Eng. & Tech. Journal, Vol.31, Part (A),No. 20, 2013

1st International Conference for Geotechnical Engineering and Transportation ICGTE in2415/4/2013

Distribution of some Heavy Metals Pollution Caused by Al- Daura Refinery in the Surrounding Region

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ABSTRACT

Due to the higher increase in the oil industry activities in Iraq, since there are a little information of the environmental status of the areas around the refinery locations, and the concerns of a possible environmental pollution that will cause health and life threats to living organisms, this study was carried out.To understand the status of heavy metals pollution in areas inside and surrounding Al-Daura refinery activities, (17) testing locations were chosen, ten locationsoutsidethe refinery and sevenlocationsinside it.One additional location was chosen in a rural (control) area, in the University of Baghdad, to compare between the heavy metals concentration in the study area and a sample from the rural area not affected by the pollution. The soil samples have been taken from (5 and 60 cm) depth from the top surface of the soil. Three samples were taken from each depth for each location to take an average of results.All the samples of soil were taken during the period from Dec/2010 to Feb/2011.The experimental work has been includes the heavy metals concentrations, such as Zinc, Nickel, Lead and Cadmium, have been measured at each selected depth for each testing locations.The results indicate that the mean concentration of Zn and Ni is (62.4 µg/g) and (100.5 µg/g) respectively and this valuesexceeded the mean allowable value by (Alloway, 1995 [2]; Kabata-Pendias and Pendias, 1992 [6]).The most concentrations of Zn, Ni and Pb, with some exceptions, accumulate at the top soil and decrease with the depth except Cd.

توزيع التلوث ببعض العناصر الثقيلة الناتجة من انبعاثات مصفى الدورة على المنطقة المحيطة

الخلاصة بسبب الزيادة الحاصلة في أنشطة الصناعات النفطية في العراق, ولأن المعلومات المتوفرة عن حالة البيئة في المناطق المحيطة بالمصافي, ووجود مخاوف من تلوث بيئي من الممكن ان يهدد صحة وحياة الكائنات الحية, أجريت هذه الدراسة. لفهم حالة التلوث بالمعادن الثقيلة في المنطقة داخل المصفى والمنطقة المحيطة به, تم اختيار (17) موقع للأختبار, اختيرت عشرة مواقع خارج المصفى و سبعة مواقع داخله. وقد تم اختيار موقع آخر من منطقة ريفية تقع في جامعة بغداد للمقارنة بين تركيز العناصر الثقيلة في منطقة الدراسة وهذه العينة التي لم تتأثر بالتلوث. وقد تم أخذ عينات التربة

https://doi.org/10.30684/etj.31.20A.13

من عمق (5 سم) وعمق (60 سم) من سطح التربة تستخدم في الفحوصات الكيميائية للتربة. أخذت ثلاث عينات من كل عمق لإيجاد معدل النتائج. ان جميع نماذج التربة والنباتات تم جمعها في الفترة الممتدة من كانون الاول/2010 لغاية شباط/2011. العمل الحقلي

تضمن قياس تراكيز العناصر الثقيلة, مثل الزنك, النيكل, الرصاص والكادميوم, في كل عمق من مواقع الإختبار المختارة. بينت النتائج بأن معدل تراكيز الزنك والنيكل هي (62,4 µg/g), (100,5 µg/g) عالتوالي وهذه القيم تتجاوز القيم المسموح حسب (Alloway, 1995 [2]; Kabata-Pendias and Pendias, 1992 [6]). ان اغلب تراكيز العناصر الزنك, النيكل , الرصاص (مع بعض الاستثنائات) تتراكم على سطح التربة وتقل مع العمق ماعدا الكادميوم.

INTRODUCTION

Due to high and rapid development in the oil industry at the last century, many different problems had occurred, one of them is the environmental pollution in all elements of the environment, such as water, soil and air, which began to raise serious questions that need a rapid solutions. Soil pollution is one of these environmental pollutions.

In general, there are many sources of soil pollution, man-made sources including automobiles, power generation and the industrial activities. They represent the main source of air pollution and thus causes soil pollution by precipitation; especially, oil industry activities using huge amount of consumable fuel, like power plants and oil refinery; due to the high rate emission of fume, solid particulates and toxic gases more than other industry in quantity [1].

These industries are more hazardous to the environment upon its existence within the limits of the cities, or its existence within urban area, and or near the agricultural terrines such as Al-Daura power plant, south Baghdad power plant and Al-Daura oil refinery.

FIELD AND EXPERIMENTAL WORK

Study Area

The study area is located at the south-west of Baghdad governorate, specifically at Al-Daura region, just 4 Km from the city centre of Baghdad, close to the western bank of Tigers River. Figure (1) shows the study area location.

Location of Samples

The selected locations of samples were as follows: (1) ten locationsoutsidethe refinery, and (2) sevenlocationsinside it, as shown in the Figure (2), those locations was chosen according to security conditions during samples collection and determinants of site.

These sample locations might reflect the heavy metals pollution arising from the oil refinery activities in all directions. Other one location was chosen in a rural (control) area, in the University of Baghdad, to compare between the heavy metals concentration in the study area and a sample from the rural area not affected by the pollution.

