RISK ASSESSMENT OF CHROMIUM AND NICKEL IN SOILS OF SHARADA INDUSTRIAL ESTATE, KUMBOTSO LOCAL GOVERNMENT AREA, KANO STATE

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ABSTRACT

Treatment of industrial chemical wastes being discharged into the environment is rarely done in Nigeria. These wastes are known to contain heavy metals which when released untreated, accumulate in the soil and pose serious environmental problems thereafter. In this study, operationally determined speciation analysis and potential mobility factor of Chromium and Nickel were carried out in the Tannery, Dye pit, Ceramic and Plastic industry soils of Sharada Industrial Estate. Levels of metals in the various fractions were determined using Atomic Absorption Spectrophotometer (Buck 211VGP AAS). The results indicated that the total concentrations of the heavy metals in these industries were 126.46, 116.28, 116.89 and 117.91 mg.kg^{-1} for Ni; 1498.54, 1446.33, 164.52, 117.93 mg.kg^{-1} for Cr, respectively. The residual fraction for Cr at the sites ranged from 61.60 mg.kg^{-1} at Plastic Industrial site to 706.85 mg.kg^{-1} at Tannery site, while that of Ni ranged from 59.80 mg.kg^{-1} at Plastic Industrial site to 84.98 mg.kg^{-1} at Tannery site. Results showed that most of the Cr and Ni fractions were bound to the residual fraction indicating that they were as a result of the lithogenic property of the soil. The mobility of Ni and Cr were calculated using Potential Mobility Factor (PMF), which for Ni across all industries gave 10.52%, 13.37%, 13.85%, 14.90%, while for Cr, the values were 0.72%, 11.08%, 8.36%, 11.55%. The PMF for Ni appeared to have a higher value compared to that of Cr, but the two values were statistically the same as they fell within the same medium stability and risk class (10 < PMF ≤ 30). Risk assessments of these metals in the soils were found to pose no immediate health challenges.

Keywords: Heavy metals, Environment, Speciation, Polluted soils, Mobility index.

INTRODUCTION

The vast development of industries in Kano State of Northern Nigeria has led to the consumption and generation of materials as waste that poses a danger to the environment. These materials are potentially harmful to both the fauna and flora communities in the immediate environment. The risk posed by these materials is due to the fact that they remain within the environment, bio accumulating in tissues of organisms over a period of time before any consequential symptoms are noticeable (Gill and Garg, 2014).

Some of these metals are found in the environment as a result of using raw materials that contain heavy metals that are necessary for the completion of manufacturing cycles (Wei and Yang, 2010). This vast industrial usage of Chromium (Cr) and Nickel (Ni) compounds

followed by the subsequent release of their effluents to the environment poses great environmental risks as they are both environmental contaminants having a very high tendency of contaminating both the surface and ground waters, thereby inducing soil pollution and water contamination (Aslam and Yousafzai, 2017). The wide public and regulatory attention Cr and Ni have generated is largely due to their ability to contaminate the ecosystems, including both microorganisms and animals under certain oxidation states (Shanker *et al.,* 2005).

Mobility of Cr and Ni within the soil is largely influenced by their species which invariably is influenced by the forms in soils (Hulanicki, 2000). These heavy metal forms especially, determine the risk potential of these metals in the environment. Thus, to produce valid evidence of potential risks

posed by metals in the soil to a given environment and the biota therein, there is the need to identify and determine the individual soil fractions and the metals associated with them. Therefore, this study was aimed at assessing the mobility and risk status of Cr and Ni in surface soils within the Sharada industrial estate, Kumbosto LGA, Kano State.

