

Characterization and assessment of heavy metal pollution levels in soils of Dana steel limited dumpsite, Katsina state, Nigeria using geo-accumulation, ecological risk and hazard indices.

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ABSTRACT: This study was carried out to quantitatively assess the heavy metal pollution level of soils collected from Dana steel limited dumpsite, katsina state, Nigeria using Potential ecological risk index, Hazard quotient and geochemical accumulation index.. Soil samples were collected from the dumpsite and control site at depths ranges 0- <20cm, 20- <40cm, 40-<60cm and 60-<80cm. Flame Atomic Absorption spectrophotometry (FAAS) was used to obtain the composition and Concentration(mg/kg) of the eight studied heavy metals (Zn, Cu, Cd, Co, Ni, Cr, Pb and As), the obtained concentrations(mg/kg) were compared with the WHO and Romanian guidelines for the legal permissible heavy metal concentration in soils. Based on these guidelines, it has been established that all the observed heavy metals in the dumpsite soils have concentrations above the WHO limit except Cobalt, world median and the Romanian threshold values. The concentrations of the heavy metals analyzed were subjected to computations of ecological risk index (ERI), geochemical accumulation index (I-geo) and hazard quotient. The obtained results were subjected to Univariate descriptive statistics. The mean geochemical accumulation index characterizes Zn and Cu in the moderate category, while Ni, Co, Cd and As in the unpolluted category. The mean Ecological risk index characterizes Zn, Ni and Cd in low potential ecological risk and Cu in considerable ecological risk. The mean Hazard quotient classifies all the studied metals in the polluted category. Inter-element correlation was observed among the concentrations of the studied heavy metals in the dumpsite and in the control area. The results reveal the pollution potential of the industrial waste dumping which suggested that the dumpsite was seriously contaminated with all the observed heavy metals and the need for proper waste management and immediate implementation of remediation measures by the relevant authority to avert the consequences that it can pose on public health and environment.

KEY WORDS: Heavy metals, flame AAS, pollution, ERF, HQ, I-geo

I. INTRODUCTION

Heavy metal is term used to describe a wide group of metallic elements with density equal or greater than 5g/cm³. such metals include Cadmium, Copper, Chromium, Lead, Nickel, Iron etc. they are trace elements when their occurrences in the environment is less than 0.2ppm. they are generally associated with pollution and toxicity (Knight et al, 1997). Trace metals occur naturally in soils (but rarely at toxic levels), sedimentary deposits and water bodies; therefore, there are normal background concentrations of these metals. These metals also find their way into soils, vegetation, water bodies and sediments through airborne particulate matter in the form of dust and vehicular emission. The pace and scale of environmental contamination by industrial activities have steadily increased in the last two centuries due to the pronounced industrial revolution (Stigliani et al., 1991). hence 40% of the USEPA's national priority list involved heavy metal contamination associated with industrial activities (Fostner, 1995) and 70% of all the metal contaminated sites involve two or more heavy metals.

Anthropogenic activities usually create wastes which constitute risks to the environment and public health, as a result of the way these wastes are handled, stored, collected and disposed off .in the urban areas, especially a rapidly urbanizing city like katsina, problems and issues of solid waste management are of immediate importance. the rapid population growth presents serious challenge to the authorities, so much that when wastes are collected they are disposed off in uncontrolled dumpsites and/or burnt, polluting water resources and air (Onibokun A.G et al, 2000: Srivastava, 2012). Dana steel limited is not an exception since the steel rolling activity has been known to be one of the most anthropogenic source of heavy metals in soil.

The Dana steel limited dumpsite has been densely engaged with various industrial wastes (see plate 1 and 2) which can consequently introduce some traces of heavy metals in to the environment. These wastes may expose near-by residents, scavengers, passers-by, staff and suppliers of raw materials to undue burden of heavy metals and may affect lots of people if it succeeds in polluting ground water which is extensively used in katsina for various purposes or are washed by rain and carried into the water channels or transported by wind. The aim of the present work is to characterize Dana steel limited dumpsite soil samples for Zinc, Copper, Cadmium, Chromium, Lead, Cobolt, Arsenic and Nickel composition and concentration so as to characterize their pollution level using geo-accumulation index, ecological risk index and hazard quotient.



Plate 1: Dumpsite Studied showing the discarded waste generated by the steel rolling activity.



Plate 2: the plate showing the dumpsite and the water way that link to river Ginzo .Note the dumpsite in higher altitude than the water way

II. MATERIALS AND METHODS

2.1 Study Area: (Description and sampling techniques)

Dana steel limited dumpsite is located in latitude $12^{\circ} 57' 43''\text{N}$ to $12^{\circ} 58' 7''\text{N}$, Longitude $7^{\circ} 37' 11''\text{E}$ to $7^{\circ} 37' 16''\text{E}$ and altitude 522.5m to 616.6m in Katsina state of Nigeria. The dumpsite was partitioned into nine (9) grid points labeled A-I. Soil samples were collected from each grid according to depth using hand auger. The depths were designated 1, 2, 3 and 4 which stands for 0- <20cm, 20- <40cm, 40-<60cm and 60-<80cm respectively. Nine (9) soil samples were collected from each depth making a total of 36 samples. Samples 1-9, 10-18, 19-27 and 28-36 were collected from depths 1, 2, 3 and 4 respectively. Control samples were collected at a distance of 3km away from the dumpsite. After removal of stones and some metal scraps, each soil sample was packed into its own secure water tight polythene bag to prevent cross contamination.

2.2 Sample preparation and analysis

All soil samples were air-dried at ambient laboratory temperature. Soil samples were grounded using mortar and pestle and sieved to pass through 2 mm sieve and stored for chemical analysis. With the aid of spatula and weighing bottle, 0.5g of each soil sample was obtained. This was placed in a Teflon beaker and transferred to a fume-cupboard for digestion. The digestion was carried out using concentrated nitric (10mL) and concentrated perchloric (5 mL) acids in the ratio of 2:1 and the oven was maintained at 200 °C. After one hour, the mixture was allowed to cool before leaching the residue with 5 cm³ of 20% HNO₃. Digested samples were then filtered and made up to 100 mL with deionized water. A blank determination was treated in the Atomic Absorption Spectrometer but without sample. Solution of samples were then taken and aspirated into Atomic Adsorption Spectrophotometer (Unicam Solar A.A.S 969 model) for analyzing metals. Blank determination was also carried out as in a similar way as described above except for the omission of the sample. A calibration graph was plotted for each element using measured absorbance and the corresponding concentration. The calibration curve was used to determine the concentration of the metal.

2.3 Heavy metal pollution characterization

2.3.1 Maximum permissible heavy metal concentration in soil.

The maximum threshold heavy metal concentration (mg/kg) in soil designated by the world health organization (WHO) and the Romanian guideline is tabulated in table 1 and 2 respectively.

