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Pollution of Oil Spills affected Soils in Parts of Bayelsa State, Nigeria.

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Abstract Concentrations of Pb, Cu, Cd, and Zn were measured in Soil samples in the study area. Averages of concentrations of Pb (55.54mg/kg), Cu (202.94mg/kg), Cd (35.47mg/kg) and Zn (51.83mg/kg) in the soil samples were compared with Canadian soil quality guidelines (CSQGs) of Canadian Council of Ministers of the Environment.(CCME), Federal Environmental Protection Agency (FEPA), Nigeria and standard of average shale. Contamination indices and ecological risk indices were analyzed to assess heavy metal contamination of agricultural soils using single and integrated indices. In this study, contamination factor (CF), ecological risk factor (Er) and index of geo-accumulation (Igeo), as single indices, and the pollution load index (PLI), the degree of contamination (Dc) and the potential ecological risk index (RI), as integrated indices, were calculated.

Keywords Pollution indices, Heavy metals, CSQGs, Soil contamination.

Introduction

Aggressive crude oil extraction in the Niger Delta by Multinational Corporations for more than fifty years, has affected the area with more environmental degradation than any visible signs of improvement in the quality of life of the host communities. The quantity of oil produced and transported between points of production, processing and distribution, or export terminals, has greatly increased as the demand of and dependence on oil has increased. Although this increase in oil production level contributes to Nigeria's economic growth, it also presents increased potential for environmental pollution and degradation. Contamination of soils with crude oil and refinery products is becoming an ever-increasing problem especially in the light of several breakdowns of oil pipelines and wells and distribution of petroleum-based products [1-3]. Nigerian crude oil is known to have about 0.003 – 42.31 mg/kg of transition metals (V, Cr, Mn, Fe, Co, Ni, Cd and Cu) [4]; some of which cannot be completely removed during the crude refining processes.

Heavy metals can be defined as trace metals with densities greater than 5 g/cm^3[5]. Many soils naturally have varying but trace amounts of heavy metals even in undisturbed environments. These amounts can be changed because many industrial processes such as smelting, burning of fossil fuels, petroleum prospecting and mining, produce heavy metals which if not properly and carefully controlled end up in soils. Any increase in these heavy metals indicates that there is contamination. When the concentrations of these metals such as cadmium (Cd) reach certain levels, they can become toxic to plants. They assume particular importance when considering bioaccumulations because there is no indication currently that most of them (with the exception of vanadium and titanium) are used by animals in their metabolic processes [6-7]. Apart from the traditional toxicological relevance of these trace heavy metals, some like nickel and vanadium that are natural constituents of crude oil, have found use as diagnostic indices of hydrocarbon degradation and oil-oil correlation [8].

Several authors have reported the detrimental effects of oil spillage to soil which has hampered agricultural activities and also adversely affected soil dependant organisms [9]. Heavy metals are often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity [5]. The general increase of heavy metal content in the soil has been largely caused by crude oil spillage [10]. Heavy metal pollution of the soil is caused by various metals especially copper, Nickel, Cadmium, Zinc, Chromium, and lead [11]. It has been observed that the pollution caused by heavy metal does not only results in adverse effects on various parameters relating to plant quality and yield but also causes changes in the size, composition and activity of the microbial activities [12].

A study by Adesina et al (2014), observed that Crude oil pollution have a negative effect on the macro-fauna such as earthworms, beetles, larva etc. which plays a vital role in the ecosystem especially in the decomposition of dead organic matter [13]. The study reported adverse effects of crude oil pollution on the growth of maize and cowpea as well as natural vegetation of the immediate environment. It concluded that crude oil pollution generally increases the heavy metal content of the soil on which it occurs.

In this study, the pollution of oil spill affected Soils in Odioama community were assessed. The concentrations of Pb, Cu, Cd and Zn were evaluated in affected Soils.