Sampling Proses

The soil samples were taken from a 5 cm depth from the top surface of the soil and at 60 cm depth by using auger (maximum depth can auger be reached about 60 cm). Three samples were taken from each depth for each location to take an average of results.All the samples were taken during the period from Dec/2010 to Feb/2011, and collected in labeled sacks and transported directly to the laboratory.

The coordinates of all locations for samples were also taken by using a geographic position system (GPS) instrument type GARMIN.

Laboratory Tests

The laboratory test includes finding the concentrations of heavy metals, such as Zinc (Zn), Nickel (Ni), Lead (Pb) and Cadmium (Cd) by using Atomic Absorption Spectrometry (AAS) device. This device was adopted in this work, and the chemical extraction was prepared in the laboratories ofthe Central Agency forStandardization and Quality Control in the Ministry of Planning.

The procedure of chemical extract preparation was as follows: [5]

1. All samples were dried in a drying oven to 105 ^{o}C for 24 hours.
2. All samples were ground and sieved with 105 mesh sizes.
3. A (1 gm) from the sieved soil was extracted with 10 ml of concentrated HNO_3 acid (Analar nitric acid) on a hot plate for heating till the volume reached 2 ml, then the sample (extracted sample) was left to stand 2 hours.
4. After that, the sample was first diluted with distilled water twice, and then, the sample was filtered on Whatman 541 papers, and finaly, a second dilution was made for the sample with distilled water for 25 ml volume.

Then the sample placed in the Atomic Absorption Spectrophotometer (AAS) to measure the heavy metals concentrations.

The results obtained from the AAS were in (mg/L) and to convert these results to (µg/g), the following formula has been applied: (Karnoob, 1986).

$$= \frac{X*V*I}{} \qquad ...(1)$$

Where:

Y: heavy metals concentration in soil sample (µg/g).

X: heavy metals concentration obtained from AAS instrument (mg/L).

V: sample volume used in the AAS = 25 ml.

I: dilution factor.

W: weight of soil extracted = 1 gm.

Results and Discussion

Heavy metals concentrations levels were measured in soil samples which were taken from the testing locations at different depths (5 and 60 cm from soil surface).

The total results of heavy metals concentration are listed in Tables (1) and (2).

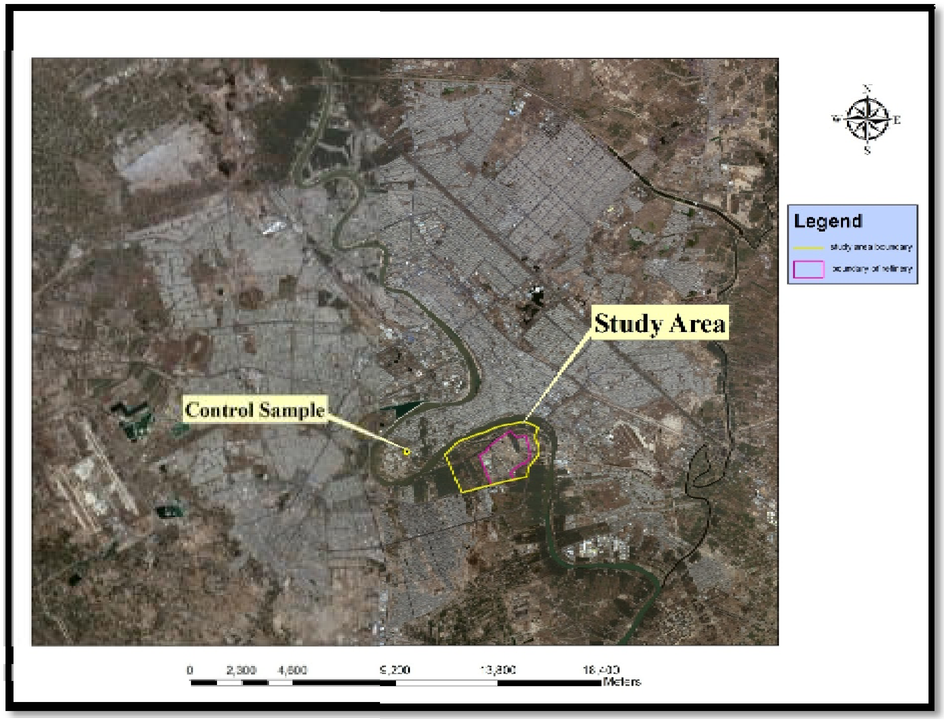

Figure (1) Study Area Location in Baghdad.