Table1: Maximum Allowed concentration limits of some toxic metals in soil (mg/kg) (WHO, 1996)

TOXIC METAL	WHO Maximum Allowed limits(mg/kg)
Nickel(Ni)	80
Copper(Cu)	30
Cadmium(Cd)	3.00
Chromium(Cr)	100.00
Lead(Pb)	100.00
Zinc(Zn)	300

Table2: Romanian guidelines on toxic metals level permitted in soil for pollution assessment (Romanian, 1997).

Element	Literature values		Romanian norms				
	European median in soil	World median	NV*	ALS*	ALLS*	ITS*	ITLS*
As	7.03	6	5	15	25	25	50
Cd	0.145	0.35	1	3	5	5	10
Cr	60	70	30	100	300	300	600
Cu	13	30	20	100	250	200	500
Ni	18	50	20	75	200	150	500
Pb	22.6	35	20	50	250	100	1000
Zn	52	90	100	300	700	600	1500

*: NV=normal value; ALS and ITS=Alert level and Intervention threshold in the sensitive area: ALLS and ITLS=Alert level and Intervention threshold in the less sensitive area.

2.3.2 Geo-accumulation index

Geo-accumulation index is used to quantify the degree of anthropogenic or geogenic accumulated pollutant loads in soil and can be determined through the following formula:

$$I_{geo} = \log_2(C_n/1.5B_n) \dots \dots \dots (1)$$

Where, C_n and B_n are the determined concentration of metals in the target and reference areas respectively. The factor 1.5 is possible anthropogenic variations of contaminants in reference areas (Lokeshwari and Chandrappa 2006; Fagboto and Olanipekun 2010). The classification of the index is tabulated below

Table3: Classification of geo-accumulation Index (after: Hakanson, 1980)

Geo accumulation Index	Classification	Level of Contamination
$5 < I_{geo} \leq 10$	6	Extremely Serious
$4 < I_{geo} \leq 5$	5	Strong to Extremely Serious
$3 < I_{geo} \leq 4$	4	Strong
$2 < I_{geo} \leq 3$	3	Moderate to Strong
$1 < I_{geo} \leq 2$	2	Moderate
$0 < I_{geo} \leq 1$	1	Light to Moderate
$I_{geo} \leq 0$	0	Non Contamination

2.3.3 Ecological risk factor

Ecological risk index (ERI) is critical to measure both risk factor and metals concentrations in soil. The potential ecological risk index can be determined through the following formula:

$$ERI = CF * TRF \dots \dots \dots (2)$$

Where ERI is the potential ecological risk factor/index, TRF represents the toxic-response factor, and CF represents contamination factor. The toxic response values for some of the toxic and trace elements are As=10, Cr=2, Cd=30, Cu=5, Pb=5, Ni=5, and Zn=1 as suggested by Hakanson (1980).

The Potential ecological risk assessment PERI as established by Hakanson (1980) is made using the following components.

(a) Contamination Factor (CF)

Contamination factor (CF) is also called single pollution index (PI). Contamination factor is the quotient obtained by dividing the concentration of metals related to the target area by reference area. Their results are mostly associated with single pollution load, while their n-root was used for integrated pollution load index. The contamination factor can be calculated through the following formula as suggested by Harikumar et al. (2009).

$$CF = C_n/B_n \dots \dots \dots (3)$$

In the above equation, C_n is the concentration of metals in the target area, and B_n is the metals concentration of the reference area. the classification is tabulated below:

Table4: Classification of contamination factor (Hakanson, 1980)

Contamination factor	Classification
$CF < 1$	Low
$1 \leq CF < 3$	Moderate
$3 \leq CF < 6$	Considerable
$CF \geq 6$	Very high

The degree of contamination (DC) of one determined area is the sum of all Contamination factors:

$$DC = \sum CF \dots \dots \dots (4)$$

Table5: Classification of degree of contamination (Hakanson, 1980)

Degree of Contamination	Classification
$DC < 1$	Low
$1 \leq DC < 3$	Moderate
$3 \leq DC < 6$	Considerable
$DC \geq 6$	Very high

(b) Potential ecological risk (PER): is given by

$$PER = TRF * CF \dots\dots\dots (5)$$

This is calculated separately for each metal. The results classifications are as follows:

Table6: Classification of Potential ecological Risk factor (Hakanson, 1980)

Potential Ecological Risk	Classification
PER<40	Low
40≤PER<80	Moderate
80≤PER≤160	Considerable
160≤PER≤320	High
PER≥320	Very high

2.3.4 Hazard Quotient

The soil Hazard Quotient (HQ) is the ratio of the heavy metal concentration of surveyed soil samples to reference permissible limit and is computed using the relation;

$$HQ=Cc/Cp \dots\dots\dots(6)$$

Where, Cp and Cc = reference maximum permissible limit of heavy metal concentration and the concentration obtained in the sampled area respectively.

III RESULTS AND DISCUSSION

3.1 Heavy metals concentration in soils

Table 7 and 8 presented the average concentrations of each of the studied heavy metals in the target and control area respectively. The average concentrations observed in the target area were seriously higher than that in the control area for all the studied heavy metals except Co. The Average concentrations in the target and control area were compared with the world health organization guideline on the maximum limits of toxic metals in the soils (WHO, 1996) as provided in table1.All the observed toxic metals in the target area were found to have concentrations above the WHO limit, while in the control area the concentrations were below the WHO limit. Zn, Cu, Cd, and Cr were found to have concentrations greater than 3 times the recommended WHO limit ,Pb was 2 times greater and Ni was Slightly(7%) above the WHO limit. The obtained concentrations of the toxic metals (mg/kg) in the dumpsite and in the control area were compared with the Romanian guideline for the allowed maximum normal legal concentration values in soils and the world median value as presented in table 2. Base on this guideline and the obtained concentrations in the target area, it could be deduced that (i) Zn, Pb, Cr and Cd concentrations (mg/kg) in the target area exceeded the world median and Intervention threshold for sensitive area. (ii) Ni and Cu exceeded the world median and the Alert level in the sensitive area. (iii) As was below the world wide median. While the concentrations in the control area were (i) Zn, Cu, As, and Pb were within the normal value (ii) Ni, Cd and Cr where above the normal legal value.