Materials and Methods

Sampling/Laboratory Analysis

The study was conducted at Odioama, Nigeria, (between latitude 04˚33'N and 04˚42'N and longitude 06˚40'E and 06˚52’E) in 2015. Twenty Surface (0 - 15 cm depth) soil samples from crude oil polluted sites and were collected from two different points with the aid of bucket auger in Odioma Community, Bayelsa state.

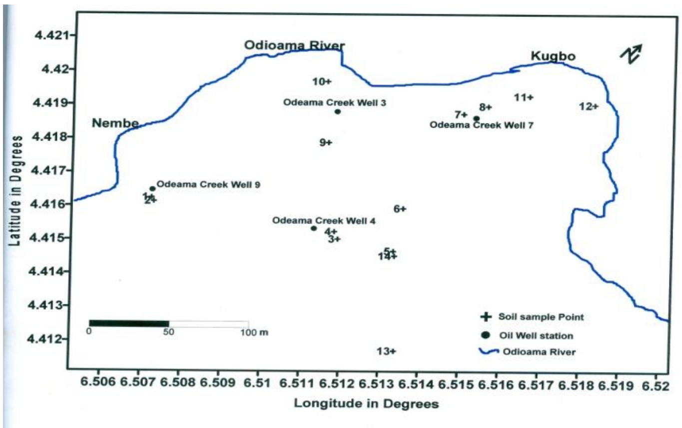

Figure 1a: Location map and sampling sites

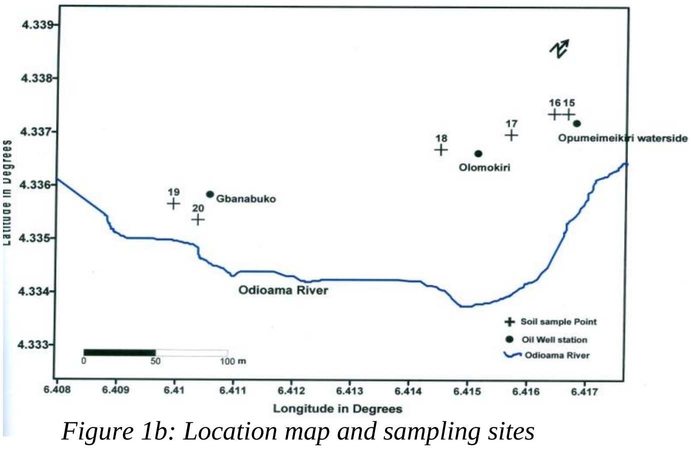

Figure 1b: Location map and sampling sites

The soil samples were mixed thoroughly, air dried and sieved with 2 mm mesh sized sieve to remove debris. Pre-metals analyses treatments of soil samples involve acid digestion of the soil samples. The weighed out gram of each of the samples was dried, sieved and transferred into a 100 mL beaker Concentrated nitric acid (HNO_3) (10 mL) and concentrated perchloric acid ($HClO_4$) (5 mL) (that is, acid volume ratio of 2:1) were added and the mixture was placed on a hot plate under fume cupboard and heated to near dryness, until its colour changed to white. This residue was allowed to cool and then dissolved with 20% nitric acid (5 mL). After filtering the mixture with filter paper, the filtrate was made up to 20 cm^3 volumes with distilled water. The various concentration standards for the various elements as well as the blank were equally prepared. Each of these preparations was then analyzed for heavy metals using elemental atomic absorption spectrophotometric method (AASUNICAM 919 model was used) [14].

Pollution Indices Calculations

In this article, the commonly used pollution indices were classified into two types: (i) single indices and (ii) integrated indices in an algorithm point of view. Single indices are indicators used to calculate only one metal contamination, which include: contamination factor, ecological risk factor, and index of geo-accumulation. Integrated indices are indicators used to calculate more than one metal contamination, which were based on the single indices. Each kind of integrated index might be composed by the single indices separately.

