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Evaluation of heavy metal pollution in soils of Dana Steel limited dumpsite, Katsina State, Nigeria using Pollution load and degree of contamination indices.

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ABSTRACT*: Evaluation of heavy metals pollution level of the soils of Dana steel limited dumpsite located in latitude 12º 57¹ 43¹¹N to 12º 58¹ 7¹¹N, Longitude 7º 37¹11¹¹E to 7º 37¹ 16¹¹E and altitude 522.5m to 616.6m in Katsina state of Nigeria was carried out using contamination factor(CF), Pollution load index (PLI) and degree of contamination (DC) 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 spectroscopy (FAAS) was used to obtain the composition and concentration of the eight studied heavy metals (Zn, Cu, Cd, Co, Ni, Cr, Pb and As).The mean concentration (mg/kg) of the heavy metals in the dumpsite were 646.228, 175.278, 85.844, 15.022, 62.361, 1096.296, 0.564 and 202.100 for Zn, Cu, Ni, Cd, Co, Cr, As and Pb respectively. Statistical significant difference was observed between the mean of toxic metal concentration in the dumpsite and control area which suggested effect of anthropogenic inputs. The contamination factors, pollution load and degree of contamination indices were computed. the pollution load index revealed that the dumpsite was polluted with all the observed toxic metals(average PLI=2.113) and the degree of contamination index indicated that the dumpsite was in very high degree of contamination category (mean DC=30.624) which suggested that the dumpsite was seriously contaminated with all the observed heavy metals and the need for 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, Pollution, PLI, DC, CF and FAAS*

I. INTRODUCTION

Pollution of the natural environment by the heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms when permissible concentration levels are exceeded (Mmolawa et al,2011).major environmental concern in the iron and steel industry in Nigeria is associated with the management of the industrial wastes generated in their different processes since it is becoming increasingly difficult for safe disposal of these volumes (Akinbinu,2010).human activity create wastes and it is the way this wastes are collected, handled, stored and disposed off that constitute risk to the public health and environment. the dumping of large amount of waste materials in sites without adequate soil protection measures results in soil surface and ground water pollution as well as degradation of abiotic and biotic components of the ecological systems (Namasivayam et al, 2001, Avwiri et al, 2011).the process of industrialization and continuous exploitation of earth resources for sustainable growth has depleted the non-renewable resources of the earth there by adversely affecting the environment. An integrated steel plant unit exhausts several harmful dusts, Fumes and substances that are quite injurious to human health, vegetation, crops, animals etc. such discharges contaminate and damage inland waters, environment, soil, food, human settlements and even plants and animals. therefore, these wastes cannot be left uncared for and that is why threshold limits for such harmful substances have been fixed and industries are required to adhere to these norms. Heavy metals through anthropogenic activities have been reported by various researchers (Onianwa and Fakayode, 2000; Martley et al, 2004; Kachenko and Singh, 2006; ngoc et al, 2009).the dumpsite studied is shown in plate1, the concentration of heavy metals in this dumpsite may be enhanced by bioaccumulation due to the presence of painted metals scraps and large volume of slags that were ubiquitous in the site.

The objective of the present work was to use Flame atomic absorption spectrophotometry to: (i) assess heavy metals concentration and contamination of environment by Zn, Cu, Cd, Cr, Pb, Co, As and Ni) using control soils obtained 3Km away from the dumpsite. (ii) Assess soil contamination of the dumpsite using contamination factor, pollution load index and degree of contamination index.

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

II. MATERIALS AND METHODS

2.1 Study Area: (Description and sampling techniques)

Dana steel limited dumpsite is located in latitude 12^{o} 57^{1} 43^{11}N to 12^{o} 58^{1} 7^{11}N, Longitude 7^{o} $37^{1}11^{11}$E to 7^{o} 37^{1} 16^{11}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 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 and was carried to laboratory for analysis.

