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Assessment of Heavy Metals Pollution in Soil Affected by Industrial Activities

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ABSTRACT

Twenty soil samples were collected in the Al-Duraa Refinery Industrial District. The soil samples displayed high concentrations of Cd, Cr, Ni, Pb and Zn than the calculated worldwide mean of unpolluted soils. The geoaccumulation index indicated that the soil samples were strongly polluted with Cd and moderately to strongly polluted with Pb. The level of pollution with Ni was moderate, whereas Cr and Zn observed unpolluted to moderately pollution. Furthermore, the result of the calculated enrichment factor (4.11-227.49) indicated significant to extremely high enriched and suggesting an important role of anthropogenic pollution due to various industrial activities done by the refinery.

Key words: Heavy metals, Geoaccumulation, Enrichment factor, Soil pollution

تقييم التلوث بالعناصر الثقيلة في الترب المتأثرة بالانشطة الصناعية

الخلاصة

تم جمع (20) نموذج من التربة في منطقة مصفى الدورة. أظهرت النتائج ان محتوى التربة من الكادميوم، الكروم، النيكل، الرصاص والزنك كان اعلى من المعدل العالمي للترب غير الملوثة. وتشير نتائج مؤشر التجمع التراكمي (Igeo) ان عينات التربة كانت عالية التلوث بالكادميوم, معتدلة إلى عالية التلوث بالرصاص ومعتدلة التلوث بالنيكل. بينما أظهرت النتائج ان التربة غير ملوثة الى معتدلة التلوث بالكروم والزنك. وعلاوة على ذلك، فقد اظهرت نتائج عامل الأغناء (4.11-227.49) زيادة معنوية الى قيم عالية للغاية مؤكدة دورا هاما للتلوث بسبب الأنشطة الصناعية الخاصة بالمصفى.

INTRODUCTION

With rapid development in industrialization, soil contamination has become a serious problem in many countries. Contamination and negative impact on the quality of air, water, and soil by population growth, rapid

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urbanization,and industrial activities have been stated by several works [1,2]. Among the most significant soil contaminants resulting from both natural and manmade sources, heavy metals are of prime importance due to their long-term toxicity effect [3,4].
In urban areas, heavy metals in soils and dusts can be accumulated in the human body via direct inhalation, ingestion, and dermal contact absorption [5,6].

Al-Duraa refinery located in the southeastern part of Baghdad city, Iraq, consists of several boards, including heavy oil, light oil, power utility, maintenance and external refineries. Products from light and heavy oil boards are the most important main products, such as the liquid gas, naphtha, jet fuel, lubricating oils, waxes, asphalt and other species. However, as a result of all these various activities carried out by the refinery, which started operations in 1955, contaminants as industrial wastes, dust emissions, and other solid, liquid and gaseous wastes can be transferred to the surrounding environment, especially the soil. Soils are regarded as the ultimate sink for heavy metals discharged into the environment [7,8], and Heavy metals can be sensitive indicators for monitoring environmental contamination [9]. Therefore, the present investigation was carried out with a goal to study the level of Cr, Cd, Cu, Pb, Zn and Ni in the soil affected by Al-Duraa Refinery activities, and to assess the degree of heavy metals contamination.

Materials and Methods

Location of the Study Site

The study site (33º 16′ N, 44º 25-44º 26′ E), is located in the Al-Duraa district in the southeastern part of Baghdad city, Iraq (**Figure 1**). The location is near to the Tigris River with a proximate area of about 2.5 km^2. It is characterized by arid to semi arid climate with dry hot summers and cold winters, where the mean annual rainfall is about 151.8 mm [10].