Table7: Univariate descriptive Statistics of the concentration of the heavy metals in the dumpsite (mg/kg) (n=36)

Toxic metal	Mean	Minimum	Maximum	Standard deviation
Zn	646.228	108.200	1189.400	340.562
Cu	175.278	0.800	841.000	206.6223
Ni	85.844	10.600	337.400	77.450
Cd	15.022	0.400	31.400	7.314
Co	62.361	6.800	82.200	18.590
Cr	1096.296	800.000	4800.00	912.090
As	0.564	0.430	0.740	0.081
Pb	202.100	91.000	818.200	208.116

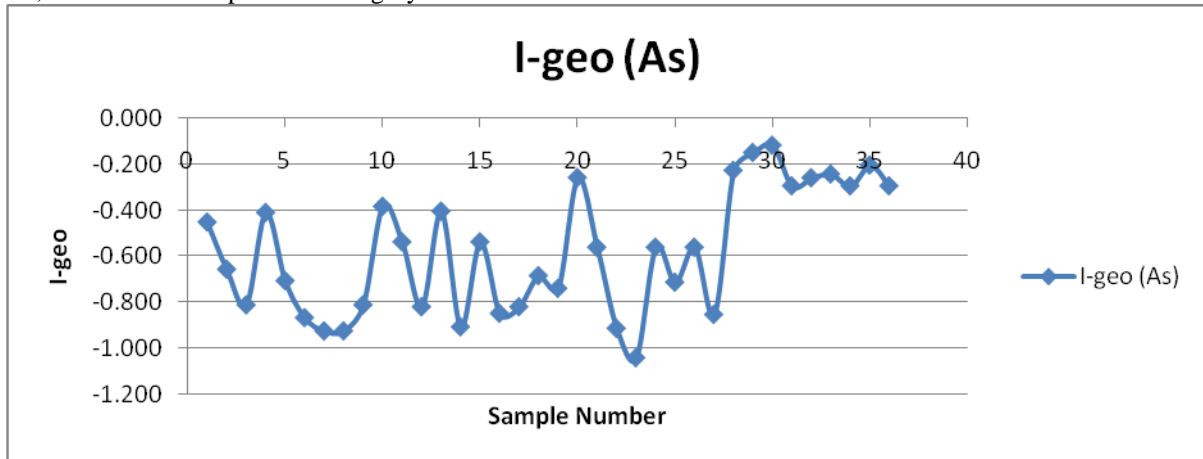
Table8: Univariate descriptive statistics of the toxic metals concentrations (mg/kg) in the control area(n=4).

Statistical parameter	Zn	Cd	Co	As	Cu	Ni	Cr	Pb
Mean	91.1	12.6	80.15	0.61	11.9	27.45	800	N/d
Minimum	59.6	10.4	72.8	0.59	7.6	20.4	N/A	N/A
Maximum	132.2	14.4	83.6	0.63	15.4	39.2	N/A	N/A
Standard deviation	30.320	1.657	5.1	0.018	3.994	8.628	N/A	N/A

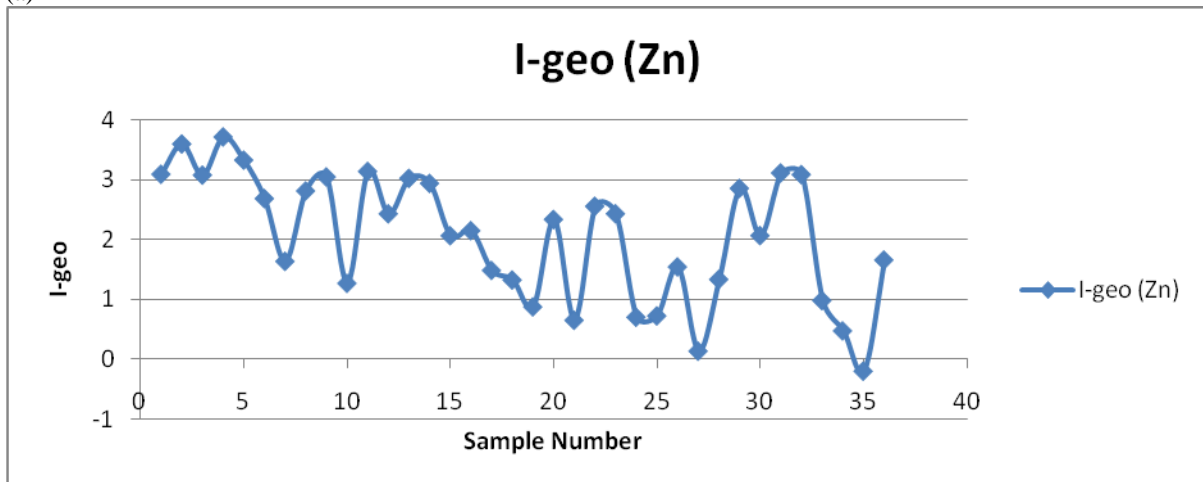
N/A means not available

3.2 Geochemical accumulation index

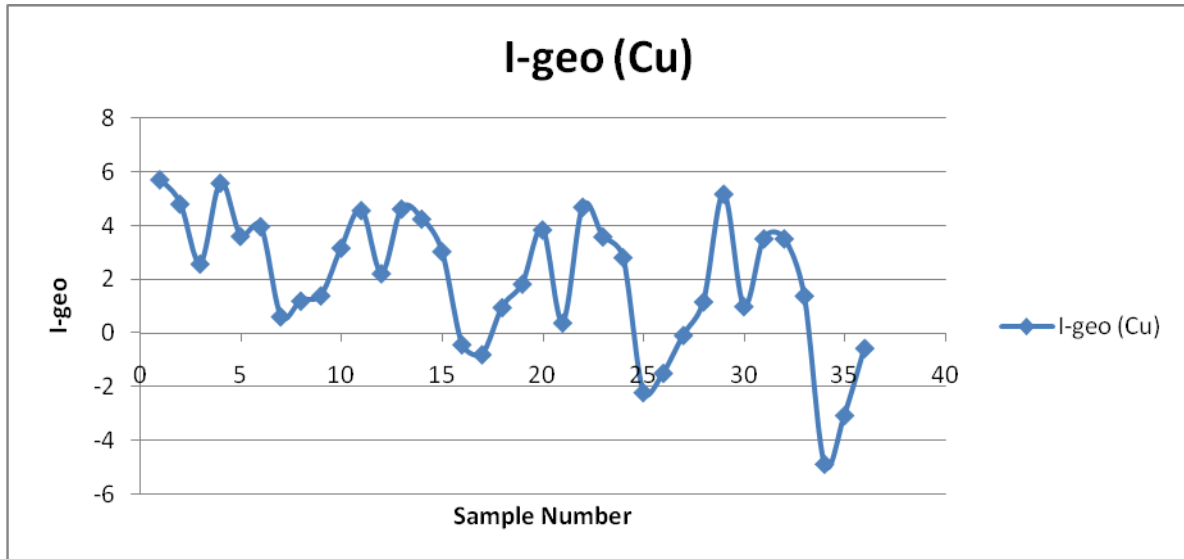
The geochemical accumulation indices were computed for all the concentrations of the sample points using equation 1. The results of this indices were presented in a scatter plot (Fig 1(a-f)) for some of the analyzed toxic metals whose background values were available. The index was not computed for Pb and Cr because their background concentration was not available as it was below detection limit. Table 9 presented the summary statistics of the computed geo-chemical accumulation indices from which the mean elemental concentration in the studied soil samples could be categorized as follows (i) Zn and Cu in Moderately polluted Category. (2) Ni, Cd, Co and As in Unpolluted Category.



