



## **Soil Pollution Assessment from Industrial Area of Erbil City**

Shelan Mustafa Khudhur and Nashmeel Saeed Khudhur

*Department of Environmental Science, College of Science, University of Salahaddin, Kurdistan Region, Iraq*

*E.mail: phdsceince09@gmail.com*

---

### **Article info**

Original: 13 May 2015  
Revised: 15 June 2015  
Accepted: 25 June 2015  
Published online:  
20 Dec. 2015

#### **Key Words:**

*Soil pollution  
Heavy metals  
Oil residues  
Industrial area*

### **Abstract**

Present study assessed soil pollution by heavy metals and spent oil in three industrial areas of Erbil City. Soil pH ranged from  $7.53 \pm 0.017$  to  $8.25 \pm 0.012$  and EC was ranged between  $103 \pm 0.882$  and  $465 \pm 9.955$ . Soils textures were loamy sand for south industry, sandy for oil selling area and north industry while loamy for control soil. The ranges of Pb, Zn and Ni were between  $1.26 \pm 0.069$  and  $17.472 \pm 0.058$ ;  $1.439 \pm 0.006$  and  $3.078 \pm 0.003$ , and  $0.399 \pm 0.061$  and  $0.982 \pm 0.048$  ppm, respectively. The concentrations of Cd and Cr were below the detection limit and Cu levels varied from  $10.307 \pm 0.334$  to  $0.063 \pm 0.003$  ppm, whereas Cu was not detected in some sites. The highest oil residue was obtained in site 6. Oil and grease content for the groundwater samples in the studied sites were zero. Pearson's correlation showed a significant positive correlation between Ni and moisture content and Ni and bulk density, beside to a moderate correlation between Pb and Zn. A high significant negative correlation was detected between bulk density and oil content. The lateral distribution of the heavy metals and oil residues showed higher average concentrations at the point of impact than 20 meters away. Relative Pollution Potential gave positive values for the metals and oil contents in all sites.

### **Introduction**

The soil is the primary recipient of a myriad of waste products and chemicals used in modern industrial society. Contamination of soil with petroleum mineral oil and mineral oil-based products is among the most common sources of pollution in industrial areas of Erbil city. The activities of each of these areas generate gaseous, liquid and solid pollutants which affect the immediate environment [1]. Repairs and servicing of automobiles and other types of machinery in mechanic workshops are sources of different pollutants in the area [2]. Among these pollutants, the spent oil, otherwise called waste-lubricating oil, obtained after servicing and subsequent draining from automobile, generators and industrial machines is disposed of indiscriminately, and has not been given the adequate attention it deserves [3]. There are several components of oil, including solvents and detergents added during the blending process, aliphatic hydrocarbons and PAHs distilled from crude oil, and heavy metals from engine wear, and these are either toxic in themselves or can combine with products of combustion to generate toxicity [4]. Heavy metals form a very important part of the non-hydrocarbon component of oil. They are described as metals occurring at  $1000 \text{ mg.kg}^{-1}$  or less in the environmental matrices. Some trace metals are hazardous while others are not, if they are in normal concentrations. A number of them are essential at low concentration but becomes deleterious at high

concentrations [5]. Heavy metal pollution of the soil is caused by various metals especially copper, nickel, cadmium, zinc, chromium, and lead [6] and the type of the metals present in certain waste depends on processes which generated this waste [3]. Oil-contaminated soils are of environmental concern because they are unsuitable for agricultural and recreational uses and are potential sources for surface and ground water contamination. Oil-polluted soil could also become unsuitable due to a reduction in the level of available plant nutrients or a rise to a toxic level of elements such as manganese [4] and also adversely affect soil dependant organisms [6]. Used oil is less viscous than unused oil; when disposed of into the soil, it adsorbs to the soil particles, reduces porosity and therefore reduces aeration of soil [7]. The heavy metals belong to types of toxic substances that have adverse effects on health. Several studies have shown that metals, such as Pb, Cd, and Ni, are responsible for certain diseases of man and animals [8]. Environment Canada (1996) reported that heavy metals might adversely affect specific tissues, reproduction and development. This may also cause anemia, nervous system disorders and depressed immune systems, resulting in mortality and effects on population levels [3]. Due to these effects, it has been found an importance to investigate the levels of soil heavy metals and oil residues within the industrial areas of Erbil city as an objective of this study with viewing of soil quality assessment due to the effect of the workshop activities.

## **Materials and methods**

### ***A/ Study area***

Erbil governorate is the capital of Iraqi Kurdistan Region (*Figure: 1*). It is one of the oldest continuously inhabited communities in the world which was founded before 2300 B.C. [9]. Geographically Erbil is elevated by 414 m a.s.l., it locates on longitude 43° 15' E and latitude 35° 11' N to 37° 24' N. It covers a total of 16484 km<sup>2</sup> with population of 1300000 [10]. The city is situated within recent sediment which belongs to palaeocin age that represents old river sedimentation which came from Bactaric formation. Their stones are composed of lentical and stratigraphs from stone, sand, silt and alluvial [11]. The soil of Erbil is calcareous because it originates from limestone and dolomite of different formation [12]. The topsoil is calcareous and may contain 1-2% organic matter and this type of soil occurs in areas with hot-dry summers and cold-rainy winters [13]. Erbil climate is most closely approaches Irano-Turanian type, characterized by cold winters, mild-growing period of springs and hot summers. It locates in semi-arid zone [14].

### ***B/ Sampling sites***

The studied sites of the present investigation were the main industrial areas of Erbil city including South Industrial Area (sites 1: 20 meters away from the industry) and (sites 2: centre of the industry or the impacted point), Oil Selling Area (sites 3: 20 meters away from the area) and (sites 4: centre of the area), North Industrial Area (sites 5: 20 meters away from the industry) and (sites 6: centre of the industry) and Greenhouse soil in the College of Science (site 7) as a control soil which is far from the influence of any industrial or traffic activity. These areas compromised as the major centre for auto-mechanics, automobile repairing, panel beaters, spraying painters and servicing and in some cases, car wash personnel. In November 2013, soil samples (0-10 cm depth) from these areas were collected into polyethylene bags using trowel. The soil samples were then taken to the laboratory for analysis.