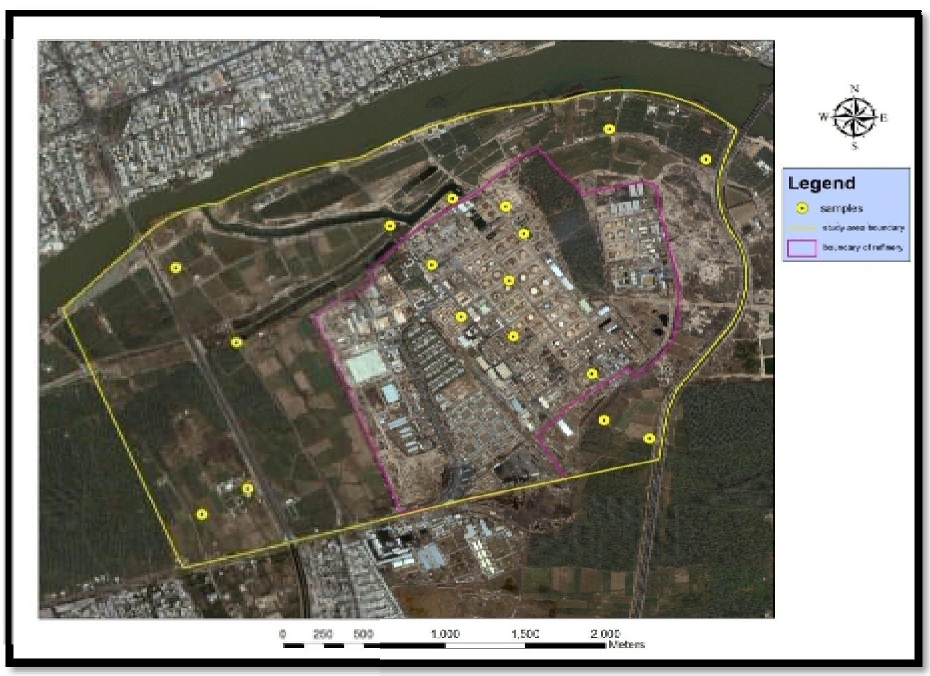

Figure (2) Location of Samples.

Table (1) the Results of Heavy Metals Concentrations outside the Refinery Location.

Sample No.	Position		Depth (cm)	Zn Av. con. (µg/g)	Ratio	Ratio	Ni Av. con. (µg/g)	Ratio	Ratio	Pb Av. con. (µg/g)	Ratio	Ratio	Cd Av. con. (µg/g)	Ratio	Ratio
	East	North													
1	447921.8	3681095	5	71.1	1.422	5.182	117.4	5.870	4.278	13	0.464	26.0	0.03	0.067	3
			60	52.7	1.054	3.841	94.8	4.740	3.455	10.8	0.386	21.6	1.22	2.711	122
2	447640.5	3681216	5	40.2	0.804	2.930	104.1	5.205	3.794	9.9	0.354	19.8	0.02	0.044	2
			60	47.6	0.952	3.469	113.4	5.670	4.133	7.3	0.261	14.6	0.61	1.356	61
3	448271.5	3682971	5	35.2	0.704	2.566	89.2	4.460	3.251	7.5	0.268	15.0	0.01	0.022	1
			60	62.6	1.252	4.563	136	6.800	4.956	8	0.286	16.0	0.24	0.533	24
4	447674.1	3683174	5	62.5	1.25	4.555	100.6	5.030	3.666	6	0.214	12.0	0.01	0.022	1
			60	58.8	1.176	4.286	128.5	6.425	4.683	14	0.500	28.0	0.01	0.022	1
5	446309.7	3682524	5	54.2	1.084	3.950	95	4.750	3.462	6	0.214	12.0	0.02	0.044	2
			60	29.7	0.594	2.165	54.5	2.725	1.986	3.5	0.125	7.0	0.25	0.556	25
6	446695.6	3682706	5	59	1.18	4.300	118.3	5.915	4.311	9.5	0.339	19.0	0.03	0.067	3
			60	52.1	1.042	3.797	105	5.250	3.827	8.3	0.296	16.6	0.5	1.111	50
7	444986.0	3682242	5	15	0.3	1.093	30.6	1.530	1.115	2.8	0.1	5.6	0.02	0.044	2
			60	16.5	0.33	1.203	37.3	1.865	1.359	5	0.179	10.0	0.02	0.044	2
8	445361.1	3681741	5	33.8	0.676	2.464	84.5	4.225	3.079	9.7	0.346	19.4	0.03	0.067	3
			60	60	1.2	4.373	127.8	6.390	4.657	5.7	0.204	11.4	1.7	3.778	170
9	445429.1	3680757	5	42	0.84	3.061	107.4	5.370	3.914	8.4	0.300	16.8	0.01	0.022	1
			60	41.5	0.83	3.025	91.3	4.565	3.327	4.9	0.175	9.8	0.02	0.044	2
10	445146.1	3680584	5	43.3	0.866	3.156	103.9	5.195	3.786	4.3	0.154	8.6	0.02	0.044	2
			60	56.6	1.132	4.125	117.8	5.890	4.293	3.8	0.136	7.6	2.1	4.667	210

Table (2) the Results of Heavy Metals Concentrations inside the Refinery Location.