MATERIALS AND METHODS

Study Area and Location
The study area was within Sharada industrial estate. It is located at Kumbosto Local Government Area of Kano State, in the northern part of Nigeria. This estate falls within an area extending between latitude 12°40' and 10°30' N and longitude 7°40' and 90°40' E (Figure 1). The industries within this industrial estate include tanneries, textiles, food and packaging/processing factories and fall within the grid spots as shown in Table 1. The mean annual rainfall experienced is about 600 mm to 750 mm usually between May and October in a given year, while the annual mean temperature ranges from 23 to about 26 $^{\circ}$C in the coolest season (December to February) and 27 to 33 $^{\circ}$C in the hottest season (April and May) (Akintola, 2001).
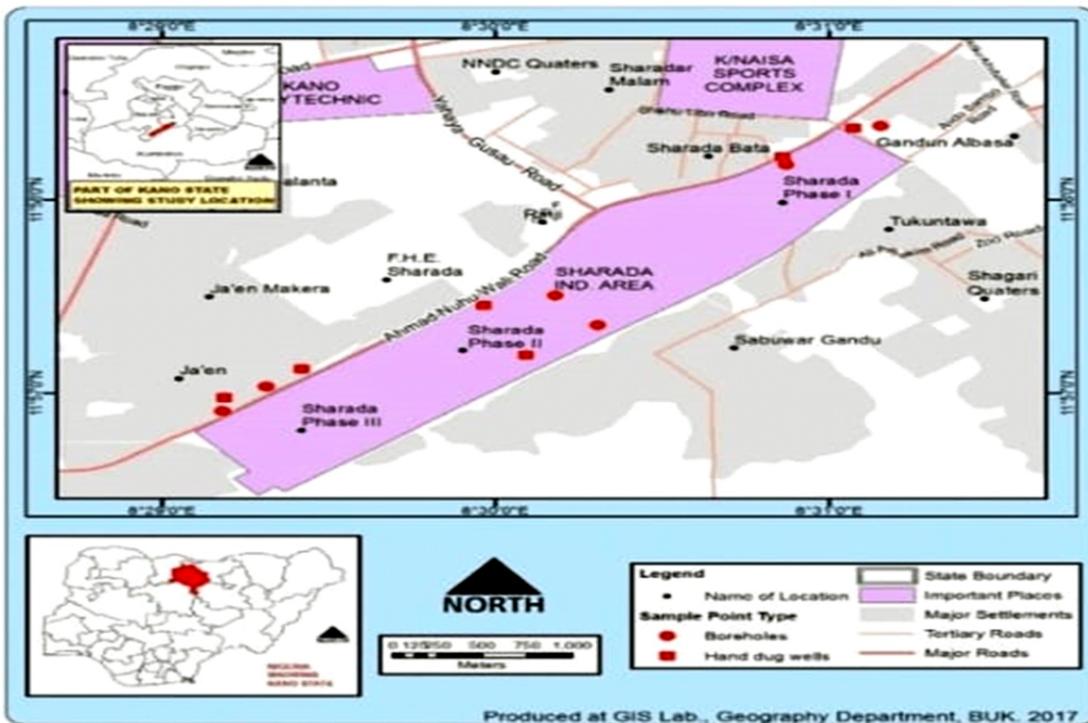
Figure 1: Georeferenced map of the study area, BUK, 2017.

Table 1: Grid locations of sampling spots

Sampling spots	Grid locations
Tannery	11° 96', 8° 51'
Dye pit	11° 97', 8° 50'
Ceramic	12° 01', 8° 52'
Plastic	11° 96', 8° 50'

Soil Sample Collection
Twenty (20) soil samples were randomly collected at 0–15 cm depth from each of the Tannery, Dye pit, Ceramic and Plastic industries located at Sharada industrial estate, Kumbosto Local Government Area of Kano State. Thus, a total of 80 samples were collected. The soil samples collected from a location were bulked, mixed and

placed in labelled sterile polythene bags for proper identification. The labelled samples were then taken to the Soil Science Laboratory of the Soil Science Department, Federal University, Dutse where they were air-dried in an enclosed environment to prevent contamination, preliminarily prepared using the standard soil preparation techniques and stored.