### ***C/ Soil physicochemical analysis***

Soils were air-dried, crushed and sieved for various physico-chemical parameters through 2-mm stainless sieve to remove debris [7]. Soil moisture content was determined by gravimetric method in which the samples were dried to constant weight as described by [15]. Bulk density was determined by core method as described by [16]. The pycnometer method described by Black (1965) was used to determine particle density. Total pore space was calculated from particle density and bulk density according to [16]. The pH and EC of the soils were determined using a calibrated pH-meter (JENWAY 3505) and an electrical

conductivity meter (JENWAY 4510) in 1:1 (soil: water suspension) in line with the method proposed by [17]. Particle size distribution and soil texture was determined by hydrometer method according to [17].

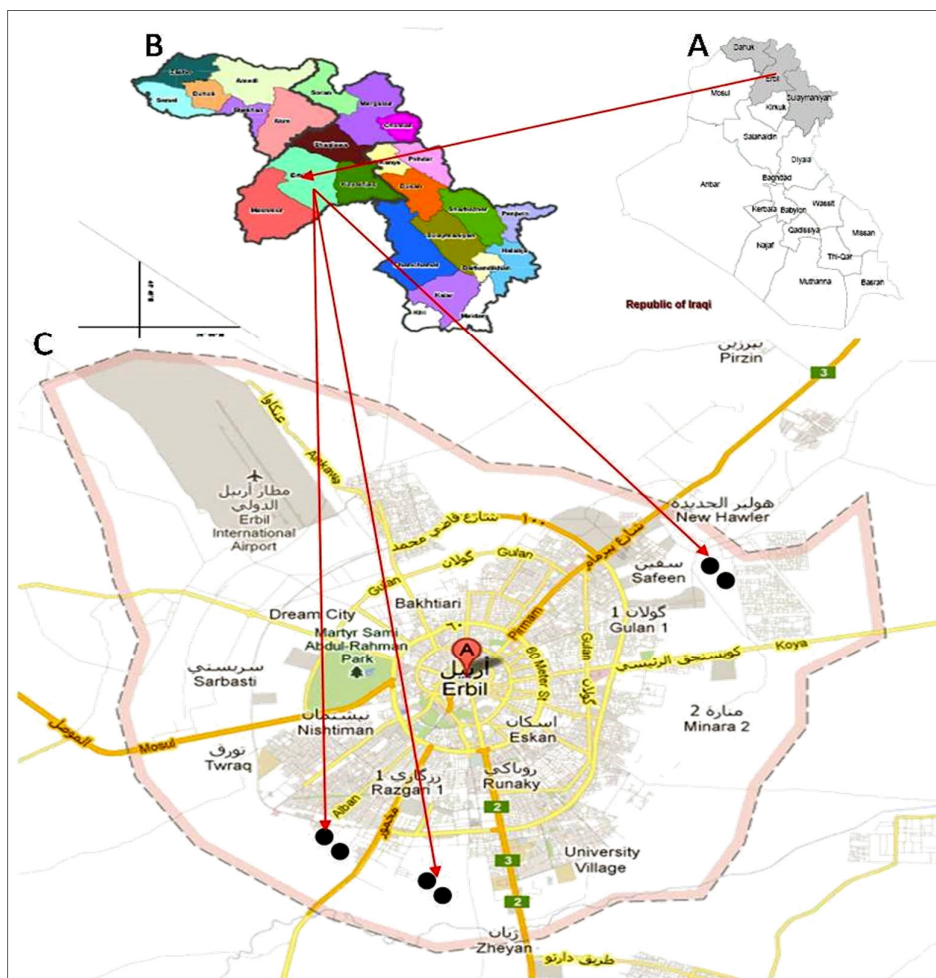


Figure-1: Map showing A. Iraq, B. Kurdistan Region and C. Erbil City with the studied area.

#### ***D/ Chemicals and solvents used***

The chemicals and solvents used for laboratory analysis were ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , toluene solvent and petroleum ether 40-60 °C which are from Analar R company-England; and the standard solutions of Pb, Cd, Cu, Zn, Ni and Cr obtained from Sigma company-U.S.A.).

#### ***E/ Soil heavy metal analysis***

Mixed-acid digestion of 1 g of each soil sample was done by using a mixture ( $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ ) at the ratio 15:5:2 (v:v), then the solutions were filtered through Whattman No. 1 filter papers and used as test samples for analyses of Pb, Cd, Cu, Zn, Ni and Cr using Flame Atomic Absorption spectrophotometer (Pg instrument AA500 Atomic Absorption) [18].

#### ***F/ Oil residue determination in the soil***

Oil residues were determined spectrophotometrically according to the toluene extraction method by taking 1 g of air-dried and homogenized soil into a 50 ml conical flasks and 10 ml of toluene added to extract the oil in the soil. After shaking vigorously, the mixture was allowed to stand for 10 minutes and then it was filtered through Whatman No. 1 filter paper. The extracted oil was diluted appropriately with fresh toluene

and the absorbance read at 420 nm in spectrophotometer (digital-JENWAY 6300) and a standard curve from known concentrations of fresh crude oil was prepared for determination of oil concentrations [19].

### ***G/ Oil and grease determination for ground water samples***

Oil and grease in groundwater samples were determined according to Best and Ross, (1977) [20] using solvent extraction method. Oil, grease and other extractable materials were dissolved in petroleum ether 40-60 °C under acidic condition and separated from the aqueous phase. The solvent layer was then evaporated, oven dried at 70 °C and the residue weighted as oil and grease.

### ***H/ Statistical analysis and quality control***

Statistical analysis for the obtained data was performed by SPSS version 11.5 and Microsoft excel 2010, using descriptive statistics and ANOVA accompanied with Duncan's test for comparing of the means at the level of significant of 0.05. Person's correlation was determined between the physicochemical characteristics with the heavy metals and oil residues as well as between particle size distribution with heavy metals and oil residues. Relative Pollution Potential computed using the scheme followed by Egharevba and Odjada reported by [21]. In order to ensure quality control in the course of the analyses, all the reagents used were analytical grades. Reagent blanks were also run in order to check purity of the reagents. Analyses were done in triplicate to ensure precision of the analytical procedure and the instruments used.

