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Chemical Speciation and Mobility of Heavy Metals in Soils Around Nasara Sack and Packaging Company Akwanga, Nigeria

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Abstract

This study quantified and assessed the mobility of iron, nickel, cobalt, and lead in soils around a sack and packaging company using indices such as mobility factor and risk assessment code. The results evaluating the mobility factor of heavy metals in soils around the sack and packaging company reveal that all the metals determined exceed the minimum limit of 10% mobility factor and are mobile with the mobility factor being in the order of Ni > Pb > Co > Fe in the test soil. The risk assessment of heavy metals in the area based on risk assessment code ranged from low risk to medium risk (1-30%) where the risk level of the heavy metals is in the order: Co > Ni > Pb > Fe in the test soil.

Keywords: Soil; Heavy Metals; Mobility Factor and Risk Assessment

1 Introduction

The ever increasing industrial activity around the world has left behind a large amount of contaminated sites on the periphery of urban areas that are characterized with high concentrations of organic and inorganic compounds such as heavy metals, among others [1]. The determination of total metal content of soils is useful for many geochemical applications. Nevertheless, the speciation of metals is more of an interest agriculturally in terms of what is biologically extractable [2]. Heavy metals are permanently fixed in soils, and they also take part in bio-geochemical cycles. Therefore, assessment of their distribution in soils is a key issue in many environmental studies [3]. Heavy metals are constituents of soil minerals, usually bound to different phases of soil particles by a variety of mechanisms such as absorption, ion exchange, co-precipitation, and complexation. Soil physiochemical properties such as organic matter content, carbonates content, oxides content, soil structure and profile development influences the mobility of heavy metals [4]. The knowledge of the binding of metals with the different soil phases and components is of major interest to assess the connections with other biotic and abiotic elements of the environment [5]. This study aims to assess the mobility of some heavy metals in soils around a sack and packaging company in Akwanga, Nigeria and determine the risk index.

2 Study Area

Nasara sacks and packaging company Akwanga is located within the geographical coordinates 8°55′20′′N (latitude) and 8°21′25″ E (longitude). The industry is situated westward of the Akwanga - Abuja road in Akwanga which is about 58.4 km from Lafia the capital of Nasarawa State located in the North-Central geopolitical zone of Nigeria. The industry though not in full operation has been in existence for over a decade.

2.2 Sample Collection

Soil samples were collected using the stratified sampling technique [6]. The sampling site was broken into four (4) stratums (small areas) north, south, east, and west with respect to Nasara sacks and packaging company.

Each strata were further subdivided into four quadrants of equal size before five (5) samples were taken randomly by grab method within the depth of 0–15 cm in the individual quadrant (smaller area) making a total of twenty (20) samples per strata (small area) and a total of eighty (80) samples from the four stratums situated at the north, south, east and west of the industry were pooled together to form the composite sample to enable detailed representation of variability within the study area. The control soil sample for the industry was collected in farmland within 1.4 km radius from the industry from a site remote to possible sources of contamination associated with the industry.

3.1 Sample Preparation

The composite and the control samples were each sorted; pebbles and coarse materials removed and then air-dried at room temperature over three days with occasional breaking of aggregated materials with wooden roller; followed by sieving through a nonmetallic sieve with mesh hole of 2 mm diameter to remove stones, plant and animals debris. The air-dried and sieved soil was employed as a soil sample for extraction and analysis.

4. Determination of Soil Physiochemical Parameters

The pH was determined by homogenizing 1g of the sample in 10 cm^3 deionized water and stirred gently to enhance H^+ (Hydrogen ions) release from soil; the mixtures were then be allowed to stand for 30 min. pH meter (JENWAY 2000) was used to read the pH value after calibration with buffer solutions of pH values 5.5, 7.0, and 8.0 respectively [6, 7].

Soil organic carbon was determined by oxidation using potassium dichromate and concentrated sulphuric acid. Considering that the average content of carbon in soil organic matter is equal to 58 % the conversion factor 1.724 was used to calculate the percentage of organic matter from the content of organic carbon [8, 9]. Nitrogen content of the soil was determined using method describe by Kjeldahl [10] while the phosphorus content using molybdate reagent by means of spectrophotometer set at wavelength of 660 nm then the cation exchange capacity was estimated using the Bray and Kurtz Hydrometer method [7, 11].