Soil Analysis

The prepared samples were subjected to routine analysis. Particle size distribution was determined using the Bouyoucous-hydrometer method (Bouyoucous, 1962). The textural classes were determined with the aid of USDA textural triangle. The pH of the soil samples were measured in water and in 0.01 M $CaCl_2$ solution, using a 1:2.5 soil: water ratio and soil: $CaCl_2$ ratio on a two-way equilibration with buffer solution at pH 4.0 and 7.0. pH was read with a glass electrode on a pH meter. Soil organic carbon (OC) in the soils was determined by the wet oxidation method of Walkley and Black as described by Nelson and Sommers (1986). Total nitrogen was determined by using the micro-Kjeldahl digestion method by Bremmer (1996). The exchangeable bases (Ca, Mg, K and Na) in the soil samples were extracted with 1 M ammonium acetate (1 M NH_4OAc) solution buffered at pH 7.0 as described by Anderson and Ingram (1993). Calcium and Mg in the extracts were determined using an atomic absorption spectrophotometer (Buck 211VGP AAS) while K and Na were determined on flame photometer. Exchangeable acidity was determined by the method outlined by Udo *et al.*, (2009). The sum of Ca, Mg, K and Na gave the total exchangeable bases. Electrical conductivity of the saturated paste extract of 1:2 soils to water ratio was determined using a conductivity meter at 25 °C (Bower and Wilcox, 1965). Available Phosphorus was determined using the Olsen method as described by Zhan *et al.*, (2015). Phosphorus in the extract was determined colometrically by the molybdate-phosphoric-blue method using ascorbic acids as a reducing agent (Reeuwijk, 1993). Cation exchange capacity of the soil samples was determined with 1 M ammonium acetate (NH_4OAc) solution buffered at pH 7.0

(Chapman, 1965). Labile extractable concentration of Cr and Ni in the soil samples was determined by the conventional EDTA (Ethylene diamine tetracetic acid) chelation method of Lindsay and Norvell (1978). To each soil sample, 0.005 mol EDTA solution was added and shaken for about 2 h. The individual suspensions were filtered using filter paper into a 100 mL volumetric flask. Extractible Cr and Ni in the filtrate were determined in AAS (Buck 211VGP AAS).

Sequential extraction analysis of Cr and Ni in the soil samples

Sequential extraction and fractionation of Cr and Ni in the soil samples were carried out using the procedures outlined by Tessier *et al.* (1979) and Onokebhagbe *et al.* (2018). The extraction steps included the use of different reagents of different binding strengths and metal specificity leading to separation of the metal species into five operationally defined fractions, namely: Exchangeable fraction (F1), Carbonate fraction (F2), Iron-Manganese fraction (F3), Organic fraction (F4), and Residual fraction (F5). The concentrations of Cr and Ni in the fractions were determined using the Atomic Absorption Spectrophotometer (Buck 211VGP AAS).

Mobility of Cr and Ni

The mobility of the individual fractions of Cr and Ni was calculated using Potential Mobility Index Factor (Kabala and Singh, 2001).

$$PMF = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \quad [1]$$

where PMF denotes Potential Mobility Factor.

Data analysis

Data obtained from the sequential extraction analysis was subjected to descriptive analysis using Excel (Microsoft Office 10). Potential mobility factor and risk assessment of Cr and Ni in the soil samples were carried out using the risk assessment table (Table 2).

Table 2: Stability and risk assessment table of heavy metals.

PMF (%)	Stability	Risk
PMF < 1	No stability	No risk
1 < PMF≤ 10	Low stability	Low risk
10 < PMF ≤ 30	Medium stability	Medium risk
30 < PMF ≤ 50	High stability	High risk
50 < PMF ≤ 75	Very high stability	Very high risk

Adopted from Shu-xuan *et al*. (2014)

RESULTS AND DISCUSSION
Physical and chemical properties of soils of the study area
The results of the laboratory analysis of the study area soils are presented in Table 3. These soil types are highly weathered, fragile with low activity clay and neutral to slightly alkaline. Active acidity (pH_{H2O}) of the soils ranged from 7.4 (Dye pit) to 8.6 (Plastic) while potential acidity (pH_{CaCl2}) of the soils ranged from 7.2 (Dye pit) to 7.6 (Plastic). The soils were predominantly sandy in nature which may be attributed to the Precambrian basement complex rocks precursor of the parent material. The organic matter statuses across the soils from the locations were low. They are also characterized by low levels of available P, except for the soils from the ceramic and plastic industry sites as well as low levels of total nitrogen and high levels of CEC as shown in Table 3.

Table 3: Physical and chemical parameters of soils of Sharada industrial estate.