## **Results**

The results of the physicochemical parameters of the soil samples collected from the studied area are presented in table 1 and figure 2. The highest moisture content was observed at site 7 and there were no significant differences between the studied sites. Bulk density was ranged between 0.791±0.029 and 1.162±0.026. The highest particle density and total pore space were in site 1 and significant differences between the studied sites were evident. The pH of the soil ranged from 7.53±0.017 to 8.25±0.012, indicating neutral to slightly alkaline soils. Significant differences between pH of the soils in sites 1, 2, and 6 were observed when compared with control. The highest EC of 424±6.928 and 465±9.955  $\mu\text{S}\cdot\text{cm}^{-1}$  was obtained in both sites 1 and 4 and the lowest EC of 103±0.882  $\mu\text{S}\cdot\text{cm}^{-1}$  was in control soil, however there were significant differences between all of the studied sites. Particle size distribution and texture classes of the studied soils were tabulated in table 2, soil of south industry was belonged to loamy sand class while both oil selling area and north industry have sandy soils, however control soil is loamy. The concentration of heavy metals from the studied soils is presented in table 3. The distributions of Pb, Zn and Ni around the studied sites are presented in figures 3, 4 and 5. Results showed a high concentration of Pb (17.472±0.058) ppm at site 6. Statistical analysis showed significant differences between the studied sites except for the sites 1 and 3 which were Pb values lower than control soil Pb and the lowest Pb level was recorded in site 1 (1.26±0.069) ppm. In spite of the recorded high level of Pb by this study, it is still below the acceptable level (table 3) except at site 6 where sudden increase occurred. The concentrations of Cd and Cr were so low that they were below the detection limit of the instrument used in this study. Copper levels varied from 10.307±0.334 ppm in site 6 and to 0.063±0.003 ppm in site 2, whereas Cu values were not detected in sites 1, 3, 4 and 7. Statistical analysis of Zn concentrations showed that there were significant differences ( $p<0.05$ ) between all of the studied sites in comparing with control soil, but the concentrations were no exceed the maximum acceptable levels (table 4). The highest Zn value in the studied soils was recorded in site 6 which was (3.078±0.003) ppm, while the lowest value was recorded in site 1 which was 1.439±0.006 ppm. Results of Ni concentrations observed that there were no significant differences between the studied sites and the range of Ni level in the studied soils were between 0.399±0.061 and 0.982±0.048 ppm in sites 3 and 7 respectively. The highest oil residue was observed in site 6 (0.034±0.001), while zero value of oil residue was in control site (table 5), and statistical analysis showed significant differences between the studied soils in comparing with control, except for the sites 1 and 5 where the same contents of oil were detected. Results of oil and grease content in groundwater samples of the studied sites indicated that there were no significant differences

( $p < 0.05$ ) between the studied sites (table 5); however zero values were recorded for all of the studied groundwater samples at all sites. The obtained results of hydrometer method showed that the soils were loamy sand for south industry, sandy for both oil selling area and north industry, while the texture was loamy for control soil. From the computation of pearson's correlation between the heavy metals and oil residues with the physicochemical characteristics of the studied soils (table 6), a significant positive correlation was obtained for Ni:moisture content (figure 6) and Ni:bulk density (figure 7) at 0.05 level of significance. A moderate correlation between Pb and Zn was observed by  $r$  value of 0.562 (figure 8). A highly significant negative correlation was detected between bulk density and oil residue content at level of significance 0.01 (figure 9). A highly significant positive correlation between particle density and total pore space was observed at level of significance 0.01 (figure 10). Results of pearson's correlation between particle size distribution with heavy metals and oil residues were presented in table 7, however, there were significant negative correlations for sand:silt, sand:clay and silt:clay by  $r$  values of -0.999, -0.998 and -0.994 respectively at level of significance 0.05. The lateral distribution of the heavy metals and oil contents of soil samples are presented in table 8; it showed that the soils at the point of impact had higher average concentrations of the metals and oil contents than 20 meters away. For the detected metals and oil residues, Relative Pollution Potential is presented in table 9. The results gave positive values for all the metals and oil residues in all sites.

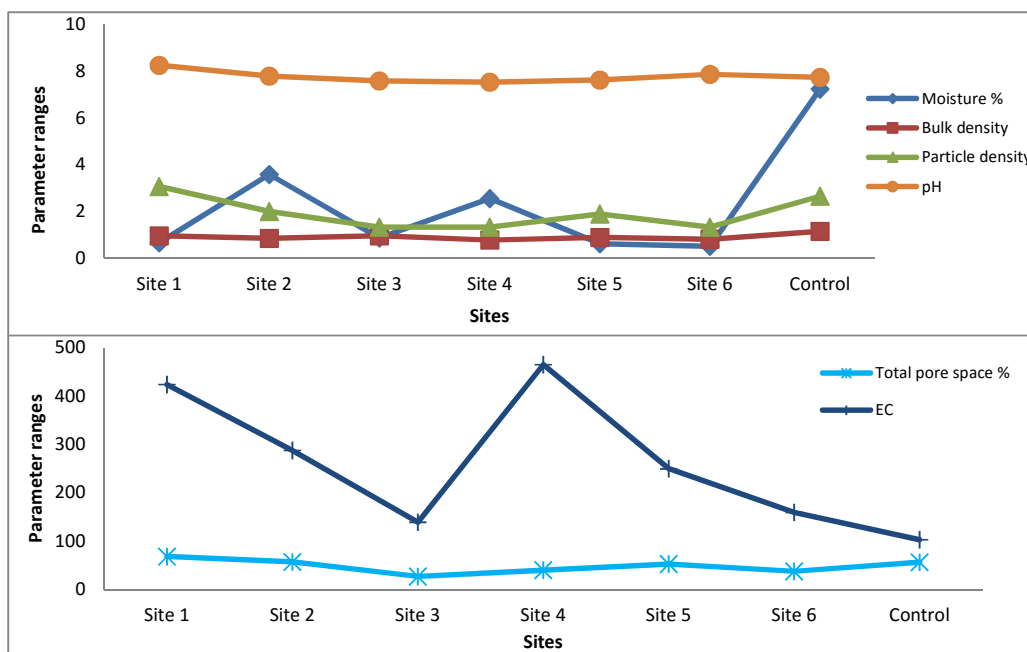


Figure-2: Variation of physicochemical properties in different studied sites.

Table-1: Physicochemical properties of the studied soils (mean  $\pm$  S.E.).