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 ^{o}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 Assessment of heavy metal contamination

2.3.1 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).

$$CF = C_n/B_n \quad \text{.................................(1)}$$

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. CF is categorized as tabulated in table1

Table 1: Classification of contamination factor. Source: Hakanson, 1980

Contamination factor	Classification
CF<1	Low
1≤CF<3	Moderate
3≤CF<6	Considerable
CF≥6	Very high

2.3.2 Pollution load index

Pollution load index (PLI) is simple statistical technique used to determine elemental contents in soil beyond the reference concentration and provide comprehensive information about the metals toxicity in respective samples (Tomlinson et al. 1996; Yang et al.2011). Pollution load index can be determined through the following formula:

$$PLI = \sqrt[n]{CF_1 * CF_2 * CF_3 * \ldots\ldots\ldots\ldots CF_n} \ldots\ldots\ldots\ldots\ldots(2)$$

Where PLI represents the pollution load index, CF is the contamination factor, and n is the number of elements. The PLI >1 indicates polluted, while PLI<1 indicates no pollution

2.3.3 Degree of contamination index

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

$$\mathrm{DC} = \sum \mathrm{CF} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

The area is classified according to DC values as follows:

Table 2: Classification of degree of contamination. Source: Hakanson,1980

Degree of Contamination	Classification
DC<1	Low
1≤DC<3	Moderate
3≤DC<6	Considerable
DC≥6	Very high

III. RESULTS AND DISCUSSION

3.1 Heavy metals concentration in soils

Fig 1(a-h) presented the concentrations in (mg/kg) of the toxic metals analyzed (Zn, Cu, Ni, Cd, Co, As, Pb, Cr) in the dumpsite soil samples. Toxic metals were detected at varying concentrations in the samples except for Pb and Cr which were not detected in some samples due to the detection limit of the machine used. The mean and standard deviations of the concentrations(mg/kg) of Zn, Cu, Ni, Cd, Co, Cr, As and Pb in the dumpsite soil samples were 646.228±340.562, 175.278±206.622, 85.844±77.450, 15.022±7.314, 62.361±18.590, 1096.296±912.090, 0.564±0.081, 202.100±208.116 respectively. The Highest concentration corresponds to Cr and the lowest corresponds to As. The increasing trend was in the order: As <Cd <Co <Ni <Co <Pb <Zn <Cr. The mean concentrations of the toxic metals in the reference areas were 91.1±30.320, 11.9±3.994, 27.45±8.628, 12.6±1.657, 80.15±5.1, 800±0, 0.61±0.018 and N/d respectively. The concentrations of all the elements in the target area were found to be higher than that obtained in the control area with greater variation in relative abundance of most of the metals.

The obtained Average concentrations in the target and reference areas were compared with the results obtained by other researchers on the Industrial Sites .Ahmad et al, 2014 Analyzed heavy metals in spinach grown in waste water agricultural soil of Sargodha Pakistan. Rahib et al (2015) Analyzed heavy metal contents in soils of gadoon Amazai industrial Estate, Pakistan. Olayiwola, 2013 Analyzed heavy metal contents in steel rolling industrial Area of Ikirun, Osun State Nigeria while Boadu, 2014 studied heavy metals contaminations of soil and water at scrap market in Accra. Their results were presented in Table3. From the table we can see that the obtained average concentration (mg/kg) in this work corroborates with the results of those researchers. The High Cr and Co Concentration observed in this study corroborates with that obtained by Olayiwola, 2013.The Observed Concentration of Cd was in Line with that obtained by Rahib et al, 2015.The observed high concentration of Pb and Ni Corroborates with the result of Olayiwola,2013.Ahmad et al, 2014.Rahib et al, 2015. Cu and Zn concentrations were also in line with the results reported by Ahmad et al, 2014 and Rahib et al, 2015.

Table3:Comparison of present Study concentrations (mg/kg) with other national and international studies.

Cr	Cd	Pb	Ni	Cu	Zn	Co	As	References
1674	-	1387	495	-	-	267	-	Olayiwola,2013
475.5	1.0	205	46	185.7	555	-	-	Ahmad et al,2014
301.6	8.8	152	58	144.8	359.4	32.5	-	Rahib et al,2015
9.57-57.73	3.47-13.80	127.83-1392.67	6.47-62.53	226.80-6291.33	173.60-899.90	17.03-64.43	-	Boadu,2014
1096.296	15.022	202.100	85.844	175.278	646.228	62.361	0.564	This work(target area)
800	12.6	N/d	27.45	11.9	91.1	80.15	0.61	This Work(Control Area)

3.2 Contamination Factor, Degree of Contamination and Pollution Load Index

Table 5 presented the calculated contamination factors of the analyzed samples. the contamination factor was used to assess the level of contamination of each element in the studied soils, base on the categories discussed in chapter2, the elemental concentrations could be categorized as follows (i) As and Co in the low contamination category (ii) Cd in the moderate contamination category (iii) Ni in the considerable contamination category (iv)Zn and Cu in the very high contamination factor category.