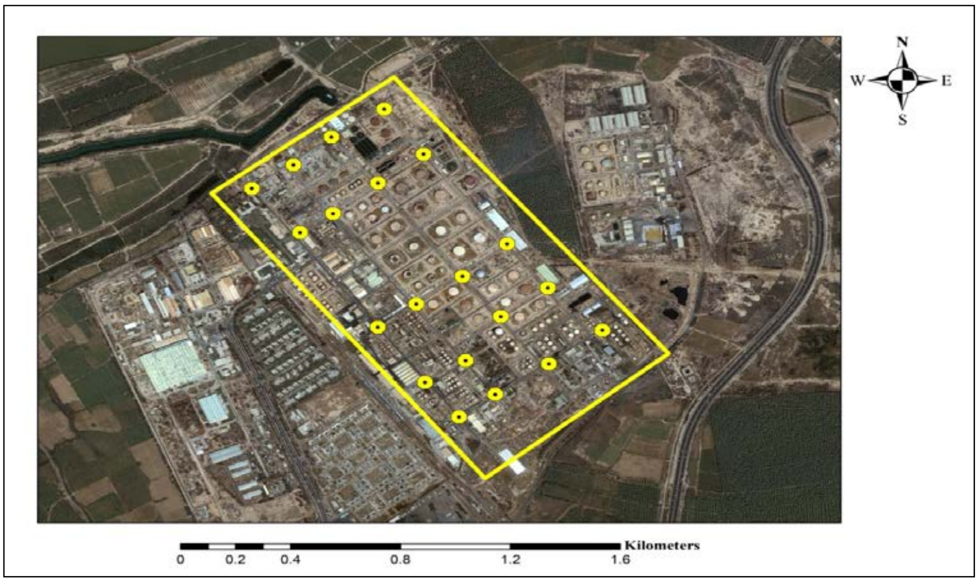

Figure (1): Sampling location in the study site

Soil Sampling and Analyses

Twenty soil samples were collected in total; each sample representing a composite sample of at least 3 subsamples in the Al-Duraa Refinery Industrial District. The sampling points were randomly distributed to cover the entire study site. All of the sampling sites were recorded using Global Positioning System (GPS) device. The soil samples were collected during November 2013. A bulk sample was prepared by collecting about 1 kg of surface soil (0-20 cm) by hand digging with a stainless steel spatula. After air drying, samples were passed through a 2 mm sieve to remove large debris, stones and pebbles, and then they were stored in plastic bags for further analysis. Samples were wet-digested using a combination of HCl and HNO_3 [11]. Metal determinations were done by Atomic Absorption Spectrometry (AAS 6300, Shimadzu, Japan) in laboratory of Environmental Research Center, University of Technology, Baghdad, Iraq.

Results and Discussion

Distribution of Heavy Metals in Soil

Descriptive statistics for the examined heavy metals in this study are shown in Table 1. High standard deviation reflecting skewed distribution and a high degree of variation. For Cu, Ni and Zn, concentrations were not normally distributed showing a skewed distribution. Therefore, for these elements, medians instead of means were used since they would describe such distributions more precisely. With the exception of Cu, all the measured metals display higher concentrations than the calculated world average of unpolluted soils [12], (Table 1).

Table (1): Heavy metal concentrations with recommended levels (mg/kg)

Element	Minimum	Maximum	Mean	Median	Std. Deviation	Skewness	Mean of Unpolluted Soils [12]
Cd	1.25	5.98	4.00	3.78	±1.55	-0.22	0.53
Cr	49.60	223.75	149.19	145.75	±53.25	-0.25	83
Cu	8.90	87.95	33.07	19.85	±23.70	1.15	24
Ni	136.89	236.22	206.61	210.83	±22.86	-1.85	34
Pb	19.97	216.34	106.09	110.62	±56.39	0.14	44
Zn	37.40	219.95	108.05	106.90	±39.81	0.83	100

Cadmium: There is a growing environmental concern about Cd as being one of the most eco-toxic metals, which exhibits highly adverse effects on soil biological activity, plant metabolism, and the health of humans and animals [12]. Cadmium pollution in soils is accepted to be a serious environmental problem. The Cd concentrations in the refinery soils vary from 1.25 to 5.98 mg/kg and the mean and median values are 4.00 and 3.78 mg/kg respectively. The observed values exceed the calculated worldwide mean of non-polluted soil (0.53 mg/kg) reported after analytical surveys [12]. Concentrations above 0.5 mg/kg could reflect the influence of the human activity [13].

The obtained results indicated that 100% of soil samples contain Cd concentration greater than the standard limit of cadmium mentioned above.

Hot spots of contamination (spots with maximum concentrations) of cadmium were near to the units of refining, hydrogenation, flare, fuel station, tanks of oil products and cross roads. These results agree with the views of [14], who stated that refining of ores is the largest source of industrial atmospheric cadmium emissions, followed by waste incineration. Also, his feature (Cd) is attributed to the wear and tear of tires which can explain the elevated level of Cd near to cross roads.

Chromium: The Cr content of topsoil is known to increase due to pollution from various sources of which the main ones are several industrial wastes [12]. The values of Cr assayed in Al Duraa Refinery ranged from (49.60 to 223.75 mg/Kg). The calculated mean and median values (149.19 and 145.75 respectively) were much higher than the average value from the world literature (84.0 mg/kg) [15] and also more than the reported world scale of unpolluted soils (83.0 mg/kg) [12].

This study shows that (90%) of all soil samples contain Cr concentration greater than the standard limit of chromium mentioned above.

Maximum concentrations of Cr were near to the flare, heavy oil units, and tanks of oil products. Emissions from these units can cause chromium pollution in the soil, since Cr could release into the environment from burning of natural oil, gas, or coal [16].

Copper: The average Cu concentration of the normal threshold value prescribed in soil (20-30 mg/kg) [15], and the typical world scale of non-polluted soil (24 mg/kg) reported by Kabata-Pendias & Pendias [12]. Copper content of soils in the study area are between 8.90 and 87.95 mg/kg with median value of 19.85 mg/kg which is applicably less than that in uncontaminated soils.

This study points out that (45%) of all soil samples contain Cu concentration greater than the standard limit of copper mentioned above.

Hot spots of Cu concentrations were near to refining, flare and heavy oil units. Sludge and atmospheric deposition can contribute to increase Cu content in soil [17]. Local Cu contamination in soils originates from corrosion of construction materials with Cu alloys (e.g. electric cables). However, the deterioration of the mechanical parts in vehicles over time will result in Cu being emitted to the surrounding environment [18].