Sites	Moisture %	Bulk density $g.cm^{-3}$	Particle density $g.cm^{-3}$	Total pore space %	pH	EC $\mu S.cm^{-1}$	
<b>South Industry</b>	1	0.673 $\pm$ 0.008 <sup>e</sup>	0.971 $\pm$ 0.012 <sup>b</sup>	3.077 $\pm$ 0.013 <sup>a</sup>	68.455 $\pm$ 0.006 <sup>a</sup>	8.25 $\pm$ 0.012 <sup>a</sup>	424 $\pm$ 6.928 <sup>a</sup>
	2	3.582 $\pm$ 0.114 <sup>b</sup>	0.860 $\pm$ 0.012 <sup>cd</sup>	2.000 $\pm$ 0.003 <sup>c</sup>	56.986 $\pm$ 0.297 <sup>b</sup>	7.78 $\pm$ 0.006 <sup>c</sup>	288 $\pm$ 6.351 <sup>b</sup>
<b>Oil Selling Area</b>	3	0.878 $\pm$ 0.007 <sup>d</sup>	0.971 $\pm$ 0.018 <sup>b</sup>	1.333 $\pm$ 0.002 <sup>e</sup>	27.163 $\pm$ 0.002 <sup>g</sup>	7.58 $\pm$ 0.017 <sup>e</sup>	139 $\pm$ 17.898 <sup>cd</sup>
	4	2.563 $\pm$ 0.018 <sup>c</sup>	0.791 $\pm$ 0.029 <sup>e</sup>	1.333 $\pm$ 0.001 <sup>e</sup>	40.665 $\pm$ 0.578 <sup>e</sup>	7.53 $\pm$ 0.017 <sup>f</sup>	465 $\pm$ 9.955 <sup>a</sup>
<b>North Industry</b>	5	0.632 $\pm$ 0.018 <sup>ef</sup>	0.898 $\pm$ 0.008 <sup>c</sup>	1.905 $\pm$ 0.003 <sup>d</sup>	52.857 $\pm$ 0.581 <sup>d</sup>	7.62 $\pm$ 0.023 <sup>e</sup>	250 $\pm$ 23.094 <sup>b</sup>
	6	0.518 $\pm$ 0.010 <sup>f</sup>	0.826 $\pm$ 0.008 <sup>de</sup>	1.333 $\pm$ 0.005 <sup>e</sup>	38.041 $\pm$ 0.578 <sup>f</sup>	7.86 $\pm$ 0.003 <sup>b</sup>	160 $\pm$ 8.660 <sup>c</sup>
<b>Control</b>	7	7.230 $\pm$ 0.017 <sup>a</sup>	1.162 $\pm$ 0.026 <sup>a</sup>	2.667 $\pm$ 0.001 <sup>b</sup>	56.420 $\pm$ 0.006 <sup>c</sup>	7.74 $\pm$ 0.003 <sup>d</sup>	103 $\pm$ 0.882 <sup>d</sup>

Table-2: Particle size distribution (%) and texture classes of the studied soils.

Sites		Particle size distribution			Texture class
		Sand %	Silt %	Clay %	
South Industry	1	59.13	25.54	15.33	Loamy sand
	2	59.02	25.59	15.39	Loamy sand
Oil Selling Area	3	94.91	5.09	0	Sandy
	4	94.89	5.11	0	Sandy
North Industry	5	94.97	5.03	0	Sandy
	6	94.92	5.08	0	Sandy
Control	7	48.94	33.19	17.87	Loam

Table-3: Concentrations of soil heavy metals (ppm) from the studied sites (mean ± S.E.).

Sites		Pb	Cd	Cu	Zn	Ni	Cr
South Industry	1	1.26±0.069 <sup>g</sup>	N.D.	N.D.	1.439±0.006 <sup>f</sup>	0.434±0.029 <sup>e</sup>	N.D.
	2	4.291±0.012 <sup>c</sup>	N.D.	0.063±0.003	2.208±0.004 <sup>c</sup>	0.476±0.021 <sup>d</sup>	N.D.
Oil Selling Area	3	2.387±0.017 <sup>f</sup>	N.D.	N.D.	1.691±0.002 <sup>e</sup>	0.399±0.061 <sup>f</sup>	N.D.
	4	3.586±0.012 <sup>d</sup>	N.D.	N.D.	1.974±0.006 <sup>d</sup>	0.519±0.084 <sup>c</sup>	N.D.
North Industry	5	8.59±0.017 <sup>b</sup>	N.D.	3.619±0.473	2.495±0.002 <sup>b</sup>	0.494±0.015 <sup>cd</sup>	N.D.
	6	17.472±0.058 <sup>a</sup>	N.D.	10.307±0.334	3.078±0.003 <sup>a</sup>	0.579±0.060 <sup>b</sup>	N.D.
Control	7	3.378±0.003 <sup>e</sup>	N.D.	N.D.	0.545±0.001 <sup>g</sup>	0.982±0.048 <sup>a</sup>	N.D.

N.D.: not detected.

Values on the same column with different superscript mean significant differences.

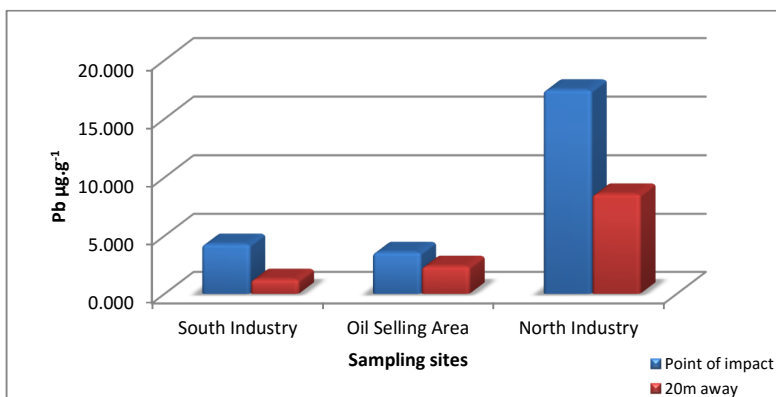


Figure-3: Relation of Pb concentrations, between the center of the industrial area and 20 meters away from the sampling sites.