Soil properties	Industry			
	Tannery	Dye pit	Ceramic	Plastic
Textural class	Sandy loam	Sandy loam	Loam sand	Sandy loam
pH (H₂O)	7.6 ±0.35	7.4 ±0.23	8.4 ±0.11	8.6 ±0.05
pH (CaCl₂)	7.5 ±0.43	7.2 ±0.15	7.5 ±0.08	7.6 ±0.12
EC	3.0 ±0.13	2.5 ±0.07	1.0 ±0.06	0.9 ±0.07
Organic Carbon (%)	1.07 ±0.14	1.75 ±0.02	0.63 ±0.10	0.71 ±0.01
Total N (%)	0.42 ±0.072	2.75 ±0.120	0.14 ±0.005	0.98 ±0.019
A. P (mg kg⁻¹)	8.30 ±0.444	6.41 ±0.224	121.81 ±4.818	171.59 ±5.902
EA (cmol₍₊₎ kg⁻¹)	0.2 ±0.04	0.2 ±0.04	0.1 ±0.01	0.1 ±0.02
CEC (cmol₍₊₎ kg⁻¹)	36.5 ±0.90	35.9 ±0.39	28.3 ±0.76	40.2 ±0.24
Ext. Cr (mg kg⁻¹)	820.21 ±4.780	450.01 ±6.117	107.90 ±1.557	101.20 ±0.288
Ext. Ni (mg kg⁻¹)	86.00 ±1.049	65.21 ±1.521	76.40 ±1.077	82.10 ±0.586

Where A.P= Available phosphorous; EA= Exchangeable acidity; CEC= Cation exchange capacity; Ext. Cr= Extractable Chromium; Ext. Ni= Extractable Nickel

Concentration of Chromium and Nickel in soil fractions of Sharada Industrial Estate
The concentrations of Cr and Ni in various fractions of the soils are presented in Table 4. Fractionation evaluation of Cr and Ni in the soils of Sharada industrial estate revealed that both metals occurred predominantly in the residual/detriteal soil fractions. As shown in Table 4 both tannery industry and dye pit had the highest content of Cr in their residual fractions (706.85 and 492.53 mg.kg⁻¹ respectively), while the lowest Cr content (3.80 mg.kg⁻¹) occurred in the carbonate fraction from soil of the tannery industry. Distributions of Cr fractions in the soils were as follows:
(a) Tannery: Residual > Organic> Oxides> Exchangeable> Carbonate;
(b) Dye pit and Ceramic: Residual > Oxides > Organic > Carbonates > Exchangeable;
(c) Plastic: Residual > Organic > Oxides > Carbonates > Exchangeable.

The abundance of Cr in its residual phase indicates a high degree of stability in the immediate environment. This result is in agreement with the result obtained by Shu-xuan *et al*. (2014). Results obtained by Shu-xuan *et al*., (2014) revealed that Cr occurred mostly in its

residual phases in studied industrial soils. This residual phase also indicates that a large percent of Cr in the sample soils is in inert form.

The highest concentration of Ni was obtained in the residual fractions of all the soils (84.98, 70.78, 68.40 and 59.80 mg.kg^{-1} (Tannery, Dye pit, Ceramic and Plastic industrial soil), while the lowest concentration of Ni was observed in the carbonate fraction. However, the total concentrations of Ni across all fractions ranged from 116.28 mg.kg^{-1} to 126.46 mg.kg^{-1}. Distributions of Ni in the soils were of the order:
(a) Tannery: Residual > Oxides >Organic > Carbonate> Exchangeable;
(b) Dye pit: Residual > Oxides > Carbonate > Organic > Exchangeable;
(c) Ceramic: Residual > Organic > Carbonate > Oxide > Exchangeable;
(d) Plastic: Residual > Organic > Oxides > Carbonates > Exchangeable.

As with Cr, Ni prevailed in the soils in its residual form therefore posing no risk to the immediate environment. This also indicates a high degree of stability in the study area. The prevalence of Ni in this inactive form is in line with other studies of industrial soils (Osakwe, 2010).