Figure 2 and 3 presented the degree of contamination and pollution load index values plotted in a scatter plot. These indices were used to assess the overall pollution level of the site resulting from the observed metals. The pollution load index results indicated that the target area was contaminated with all the observed toxic metals (mean PLI=2.113) .The Results of the Degree of contamination index indicated that the target area is in very high degree of contamination category (Mean DC=30.624 which is greater than 4m (m=6)) base on the categories described in chapter2.

3.3 T-test

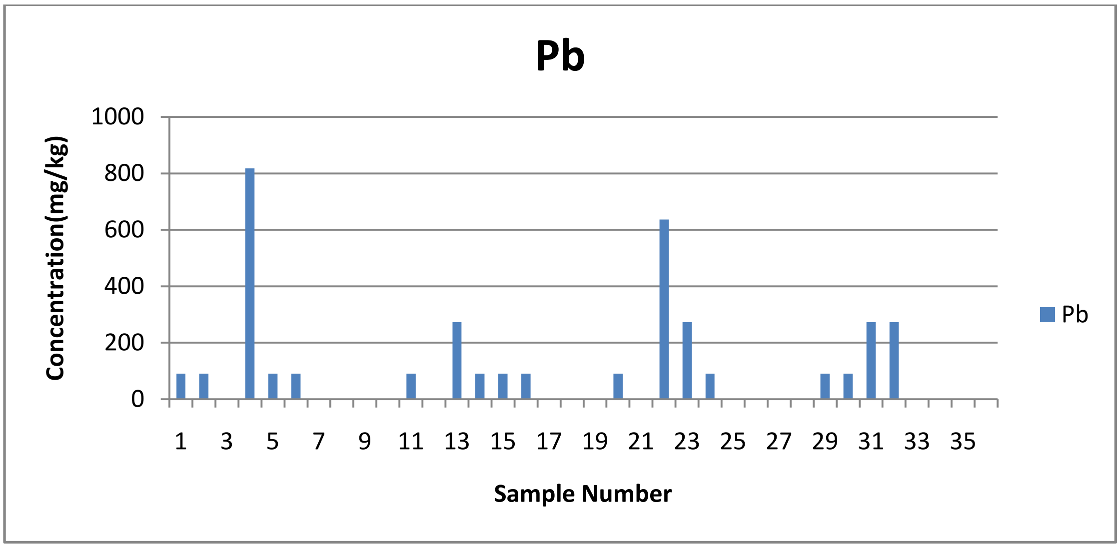
In order to understand the level of difference between the means at each depth of the observed toxic metals concentrations in the target and control area to ascertain the cause of the variation, the mean concentration(mg/kg) of each metal in the target and control area were analyzed using Microsoft excel 2007 T-test (Pair two samples for means) at $P<0.05$ significance (one-tail).the result of the test was displayed in table 4.The Results showed significant difference in the means of Zn, Cu, Ni, Co, As and Insignificant difference in respect of Cd. This suggested that all the significant toxic metals concentrations can be attributed to the industrial activity.

Table4: T-tests (Pair two sample for means) between toxic metals concentration in dumpsite soil and control site ($P<0.05$) one tail.

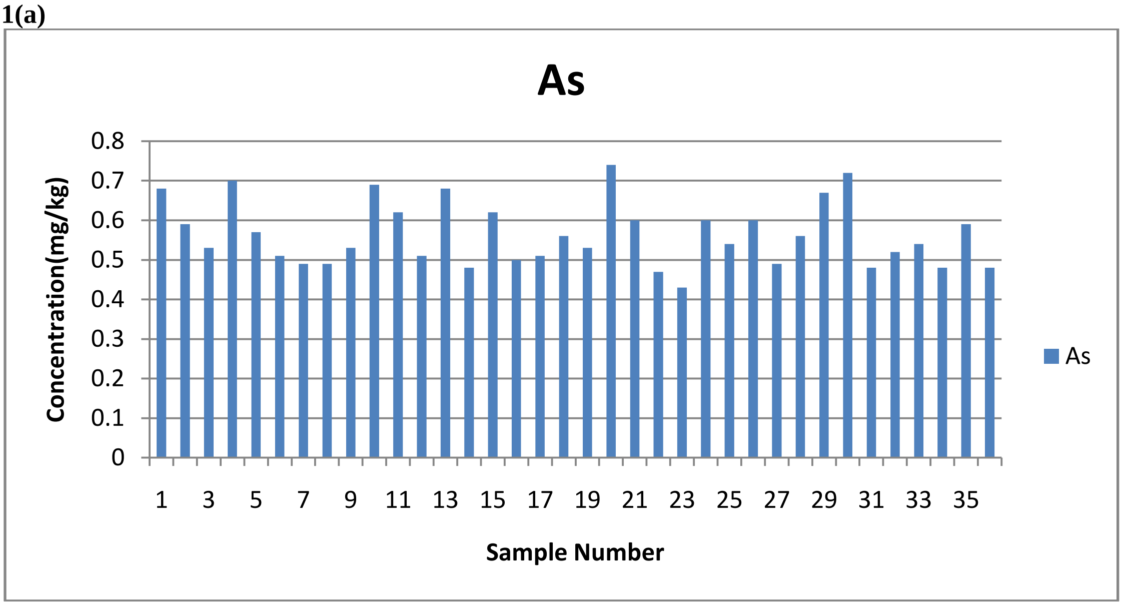
Toxic Met al	t-stat	P value	Level
Zn	-9.041	0.001	Significant
Cu	-10.657	0.0009	Significant
Ni	-6.951	0.003	Significant
Cd	-1.734	0.091	Not Significant
Co	5.995	0.005	Significant
As	-4.631	0.009	Significant