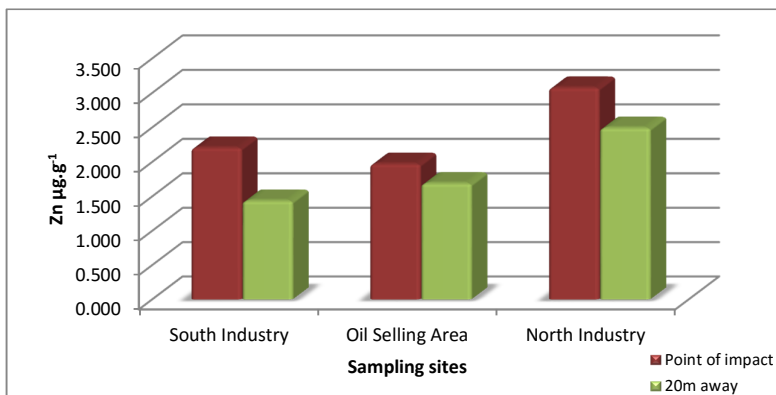


Figure-4: Relation of Zn concentrations, between the center of the industrial area and 20 meters away from the sampling sites.

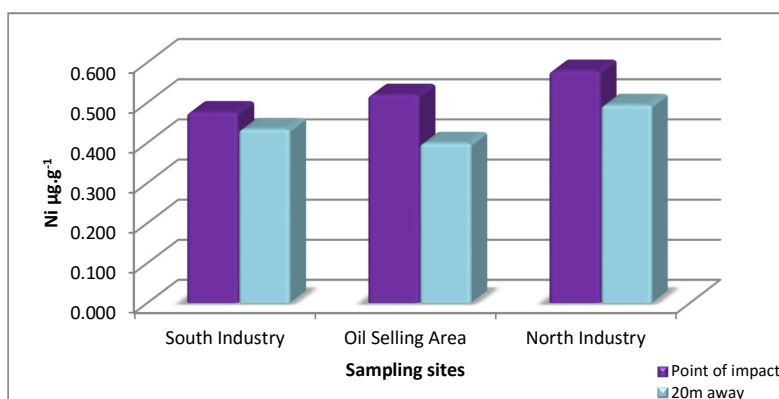


Figure-5: Relation of Ni concentrations, between the center of the industrial area and 20 meters away from the sampling sites.

Table-4: Contents and acceptable limits of the studied heavy metals in soil.

<i>Element</i>	<i>Content (mg.kg<sup>-1</sup>)</i>	<i>Acceptable limit (µg.g<sup>-1</sup>)</i>
<i>Cd</i>	0.01-0.70	0.03-0.30
<i>Cr</i>	1-1000	70
<i>Cu</i>	2-100	30-40
<i>Ni</i>	5-500	30-70
<i>Pb</i>	2-200	85-450
<i>Zn</i>	10-300	135-150

Soil contents of the studied metals taken from [32] and the acceptable limits taken from [7] and [33].

Table-5: Oil residue in the studied soils and oil and grease content in the groundwater samples of the studied sites.

<i>Sites</i>	<i>Oil residue (ppm) in soil samples</i>	<i>Oil and grease (ppm) in groundwater samples</i>
<i>South Industry</i>	1	0.015±0.001 <sup>d</sup>
	2	0.025±0.001 <sup>b</sup>
<i>Oil Selling Area</i>	3	0.010±0.001 <sup>e</sup>
	4	0.022±0.001 <sup>c</sup>
<i>North Industry</i>	5	0.015±0.001 <sup>d</sup>
	6	0.034±0.001 <sup>a</sup>
<i>Control</i>	7	0.000±0.000 <sup>f</sup>

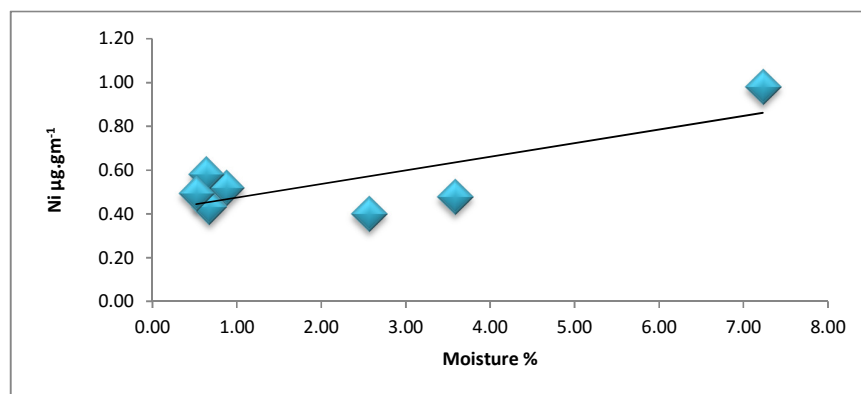


Figure-6: Correlation between moisture and Ni in soil samples of the studied sites.

Table-6: Pearson’s correlation coefficients between the heavy metal concentrations and oil residues with soil physicochemical properties of different sites.

	Moisture %	Bulk density	Particle density	Total pore space %	pH	EC	Pb	Zn	Ni	Oil residues
Moisture %	1									
Bulk density	0.612	1								
Particle density	0.353	0.642	1							
Total pore space%	0.275	0.308	0.900**	1						
pH	-0.172	0.181	0.721	0.673	1					
EC	-0.280	-0.516	0.142	0.358	0.243	1				
Pb	-0.332	-0.423	-0.458	-0.302	-0.038	-0.346	1			
Zn	-0.726	-0.697	-0.534	-0.270	-0.223	0.033	0.562	1		
Ni	0.780*	0.851*	0.388	0.183	-0.127	-0.665	-0.082	-0.549	1	
Oil residues	-0.530	-0.890**	-0.518	-0.211	0.082	0.289	0.656	0.624	-0.716	1

\* Correlation is significant at the 0.05 level (2-tailed).

\*\* Correlation is significant at the 0.01 level (2-tailed).

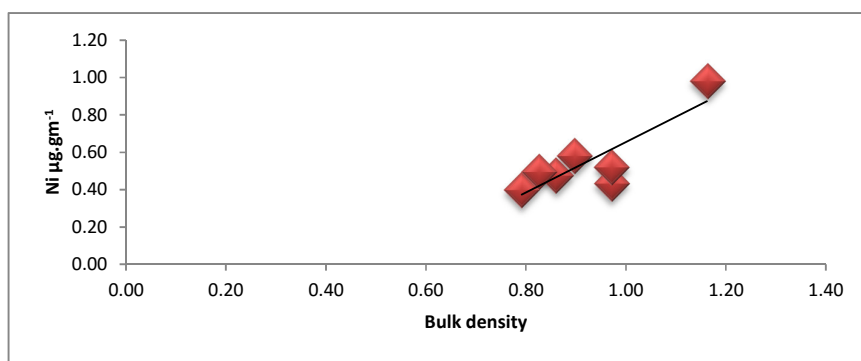


Figure-7: Correlation between bulk density and Ni in soil samples of the studied sites.