Sample No.	Position		Depth (cm)	Av. Zn con. (μg/g)	Ratio	Ratio	Av. Ni con. (μg/g)	Ratio	Ratio	Av. Pb con. (μg/g)	Ratio	Ratio	Av. Cd con. (μg/g)	Ratio	Ratio
	East	North													
11	446569.8	3682261	5	101.8	2.036	7.420	110.1	5.505	4.012	64.4	2.300	128.8	0.21	0.467	21
			60	51.2	1.024	3.732	90	4.500	3.280	7.9	0.282	15.8	0.06	0.133	6
12	447027.4	3682652	5	77.5	1.55	5.649	106.1	5.305	3.867	5.1	0.182	10.2	0.06	0.133	6
			60	101.3	2.026	7.383	145.5	7.275	5.302	7.2	0.257	14.4	2.31	5.133	231
13	447144.6	3682469	5	60.9	1.218	4.439	89	4.450	3.243	1.45	0.052	2.9	0.01	0.022	1
			60	48.7	0.974	3.550	79.6	3.980	2.901	0.5	0.018	1.0	0.12	0.267	12
14	447567.7	3681528	5	52.6	1.052	3.834	90.8	4.540	3.309	1.4	0.050	2.8	0.05	0.111	5
			60	44.2	0.884	3.222	85.6	4.280	3.120	0.7	0.025	1.4	0.07	0.156	7
15	447075.4	3681779	5	66.8	1.336	4.869	120.9	6.045	4.406	48.4	1.729	96.8	0.03	0.067	3
			60	50.2	1.004	3.659	103.9	5.195	3.786	9.4	0.336	18.8	0.64	1.422	64
16	447048.9	3682156	5	115.1	2.302	8.389	124.4	6.220	4.534	6.8	0.243	13.6	0.04	0.089	4
			60	86.2	1.724	6.283	97	4.850	3.535	2.7	0.096	5.4	0.07	0.156	7
17	446751.8	3681911	5	128.9	2.578	9.400	116.2	5.810	4.235	10	0.357	20.0	0.01	0.022	1
			60	76.2	1.524	5.554	104.3	5.215	3.801	5.6	0.200	11.2	1.3	2.889	130

Zinc: The Zn concentration in the study area at the top soil varies from (15- 128.9 µg/g) with a mean value of (62.4 µg/g). The observed values have been reportedly higher than the common world average for total Zn concentrations in soil (50 µg/g) [2]. It is also higher than the mean concentrations of trace elements calculated on the world scale for silty soil (60 µg/g) [6].

At (60 cm) depth from soil surface, the Zn concentration varies from (16.5- 101.3 µg/g) with a mean value of (55.1 µg/g). This mean value has been higher than the common world average illustrated above.

This study indicates that (64.7%) of all soil samples contain zinc concentration greater than the standard limit of zinc in soil; and (100%) of all samples contain zinc concentration greater than (13.72 µg/g) which is the zinc concentration in soil sample from the rural area.

The maximum concentrations of Zn inside the refinery were near the old storage basins and in the center of refinery, and the maximum value outside the refinery was near the expressway (Mohammed Al-Kasim), which is agricultural area, because the main sources of Zn have been reported as an agricultural use of sewage and composted materials and the use of agrochemicals, such as fertilizers and pesticides [2]. Some of the studies have also linked the high Zn levels to accumulation from the traffic and industry input [4], and also from the vehicle emissions and tire and brake abrasion [9].

Rainfall was the main reason that makes the fluctuation in the path of Zn concentration with soil depth, because the solubilization of Zn minerals during weathering produces mobile Zn^{+2}, especially in acid, oxidizing environments [6].

The distribution of Zn levels at the top soil and 60 cm depth from surface in the study area is illustrated in Fig.(3) and Fig.(4), respectively.

Nickel: The Ni content in the study area at the top soil varies from (30.6- 124.4 µg/g) with a mean concentration of (100.5 µg/g). The observed mean value is higher than the world average concentration of Ni in soil, which is around (20 µg/g) [2]. These results exceed the calculated world mean for silty soil (26 µg/g) [6].

At (60 cm) depth from soil surface, the Ni concentration varies from (37.3- 145.5 µg/g) with a mean value of (100.7 µg/g). This value is also exceeding the above mean values.

This study points out that (100%) of all soil samples contain nickel concentration greater than the standard limit of nickel in soil; and (100%) of all samples contain nickel concentration greater than (27.44 µg/g) which is the nickel concentration in soil sample from the rural area.

Maximum concentrations of Ni inside the refinery were in the center of refinery and near the flare, and the maximum value outside the refinery was near the expressway (Mohammed Al-Kasim) and near to the flare. It is evident that local solid waste litter and anthropogenic activities, such as burning of fuel and residual oil contribute to the increase in Ni content in the soil of the study area [2].

Ni is easily mobilized during weathering. However, unlike Ni^{+2} is relatively stable in aqueous solutions and is capable of migration over a long distance, therefore, the Ni concentration path is with the soil depth are fluctuated.

Figures (5 and 6) show the distribution of Ni levels at the top soil and 60 cm depth from surface in the study area, respectively.

Lead: The Pb content in the study area varies from (1.4- 64.4 µg/g) at top soil with a mean value of (12.6 µg/g). The observed values are less than the calculated world average of silty soil (28 µg/g) [6].

Also, the Pb contents at 60 cm depth from soil surface (0.5-14 µg/g) are less than the calculated world average value.

This study indicates that (6%) of all soil samples contain lead concentration greater than the standard limit of lead in soil; and (97%) of all samples contain lead concentration greater than (0.5 µg/g) which is the lead concentration in soil sample from the rural area

The maximum concentrations of Pb inside the refinery were near the power former unit, and the maximum values outside the refinery were at samples near the road sides. Deposition related to the automobile emissions and transportations sector, in general (considering the long residence time of Pb), may be the major source of increase in Pb content [3]; [7]; Imperato et al., 2003).

Pb is reported to be the least mobile among the other heavy metals [6], therefore, the Pb content paths with the depth of soil were less fluctuated among other heavy metals.

Figures (7 and 8) depict the distribution of Pb levels at the top soil and 60 cm depth from surface in the study area, respectively.