Table 4: Chromium and Nickel fractions in soils of Sharada industrial estate

| | Fractions | | | | | |
Industry	Exchangeable	Carbonate	Oxides	Organic	Residual	Total
	Cr (mg.kg^{-1})					
Tannery	7.31±0.315	3.80±0.004	376.74±4.053	403.84±6.042	706.85±8.041	1498.54±3.691
Dye pit	6.78±0.112	153.49±3.056	400.93±5.012	392.60±3.102	492.53±4.206	1446.33±5.163
Ceramic	5.08±0.104	8.67±1.041	36.10±1.062	34.19±1.301	80.48±2.012	164.52±1.104
Plastic	5.34±0.130	8.28±1.211	20.22±0.941	22.49±4.071	61.60±2.062	117.93±1.683
	Ni (mg.kg^{-1})					
Tannery	0.25±0.001	13.08±0.142	14.62±1.702	13.53±2.021	84.98±2.401	126.46±1.253
Dye pit	0.16±0.010	15.27±0.216	15.52±2.013	14.55±1.004	70.78±3.035	116.28±1.256
Ceramic	0.16±0.002	16.03±0.602	15.92±1.045	16.38±1.304	68.40±1.041	116.89±0.799
Plastic	3.40±0.021	14.21±2.003	17.72±2.010	22.78±2.016	59.80±3.076	117.91±1.825

Percentage Distribution of Chromium and Nickel in soil fractions of Sharada Industrial Estate

Figure 2 shows the percentage distribution of Cr in the study soils of Sharada industrial estate. The exchangeable fraction was found to be lowest in the tannery industry (0.2%), while the highest value (2.88%) was obtained at the plastic industry. The carbonate fraction was highest at the ceramic industry (13.71%), while it was lowest at the tannery industry. Meanwhile, the highest percentage (13.34%) distribution (Fe-Mn bound) was found at the tannery industry and lowest (11.60%) at the dye pit. More so, the highest and lowest value for the organic-bound fraction was 10.7% and 19.32% at both the tannery and dye pit respectively. Lastly, the residual value was found to be highest at the tannery industry (67.2%) and lowest at the plastic industry (50.72%).

The percentages of the mobile fractions (exchangeable and carbonate) of Cr reported in the soil samples was low. These fractions are the most reactive and bio-available fractions that can be accessed easily by plants and animals (Asagba *et al.*, 2007). The low range of these percentages is similar to the report by Chaudhary and Banerjee (2006) on chromium in contaminated industrial soils of New Delhi. Pavlović *et al.*, (2018) reported that Cr exists in soil in a stable state thus indicating that it was unavailable biologically for plant uptake.
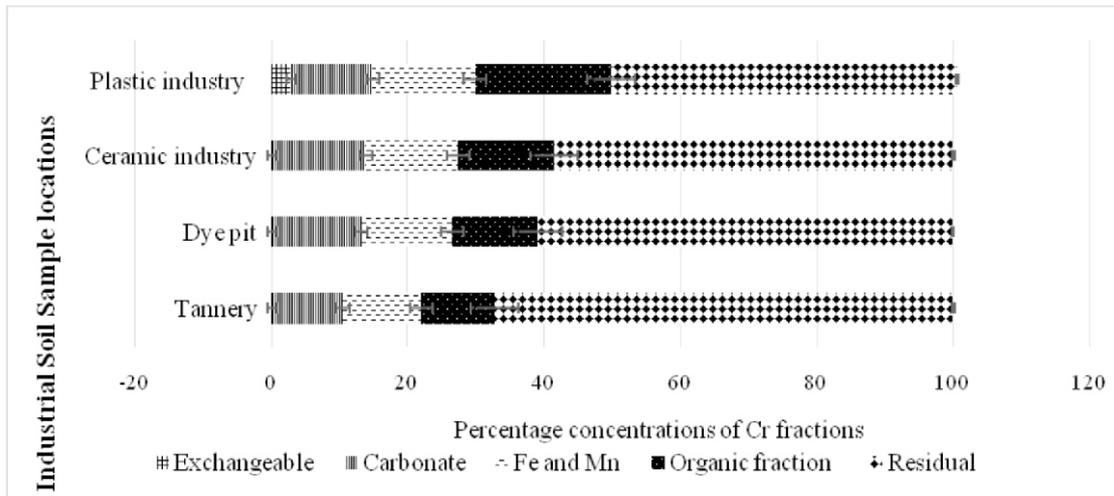
Figure 2: Percentage Distribution of Chromium fractions in soils of Sharada Industrial Estate.