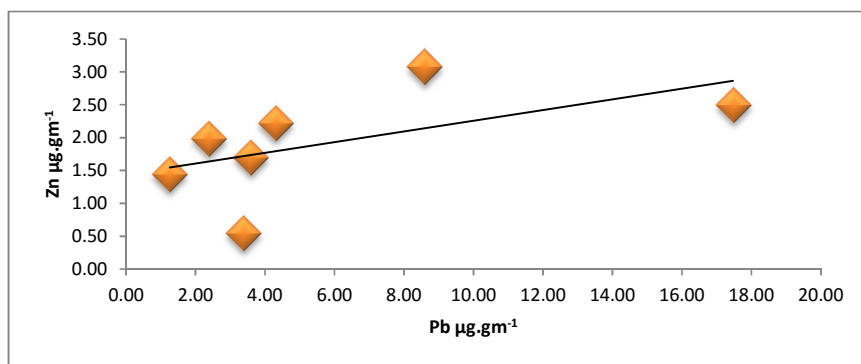


Figure-8: Correlation between Pb and Zn in the studied soil samples.

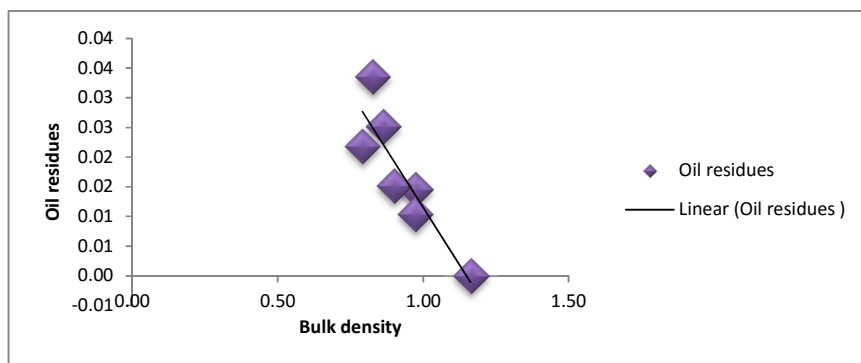


Figure-9: Correlation between bulk density and oil residues in the studied soils.



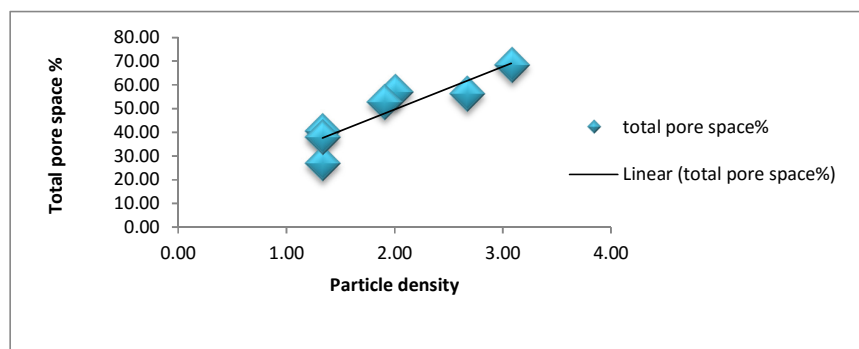


Figure-10: Correlation between particle density and total pore space in the studied soils.

Table-7: Pearson’s correlation coefficients between particle size distribution with heavy metals and oil residues of different sites.

	<i>Sand %</i>	<i>Silt %</i>	<i>Clay %</i>	<i>Pb</i>	<i>Zn</i>	<i>Ni</i>	<i>Oil residues</i>
<i>Sand %</i>	1						
<i>Silt %</i>	-0.999*	1					
<i>Clay %</i>	-0.998*	-0.994*	1				
<i>Pb</i>	0.467	-0.462	-0.473	1			
<i>Zn</i>	0.679	-0.697	-0.650		1		
<i>Ni</i>	-0.497	0.533	0.445	-0.082	-0.549	1	
<i>Oil residues</i>	0.437	-0.460	-0.401	0.656	0.624	-0.0716	1

\*Correlation is significant at the 0.05 level (2-tailed).

Table-8: Lateral distribution of the metals ( $\mu\text{g.g}^{-1}$ ) and oil content (ppm) in soils 20m away from the industrial areas.

<i>Metals</i>	<i>Sites</i>	<i>Point of impact</i>	<i>20m away</i>
<b><i>Pb</i></b>	<i>South Industry</i>	4.291	1.26
	<i>Oil Selling Area</i>	3.586	2.387
	<i>North Industry</i>	17.472	8.59
<b><i>Cu</i></b>	<i>South Industry</i>	-	-
	<i>Oil Selling Area</i>	-	-
	<i>North Industry</i>	10.307	3.619
<b><i>Zn</i></b>	<i>South Industry</i>	2.208	1.439
	<i>Oil Selling Area</i>	1.974	1.691
	<i>North Industry</i>	3.078	2.495
<b><i>Ni</i></b>	<i>South Industry</i>	0.476	0.434
	<i>Oil Selling Area</i>	0.519	0.399
	<i>North Industry</i>	0.579	0.494
<b><i>Oil residues</i></b>	<i>South Industry</i>	0.025	0.015
	<i>Oil Selling Area</i>	0.022	0.010
	<i>North Industry</i>	0.034	0.015

Table-9: Relative Pollution Potential of the studied metals.