Contamination indices and ecological risk indices were analyzed to assess heavy metal contamination of oil spills affected soils using single and integrated indices. In this study, contamination factor (CF), ecological risk factor (Er) and index of geo-accumulation (Igeo), as single indices, and the pollution load index (PLI), the degree of contamination (Dc) and the potential ecological risk index (RI), as integrated indices, were calculated.

Contamination factor (CF) and Pollution load index (PLI)

The level of contamination can be expressed by the contamination factor (CF). The CF is calculated according to Hökanson,1980 [15] .

$$CF = \frac{\text{Cmetal}}{\text{Cbackground}} \qquad (1)$$

The CF is the ratio obtained by dividing the concentration of each metal (C_{metal}) in the sediment by the baseline or background value. The background value ($C_{background}$) corresponds to the baseline concentrations reported by (Turekian and Wedepohl, 1961) and is based on elemental abundances in sedimentary rocks (shale). The following terminologies are used to describe the contamination factor: CF<1, low contamination factor; 1≤ CF <3, moderate contamination factors; 3≤ CF <6, considerable contamination factors; and CF ≥6, very high contamination factor [16].

The PLI as proposed by Tomlinson et al. (1980) provide information about the quantity of a component in the environment. For a single site, the PLI is the nth root of n number of metals multiplied by Contamination factor (CF) values. A PLI value of zero indicates perfection; a value of one indicates the presence of only baseline levels of pollutants, and values above one would indicate progressive deterioration of the site and estuarine quality [17]. The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution [18-19].

$$PLI = (CF1 \times CF2 \times CF3 \times \cdots \times CFn)^{1/n} \qquad (2)$$

Where, n is the number of metals (Four in the present study).

Degree of contamination (Dc)

The degree of contamination is another index that can be derived from the CF values. Degree of contamination (Dc) is defined as the sum of all contamination factors for a given site [15]:

$$DC=\Sigma^{n}_{i}CF \qquad (3)$$

Where CF is the single contamination factor and n is the count of the elements present. Dc values less than n would indicate low degree of contamination; n≤Dc<2n, moderate degree of contamination; 2n≤Dc<4n, considerable degree of contamination; and Dc>4n, very high degree of contamination [20].

For the description of the degree of contamination in the study area the following terminologies have been used: Dc<4 low degree of contamination; 4<Dc<8 moderate degree of contamination; 8≤Dc<16 considerable degree of contamination; Dc >16 very high degree of contamination. Where, n=4= the count of the studied heavy metals.

Index of geo-accumulation **(Igeo)**

A common criterion to evaluate the heavy metal pollution in sediments is the geo-accumulation index. Geo-accumulation index was originally proposed by Muller in 1969 to determine metal contamination in sediments, by comparing current concentrations with pre-industrial levels [18, 21-22]. It can be calculated using the following formula:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (4)$$

Where, C_n is the measured concentration of a heavy metal in sediments, B_n is the geochemical background value in average shale of element n and 1.5 is the background matrix correction due to Terrigenous effects . The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the sediment. The geo-accumulation index (Igeo) was distinguished into seven classes Igeo≤0, class 0, unpolluted; 0<Igeo≤1, class 1, from unpolluted to moderately polluted; 1<Igeo≤2, class 2, moderately polluted; 2<Igeo≤3, class 3, from moderately to strongly polluted; 3<Igeo≤4, class 4, strongly polluted; 4<Igeo≤5, class 5, from strongly to extremely polluted; and Igeo>5, class 6, extremely polluted [23-26].

Ecological risk factor (Er)

An ecological risk factor (Eri) was proposed by Håkanson (1980) to quantitatively express the potential ecological risk of a given contaminant

$$Er = Tr \times CF \quad (5)$$

Where Tr is the toxic-response factor for a given substance, and CF is the contamination factor. The Tr values of heavy metals suggested by Håkanson (1980) for Pb, Cu, Cd and Zn are 5, 5, 30 and 1, respectively. The following terminologies are used to describe the risk factor: Er<40, low potential ecological risk; 40≤Er<80, moderate potential ecological risk; 80≤Er<160, considerable potential ecological risk; 160≤Er<320, high potential ecological risk; and Er≥320, very high ecological risk [15].