5. Sequential Extraction Procedure

The five-step sequential extraction procedure described by Tessier *et al*. [12] where the chemical partitioning of heavy metals allows distinguishing five fractions representing the following chemical phases: exchangeable metals, bound to carbonates, bound to Fe–Mn oxides, organic matter and residual fraction. The procedure was carried out with an initial weight of 1 g of the sieved dry soil sample. Deionized water was used in preparing blank solutions for each step of the leaching procedure. The same process was repeated in the control sample.

Fraction 1—Exchangeable fraction (F1)

One gram of the soil sample was extracted at room temperature for 1 hour with 16 mL of magnesium chloride solution (1 M $MgCl_2$) at pH 7. Soil and extraction solution was thoroughly agitated throughout the extraction. The extracted metals were then decanted from the residual soil, filtered and stored for AAS analysis.

Fraction 2—Bound to carbonates (F2)

The residue of Fraction 1 was extracted with 16 mL of 1 M sodium acetate/acetic acid buffer at pH 5 for 5 hours at room temperature. The extracted metal solution was filtered from the residual soil, and the filtrate was stored for AAS while the residual soil was used for the next extraction.

Fraction 3—Bound to oxides (F3)

The residue from fraction 2 was extracted under mild reducing conditions. Hydroxyl amine hydrochloride ($NH_2OH{\cdot}HCl$) (13.9 g) was dissolved in 500 mL of distilled water to prepare 0.4 M $NH_2OH{\cdot}HCl$. The residue was extracted with 20 mL of 0.4 M $NH_2OH \cdot HCl$ in 25% (v/v) acetic acid with agitation at 96°C in a water bath for 6 hours. To release metals bound to Fe (III) and Mn (IV). The extracted metal solution was filtered from the residual soil, and the residue was used for the next extraction.

Fraction 4—Bosund to organics (F4)

To release metals bound to organic matter, the residue from fraction 3 was oxidized as with 3 mL of 0.02 M HNO_3 and 5 mL of 30% (v/v) hydrogen peroxide, which has been adjusted to pH 2. The mixture was heated to 85°C in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3 mL of 30% hydrogen peroxide, adjusted to pH 2 with HNO_3, was then added. The mixture was heated again at 85°C for 3 h with occasional agitation and allowed to cool down. Then 5 mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid was added, followed by dilution to a final volume of 20 mL with de-ionized water. The extracted metal solution was filtered from the residual soil, which was used for the next extraction.

Fraction 5—Residual or inert fraction (F5)

To extract metals firmly bonded within crystal structure of the minerals comprising the soil, the residue from Fraction 4 was oven-dried at 105°C. Digestion was carried out with a mixture of 5 mL conc. HNO_3 (HNO_3, 70% w/w) and 10 mL of perchloric acid ($HClO_4$, 60% w/w) in a beaker.

6. Determination of Heavy Metals

The concentration of the heavy metal in the various fractions was determined using Atomic Absorption Spectrophotometer (PG 990 model) equipped with Zeeman's background correction. Prior to sample analysis, the flame condition was optimized for maximum absorbency and linear response while aspirating known standards.

Mobility Factor (**MF**): The mobility of metals in soil samples may be evaluated based on the absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was calculated as a 'mobility factor' (MF) [13, 14]. The MF was calculated using equation (3); where F1 to F5 are the various geochemical fractions. Where MF values ≤ 10 indicates stability.

$$\text{Mobility Factor} = \frac{F1+F2+F3}{F1+F2+F3+F4+F5} \text{ X } 100 \quad (3)$$

Risk assessment code (RAC): The guideline was based on the percentage of metal in the exchangeable and acid-soluble fraction (fraction I) described by Singh *et al.* [15]. The Risk Assessment Code classification indicates no risk < 1 %; low risk 1-10 %; medium risk 11-30 %; high risk 31-50 %; very high risk > 50 %. The RAC classification was used to assess the risk connected with the release of heavy metals from the soils

7 Results and Discussion

The pH, organic carbon, and organic matter content the test soils were 8.40, 1.76% and 3.03% respectively. The pH value was slightly alkaline; the organic carbon and organic matter content are within the limit of agricultural and natural resource of 1.0 to 6.0 [16]. Soil organic matter is the organic matter component of soil; it help in improving soil structure, enhanced cation exchange capacity in order to retain nutrient and also minimize erosion [17].