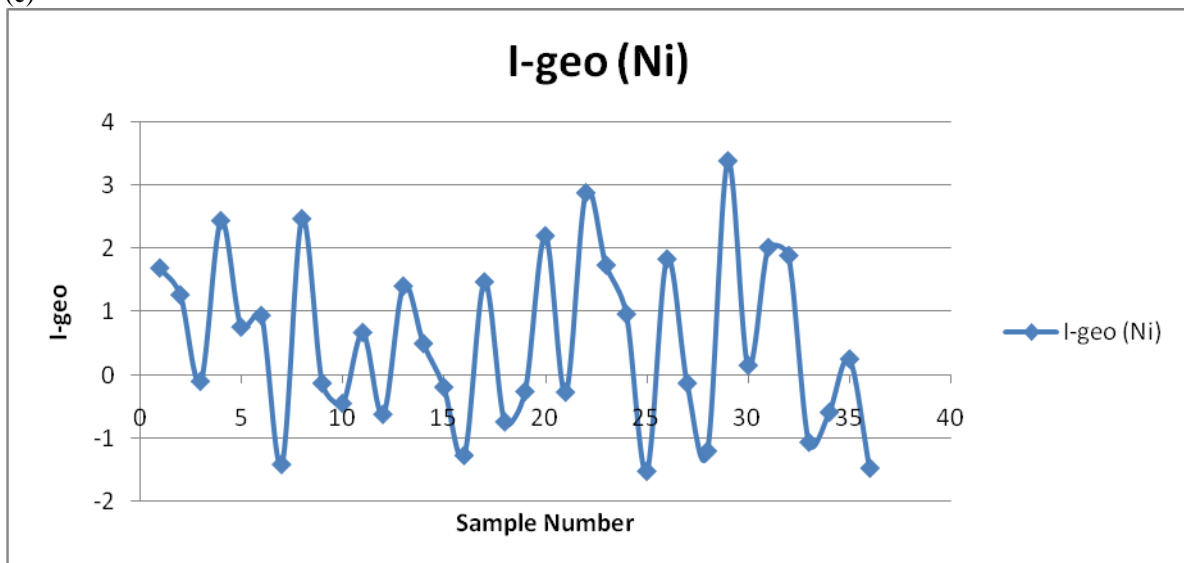
(a)



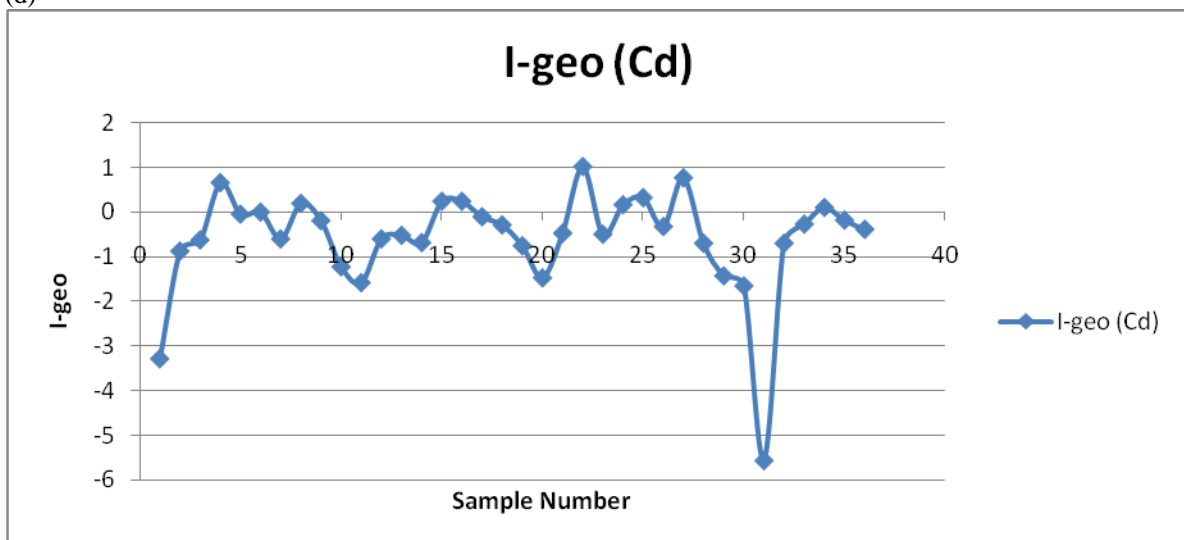
(b)



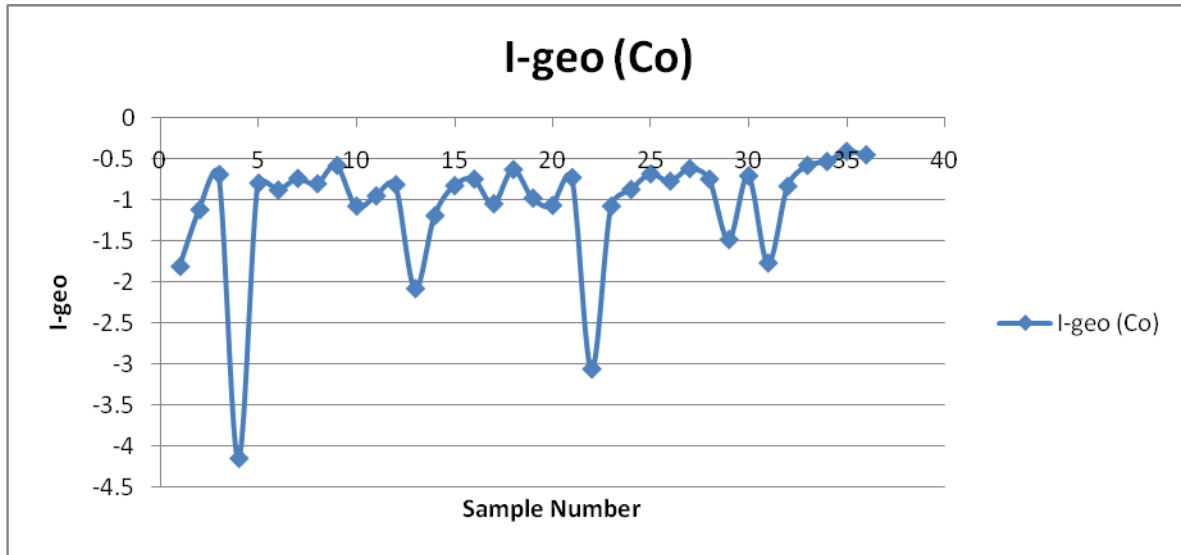
(c)



(d)



(e)



(f)

