



Mobility Profiles of Some Heavy Metals in Soil Samples from Selected Areas of Ado Local Government Area, Benue State, Nigeria

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ABSTRACT

During the rainy season, soil samples (at depths of 5 cm, 10 cm, and 15 cm) were collected from 15 different spots from five selected locations (NFS, NRL, NS1, NS2, and NR as control) in Ukwonyo Utonkon in Ado Local Government Area of Benue State, and analyzed for total metal concentration and mobility using standard methods. The percent loss on ignition (% LOI) at the different soil depths, which measures the organic matter content of the soil, showed that sample NRL was highest in organic matter loss (17.30%) at 5 cm soil depth. The total heavy metals concentration of the soil samples showed no specific trend in the level of heavy metals at the different soil depths. However, the metals distribution ranged from 4 mg/kg of Ni (for sample NRL3) to 1000 mg/kg of Ag (for sample NFS3) at 15 cm that showed a high potential for Ag content. Hg, Pb, and Sn were not detected in all the soil samples. The mobility of the metals in the soils varied considerably from one area to another with random increase and decrease according to soil depths. Mobility was highest for Ag (69.4 mg/g) in soil sample NFS, but Zn was not detected in the control sample NR at mean depth. The concentrations of the metals in soils from this study area were lower than their recommended levels for soil quality and indicated no threat to human health by the use of the soils for agricultural purposes.

Keywords: Heavy metals, Mobility, Soil.

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1. INTRODUCTION

Soil is very important in ecosystem research, as it is the medium where many kinds of interactions take place between minerals, air, water and biota. The soil which is an open system has been subjected to more physical and chemical stress than ever before by paving, excavation and inputs of foreign substances. One aspect of chemical pollution is the increase in the geogenic heavy metals concentration caused by emission from industries, transportation and agriculture. Nubi et al, [22], Uba et al, [28] and Elaigwu et al, [13] reported that solid wastes introduce additional heavy metals into the surrounding soil and ground water. As a result,

large amounts of these heavy metals are released into the soil due to increased anthropogenic activities such as agricultural practices, industrial activities, energy consumption and waste disposal methods, thus leading to contamination of the soils [11, 12, 23, 20].

Total metal content of soils is useful for many geochemical applications but often the speciation (bioavailability) of these metals is more of an interest agriculturally in terms of what is biologically extractable. Heavy metals contamination of soil is a far more serious problem than either air or water pollution because they are more tightly bound by soil and may persist for centuries or millennia, depending on the conditions. More so, the soil is an important geochemical sink which accumulates heavy metals and usually depletes them very slowly by leaching into the ground water aquifers or bioaccumulate in plants [3]. Contamination and subsequent pollution of the environment by toxic heavy metals have become an issue of global concern due to their sources, widespread distribution and multiple effects on the ecosystem [21]. Due to their cumulative behaviour and toxicity, they have a potential hazardous effect not only on crop plant but also on human health [9]. The immobilization process enables the soil to function as filler for ground water. However, the side effect of it is that the soil collects not the nutrients but also pollutants like heavy metals. Consequently, the increase in heavy metal concentration in the soil caused by human has led to considerable accumulation in some cases [16].

In this study, the determination and mobility of heavy metals in soil samples of Utonkon in Ado LGA of Benue State were investigated and reported to furnish their profiles and potency for bioavailability.

2. MATERIALS AND METHODS

2.1. Sampling and Sample Location

Ado Local Government Area is one of the 23 LGAs in Benue State (Figures 1 and 2). Its name is derived from the Ado stream which was created in 1989 with five districts: Agila, Igumale, Ulayi, Ijigban, and Utonkon, with its headquarters in Igumale. The LGA shares boundary with Otukpo, Okpokwu, Obi, and Oju LGAs of Benue State and with Ishielu and Ohaukwu LGAs of Ebonyi State. Ado LGA lies in latitude $7^{\circ}5'$ and $7^{\circ}15'$ north and longitude 9° and $9^{\circ}6'$ east of the equator. The area is renowned for yam, rice, cassava, maize, and palm oil production. Fishing is a lucrative occupation in the area due to the presence of Okpokwu, Ogege, Awu, Atsani, and Ado streams. There is a large number of blacksmiths in the area producing hoes, cutlasses and other basic farm implements. The population of the local government area is about 184,389, and the populace speak predominantly Idoma and Ufia languages.