The available phosphorus content, nitrogen and effective cation exchange capacity of the test soil samples were 3.62 mg/kg, 0.251% and 65.95 Meq/100g respectively, where available phosphorus grossly below 15-30% limits of normal agronomical soil stipulated by Ohio State University Extension on soil resources. The effective cation exchange capacity of the of the test soil is high, hence indicating the capacity of the soil to retain cation

Table 1: Physicochemical parameters of soil samples around sack and packaging company

S/no	**Parameter**	**Test soil**	Agriculture and Natural Resources guideline
1	pH	8.4±0.20	6.3-7.0
2	Organic carbon (%)	1.76±0.03	-
3	Organic matter (%)	3.03±0.33	1.0-6.0
4	Nitrogen (%)	0.251±0.01	-
5	Avail P(mg/kg)	3.62±0.02	15-30
6	ECEC (Meq/100g)	65.59±0.05	-
7	Sand (%)	46	1-5
8	Silt (%)	49	6-20
9	Clay (%)	5	21-30
10	Textural class base on USDA standard	Sandy Loam	Sandy Loam

Guideline sourced from [16].

Table 2: Mobility factor (%) and Risk Assessment Code base on Exchangeable fraction (%) of heavy metals in soils around sack and packaging company

	Metal	**Fe**	**Ni**	**Co**	**Pb**
Mobility factor (%)	**Test soil**	29.62	61.69	35.04	57.64
	Remark	mobile	mobile	Mobile	Mobile
	Control soil	15.87	49.24	68.61	51.33
	Remark	mobile	mobile	Mobile	Mobile
Exchangeable fraction (%)	**Test soil**	1.27	14.41	17.73	9.00

	Remark	low risk	medium risk	medium risk	low risk
	Control soil	0.81	12.61	11.49	9.78
	Remark	no risk	medium risk	medium risk	low risk

7.1 Determination of iron concentration

The mean concentration of iron in the various geochemical fractions F1 to F5 were in the order: F5> F3> F4> F2> F1 for the test soil and F5> F3> F2> F4> F1 for the control soil implying bulk of the iron content are from lithogenic source while the respective mobility factors were 29.62% and 15.89% which is greater than 10% threshold limit of mobility index as shown in Figure 1 and Table 4 respectively [14]. This implies that iron is labile in the respective soil; nevertheless, the mobility factor of iron in soil around the industry is about twice the factor in the control soil. The Risk Assessment Code classification of 1.27% and 0.81% exchangeable fraction for the test and control soil falls within low risk and low risk as describe by Singh et al. [15] Also the high concentration of iron in the residual fraction suggests metal stability and the likely source of iron in the soil is the parent material and not due to anthropogenic activity. Metals with anthropogenic origin are mainly extracted in the first step of sequential extraction procedures while lithogenic minerals are found in the last step of the process corresponding to the residual fraction [18].

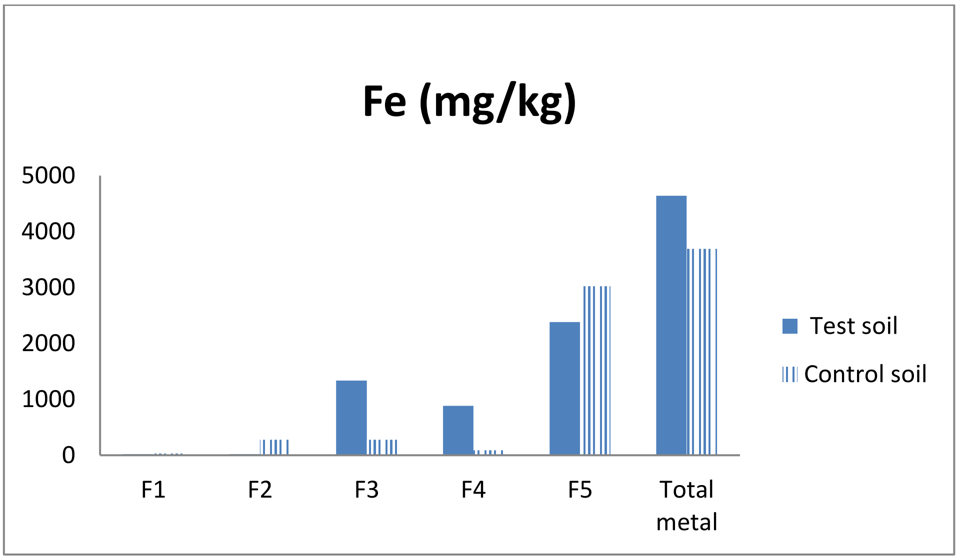

Figure 1: Mean Concentration (mg kg^{-1}) of Iron in each Fraction of the Soil Samples