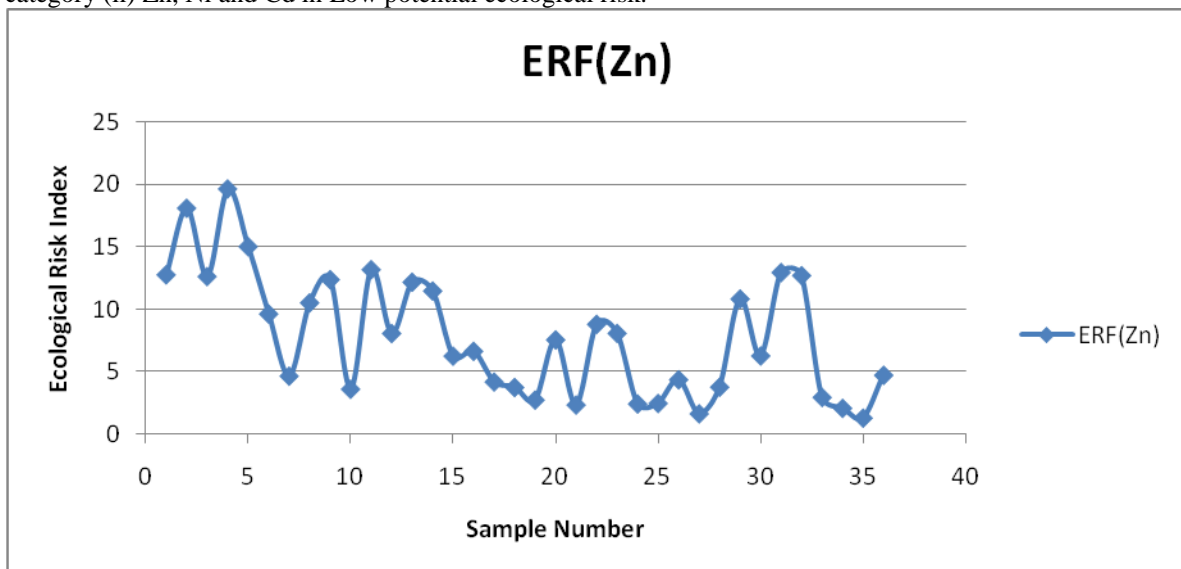
Fig1 (a-f): Scatter Plot of geochemical accumulation Index for Some elements in the analyzed dumpsite soil samples.

Table9: Univariate Descriptive statistics of the geochemical accumulation Indices of the analyzed dumpsite soil samples.

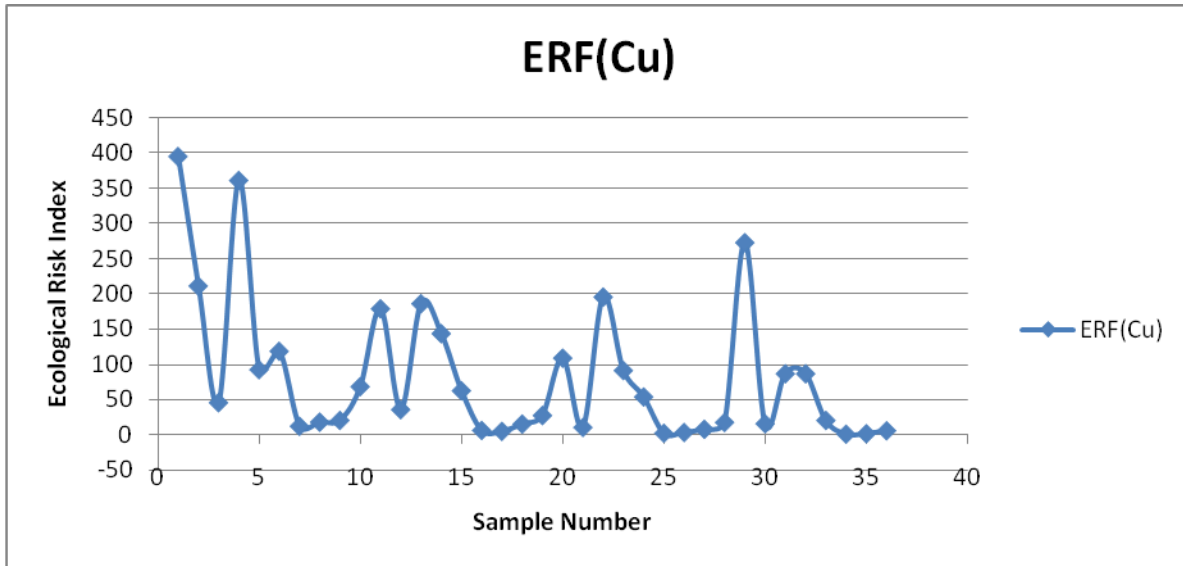
Geochemical accumulation index	mean	minimum	maximum	Standard deviation
I(Zn)	2.060	-0.192	3.711	1.054
I(Cu)	2.004	-4.852	5.722	2.544
I(Ni)	0.534	-1.530	3.381	1.357
I(Cd)	-0.598	-5.563	1.009	1.164
I(Co)	-1.066	-4.153	-0.410	0.738
I(As)	-0.577	-1.041	-0.118	0.270

3.3 Ecological Risk Factor

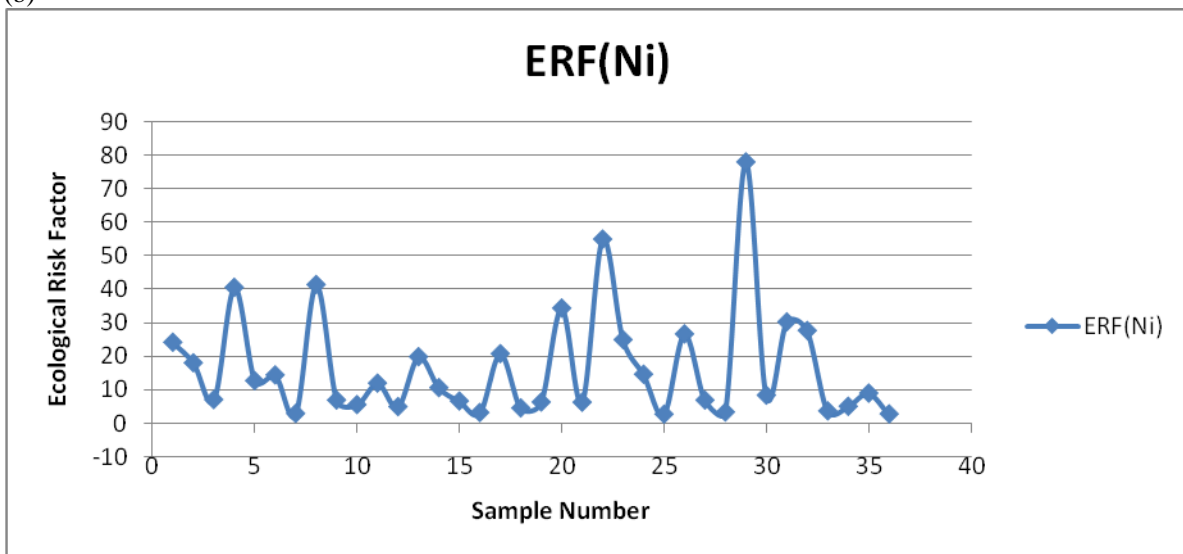
The Ecological risk Factors (ERF) was calculated for some metals studied in each of the samples utilizing equation5. Fig 3(a-d) displayed the calculated values of this index in a scatter plot. The Ecological risk factors of the other heavy metals studied were not computed due unavailability of their toxic response factors in literatures The Summary Statistics of this Index for some of the studied metals (those whose toxic response factor is in literatures and the contamination factor has been calculated) were presented in table. The mean elemental concentration could be categorized base on this index into (i)Cu in considerable Ecological risk category (ii) Zn, Ni and Cd in Low potential ecological risk.