The potential ecological risk (RI) of the heavy metals is quantitatively evaluated by the potential ecological risk index (Er) (Håkanson,1980; Zhu et al., 2008), which takes into account both contamination factor (CF), and the "toxic-response" factor. The potential ecological risk values obtained were compared with categories grade of Er and RI of metal pollution risk on the environment as suggested [15, 27]. The potential ecological risk index (RI) just like the degree of contamination was defined as the sum of the risk factors.

$$RI = \Sigma^{n}_{i}Er \quad (6)$$

Where Er is the single index of ecological risk factor, and n is the count of the heavy metal species. The following terminology was used for the potential ecological risk index: RI<150, low ecological risk; 150≤RI<300, moderate ecological risk; 300≤RI<600, considerable ecological risk; and RI>600, very high ecological risk [15]. Where, Er and RI denote the potential ecological risk factor of individual and multiple metals, respectively.

Results and Discussion

Concentrations of heavy metals (Pb, Cu, Cd and Zn) were measured in twenty (20) surface soil samples (0- 15 cm depths) from two sites in Odioama Community, affected by oil spill. Average concentration of heavy metals in the size fraction (2mm) are (Table 1) in the following order: Cu> Pb> Zn >Cd.

The concentration of lead in the top layer of soils varies considerably due to the deposition and accumulation of pollutants from anthropogenic sources. The lead concentration in soil generally decreases as the distance from the contaminating sources increases. From Table 1, it can be seen that lead (Pb) concentration is high at around Odeama Creek well 9, and Odeama Creak well 4, this is due to the closeness of the area to the well from where the spills occurred.

The concentrations of copper (Cu) is at location 3,7,10 and 14. (Table1). According to Mathew et al., (2013) in the absence of any major industry, petroleum products (from oil spills,motor vehicles e.t.c) are considered the point sources of heavy metals such as cu to Soils [28].

The mean cadmium level in unpolluted topsoil's in the United States is approximately 0.25mg/kg, in urban garden and allotment soils in the United Kingdom the geometric mean was 0.53mg/kg in 1987/1988, and unpolluted Paddy Soils in Japan it amounted to 0.4mg/kg. Cadmium concentrations in topsoil of Europe vary from <0.03 to >0.8mg/kg. The medium value being 0.14mg/kg.

From Table 1, it can be seen that cadmium concentration in the soils is high. The concentration range from 23.40 to 47, 66mg/kg. The highest values were found in sample 5 (46.88 mg/kg), 9 (46.78 mg/kg) and 10 (47.66 mg/kg) respectively. This result is in agreement with a study by Nwachukwu et al., (1995), which opined that

Nigerian crude oil is known to have about 0.003 – 42.31 mg/kg of transition metals (V,Cr, Mn, Fe, Co, Ni and Cu) [4].

In Nigeria, the average cadmium contents in different unpolluted soils types is <0.2mg/kg [29]. Adesina et al., (2014) reported 7.2ppm of cadmium in unpolluted soils and 11.7ppm of cadmium in oil polluted oils in parts of Nigeria. The study revealed that a measure of high cadmium contents in soils around oil and gas activities is related to pollution from hydrocarbon which is enriched with cadmium [13].

Zinc is an essential trace element, which is present in soils. Soils microbial processes are particularly sensitive to Zn. Zinc can cause symptoms of deficiency and can be toxic when exposures exceed psychological needs. People are exposed to Zn primarily from food, although oral exposure can became excessive through non-dietary source. [30]. From Table 1, the concentration of zinc ranges from 35.64 to 67.86mg/kg. Matthew et al., (2013) reported that industries act as point sources for heavy metals in soils [28].