IV. CONCLUSION

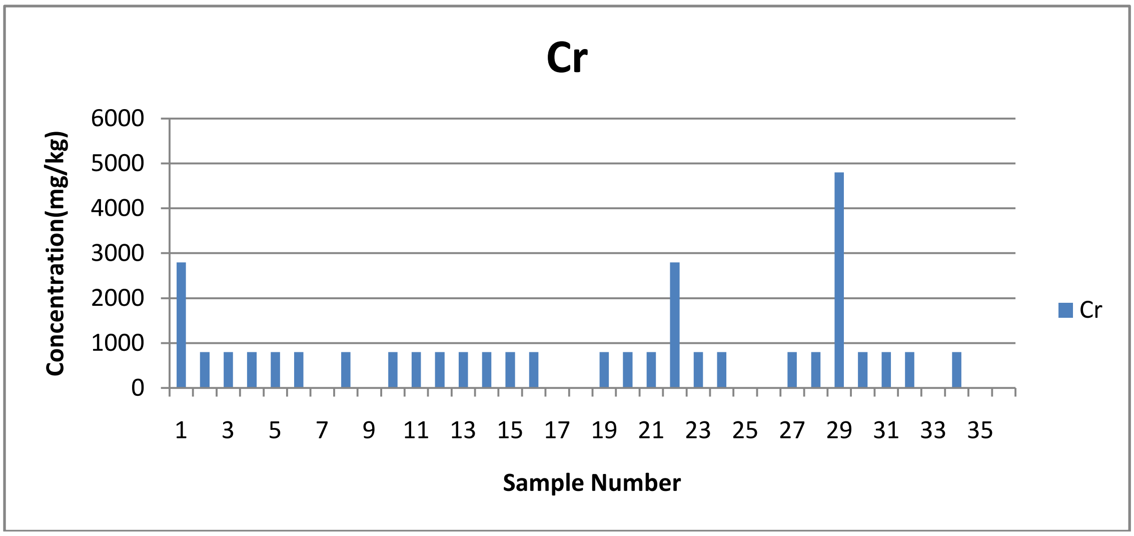
Soils samples have been collected from the Dana steel limited dumpsite in Katsina state and were analyzed for toxic metals' (Zn, Cu, Cd, Co, Ni, As, Pb and Cr) composition and concentration using flame atomic absorption spectrophotometry. The obtained concentrations (mg/kg) were used in computations of heavy metals hazard indices including contamination factors, pollution load index and degree of contamination index. On the basis of these indices, it has been established that the soils of Dana steel limited has been highly affected by depositions of heavy metals in the industry. These heavy metals can cause environmental problems in ecosystem of the area due to the release of toxic metals from the contaminated soil to the ground water system and also in the plants grown in the soil. This alarming situation should be regularly monitored for health related problems in the inhabitants of the area. It is therefore strongly recommended that Phyto and bio-remedial measures be considered by appropriate authorities in order to minimize the extent of accumulated pollutant loads.