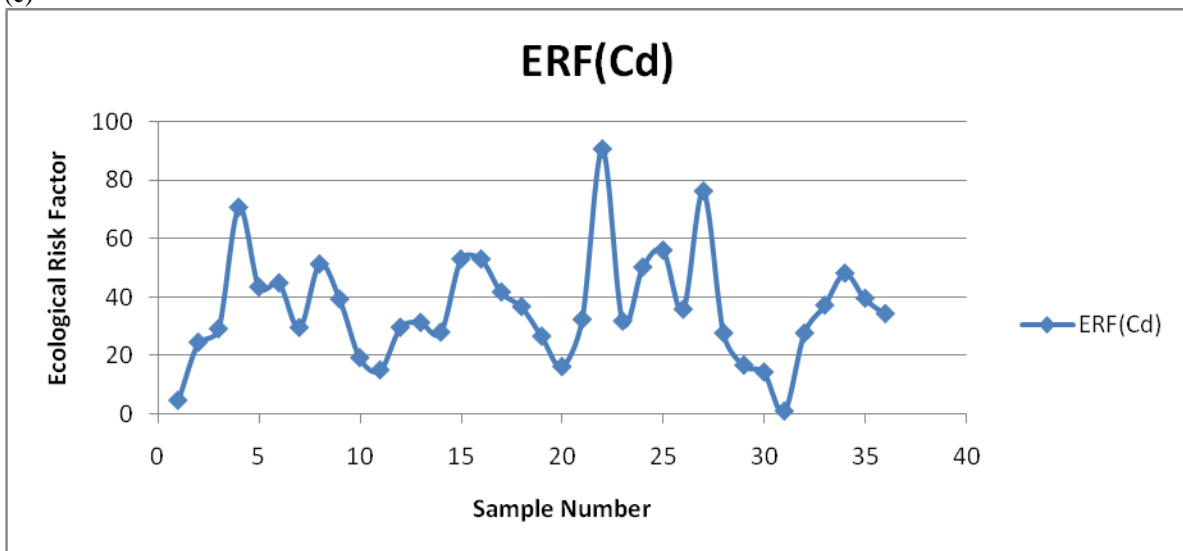
(a)



(b)



(c)



(d)

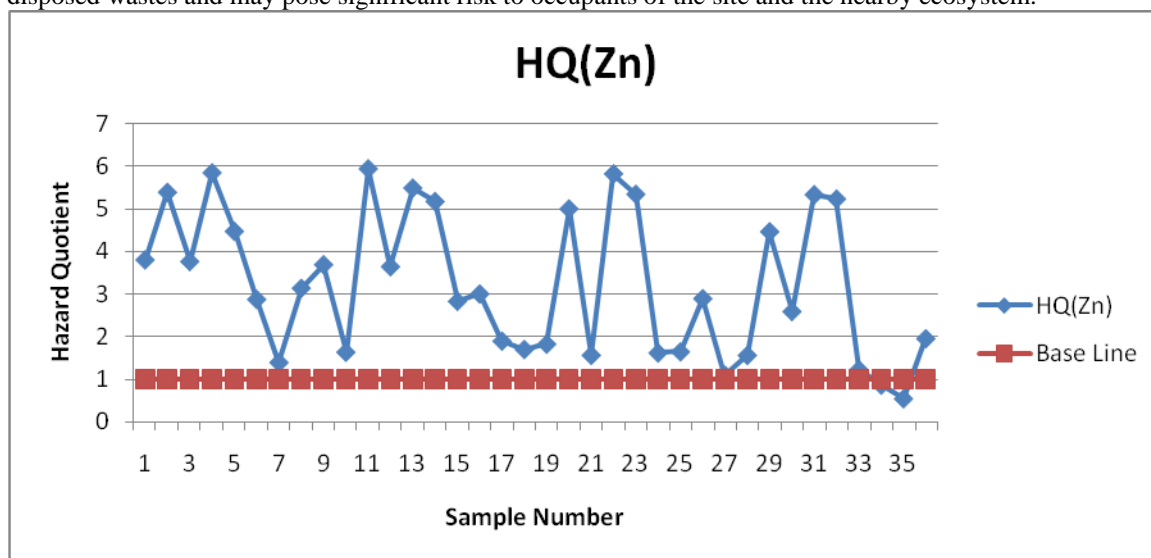
Fig3 (a-d): Scatter Plot showing the values of the calculated Ecological risk factors for the determined toxic metals in the dumpsite soil samples analyzed.

Table10: Univariate Descriptive Statistics of the determined Ecological risk Factors

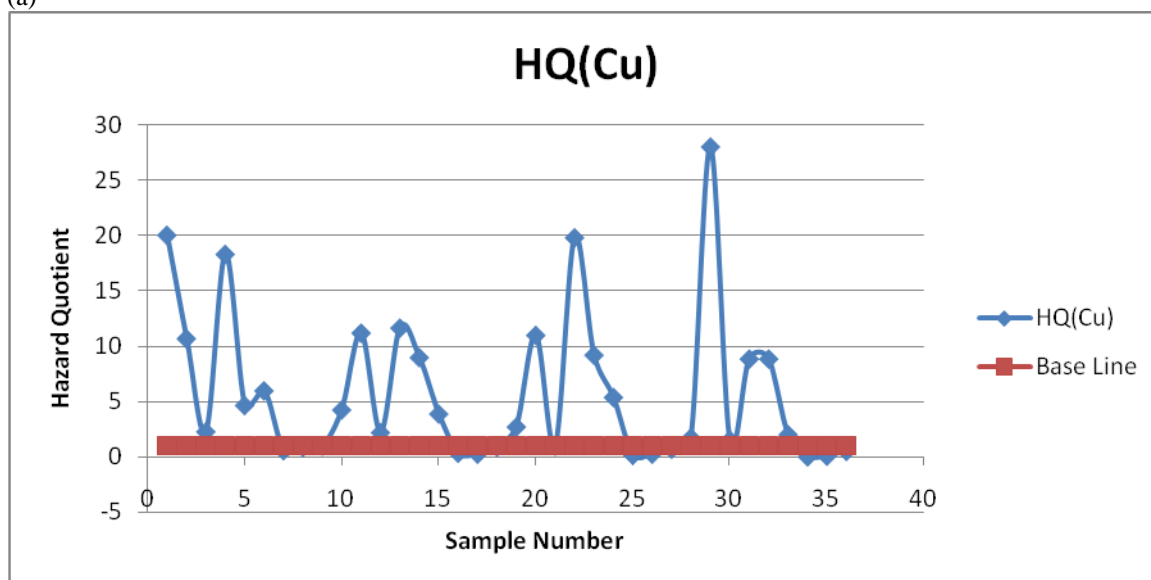
Ecological Risk Factor	mean	Minimum	Maximum	Standard deviation
ERF(Zn)	7.866	1.313	19.644	4.925
ERF(Cu)	82.558	0.26	395.789	101.661
ERF(Ni)	16.660	2.598	78.102	16.729
ERF(Cd)	36.266	0.952	90.577	18.761