Table 1: Concentrations of heavy metals in Samples of the Study Area

Samples	Pd	Cu	Cd	Zn
1	82.79	187.2	33.20	67.86
2	88.64	176.8	28.75	54.61
3	61.45	209.8	37.60	52.79
4	88.60	196.8	43.70	48.66
5	85.49	188.9	46.88	45.33
6	74.70	166.6	37.80	43.79
7	64.78	258.8	23.44	56.64
8	68.70	187.8	28.67	66.77
9	54.89	143.9	46.78	35.64
10	69.11	208.9	47.66	61.48
11	48.54	188.6	39.10	63.73
12	44.54	188.6	28.69	51.60
13	56.61	321.6	33.45	48.70
14	66.78	227.5	27.45	39.45
15	32.65	198.7	36.66	53.43
16	23.42	177.6	42.48	48.68
17	31.44	243.8	28.83	57.75
18	24.17	233.7	23.40	39.31
19	18.66	187.9	33.18	46.63
20	24.71	165.3	41.72	53.80
CSQGS of agricultural soils	70	63	1.4	200
Average Shale	20	45	0.3	95
Tr	5	5	30	1
FEPA (1991)	0.010	1.000	0.003	3.000

Finally, the concentrations of heavy metals in oil spill affected soils in Odeama in Bayelsa State were high (except Zn) due to the introduction of elevated levels of heavy metals to the soils. CSQGS: Canadian soil quality guidelines for Agricultural Soils – Average Shale, after Turekian and wedepoli (1991) Tr: toxic- response factor of Hakanson (1980) and FEPA – Federal Environmental Protection Agency.

Pollution Indices**.**

Concentrations of Pb,Cu,Cd and Zn in the Soil samples in Odioama Community (Table1) were compared with Canadian soil quality guidelines (CSQG) of the Canadian Council of Ministers of the Environment CCME (2007), Federal Environmental Protection Agency (FEPA, 1991) and average shale of Turekian and Wedepohl (1961).

Pb concentrations in the study area are less than values of CSQG (except in samples 1, 2, 4, and 6) and more than FEPA values and average shale of Turekian and wedepohl (1961) (Table 1).

Cu concentrations of the study area are more than that of CSQG, FEPA and average shale of Turekian and wedepohl (1961). Most copper compounds will settle and be bound to water, sediment or soil particles which is also related to oil spills [31].

Cd concentration of the study area is more than the values for CSQG, FEPA and average shale of Turekian and wedepohl (1961). Studies in Nigeria have suggested that the enrichment of heavy metals like Cd in soils, is related to anthropogenic sources such as oil spill [13-29].

The concentration of Zn in soils of study area are less than that of CSQG and average shale of Turekian and wedephol (1961) but higher than that of FEPA [31].

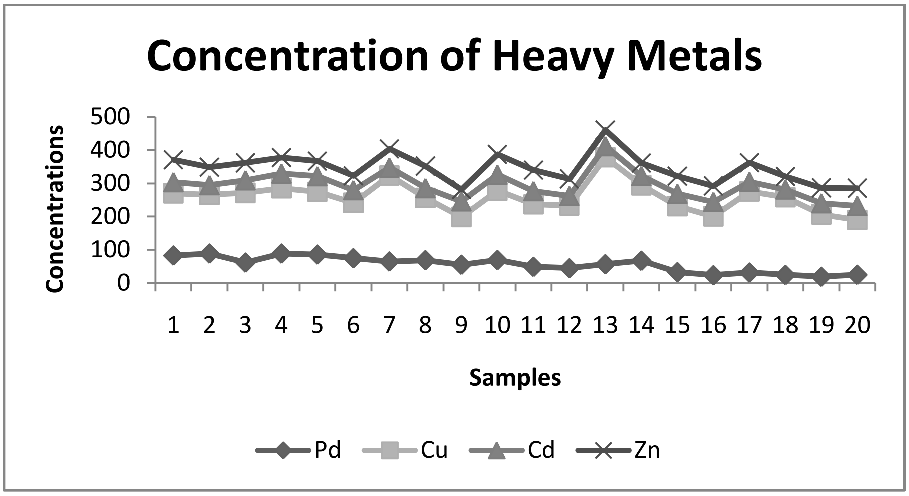

Figure 2: Concerntrations of heavy metals in Soils of the study area.