The percentage distribution of Ni fractions in the study soils are shown in Figure 3. The exchangeable fraction was highest at the plastic industry (4.53%) and lowest at the tannery industry (0.2%). The carbonate was highest at the dye pit and lowest at the ceramic industry. Meanwhile the Fe-Mn fraction was highest at the dye pit (27.72%) and lowest the tannery (11.56%). The highest value for the organic fraction was obtained at the dye pit (27.14%), while the lowest value was obtained at the tannery (10.7%). The highest value for the residual fraction was obtained at the tannery (67.2%) while the lowest value was obtained at the dye pit (34.05%). This further shows that Ni occurred in the soil samples,

largely in residual forms apart from the dye pit soil samples of which the residual form was less than 40% of the total concentration of Ni. This further shows that their occurrence in other forms in the soil samples from the dye industry was probably due to anthropogenic activities. On average, Ni occurred in equal proportions in both oxide (27.72%) and organic substrates (27.14%) in soil samples from the dye pit (Figure 3). Similar equal distribution of Ni in both fractions was obtained by Pavlović *et al*., (2021) in soil samples obtained from industrial sites of Hellbrunn and Košutnjak, Poland. This was further explained by Kabata-Pendias and Mukherjee (2007) to be due to the high affinity of Ni to organic matter.
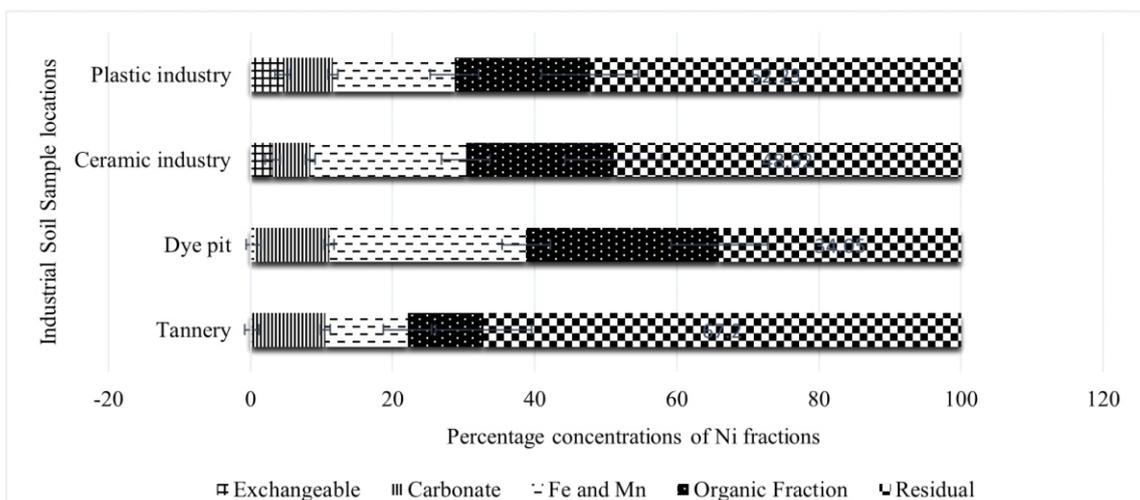
Figure 3: Percentage distribution of Nickel fractions in soils of Sharada Industrial Estate

Distribution of the various Cr and Ni species in the study area were not consistent. Although species of Cr and Ni were in varied quantities in the study soils, they occurred mostly in their residual forms. It is important to note that the residual fractions of heavy metals in soils unlike the exchangeable fractions are not in the soil solution, hence they are not available to the plants for uptake and they are permanently bound in crystal lattice of the mineral components. For now this might not be a source of concern with regards to the health of the environment.

Mobility of Chromium and Nickel fractions of Soils in Sharada Industrial Estate
The determined mobility indexes (percentage) of Cr and Ni in the studied soils are presented in Table 5. For Cr as shown in Table 5, the soil samples obtained from the tannery industry had the lowest mobility index of 0.8%, while Cr in soil obtained from the plastic industry had the highest mobility index of 12%. An index of 8% was obtained from soil of the ceramic industry while for the dye pit, a mobility index of 11%. The average potential mobility ranking of Cr in these soils is as follow: Plastic industry > Dye pit > Ceramic industry > Tannery industry.

For Ni, the Plastic industry (15%) had the highest mobility index, followed by the Ceramic industry and Dye pit which gave a mobility index of 14 and 13% respectively. Lastly, the least mobility index was recorded at the Tannery industry, having a mobility index of 11%. The average potential mobility ranking of Ni obtained from the soils is as follow: Plastic industry > Ceramic industry > Dye pit > Tannery industry.