Pb
1000
800
600
400
200
0
Concentration(mg/kg)
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
Sample Number
Pb

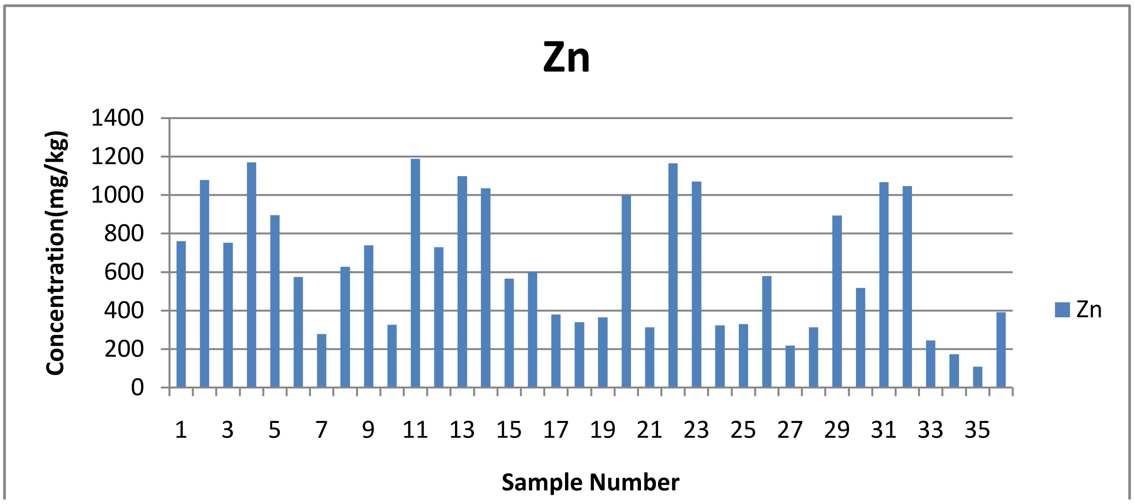
1(a)


As
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Concentration(mg/kg)
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
Sample Number
As

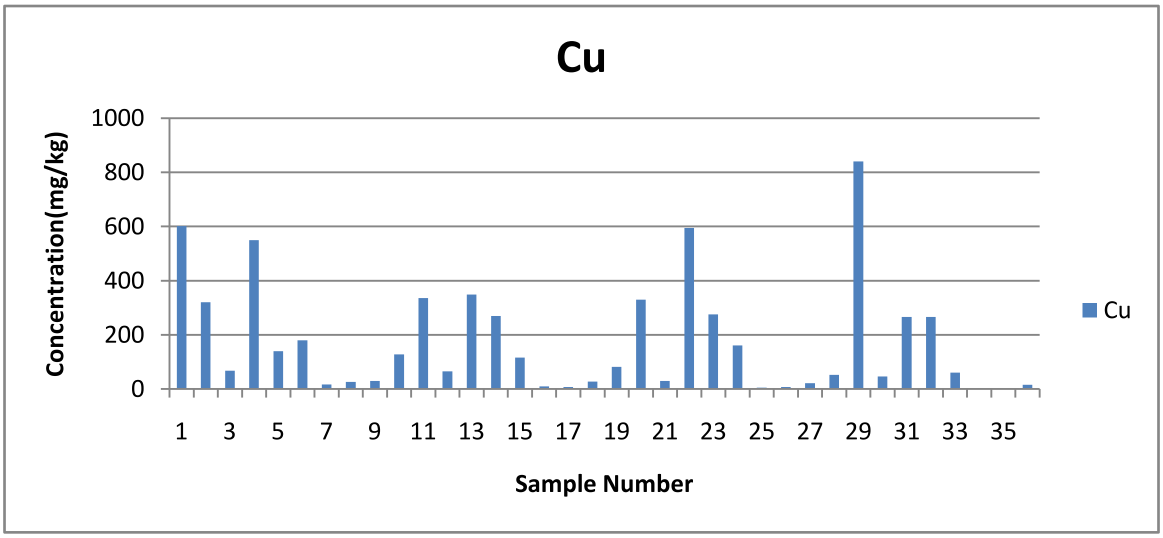
1(b)


Cr
6000
5000
4000
3000
2000
1000
0
Concentration(mg/kg)
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
Sample Number
Cr