Cadmium: The Cd content in the study area varies from (0.01- 0.21 µg/g) at top soil with a mean value of (0.035 µg/g). The observed values are less than the calculated world mean for silty soil (0.45 µg/g) [6].

At (60 cm) depth from soil surface, the Cd concentration varies from (0.01- 2.31 µg/g) with a mean value of (0.66 µg/g). This mean value has been higher than the common world mean illustrated above.

This study shows that is (20.6%) of all soil samples contain cadmium concentration greater than the standard limit of cadmium in soil; and (82.35%) of all samples contain cadmium concentration greater than (0.01 µg/g) which is the cadmium concentration in soil sample from the rural area.

The maximum concentrations of Cd inside the refinery were near the flare, and the maximum values outside the refinery were at samples near the roadsides, which were agricultural areas. Cadmium has a wide range of uses in the industry [8], and a significant source of Cd in soils is the phosphate fertilizers [6].

Among the other trace metals, Cd is known to be most mobile under conditions of different soils [6], therefore, the concentration of Cd increases with soil depth.

Figures (9 and 10) reveal the distribution of Cd levels at the top soil and 60 cm depth from surface in the study area, respectively.

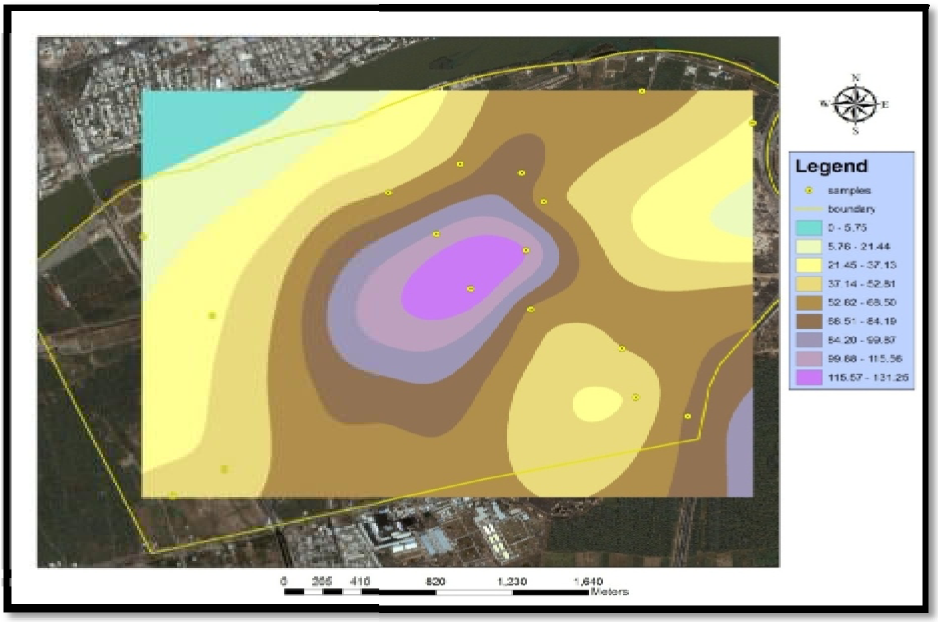

Figure (3) Distribution of Zinc at Top soil.

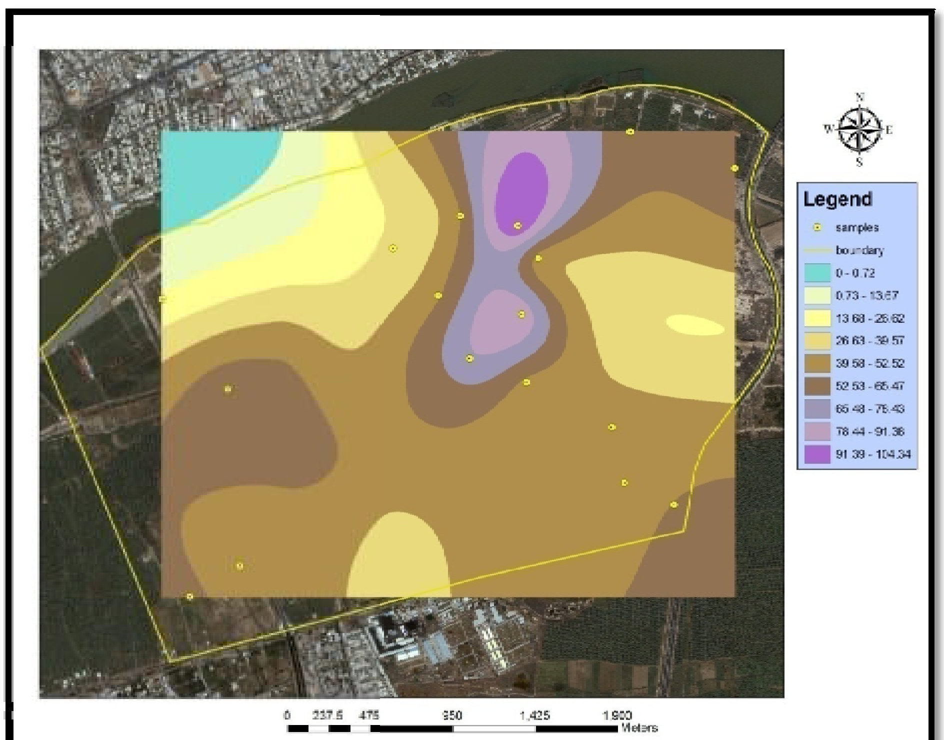

Figure (4) Distribution of Zinc at 60 cm Depth from Soil Surface.