Several calculation methods have been proposed for estimating the level of metal pollution in soils of the immediate environment. In the present study, contamination factor (CF) and pollution load index (PLI), Degree of contamination (DC), index of geo-accumulation (Igeo), Ecological risk factor (Er) and potential ecological risk (RI) have been used to assess the heavy metal contamination level in the top soils samples collected from areas affected by oil spill.

The contamination factors (Table 2) calculated for all metals in all samples showed considerable contamination factors ($3 \leq CF < 6$) except in samples 13 – 20 with moderate contamination factors ($1 \leq CF < 3$).

The CF of Cu showed considerable contamination factors ($3 \leq CF < 6$) except in samples 13 with very high contamination factors ($6 \leq CF$). The CF of Cd showed considerable contamination factor ($6 \leq CF$) in all the soil samples. The CF of Zn in all the samples have low contamination factor ($CF < 1$).

The PLI values >1 in all samples indicate pollution (Table 2 and Fig 3).

For the description of the degree of contamination in the study area, the following terminologies have been used: $4 < DC < 8$ moderate degree of contamination:$8 \leq DC < 16$ considerable degree of contamination and $DC > 16$, very high degree of contamination as in all the samples (Table 2 and fig 3) where n=4. The count of the studied heavy metals.

The calculated values of Geo – accumulation index (Igeo) in oil spill affected soils of the study area are shown in Table 3 and fig.4. The negative values of Zn and Pb (samples 16- 20), according to contamination classification of Muller (1969) indicated that the soils were not polluted by these metals. Base on the results of Geo-accumulation index values for Pb in soils of samples 1 – 15 showed unpolluted as in samples 9 – 15 and moderately polluted as in samples 1 – 10. Igeo values for Cu revealed moderately polluted soils. Igeo values for Cd in all the samples showed that the samples are extremely polluted.

The ecological risk assessment results of toxic metals in soils of the study area are summarized in Table 4. The Er values of Pb, Zn and Cu in all the samples showed $Er < 40$, to have low potential ecological risk. The Er values of Cd showed $Er \geq 320$, very high ecological risks in all the samples. In order to quantify the overall potential ecological risk observed metals in soils in study area. RI was calculated as the sum of all calculation risk factors (Table 3 and fig.5). RI could characterize sensitivity of local ecosystem to the toxic metals and represents the ecological risk resulting from the overall contamination (Shi et al: 2010). RI values revealed RI >600, very high ecological risk in all the samples.

Table 2: Contamination Factor (CF) Pollution Load index (PLI) and Degree of Contamination (DC) of Oil Spills affected Soils

Samples	Pb	Cu	Cd	Zn	PLI	DC
1	4.14	4.16	110.67	0.71	6.07	119.68
2	4.43	3.93	95.8	0.57	5.55	104.73
3	3.07	4.66	125.33	0.56	5.63	133.62
4	4.43	4.37	145.67	0.51	6.16	154.98
5	4.27	4.19	156.27	0.48	6.05	165.21
6	3.74	3.70	126.0	0.46	5.32	133.9
7	3.24	5.75	78.13	0.60	5.44	87.72
8	3.44	4.17	95.57	0.70	5.57	103.88
9	2.75	3.19	155.93	0.38	4.77	162.25
10	3.46	4.64	158.87	0.65	6.38	167.62
11	2.43	4.19	130.33	0.67	2.89	137.62
12	2.23	4.19	95.63	0.54	4.69	102.59
13	2.83	7.15	111.5	0.51	5.82	121.99
14	3.34	5.06	91.5	0.42	5.05	100.32
15	1.63	4.42	122.2	0.56	4.71	128.21
16	1.17	3.95	141.6	0.51	4.27	147.23
17	1.57	5.42	96.1	0.61	4.73	103.7
18	1.21	5.19	78.0	0.41	3.76	84.81
19	0.93	4.18	110.6	0.49	3.81	116.2
20	1.24	3.67	139.06	0.57	4.36	144.54