Table 5: Mobility of Chromium and Nickel fractions in industrial soils

	Industry			
	Tannery	Dye pit	Ceramic	Plastic
Cr				
Mobility Index	0.01	0.11	0.08	0.12
% Mobility	1	11	8	12
Ni				
Mobility Index	0.11	0.13	0.14	0.15
% Mobility	11	13	14	15

Mobility indexes of the two metals were low across all studied soils. The low mobility indexes are an indication of the fact that these metals in the soils posed no risk to the environment. This might be directly linked to the high levels of the residual forms of the metals. It has also been established that when these metals occur in residual forms, they pose no risk to the environment (Howari and Banat, 2001). Soil reaction has also been found to play a major role in the occurrences of heavy metals in their residual forms. Heavy metals have been found to occur as hydroxides and precipitate under high pH conditions in soil. This is further supported by the reports of Sintorini *et al*. (2021) who stated that at higher pH, these metals occur in the form of hydroxides in the solid matrix of the environment thereby minimizing their potential mobility in the soil.

Stability and risk assessment of Chromium and Nickel in soil fractions of Sharada Industrial Estate
Table 6 shows the stability of Cr and Ni in soil fractions of the study area. Classes of PMF obtained for Cr ranged from low to medium stability and risk assessment group. Low PMF values were obtained from soils within the tannery (0.74%) and ceramic (8.36%) industrial sites while medium PMF classes (11.08 and 11.55%) for Cr were obtained from dye pit and plastic industrial sites. Potential mobility factor classes obtained for Ni were all within the medium stability and risk assessment group as PMF values obtained from the soils ranged from 10.52 to 14.90%.

Table 6: Stability and Risk Assessment of Chromium and Nickel in soils of Sharada Industrial Estate

Locations	Cr (%)	Stability	Risk	Ni (%)	Stability	Risk
Tannery	0.74	Low	Low	10.52	Medium	Medium
Dye pit	11.08	Medium	Medium	13.37	Medium	Medium
Ceramic industry	8.36	Low	Low	13.85	Medium	Medium
Plastic industry	11.55	Medium	Medium	14.9	Medium	Medium

The risk assessment of Cr and Ni was largely based on their exchangeable and carbonate fractions. These two fractions are of importance to the soil, because they exist in the soil solution and thus are readily available for the plant uptake. These fractions are what usually pose problems to the environment. In situations where there are high occurrences of metals in their exchangeable and carbonate fractions, there is then the potential for these elements to contaminate the environment.

The low to medium stability and risks classes obtained from this study can be directly linked to the pH and organic matter content of the study soils. The high pH values obtained from the soils show that there are low number of oxidative reactions going on within the immediate environment hence minimum acidification thereby leading to less mobility of Cr and Ni in the soils. In other words, the lower the mobility, the more unavailable these metals are within the soil hence the lower the potential risk these metals pose to the environment. A similar scenario was assumed to have played out with the low status of organic matter content in soils thereby leading to low mobility classes of Cr and Ni. Aigberua (2018) established a positive relationship between mobility factors of heavy metals and elevated levels of organic matter in the soils. This he portrayed by depicting the increasing mobility of heavy metals with increasing organic matter content in the soils. This low level of organic matter status in the soils will lead to probable absence of complexes and chelates formation in the soil thereby resulting in fixation of these metals by the sorption sites of the soil matrix.

CONCLUSION

This study revealed that although there were high concentrations of Cr and Ni in the surface soils of Sharada Industrial Estate, they occurred mostly in the residual fractions. Distribution of these metals was not consistent across the soils used for the study. More than 70% of Cr and Ni occurred in their residual forms in the soils obtained from tannery industrial site while percentages of Cr and Ni from other study soils ranged from 50 to 70%, hence low bioavailability for plant uptake. These results indicated low contamination status of the soils within the Industrial layout. The results also revealed that sources of Cr and Ni were naturally occurring crystal lattices of the soil samples in the study areas indicating lithogenic origins. An assessment of the potential mobility of these metals revealed that these metals had low mobility and posed low to medium health risk to the environment. But a medium mobility index, if not monitored over time, could, however, become a major threat to the environment. This can only be possible when oxidising conditions set in within the soils. Hence appropriate management activities should be carried out to ensure that monitoring and remedy steps are taken to guarantee a continuous controlled situation.

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