Temperatures of the area are generally very high during the day, particularly in March and April. Maximum temperatures range from 35°C (during the rainy season) to 37°C (in the dry season). The vegetation of the area consists of rain forest and Guinea Savannah.

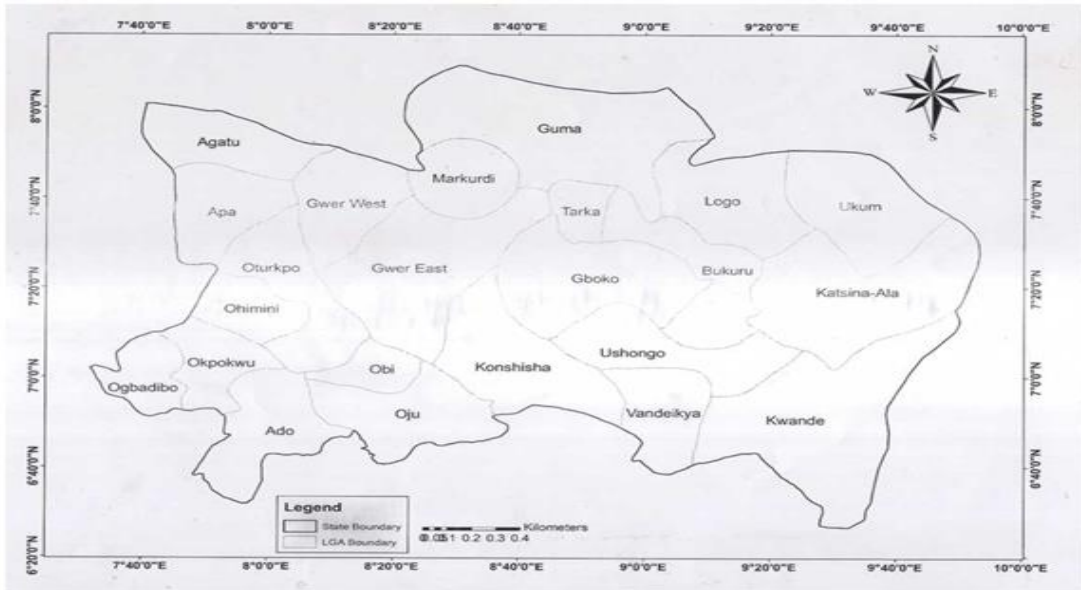


Figure-1. Map of Benue State showing the twenty-three Local Government Areas.