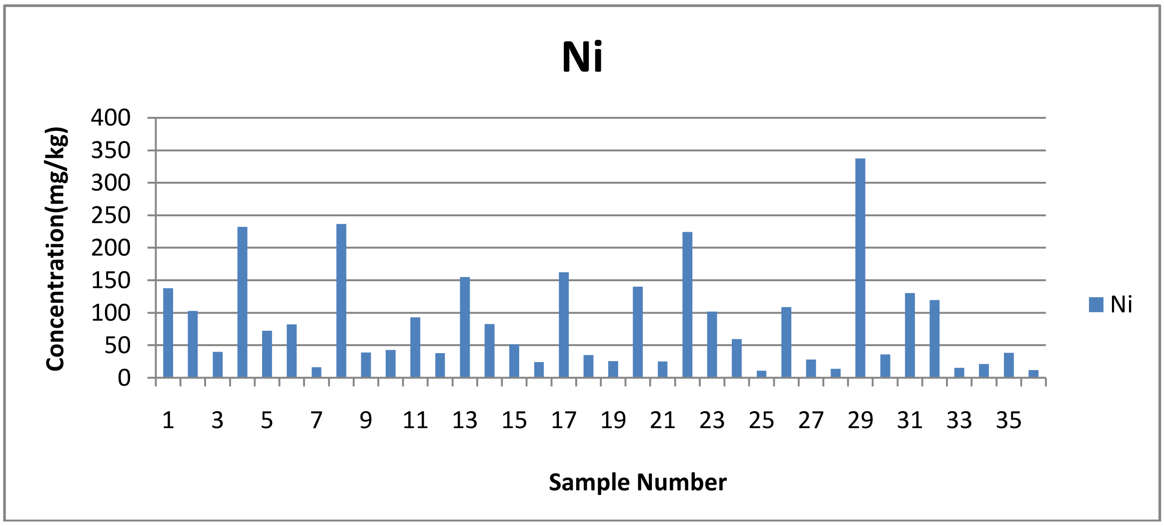
1(c)


Zn
1400
1200
1000
800
600
400
200
0
Concentration(mg/kg)
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
Sample Number
Zn

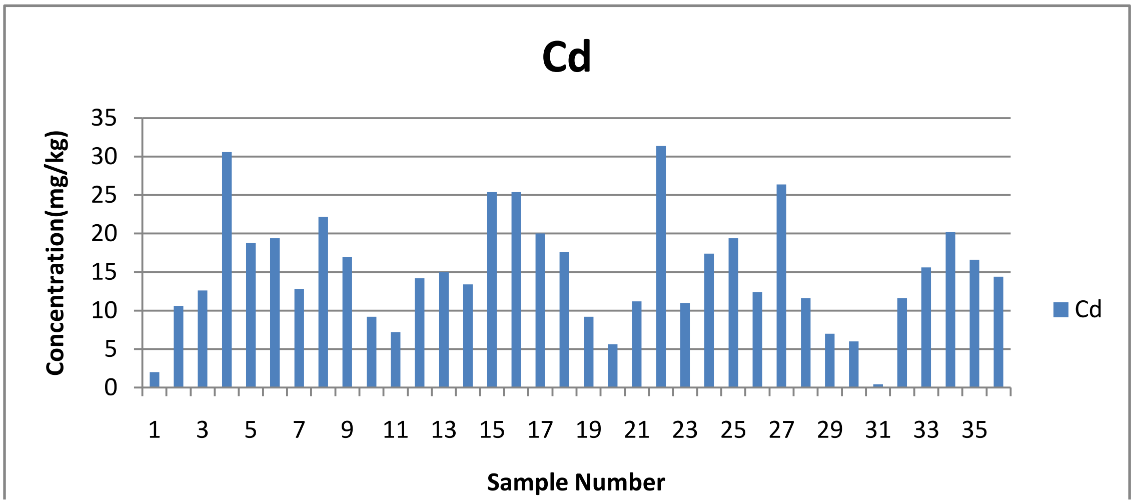
1(d)


Cu
1000
800
600
400
200
0
Concentration(mg/kg)
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
Sample Number
Cu