3.4 Hazard Quotient

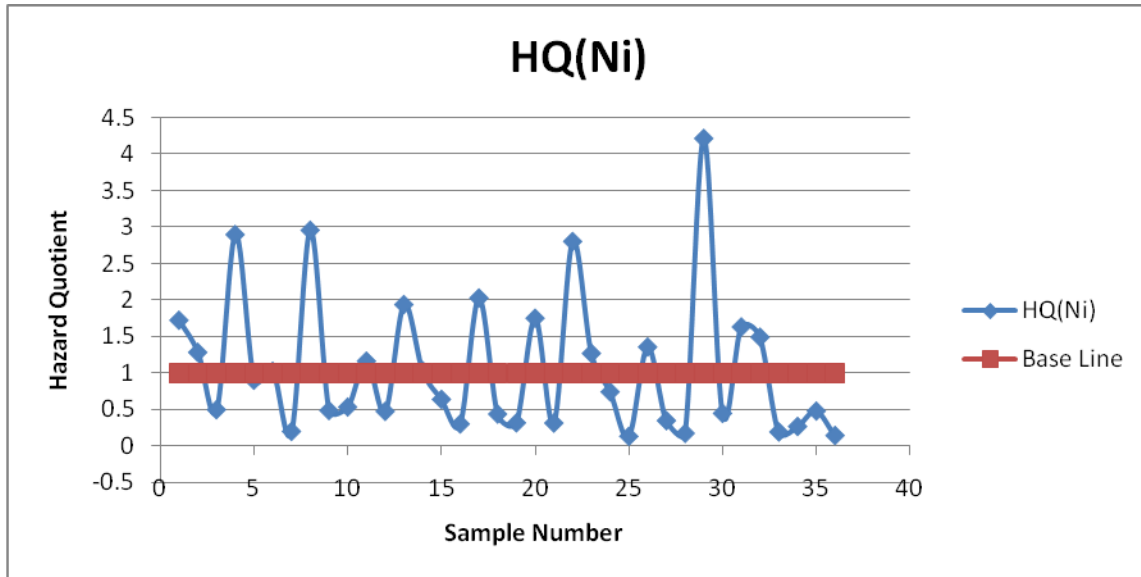
The Hazard Quotient for each heavy metal in each of the samples in the target area was calculated using equation 6 and WHO recommended threshold limit for concentrations of metals in soils (provided in table 1). The results of the calculated Hazard quotient were presented in a scatter plot (Fig 4 (a-e)) in the case of Zn, Cu and Ni and in Histogram in the case of Pb, Cr and Cd. the Base line (maximum permitted hazard quotient for the soil to be unpolluted) was plotted along the hazard quotients of the samples for comparison sake. The hazard quotients of the samples were subjected to Univariate descriptive statistics and the summary was presented in Table 11. the mean Hazard quotients for all the toxic metals studied (Zn, Cu, Ni, Pb, Cr and Cd) were far greater than unity except Ni which was slightly greater indicating that the dumpsite has been heavily polluted by the disposed wastes and may pose significant risk to occupants of the site and the nearby ecosystem.



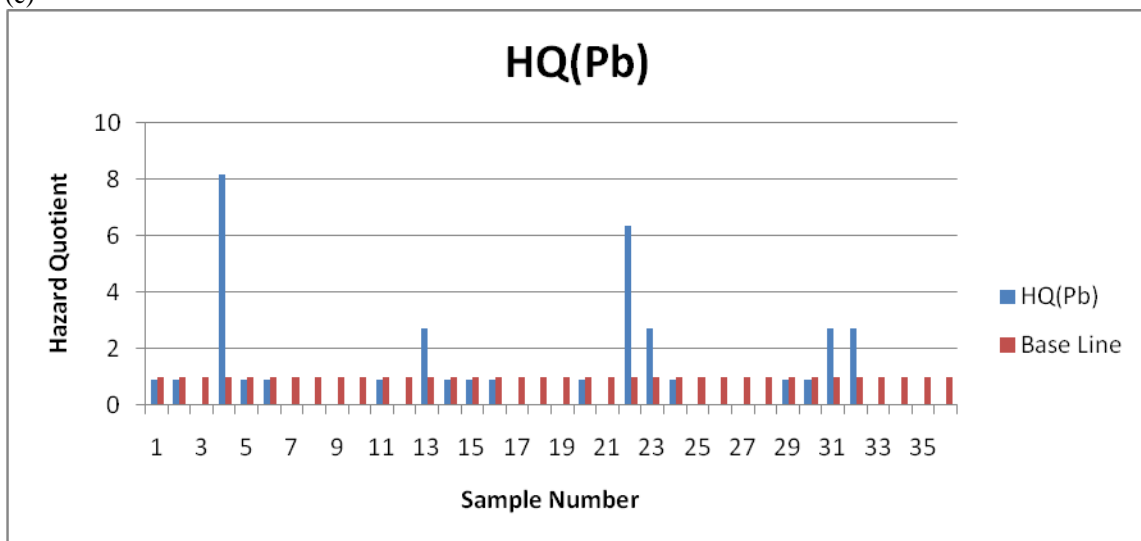
(a)