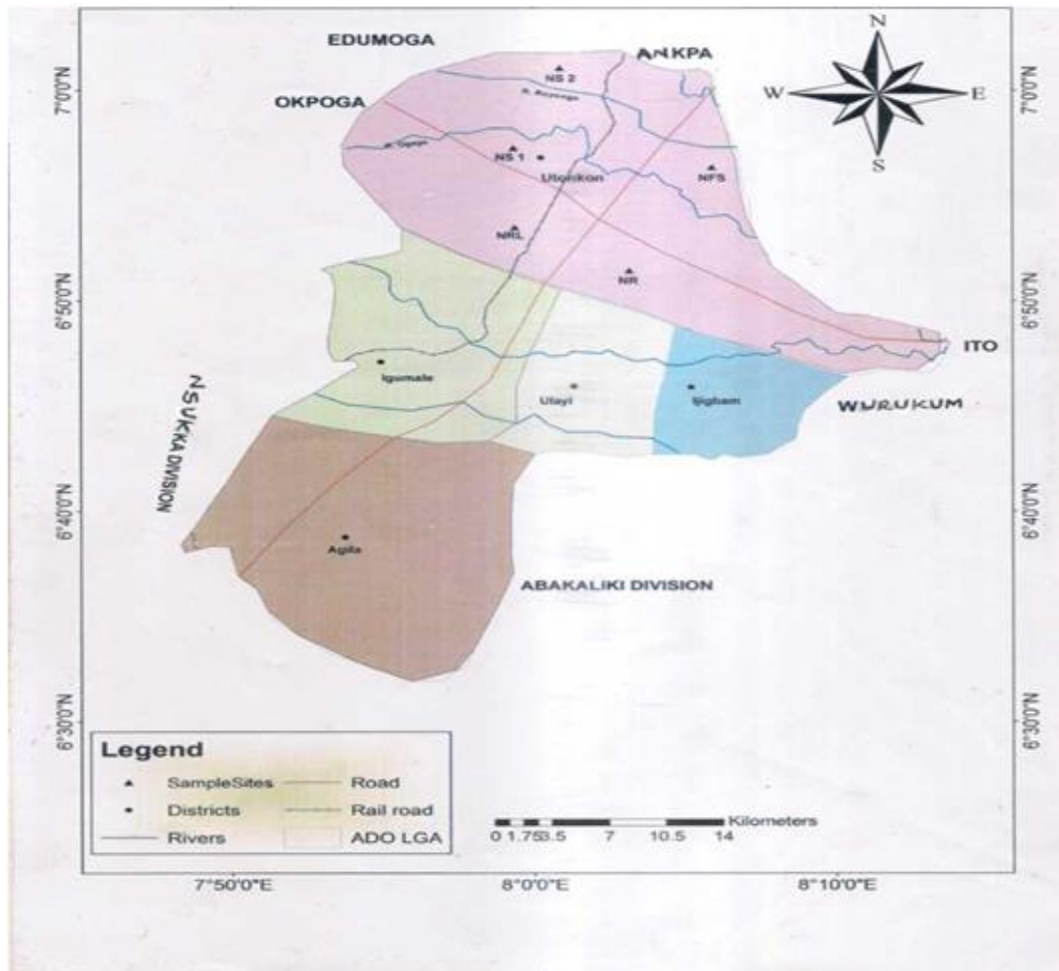


Figure-2. Map of Ado Local Government Area showing the Sites of Samples

2.2. Collection of Samples

During the rainy season, 15 soil samples from five selected locations in Ukwonyo Utonkon in Ado Local Government Area of Benue State. The locations include Near the Farm Site (1), Near the Rail (2), Near Ogege Stream 1 (3), Near Royongo Stream 2 (4), and Near Residence (5) (Figure 2). Three samples of different depths (5 cm, 10 cm, and 15 cm) were collected from each of the five different locations. A control sample of different depths 5 cm, 10 cm, and 15 cm was also taken from Near Residential homes. All analyses were in duplicate. A stainless steel spoon was used for scooping the soil samples into polyethylene envelopes which had been previously pre-cleaned in dilute nitric acid for 24 h, rinsed with distilled water and dried. Each sample was air dried for one week before further analysis.

2.3. Sample Preparation

Each of 20.00 g of the samples was finely ground and passed through a 200 µg mesh sieve size. The samples were then dried in an oven at 105 °C for 1 h and cooled. Thereafter, the samples were mixed with cellulose flake binder in the ratio of 5:1 and pelletized at a pressure of 10 – 15 torrs /inch² in a pelletizing machine. The pelletized samples were then stored in desiccators ready for analysis.

2.4. Determination of Loss on Ignition (LOI)

From the 200 µg sieve fraction, 1 g was weighed into an empty weighed crucible (previously fired at 1000 °C for 1 h) and heated slowly and then finally at 100°C for 1 h. This was removed and placed in a desiccator to cool. It was then reweighed and the loss in weight noted.

2.5. Determination of Total Metal Content

The total metal content of the soil samples was determined using the method of routine instrumental analytical procedure for samples by National Metallurgical Development Centre in Jos (NMDC). The Energy Dispersion X-ray Fluorescence Spectrometry (ED – XRFS) machine was switched on and allowed to warm up for 2 h. The appropriate programs for the various elements of interest were then employed to analyze the sample materials for their presence or absence. The results of the analysis were reported in (mgkg⁻¹) for major and minor concentrations of elements evaluated from intensity measurements.

2.6. Calculation of Mobility, q of Metals in the Soil Samples of Study Areas

Calculation of the mobility of metal in the soil sample [4] is as shown in Equation 1:

$$Q = \frac{(C_0 - C_e) \times V}{w} \quad \dots \quad 1$$

Where, q = amount of metal absorbed on the soil (mg g⁻¹)

C₀ = initial concentration of the metal in solution (mg g⁻¹)

C_e = concentration of metal at equilibrium (mg g⁻¹)

V = volume of solution (ml); w = weight of air-dried soil sample (g)

3. RESULTS AND DISCUSSION

Table 1 showed the results of percent Loss on Ignition (LOI) in 15 different samples of 5 selected spots from Ukwonyo Utonkon in Ado Local Government Area of Benue State. The different soil depths showed varying %LOI. At 5 cm soil depth, LOI varied from 4.00% (for NS2) to 17.30% (for NRL). At 10 cm soil depth, LOI varied from 4.60% (for NR) to 16.50% (for NRL). At 15 cm soil depth, LOI varied from 4.40% (for NR) to 16.90% (for NRL).