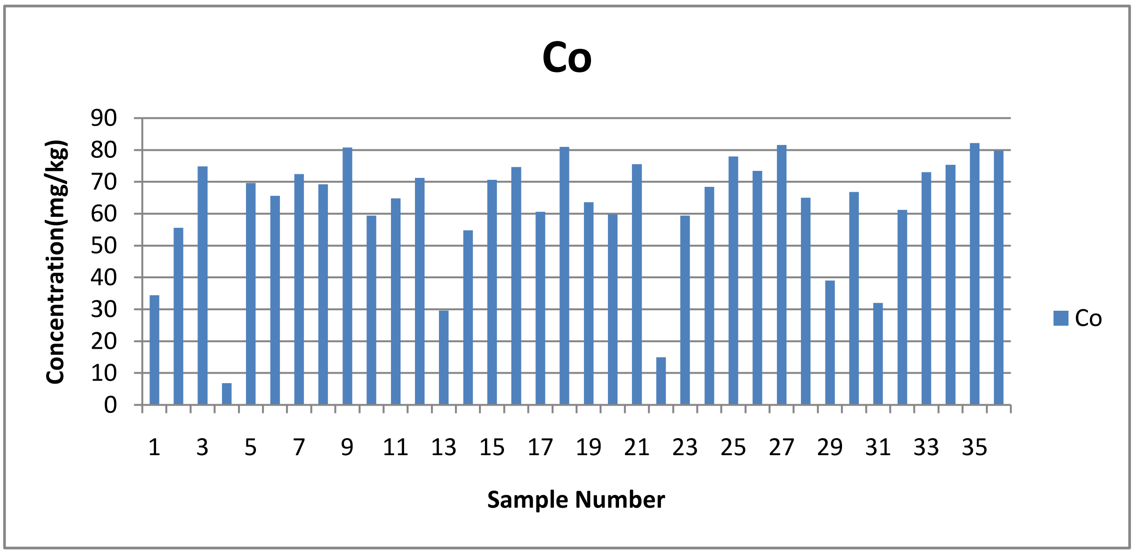
1(e)


Ni
400
350
300
250
200
150
100
50
0
Concentration(mg/kg)
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
Sample Number
Ni

1(f)



1(g)



1(h)

Fig 1(a-h): Histogram representing the determined toxic metals concentration of the dumpsite Soil Samples (mg/kg)

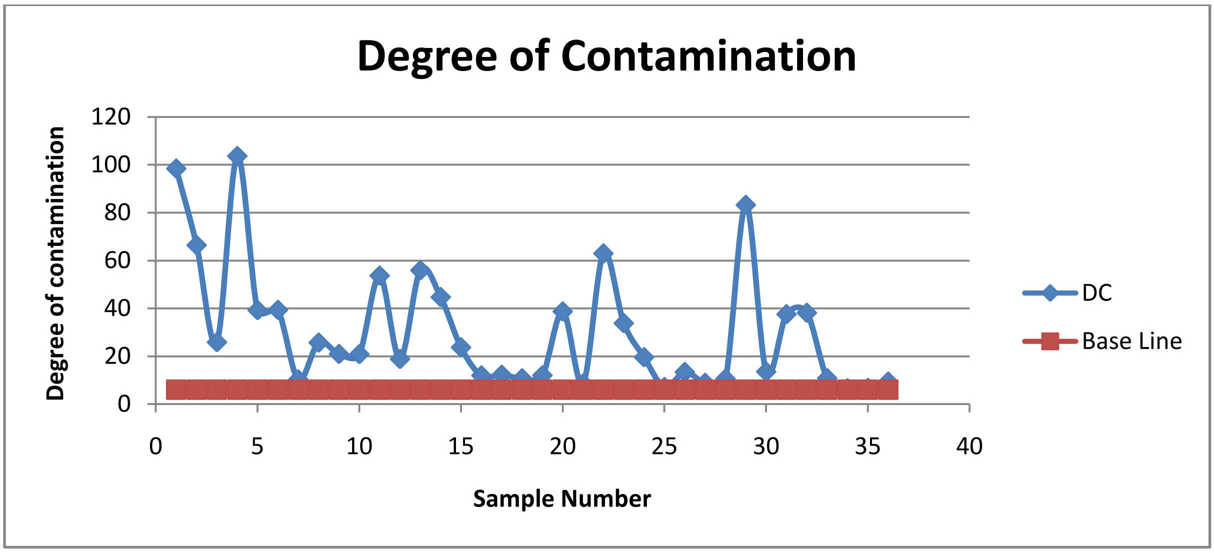


Fig2: A Scatter Plot showing the Degree of Contamination of the dumpsite soil samples