Table 3: Geo- accumulation index of Oil Spill affected Soils in Study Area

Samples	Pb	Cu	Cd	Zn
1	1.46	1.47	6.21	-1.07
2	1.56	1.39	5.99	-1.38
3	1.03	1.64	6.38	-0.43
4	1.56	1.54	6.60	-1.55
5	1.51	1.48	6.70	-1.65
6	1.32	1.30	6.39	-1.70
7	1.11	1.94	5.70	-1.33
8	1.19	1.48	5.99	-1.09
9	0.87	1.09	6.69	-1.99
10	1.20	1.63	6.73	-1.21
11	0.69	1.48	6.44	-1.16
12	0.57	1.48	5.99	-1.47
13	0.92	2.25	6.21	-1.55
14	1.15	1.75	5.93	-1.85
15	0.12	1.56	6.35	-1.42
16	-0.36	1.39	6.56	-1.55
17	0.07	1.85	6.00	-1.30
18	-0.31	1.79	5.70	-1.86
19	-0.69	1.48	6.20	-1.61
20	-0.28	1.29	6.53	-1.41

Table 4: Ecological Risk Factors (Er) and Risk indices (RI) of Oil Spill affected Soil in Study Area

Samples	Pb	Cu	Cd	Zn	RI
1	20.7	20.8	3320.1	0.71	3,362.31
2	22.15	19.65	2874	0.57	2,916.37
3	15.35	23.3	3759.9	0.56	3,799.11
4	22.15	21.85	4350	0.51	4,394.51
5	21.35	20.95	4688.1	0.48	4,730.88
6	18.7	18.5	3780	0.46	3,817.66
7	16.2	28.75	2343.9	0.60	2,389.45
8	17.2	20.85	2867.1	0.70	2,905.85
9	13.76	15.95	4677.9	0.38	4,707.99
10	17.3	23.2	4766.1	0.65	4807.25
11	12.15	2095	3909.9	0.67	3,943.67
12	11.15	20.95	2868.9	0.54	2,901.54
13	14.15	35.75	3345	0.51	3,395.41
14	16.7	25.3	2745	0.42	2,787.42
15	8.15	22.1	3666	0.56	3,696.81
16	5.85	19.75	4248	0.51	4,274.11
17	7.85	27.1	2883	0.61	2,918.56
18	6.05	25.95	2340	0.41	2,372.41
19	4.65	20.9	3318	0.49	3,344.04
20	6.2	18.35	4171.8	0.57	4,196.92

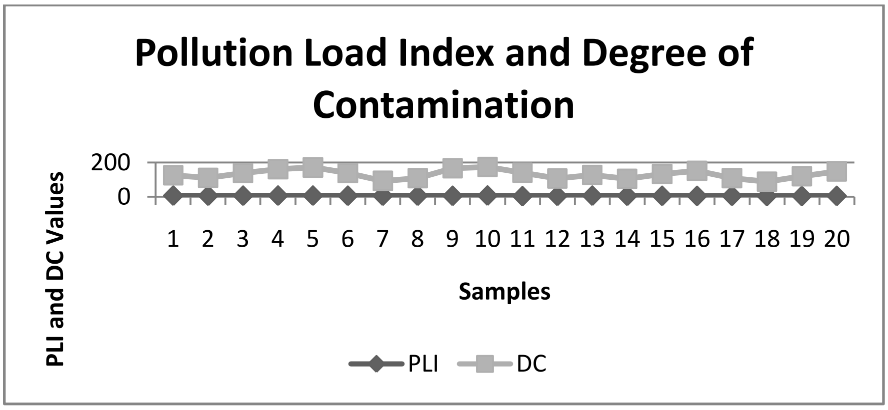

Figure 3: PLI and Dc of the Soils of the study area.