Table-1. Loss on Ignition (LOI) of the Soil Samples

S/N	Location (Spot)	Depth (cm)	% LOI
1.	NFS ₁	5	16.60
2.	NFS ₂	10	12.30
3.	NFS ₃	15	12.00
4.	NRL ₁	5	17.30
5.	NRL ₂	10	16.50
6.	NRL ₃	15	16.90
7.	NR ₁	5	4.70
8.	NR ₂	10	4.60
9.	NR ₃	15	4.40
10.	NS1 ^a	5	14.00
11.	NS1 ^b	10	15.60
12.	NS1 ^c	15	15.40
13.	NS2 ^a	5	4.00
14.	NS2 ^b	10	6.70
15.	NS2 ^c	15	10.40

NFS = Near Farm Site; NRL = Near the Rail; NR = Near Residence; NS1= Near Stream 1

NS2 = Near Stream 2;

The loss on ignition (LOI) measures the organic matter content of the soil and shows the level of human activity leading to geo-thermal conversion of the organic matter. The sites near the farm (NFS) and rail line (NRL) showed the higher organic matter loss compared to the other sites of this study. This may suggest a higher use of manure/fertilizer as part of the human activity in these sites. The conversion of the organic matter content also varies with vegetation/soil type, degree of decomposition, land management practice, and age of organic matter (fossil) [6, 17]. A comparison of the LOI values of the study area with other studies revealed that the LOI found in soils of the study area were generally lower compared to those from other studies (Table 2). For instance the mean % LOI of the study area near the rail was 16.90% (Table 2), and this was lower than the levels found in Big Cypress National Preserve of north-central United States [17] with a value of 231.00%. The levels of LOI found in the entire study area were far below the standard set for commercial agriculture since a lower LOI value signifies a lower organic –matter content (Table 2).

Table-2. Summary of Loss on Ignition (LOI) of Study Areas compared with other Studies (%)

This Study	Mean LOI (%)
NFS	13.63
NRL	16.90
NR	4.57
NS1	15.00
NS2	7.03
*Other Studies:	
Big Cypress National Preserve Central	275.00
Big Cypress National Preserve South	231.00
East coast buffer strip	593.00
Everglades National Park	463.00
Holy land wildlife Management Area	750.00

*Source: Alan et al, [2]

The total heavy metals concentration of the soil samples as shown in Table 3 revealed no specific trend in the distribution/level of heavy metals in the soils.

Table-3. Total heavy metals concentration (mgkg^{-1}) in the soil samples

S/N	Sample code	Soil Depth (cm)	Ag	Hg	Pb	Cu	Mn	Mo	Ni	Sn	Zn
1.	NFS ₁	5	30.0	ND	ND	50.0	90.0	ND	50.0	ND	10.0
2.	NFS ₂	10	100.0	ND	ND	60.0	330.0	ND	60.0	ND	20.0
3.	NFS ₃	15	1000.0	ND	ND	60.0	130.0	ND	10.0	ND	20.0
4.	NRL ₁	5	50.0	ND	ND	40.0	110.0	ND	10.0	ND	10.0
5.	NRL ₂	10	50.0	ND	ND	40.0	90.0	ND	7.0	ND	7.0
6.	NRL ₃	15	10.0	ND	ND	40.0	70.0	ND	4.0	ND	ND
7.	NR ₁	5	570.0	ND	ND	50.0	120.0	ND	8.0	ND	ND
8.	NR ₂	10	220.0	ND	ND	30.0	90.0	ND	5.0	ND	ND
9.	NR ₃	15	580.0	ND	ND	40.0	70.0	ND	7.0	ND	ND
10.	NS1 ^a	5	60.0	ND	ND	50.0	600.0	ND	10.0	ND	9.0
11.	NS1 ^b	10	100.0	ND	ND	70.0	380.0	ND	20.0	ND	2.0
12.	NS1 ^c	15	100.0	ND	ND	80.0	360.0	ND	20.0	ND	2.0
13.	NS2 ^a	5	300.0	ND	ND	50.0	100.0	ND	7.0	ND	5.0
14.	NS2 ^b	10	1000.0	ND	ND	60.0	130.0	ND	10.0	ND	8.0
15.	NS2 ^c	5	200.0	ND	ND	50.0	180.0	ND	8.0	ND	10.0