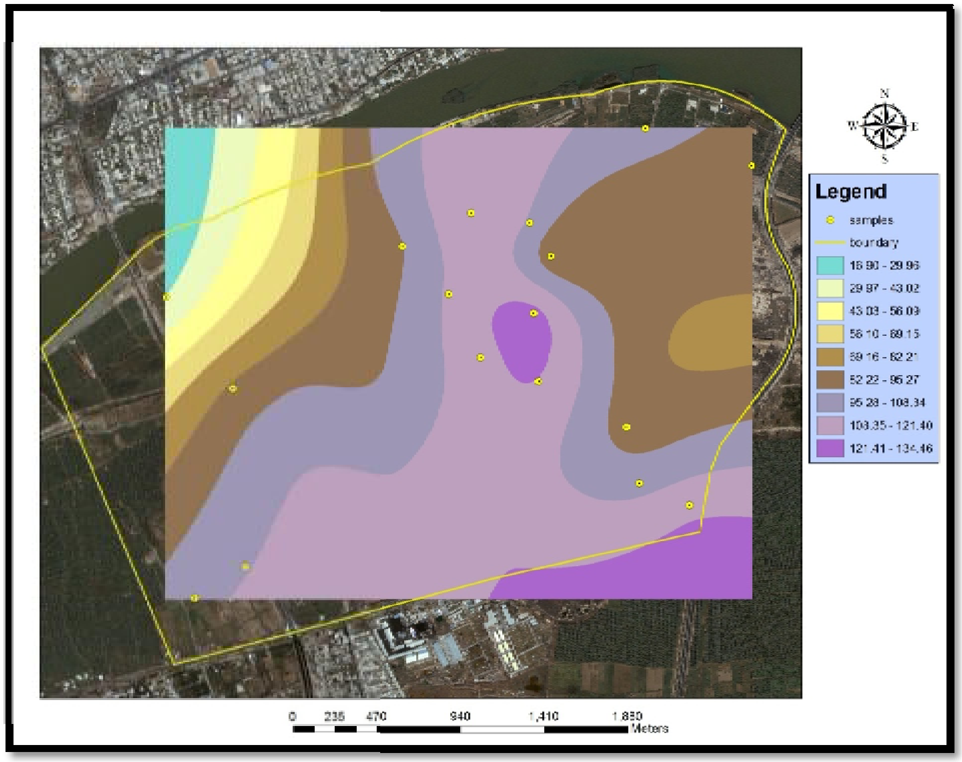

Figure (5) Distribution of Nickel at Top soil.

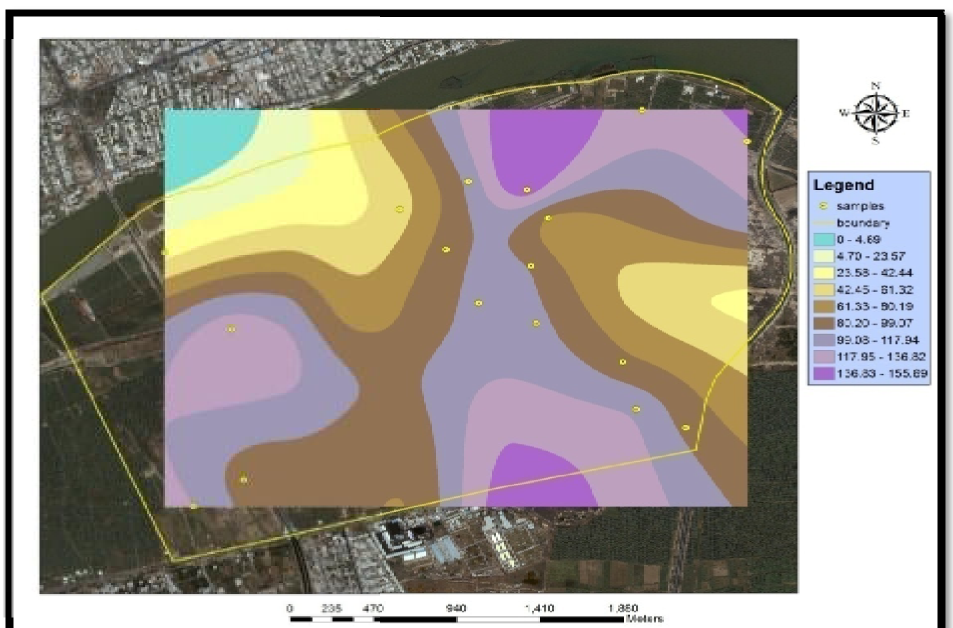

Figure (6) Distribution of Nickel at 60 cm Depth from Soil Surface.