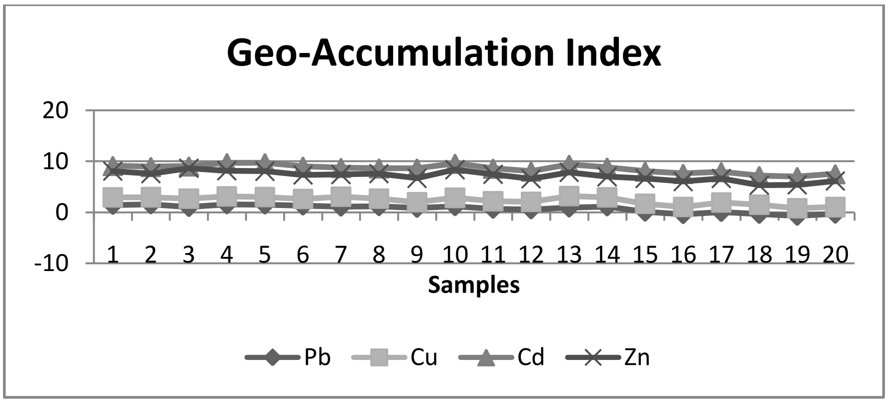

Figure 4: Igeo of the Soils in study area.

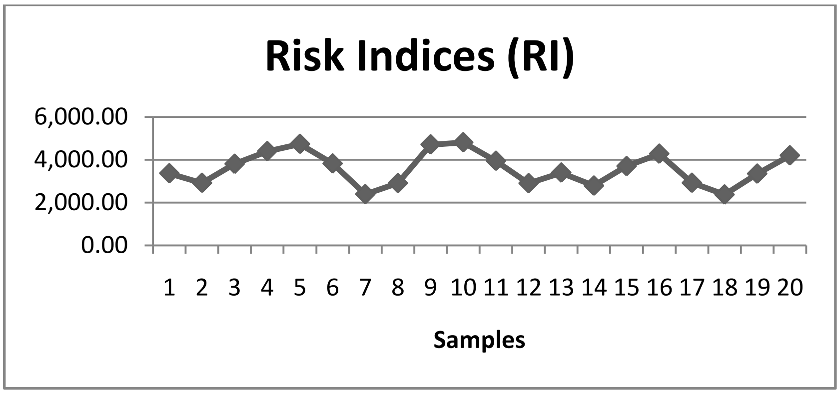

Figure 5: RI of the soils of the study area

Conclusions

The concentrations of heavy metals in soils of the study area were high due to the oil spills into soils of the study area. Average concentration of heavy metals are in the following order Cu>Pb>Zn>Cd.

The concentration of Pb in the study area is more than that of CSQG (except in samples 3, and 7 -12) and the average Turekian and wedepohl (1961). Cu and Cd concentrations of the study area are more than that of CSQG and more than FEPA and Turekian and wedepohl (1961). Zn concentrations in all the samples are less than that of CSQG, and average Turekian and wedepohl (1961) but more than FEPA (1991).

The contamination factor of Pb in all samples showed moderate in samples 15-20 (1≤Cf <3) to considerable contamination factors (3≤Cf <6), in samples1-14. The Cf of Cu showed a considerable contamination factors samples 1-12 and 14-20 and very high contamination factor (sample 13). For Zn, the Cf revealed low contamination in all the samples. The Cf of Cd showed very high contamination factor in all the samples.

The Er values Pb, Zn and Cu showed low potential ecological risk (Er <40) in all the samples. The Er values for Cd revealed very high potential ecological risk (Er≥320) in all the samples. The potential ecological risk index RI, for all the metals and samples were of very high ecological risk (RI >600).

The soils of the study areas are contaminated and the contamination is due to oil spills.

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