ND = Not detected; NFS = Near Farm Site; NRL = Near the Rail; NR = Near Residence; NS1 =Near Stream 1; NS2 = Near Stream 2

However, the levels of Ag ranged from 30 mg/kg for NFS1 at 5 cm depth to 1000 mg/kg for NFS3 at 15 cm depth, which showed a high potential for Ag content. Cu levels ranged from 30 mg/kg for NR2 at 10 cm depth to 60 mg/kg for NFS2 and increased to 80 mg/kg for NS1c at 15 cm depth. Mn concentration ranged from 70 mg/kg for NR3 and NRL3 at 15 cm to 600 mg/kg for NS1a at 5 cm depth. For Ni, the concentration ranged from 4 mg/kg (NRL3) at 15 cm to 60 mg/kg for NFS2 at 10 cm depth. Zn levels ranged from not detected to 20 mg/kg for NFS2 and NFS3 at 10 cm and 15 cm depths, respectively. Hg, Pb, Mo, and Sn were not detected in the soil samples at the different depths. The mean concentration of the metals (Table 4) showed that Ag ranged from 36.67 mg/kg (for NRL) to 500 mg/kg (for NS2). Cu concentrations ranged from 40 mg/kg (for NR

and NRL) to 66.67 mg/kg (for NS1). For Mn, the levels ranged from 90.00 mg/kg (NRL) to 446.67 mg/kg (for NS1). Ni was highest in NFS (40.00 mg/kg) but lowest in NR (6.67 mg/kg). Zn concentrations ranged from not detected (for NR) to 16.67 mg/kg (for NFS).

Table-4. Mean Concentrations of heavy metals (mgkg⁻¹) in soils of the study areas

Metal	Near Residence (Control)	Near Farm Site	Near Rail	Near Stream 1	Near Stream 2
Ag	456.67	376.67	36.67	86.67	500.00
Cu	40.00	56.67	40.00	66.67	53.33
Mn	93.33	183.33	90.00	446.67	136.67
Ni.	06.67	40.00	07.00	16.67	08.33
Zn	ND	16.67	05.67	04.33	07.67

The levels and distributions of Pb, Cr and Cu in the soil and pepper (*Capsicum annun*) on the bank of river Challawa, Nigeria reveals high metal ranges 60.00 – 143.30 mgkg⁻¹ for Pb, 104.20 – 230.00 mgkg⁻¹ for Cr, and 58.30 – 207.50 mgkg⁻¹ for Cu in soil samples; while 11.33 – 27.00 mgkg⁻¹ for Pb, 10.40 – 35.10 mgkg⁻¹ for Cr, and 7.56 – 21.07 mgkg⁻¹ for Cu in pepper samples. The study also revealed the presence of correlation between metals in soil and pepper which indicates possible transfer of these metals into the food chain [5]. Similar investigation of the heavy metals in soil and carrot samples obtained in Maiduguri ranged from 0.48 ± 0.02 µg/g for Cd to 52.00 ± 2.58 µg/g for Cr. Levels of the heavy metals in the soil samples also ranged from 0.56 ± 0.05 µg/g for Cd to 76.18 ± 5.49 µg/g for Cr. The levels of the metals in the corresponding vegetables and soil samples were higher than in the control samples [29]. Pb, Cd, Hg, and As are reported to be widely dispersed in the environment. These elements have no beneficial effects in humans, and there is no known homeostasis mechanism for them [10]. They are generally considered as toxic to humans and animals; the adverse human health effects associated with exposure to them, even at low concentrations are diverse and include, but are not limited to neurotoxic and carcinogenic actions [1, 7, 15, 27]. Lead as a toxicologically relevant element has been brought into the environment by human in extreme amounts, despite its low geochemical mobility and has been distributed worldwide. Lead amount in deep ocean water is about 0.01 – 0.02 µg/L, but in surface ocean waters is 0.3 µg/L [7]. The Joint FAO/World Health Organization Expert Committee on Food Additives (JECFA) have established a provisional tolerable weekly intake (PTWI) for lead as 0.025 mg/kg body weight [14]. WHO provisional guideline of 0.01mg/L has been adopted as the standard for drinking water [30]. The Joint FAO / WHO has recommended the PTWI as 0.007 mg/kg body weight for Cd [14]. The EPA maximum contaminant level for cadmium in drinking water is 0.005mg/L whereas the WHO adopted the provisional guideline of 0.003mg/L [30]. Critical early indicators of Cd damage to nephrons in kidneys include low molecular weight protein (2-microglobulin), Glycosuria, aminoaciduria, and reduced ability of the kidney to secrete polyaromatic hydrocarbons (PAHs) [18]. Exposures to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys and developing foetus [31]. The toxicity of mercury depends on its chemical form (ion < metallic < organic) [8]. However, it has been reported that up to 90% of most organic mercury compounds are absorbed from food and beverages at levels of <1 to 50 µg/kg. Higher levels are often found in marine foods. Organic mercury compounds easily pass across biomembranes and are lipophilic [24]. Therefore elevated mercury concentrations are mainly found in liver of