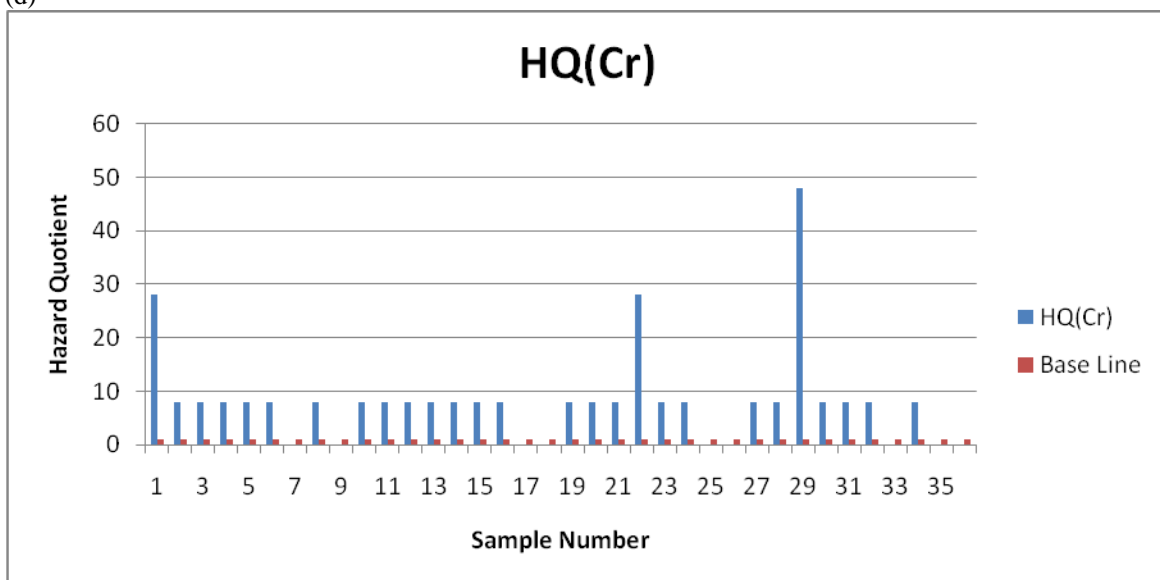
(b)



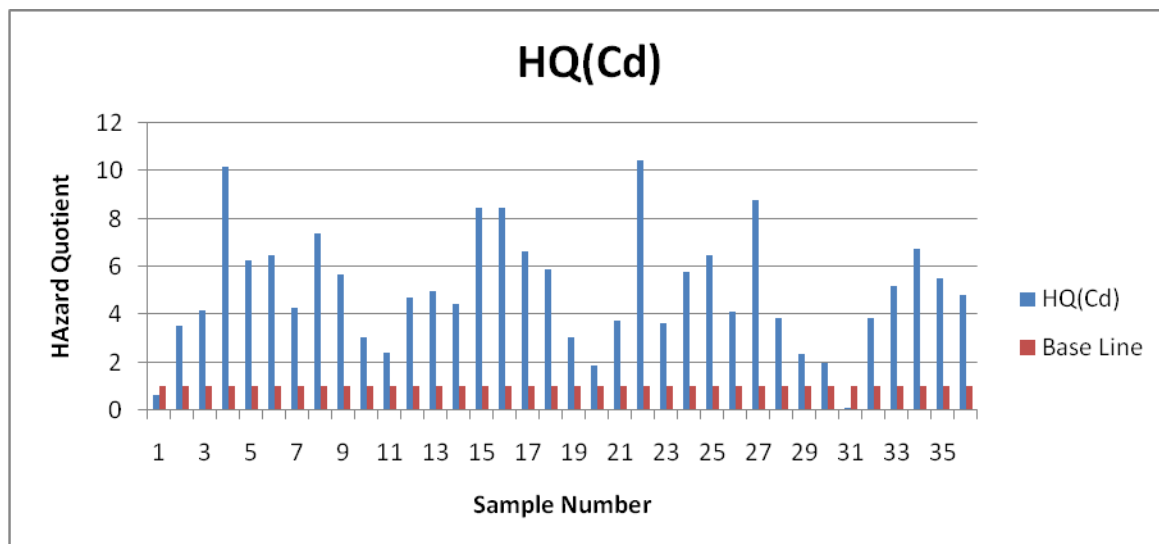
(c)



(d)



(e)



(f)

Fig 4 (a-e): Histogram showing the calculated Hazard quotient for the sampled points in the site and the base line provided by world health organization.

Table11: Univariate descriptive Statistics for the Calculated Hazard Quotient in the determined toxic metals in the dumpsite soil samples.

Hazard Quotient	Mean	Minimum	Maximum	Standard deviation
HQ(Zn)	3.231	0.541	5.947	1.703
HQ(Cu)	5.843	0.027	28.033	6.887
HQ(Ni)	1.073	0.133	4.218	0.968
HQ(Pb)	2.021	0.910	8.182	2.081
HQ(Cr)	10.963	8.000	48.000	9.121
HQ(Cd)	5.007	0.133	10.467	2.438

3.5 Correlation

The trend in the concentration of the toxic metals in the dumpsite soil samples indicated a certain measure of similarity between the different sets of samples. This similarity is expected since these concentrations could be influenced by the same steel rolling industrial activity. In an attempt to unravel the relationship between the toxic metals concentrations in the dumpsite, the concentrations of the elements (mg/kg) were subjected to Correlation Analysis using Microsoft office 2007.the correlation coefficients were displayed in Tables 12 and 13 for the dumpsite and the control area respectively.

The results of this correlation in the control area indicated a significant Positive correlation between the pairs depth/Cu, Zn/Cu, Ni/Cd and Significant negative Correlation between depth/Ni, Cu/Ni, Zn/Cd, Cu/Cd and Depth/Co. The results of Pearson correlation in the target area showed a significant positive correlation between Zn/Cu, Zn/Ni, Cu/Ni and Significant negative correlation between Zn/Co, Cu/Co, and Ni/Co.

Table12: correlation matrix for concentration (mg/kg) of pairs of elements in the dumpsite Area.

	Zn	Cu	Ni	Cd	Co
Zn	1				
Cu	0.70301	1			
Ni	0.6113	0.78075	1		
Cd	-0.133	-0.1573	0.04392	1	
Co	-0.6734	-0.8295	-0.7322	0.00305	1

Table13: Pearson correlation matrix for concentration of pairs of elements (mg/kg) in control samples with depth

	Depth	Zn	Cu	Ni	Cd	Co
Depth	1					
Zn	0.47007	1				

Cu	0.94361	0.66838	1		
Ni	-0.5955	-0.364	-0.7549	1	
Cd	-0.4051	-0.6941	-0.6787	0.86535	1
Co	-0.5923	0.40625	-0.4074	0.45249	-0.0473 1

IV. CONCLUSION

Flame Atomic absorption spectrometry technique has been employed in order to evaluate pollution of Dana steel limited dumpsites soils with heavy metals. from the experimental results presented in this work it can be seen that the concentrations of heavy metals studied in the target area exceeded the world health organization limit of heavy metals in soils, the maximum values admitted by the Romanian guidelines as well as the concentrations of all the heavy metals in the control area except cobalt. The calculated indices used in this characterization reveal the pollution potential of some of these metals. Based on the results of this work it must be stressed that pollution impact on the environment by this heavy metals is present. The situation can be labeled as “potentially significant pollution”. in this case, the competent authorities should take actions to reduce the pollutants emission in to the air as well as excessive dumping of metal slags and scraps in the dumpsite so as to diminish the possibilities of contaminating the underground water and the ecosystem around the area.

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