<i>Sites</i>	<i>Pb</i>	<i>Cu</i>	<i>Zn</i>	<i>Ni</i>	<i>Oil residues</i>
<i>South Industry</i>	0.706	-	0.348	0.088	0.400
<i>Oil Selling Area</i>	0.334	-	0.143	0.231	0.545
<i>North Industry</i>	0.508	0.649	0.189	0.147	0.559

## Discussion

The moisture content observed in the present study is similar to that obtained by [31] in industrial area of Mysore. The observations of [23] in old gasoline-contaminated site in Anand appear to be close to the present findings with regard to bulk density. Soil pH is one of the main parameter for determining the extent of pollution; it has been identified as a principal factor that affects the mobility and availability of metals in soil [24]. The pH of the soil ranged from  $7.53 \pm 0.017$  to  $8.25 \pm 0.012$ , indicating neutral to slightly alkaline soils, the finding is closed to those obtained by [25] and [26]. Such pH values are characteristic of soils in areas where leaching is less pronounced due to low precipitation, resulting in the concentration of base forming cations in the place of acid contributing cations such as  $Al_3^+$  and  $H^+$  [26]. The highest EC was obtained in both sites 1 and 4 which is similar to the observations of [23]; [26] and [21] in Kakuri industrial area, old gasoline-contaminated site in Anand and automobile workshops in Abraka respectively. The lowest EC in control soil is close to that observed by [26]. The variation in the electrical conductivity values could be attributed to differences in the soluble salt content of the soils [26] or it could be attributed to the reactions between some spilled acids from batteries and some metals from vehicle scraps leading to formation of some soluble and ionisable inorganic salts in the soils [21]. A high concentration of Pb ( $17.472 \pm 0.058$ ) ppm which observed at site 6 is closed to that obtained by [21] in eight sites out of twenty-four sites in cement factory of Anbar. As well, the obtained Pb in south industry and oil selling area is closed to that obtained by [27] in soils around Apir auto-mechanic shop refuse dumpsites in Makurdi metropolis, while the environment surrounding the workshops is highly polluted with Pb and Cu in a similar study conducted by [28] in the same textured soil containing a range of sand 73.5-90.1% and this high mean values in these areas could be attributed largely to the activities in the auto mechanic clusters and it is possible that these levels of Pb is elevated by the amount of waste oil, presence of automobile emissions, and expired motor batteries indiscriminately dumped by battery chargers and auto mechanics in the surrounding areas. Site 6 in the present study, is not only a major service centre for light and medium vehicles, but also a centre for autobike, motorskile and electricity, generator repairs and service. The elevated value of Pb at this site could be also attributed to its proximity to the main commercial and touristic road of Shaqlawa resulting to discharge from vehicular and automobile emissions as well as its vicinity to the electricity generation power plant of 29 Megawatt and possible spill from there could have caused the high level of Pb concentration and oil residue. In spite of the recorded high level of Pb by this study, it is still below the acceptable level (table 4). The not detected limits of Cd at sites out of 8 studied sites by [26] seem to confirm the present finding. The detected level of Cu in sites 5 and 6 are however higher than those reported by [21] and this may refer to the used oils that sink into the ground as leachates contain high proportions of copper as well as lead and antimony. Metal bearing wears are also a possible source of copper as well as copper cables are used as electrical light source. Statistical analysis of Zn concentrations showed that there were significant differences ( $p < 0.05$ ) between all of the studied sites in comparing with control soil, and this increase may refer to the oil spills from these area, but the concentration were no exceed the maximum acceptable levels (table 4). Zinc values were ranged between  $1.439 \pm 0.006$  and  $3.078 \pm 0.003$  ppm in sites 1 and 6 respectively and results of [5] in oil spillage sites close to the present findings, while higher levels recorded by [21]. Zinc in form of zinc oxide is a component of paint, so zinc levels in the soils could be as a result of the activities of the spray painter and also vehicle body paints. It is also a component of crude oil tyre and automobile exhaust and so its concentration could also be attributed to this. Zinc is involved in various metabolic activities of many organisms [29]. Results of [5] regarding to Ni in oil spillage sites close to the results obtained in the main industrial areas by this study. Nickel and Chromium are toxic, so the low concentrations of the former and the not detected limits of the later is good for the environment and this may be due to the spilled oil being low in these metals [8]. The obtained oil content range by this study (table 5) was near to that obtained by [30] in sand to loamy sand soil who obtained a range of 0.002-1.798 ppm in a medium impacted zone by oil content in Nigerian soil. The zero levels of oil and grease content of groundwater indicated that there is no leaching of spent oil in the industrial area. Pearson's correlation was computed for the investigated heavy metals, oil residues, physicochemical characteristics and particle size distribution to determine their

interrelationship with each other (tables 6 and 7). The moderate correlation between Pb and Zn (figure 8) by  $r$  value of 0.562 is similar to the observation of [31] by a correlation coefficient value of 0.47 at level of significance 0.05. The lateral distribution of the heavy metals and oil residues showed that the soils at the point of impact had higher average concentrations than 20 meters away. This is consistent with some other reports [8]; [22] and [21] regarding to the heavy metals. Relative Pollution Potential is a measure of the level of chemical interaction between the pollutant and the recipient. For the detected metals and oil residues, Relative Pollution Potential gave positive values for all the metals and oil residues in all sites indicating that the soils were contaminated at the point of impact.

## **Conclusion**

The study concluded that, the detected heavy metal contents are introduced by so many sources, proximity to the main roads and human activities, whereas the spent oil residues came from man's activities in the industrial area. The lateral distribution of the heavy metals and spent oil residues showed that the soils at the point of impact had higher average concentrations than 20 meters away. Industrial areas have been implicated for elevated concentration of Pb, Cu, Zn and Ni in soils as well as spent oil residues and relative pollution potential for these pollutants indicated that the soils were contaminated at the point of impact, but the metal levels are still below the maximum acceptable levels described by EPA and they are non-toxic to human health.

## **Acknowledgment**

The authors are grateful to Mr. Sarkar Syamand Jalal fellowship, in the Directorate of Environment, for providing laboratory facility.