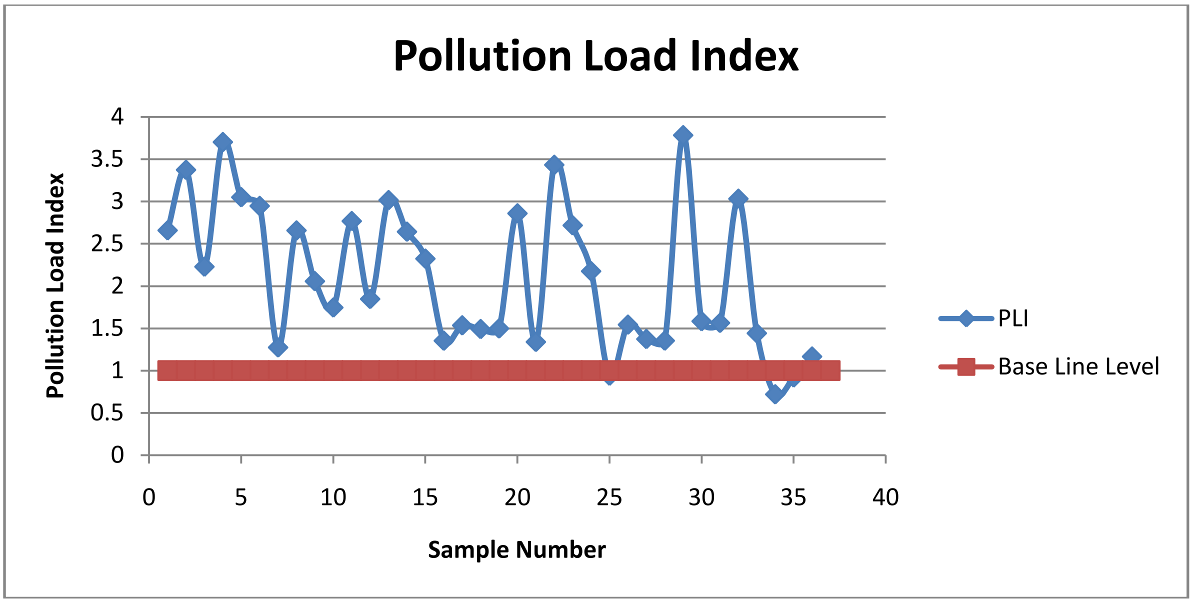


Fig3: A Scatter Plot showing the pollution Load Index of the determined toxic metals in the analyzed dumpsite soil samples.

Table5: Calculated contamination factors (CF) for some of the heavy metals analyzed in the dumpsite soil samples.

Depth	Sample No	CF(As)	CF(Zn)	CF(Cu)	CF(Ni)	CF(Cd)	CF(Co)
0-<20cm	1	1.097	12.772	79.158	4.825	0.154	0.427
	2	0.952	18.104	42.263	3.594	0.815	0.690
	3	0.855	12.638	9.026	1.392	0.969	0.928
	4	1.129	19.644	72.342	8.112	2.354	0.084
	5	0.919	15.030	18.421	2.524	1.446	0.864
	6	0.823	9.648	23.658	2.867	1.492	0.814
	7	0.790	4.671	2.316	0.559	0.985	0.898
	8	0.790	10.534	3.474	8.280	1.708	0.859
	9	0.855	12.389	3.974	1.364	1.308	1.002
	10	1.150	3.623	13.596	1.092	0.639	0.711

20-<40cm	11	1.033	13.186	35.766	2.378	0.500	0.775
	12	0.850	8.084	7.043	0.969	0.986	0.852
	13	1.133	12.184	37.213	3.959	1.042	0.354
	14	0.800	11.481	28.702	2.107	0.931	0.656
	15	1.033	6.275	12.426	1.306	1.764	0.844
	16	0.833	6.659	1.128	0.617	1.764	0.892
	17	0.850	4.204	0.872	4.143	1.389	0.725
	18	0.933	3.765	2.936	0.893	1.222	0.969
40-<60cm	19	0.898	2.761	5.382	1.245	0.885	0.761
	20	1.254	7.573	21.711	6.873	0.538	0.715
	21	1.017	2.365	1.974	1.235	1.077	0.904
	22	0.797	8.818	39.118	11.000	3.019	0.179
	23	0.729	8.091	18.184	4.980	1.058	0.711
	24	1.017	2.448	10.645	2.912	1.673	0.818
	25	0.915	2.487	0.329	0.520	1.865	0.933
	25	1.017	4.380	0.539	5.324	1.192	0.878
	27	0.831	1.654	1.434	1.363	2.538	0.976
60-<80cm	28	0.889	3.789	3.403	0.648	0.921	0.893
	29	1.063	10.842	54.610	15.620	0.556	0.536
	30	1.143	6.289	3.013	1.657	0.476	0.918
	31	0.762	12.959	17.273	6.046	0.032	0.440
	32	0.825	12.714	17.273	5.528	0.921	0.841
	33	0.857	2.968	3.961	0.713	1.238	1.003
	34	0.762	2.092	0.052	0.991	1.603	1.036
	35	0.937	1.313	0.182	1.778	1.317	1.129
	36	0.762	4.740	1.026	0.537	1.143	1.096

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