7.2 Determination of nickel concentration

The mean concentration of Ni in the various geochemical fractions F1 to F5 were in the order: F2> F5> F3> F1> F4 for the test soil and F5> F3> F2> F1> F4 for the control soil implying the bulk content of the Ni content in test soil is in the bound to carbonate fraction (F2) while the respective motility factors were 61.69% and 49.24% as shown in Table 2 respectively suggesting that the Ni content is highly mobile and the source is likely anthropogenic.

Based on Risk Assessment Code classification the 14.41% and 12.61% exchangeable fraction for the test and control soil falls within 11-30% values termed medium risk as described by Singh et al. [15]

Nickel is a potentially toxic metal and its present in all soils average between 20 to 30 mg/kg, sometimes exceeding 10,000 mg/kg in ultramafic soils. The eco-toxicological risk of Ni in soils to organisms is controlled by its availability [19].

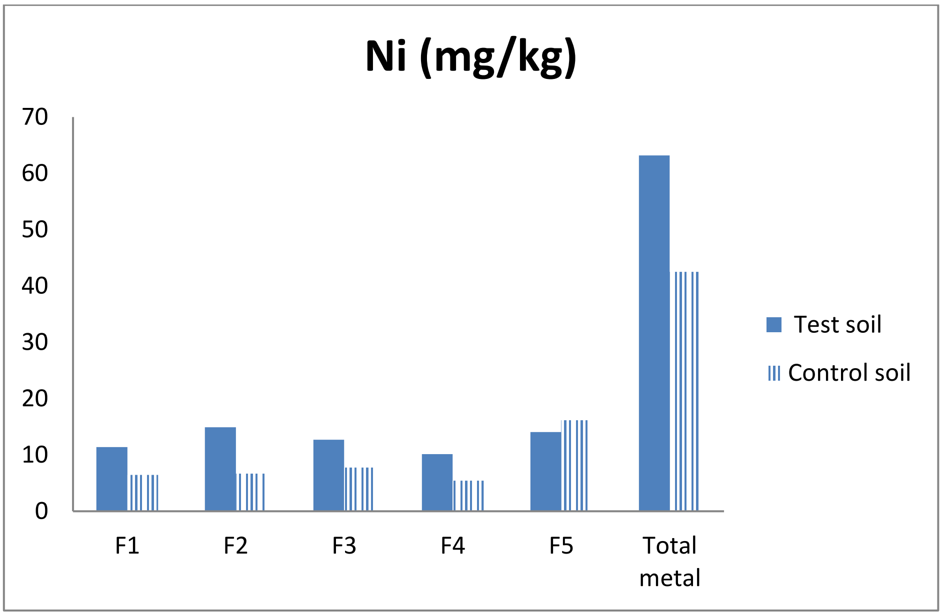

Figure 2: Mean Concentration (mg kg^{-1}) of Nickel in each Fraction of the Soil Samples

7.3 Determination of cobalt concentration

The mean concentration of cobalt in the various geochemical fractions F1 to F5 were in the order: F5> F3> F4> F2> F1 for the test soil and F5> F3> F4> F2> F1 for the control soil while the respective motility factors were 38.04% and 68.61% as shown in Table 2. This implies that the mobility factor exceeds the 10% minimum limit hence, cobalt is mobile. Based on Risk Assessment Code classification the 17.73% and 11.49% exchangeable fraction for the test and control soil falls within 11-30% values termed medium risk as described by Singh et al. [15] Cobalt is an essential component of Vitamin B12 nevertheless excessive levels of available cobalt in the soil elevates the amount in plant tissues leading to iron deficiency which in turn results in stunted growth, loss of leaves and hence decreases the amount of oxygen produced by plants during photosynthesis and eventually death of the plant [20].