lean species and in fatty fish species. Because of the extreme health effects associated with mercury exposure, the regulatory standard by EPA and WHO for Hg in drinking water is 0.002 mg/L and 0.001 mg/L, respectively [30]. As occurs in natural waters in oxidation states III and V in the form of Arsenous acid (H_3AsO_3) and its salts, and arsenic acid (H_3AsO_5) and its salts, respectively [25]. The toxic effects of arsenic depend especially on oxidation state and chemical species among others. Inorganic arsenic is considered carcinogenic and is related mainly to lung, kidney and skin disorders [1]. The toxicity of arsenic in its inorganic form is known for decades [19, 26].

The mobility, q of metals in soils of the study areas varied considerably from one area to another (Table 5). For most soils sampled in these study areas, the mobility (q) tends to increase and decrease randomly in their order of depths (5cm, 10cm and 15cm) respectively.

Ag has the highest mobility, q (69.4 mgg^{-1}) in soil sample NFS while it was lowest in sample NRL (2.70 mgg^{-1}). For the control sample NR, mobility of the heavy metals ranged from not detected (for Zn) to 22.60 mgg^{-1} (for Ag), showing that Ag was the most mobilized heavy metal in the areas of human residence. The soil sample NS1 showed the highest mobility of 3.70 mgg^{-1} for copper but lowest in sample NRL (0.00 mgg^{-1}). The mobility of Mn was highest in sample NS1 (30.6 mgg^{-1}) but lowest in sample NRL (4.0 mgg^{-1}). Ni had the highest mobility of 2.0 mgg^{-1} in sample NFS but lowest in samples NR and NS2 (0.20 mgg^{-1}). Zn was not detected in NR samples but the mobility increased to 1.40 mgg^{-1} in sample NFS.

Table-5. Mobility profiles of the Heavy Metals (mgg^{-1}) in soils samples of the study areas

Mobility (q, mgg^{-1})	Mean Depth, \bar{x} (cm)				
	NR	NFS	NRL	NS1	NS2
Ag	4.60	3.80	0.40	0.90	5.00
q	22.60	69.40	2.70	5.40	40.00
Cu	0.40	0.60	0.40	0.70	0.53
q	2.00	1.40	0.00	3.70	0.60
Mn	0.90	2.50	0.90	4.50	1.40
q	5.40	8.00	4.00	30.60	7.40
Ni	0.07	0.40	0.07	0.20	0.08
q	0.20	2.00	0.60	1.40	0.20
Zn	ND	0.20	0.09	0.04	0.08
q	ND	1.40	0.80	0.80	0.60

q = The amount of heavy metal absorbed in the soil, mobility (mg g^{-1}); NR = Near the Residence; NFS = Near Farm Site; NRL

= Near the Rail; NS1= Near Stream 1; NS2 = Near Stream 2.

4. CONCLUSIONS

The percent loss on ignition (LOI) at the different soil depths, which measures the organic matter content of the soil, showed that sample NRL was highest in organic matter loss (17.30%) at 5 cm soil depth. The total heavy metals concentration of the soil samples showed no specific trend in the distribution/level of heavy metals in the soil depths of 5 cm, 10 cm, and 15 cm. However, the metals distribution ranged from 4 mg/kg of Ni (for sample NRL3) to 1000 mg/kg of Ag (for sample NFS3) at 15 cm, which showed a high potential for Ag content. Hg, Pb, and Sn were not detected in all the soil samples. The mobility of the metals in soils varied considerably from one area to another with random increase and decrease according to soil depths. Mobility

was highest for Ag (69.4 mg/g) in soil sample NFS but was not detected in Zn for the control sample NR at mean depth. Levels of heavy metals in soils of the study areas were not generally higher than in control soil samples, a suggestion that anthropogenic activities were almost at same rate in the entire soils sampled.

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