. Values of the Pearson correlation between the fractions and the total concentration

Element	Fraction	Exchangeable	Reducible	Oxidisable	Residual	Total content
		1 1	0.823 0.896	0.544 -0.466	0.519 0.563	0.822 0.457
Cr Ni	Reducible	0.391 -.129	1 1	0.413 -0.193	0.156 -0.429	0.597 -0.031
Cr Ni	Oxidisable	0.456 -0.433	0.413 -0.193	1 1	0.804 -0.001	0.869 0.316
Cr Ni	Residual	0.410 -0.073	0.156 -0.429	0.804 -0.001	1 1	0.799 0.129

Table 6. Values of the Pearson correlation between the fractions pH and TOC

BCR steps	Element	pH	T.O.C
Exchangeable	Cr Ni	0.054 (p- value 0.684) 0.045 (p- value 0.733)	-0.334 (p- value 0.009) -0.111 (p- value 0.398)
Reducible	Cr Ni	-0.058 (p- value 0.659) 0.095 (p- value 0.468)	-0.179 (p- value 0.170) 0.170 (p- value 0.195)
Oxidisable	Cr Ni	0.039 (p- value 0.769) -0.089 (p- value 0.497)	-0.312 (p- value 0.015) -0.064 (p- value 0.629)
Residual	Cr Ni	0.034 (p- value 0.796) -0.020 (p- value 0.881)	-0.224 (p- value 0.085) -0.184 (p- value 0.159)

Some researchers have shown that correlations exist between the levels of heavy metal in the exchangeable fraction with some physicochemical characteristics[80,81]. Correlation coefficients between the total concentrations of the metal and the soil pH and total organic carbon (T.O.C) were determined as shown in table 6. The levels of the metal in the exchangeable (acid –soluble) fraction correlated positively with the pH and negatively with the T.O C. Levels of Ni in the reducible fraction gave a positive correlation with the pH and T.O C. For the oxidizable fraction levels of Cr had a positive correlation with pH while both metals correlated negatively with T.O C. Chromium levels in the residual fraction were found to correlate positively with pH. This is an indication that bioavailability of the metals in contaminated soils is influenced by the pH and T.O.C. as suggest by literature reports[82,83].

3.6. Concentration of Cr and Ni in Grass and Water

As expected from mobility results, the levels of these metals in the garage water pools and run off were found to be high as shown in table 7. They ranged from 0.96 to 4.66, and 3.00 to 5.90mg/kg for Cr and Ni respectively. Further the metal levels upstream were found to be higher than downstream due to heavy metal translocation from the garage to the surrounding environment. These concentrations in water near and within the garage were significantly high than the minimum allowed limits indicating considerable pollution. This means that the heavy metals may leach into surface and ground water and affect their quality[84].

The levels of these metals in nearby grass were also found to be high. The concentration of Ni was the highest in grass at mean of 176.85±5.38 followed by Cr at 160.76±4.64 ppm. Since the heavy metals can be transferred through food chain, there is a potential risk for ruminant animals grazing within or near automobile mechanic garages[85].

Table 7. Levels of Cr and Ni in ppm in the nearby grass and water

Sample	Cr (Mean±SE) ppm	(Ni Mean±SE) ppm
Grass	160.76±4.64	176.85±5.38
Water (100 m upstream)	2.25±0.00	3.00±0.00
Water (200m upstream)	0.96±0.00	3.00±0.00
Water (100m downstream)	3.54±0.00	4.61±0.00
Water (200m downstream)	4.50±0.00	5.90±0.00
Water (at garage pools)	4.66±0.07	4.45±0.22
Water (site run off)	4.18±0.07	3.78±0.12
p-value	<0.001	<0.001

4. Conclusions

The results indicate that the metal concentration levels in the top 10.0 cm of soil of the ten site are above the maximum allowed limits and have caused severe to excessive pollution capable of serious ecological and public health hazards. This implies that metal pollution levels at the study site are not of natural geology or the processes of weathering and deposition. The study also revealed the geochemical nature of the two heavy metals and their probable association with different chemical forms in the soils within and around the automobile mechanic workshops. The heavy metal concentrations found in the non-residual fractions was higher than those observed in the residual fraction for the two metals indicating that a high percentage of the metals in a bio-available form and could easily enter the food chain. The relatively high mobility factor observed in the metals confirms the high liability, and biological availability of the metals in the soils studied. The metals studied do pose environmental risks since their total concentration was very high and a high proportion is in non-residual fractions. Consequently authorities can be encouraged to institute environmentally friendly automobile mechanic workshop concepts for the disposal of oil and other wastes. The poor infrastructural development common at such workshops also calls for immediate action of redevelopment. Continuous education and training should be provided to the mechanics, emphasizing on the environmental implications of their poor occupational waste management. Code of practice and specific regulations guiding the establishment and the operation of the automobile workshops must be put in place and enforced. Efficient and affordable soil remediation programs are also recommended at the site.

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