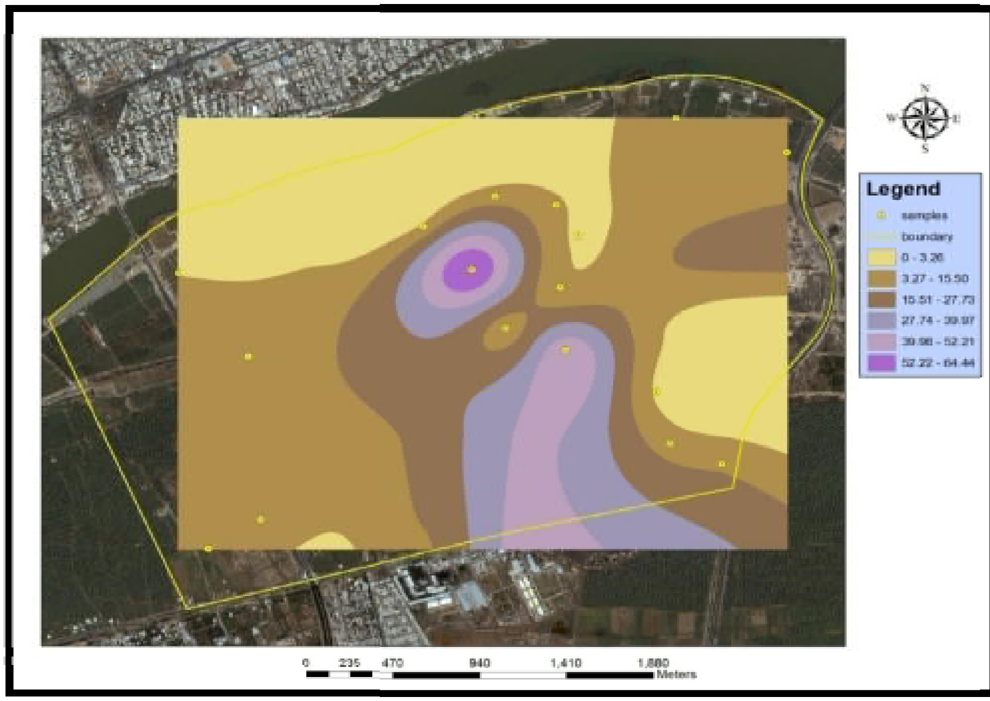

Figure (7) Distribution of Lea d at Top soil.

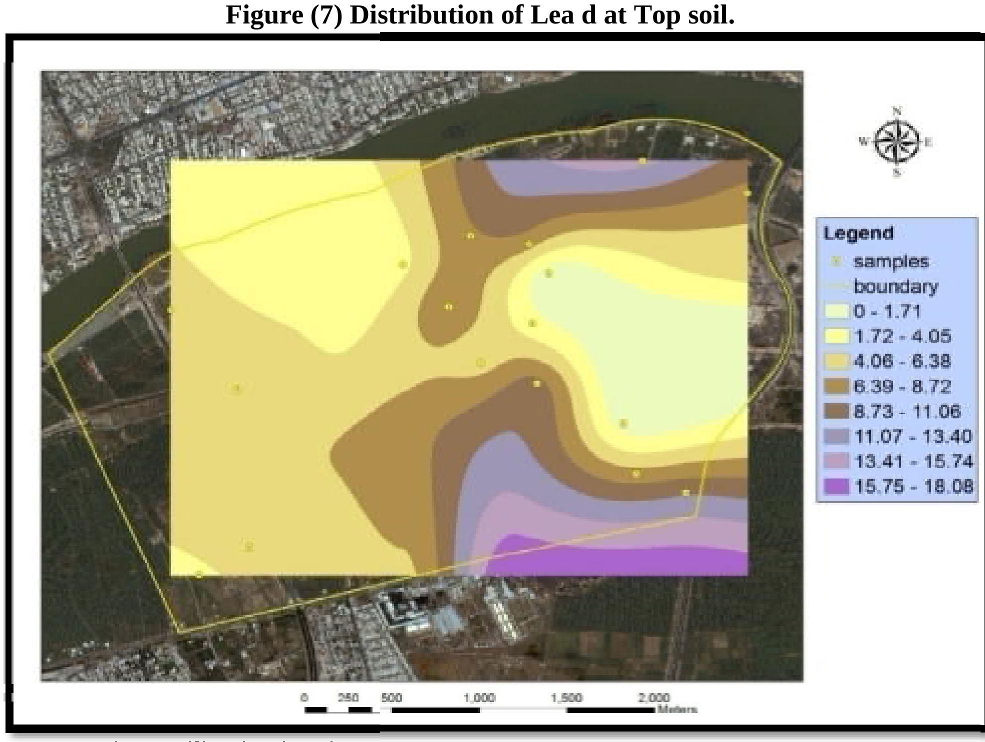

Figure (8) Distribution of Lead at 60 cm Depth from Soil Surface.