## **References**

- [1]Ma, L.Q. and Rao, N. Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *Journal of Environmental Quality*. 26: 259-264. 1997.
- [2]Iwegbue, C.M.; Isirimah, N.O.; Igwe, C. and William, E.S. Characteristics levels of heavy metals in soil profile of automobile mechanic waste dumps in Nigeria. *Environmentalist*. 26: 131-137. 2006.
- [3]Adesodun, J.K. and Mbagwu, J.S.C. Distribution of heavy metals and hydrocarbon contents in an alfisol contaminated with waste-lubricating oil amended with organic wastes. *Bioresour. Technol.* Elsevier Ltd. doi:10.1016/j.biortech.2007.05.048. 2007.
- [4]Ikhajiagbe, B.; Anoliefo, G.O.; Oshomoh, E.O. and Airhienbuwa, N. Changes in heavy metal contents of a waste engine oil polluted soil exposed to soil pH adjustments. *British Biotechnology Journal*. 3(2): 158-168. 2013.
- [5]Osuji, L.C. and Achugasim, O. Trace metals and volatile aromatic hydrocarbon content of Ukpeliede-I oil spillage site, Niger Delta, Nigeria. *J. Appl. Sci. Environ. Manage.* 14(2): 17-20. 2010.
- [6]Adesina, G.O. and Adelasoye, K.A. Effect of crude oil pollution on heavy metal contents, microbial population in soil, and maize and cowpea growth. *Agricul. Scie.* 5(1): 43-50. 2014.
- [7]Warmate, A.G.; Ideriah, T.J.; Tamunobereton, I.T.; Udonam, U.E. and Ibaraye, T. Concentrations of heavy metals in soil and water receiving used engine oil in Port Harcourt, Nigeria. *J. Ecol. Natural Environ.* 3(2): 54-57. 2011.

- [8]Bada, B.S. and Olarinre, T.A. Characteristics of soils and heavy metal content of vegetation in oil spill impacted land in Nigeria. Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy: Vol. 17, Article 2. 2012.
- [9]Atlas. World Atlas. Compact Disk England. 2000.
- [10]World Food Programme WFP. Statistical Report on Population of Iraqi Kurdistan Region. 2002.
- [11]Hussein, T. Hydrogeological study of Bastora area. M.Sc. Thesis. Univ. of Mousl, Iraq. 1980.
- [12]FAO: Food and Agriculture Organization. Study of agro-ecological zoning for Diana, Mergasor, Barzan, and Sheruan-Mazn/Rubar Barazgird valley areas. FAO Representation in Iraq. FAO Coordination Office for Northern Iraq. 2001.
- [13]Guest, E. Flora of Iraq. Vol.1. Ministry of Agriculture, Baghdad, Iraq. 1966.
- [14]Maulood B.K.; Hinton G.C.F. and Al-Dosky, H.S. A study on the blue green algae of Arbil province, Iraq. Zanco Sci. Jour. Univ. of Sulaimaniya, Iraq. Series A. 6(2): 67-90. 1980.
- [15]Pansu, M. and Gautheyrou, J. Handbook of Soil Analysis: Mineralogical, Organic and Inorganic Methods. Springer-Verlag Berlin Heidelberg. 2006.
- [16]Jaiswal, P.C. Soil, Plant and Water Analysis. Kalyani Publisher. 441pp. 2003.
- [17]Ryan, J.; Estefan, G. and Rashid, A. Soil and Plant Analysis Laboratory Manual. Second Edition. International Center for Agricultural Research in the Dry Areas (ICARDA), Aleppo, Syria. 2001.
- [18]Hseu, Z.Y.; Chen, Z.S.; Tsai, C.C.; Cheng, S.F.; Liu, C.L. and Lin, H.T. Digestion methods for total heavy metals in sediments and soils. J. Water Air Soil Pollut. 141: 189-205. 2002.
- [19]Odu, C.T.I., Nwoboshi, L.C., Fagado, S.O. & Awani, P. E. Post-impact study of SPDC'S Nun River 8" delivery line oil spillage. Final report. SPDC, Nig., 95 pp. 1989.
- [20]Best, G.A. and Ross, S.L. River Pollution Studies. Liverpool University Press. 92 pp. 1977.
- [21]Lafta, J.G.; Fadhil, H.S. and Hussein, A.A. Heavy metals distribution and the variation of soil properties around Alqaim cement factory in Anbar Governorate-Iraq. International J. of Engineering and Advanced Technology. 3(1): 289-291. 2013.
- [22]Sharma, M.C.; Baxi, S.K.; Sharma, K.K.; Singh, M. and Patel, S. Heavy metal ions levels and related physicochemical parameters in soils in the vicinity of a paper industry location in Nahan area of Himachal Pradesh. J. Environ Anal Toxicol. 4:6. 2014.
- [23]Damian, F.; Damian, G.; Lăcătușu, R. and Iepure, G. Heavy metals concentration of the soils around Zlatna and Coșsa Mică smelters Romania. Carpth. J. of Earth and Environmental Sciences. 3(2): 65-82. 2008.
- [24]Inobeme, A.; Ajai, A.I.; Iyaka, Y.A.; Ndamitso, M. and Uwem, B. Determination of physicochemical and heavy metal content of soil around paint industries in Kaduna. International Journal of Scientific & Technology Research. 3(8): 221-225. 2014.
- [25]Khan, S.R.; Kumar, J.I.; Kumar, R.N. and Patel, J.G. Physicochemical properties, heavy metal content and fungal characterization of an old gasoline-contaminated soil site in Anand, Gujarat, India. Environmental and Experimental Biology. 11: 137-143. 2013.
- [26]Anapuwa, O.S. Heavy metal contamination and physicochemical characteristics of soils from automobile workshops in Abraka, Delta State, Nigeria. International Journal of Natural Sciences Research. 2(4): 48-58. 2014.
- [27]Luter, L; Akaahan, T.J. and Attah, S. Heavy metals in soils of auto-mechanic shops and refuse dumpsites in Makurdi Nigeria. J. Appl. Sci. Environ. Manage. 15(1): 207-210. 2011.
- [28]Pam, A.A.; Sha'Ato, R. and Offem, J.O. Evaluation of heavy metals in soils around auto mechanic workshop clusters in Gboko and Makurdi, Central Nigeria. Journal of Environmental Chemistry and Ecotoxicology 5(11): 298-306. 2013.

- [29]Adriano, D.C. Trace Elements in Terrestrial Environment. Second edition. New York: Springer-Verlag Company. 2001.
- [30]Amadi, A.; Abbey, S.D. and Nma, A. Chronic effects of oil spill on soil properties and microflora of a rainforest ecosystem in Nigeria. *Water, Air and Soil Pollution*. 86:1-11. 1996.
- [31]Rakesh, M.S. and Raju N.S. Correlation of heavy metal contamination with soil properties of industrial areas of Mysore, Karnataka, India by cluster analysis. *Int. Res. J. Environment Sci.* 2(10): 22-27. 2013.
- [32]Lindsay, W.L. *Chemical Equilibria in Soils*. John Wiley and Sons. New York. 1979.
- [33]EPA US: Environmental Protection Agency-United States. *Effects of Pollution: Water, Air and Soil*. 2011.