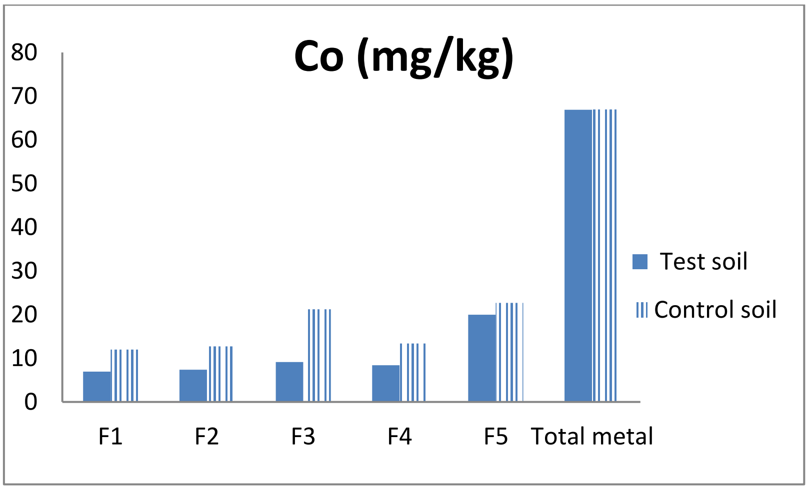

Figure 3: Mean Concentration (mg kg^{-1}) of Cobalt in each Fraction of the Soil Samples

7.4 Determination of lead concentration

The mean concentration of lead in the various geochemical fractions F1 to F5 were in the order: F3> F5> F4> F1> F2 for the test soil and F5> F3> F4> F1> F2 for the control soil while the respective motility factors were 57.64% and 51.33% as shown in Table 2. The mobility factor of lead in the test soil and control soil was more than 5 times the 10% threshold for mobility [14]. While the 9.0% and 9.78% lead in the exchangeable fraction falls within 1-10% classified as low risk based on the Risk Assessment Code describe by Singh et al. [15]

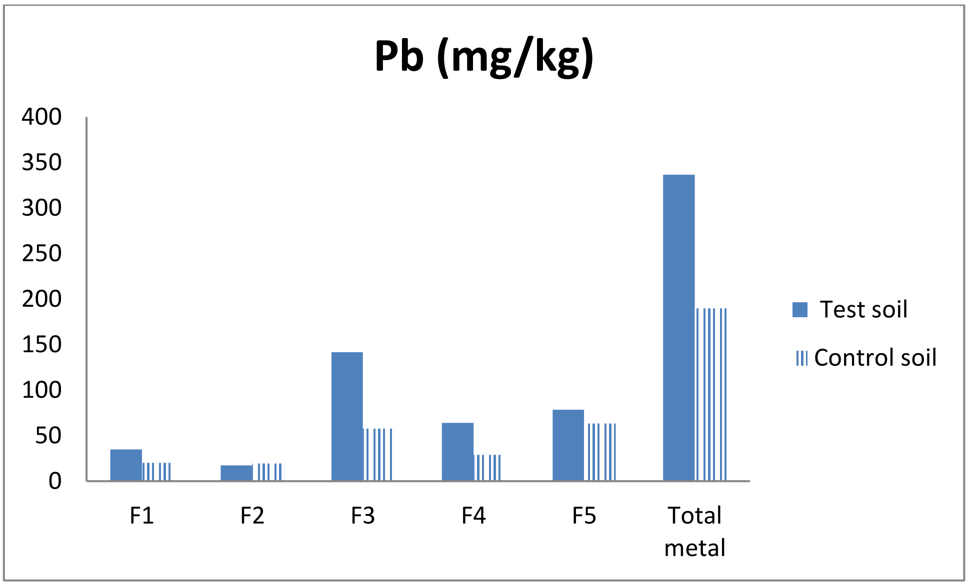

Figure 4: Mean Concentration (mg kg^{-1}) of Lead in each Fraction of the Soil Samples

9. Conclusion

The results evaluating the mobility of heavy metals in soils around sack and packaging company reveals that all the minerals determine are mobile with a mobility factor in the order: Ni > Pb > Co > Fe in the test soil. While the risk assessment of the heavy metals base on risk assessment code ranged from low risk to medium risk (1-30%) where the risk level of the heavy metals is in the order: Co > Ni > Pb > Fe in the test soil.

Conflicts of Interest

Authors have declared that no conflicting interests exist.

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