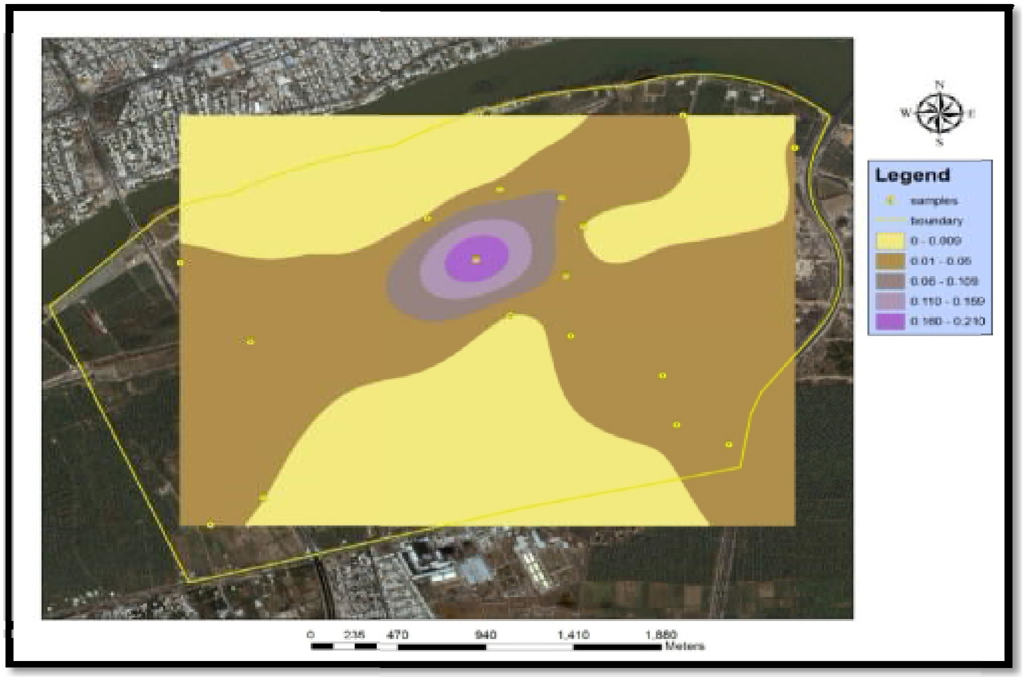

Figure (9) Distribution of Cadmium at Top soil.

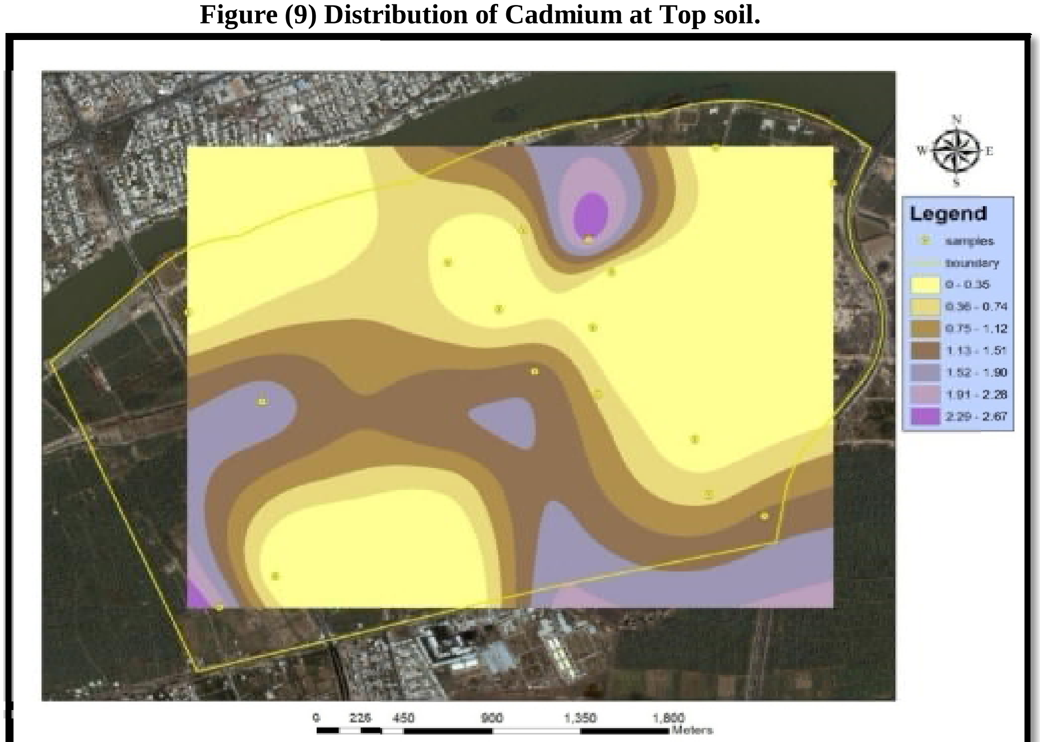

Figure (10) Distribution of Cadmium at 60 cm Depth from Soil Surface.

CONCLUSIONS

1. Zn, Ni and Pb concentrations are accumulated in the top soil and decreased with the depth inside the soil (except Cd).
2. This study indicates that (64.7%), (100%), (6%) and (20.6%) of all soil samples contain zinc, nickel, lead and Cadmium concentration (respectively) greater than the standard limit of their concentrations in soil.
3. This study, also indicates that (100%), (100%), (97%) and (82.35%) of all soil samples contain zinc, nickel, lead and Cadmium concentration (respectively) greater than their concentrations in soil sample from the rural area.
4. The highest concentrations value of zinc and nickel were in the center of the refinery; and the highest lead concentration were near the power former unit; and the cadmium highest value was near the flare.

RECOMMENDATIONS

1. Immediate medical intervention measures should be thought in order to determine the extent and effects of human diseases associated with refining pollution in all over the areas surrounding the refining activities.
2. Maintenance of all the refinery units that cause emissions.
3. Add treatment materials to refining operations for the purpose of reducing the emissions of heavy metals from the refinery.
4. Compulsion the maintenance on the automobile to reduce the emissions from it.

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