Nickel: Ni content varies from 136.89 to 216.34 mg/kg with a median value of 210.83 mg/kg. The observed values are higher than the world average concentration of Ni in soil which is around 20 mg/kg [15]. Results also exceed the calculated world mean of unpolluted soil (34 mg/kg) [12]. In soils, Ni is usually present in the organically bound forms which under acidic and neutral conditions increase its mobility and bioavailability.

Results indicated that (100%) of all soil samples contain Ni concentration greater than the standard limit of nickel mentioned above. Ni has been traditionally related to atmospheric accumulation from burning of coal, diesel oil and fuel oil, the incineration of waste as well as, from miscellaneous industrial sources [19].

Lead: The common use of Pb makes its concentration in all environmental media elevated [20]. The Pb content varies from 19.97 to 216.34 mg/kg with a mean and median value of 106.09 and 110.62 mg/kg respectively. The observed values are higher than the calculated world average of unpolluted soils (44.0 mg/kg) [12].

This study shows that (80%) of all soil samples contain Pb concentration greater than the standard limit of lead mentioned above. elevated concentrations of Pb may be related to vehicle emission and transportation which are considered the principal source of Pb in the soil. Although the use of leaded petrol had been banned in the recent years and the content of Pb in the troposphere has decreased [21], the concentration of Pb in soils still reflects the significant degree of historical Pb contamination and the long half-life of Pb in soils [22]. Other sources of Pb contamination in the study area might be from pesticides, fertilizer impurities; atmospheric fallout from the combustion of fossil fuels [23].

Zinc: Environmental contamination of Zn is mainly related to anthropogenic input. The anthropogenic sources of Zn are related to industries, waste combustion and may be derived from mechanical abrasion of vehicles, as they are used in the production of brass alloy itself and come from brake linings, oil leak sumps and cylinder head gaskets [24,25]. The Zn content varies from 37.40 to 219.95 mg/kg. The calculated median values were reportedly within the common world range for total Zn concentrations in soil (10-300 mg/kg) [15], but little higher than average for un-polluted soil which is reported as 100 mg/kg [12], with (70%) of all soil samples containing Zn concentration greater than the standard limit of zinc in soil.

Contamination Level Assessment

In the present study, Igeo and EF were used to assess the metal contamination levels in the soil samples. Reference values (Earth crust averages) of the studied metals which were used as background values were taken from Riley and Chester [26].

Index of Geoaccumulation

The index of geoaccumulation (Igeo) enables the assessment of contamination by comparing current and preindustrial concentrations. This method which has been used by Müller [27] since the late 1960s was applied to several trace metals. It is computed using the following equation:

$$Igeo = \log_2 (C_n / 1.5B_n)$$

Where

C_n is the measured concentration of the examined metal in the soil and B_n is the geochemical background concentration of the same metal. The constant 1.5 is introduced to minimize the effect of possible variations in the background values, which may be attributed to anthropogenic influences [28,29]. The following classification is given for the geoaccumulation index: < 0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted, and > 5 = extremely polluted [27].

Table 2 shows I_{geo} values for the measured heavy metals in the tested soil. The pollution levels of these metals in the environment expressed in terms of geoaccumulation index indicated that the soil samples in the study area were strongly polluted with Cd and moderately to strongly polluted with Pb. The obtained I_{geo} for Ni and Zn revealed that most of the soil samples examined fall into class unpolluted to moderately polluted, and for Cr and Cu the I_{geo} was mostly negative, pointing to the lack of contamination.

Table (2): Geoaccumulation index values

Elements	Geoaccumulation index
Cd	3.74
Cr	-0.01
Cu	-2.06
Ni	0.91
Pb	2.50
Zn	0.03

Enrichment factor (EF)

This method is based on standardization of an element tested against a reference element. The most common reference elements are Sc, Mn, Ti, Al, Ca, and Fe [30,31,32]. In this study iron was used as a conservative tracer to differentiate natural from anthropogenic components, following the assumption that its content in the crust has not been disturbed by anthropogenic activity and it has been chosen as the element of normalization because natural sources (98%) vastly dominate its input [33]. According to Rubio *et al.* [34], the metal enrichment factor (EF) is defined as follows:

$$EF = \frac{(M/Fe)sample}{(M/Fe)background}$$

Where

EF is the enrichment factor, (M/Fe) sample is the ratio of metal and Fe concentration of the sample and (M/Fe) background is the ratio of metal and Fe concentration of a background. Five contamination categories are recognized on the basis of the enrichment factor [35].

EF < 2 deficiency to minimal enrichment
EF = 2-5 moderate enrichment
EF = 5-20 significant enrichment
EF = 20-40 very high enrichment
EF>40 extremely high enrichment

The results of the calculated enrichment factor shown in Table 3 suggest that the origin of heavy metals may not come from the local soil background but other natural and/or anthropogenic sources in industrial areas, including industrial discharges and other activities [1]. The values of EF from 4.11 to 227.49 show that significant heavy metal pollution was likely to originate from the industrial activities of the refinery. Furthermore, the results of EF indicated that the soils of the study area were extremely high enriched with metals such as Cd and Pb, very high enriched with Ni and moderate enriched with Cu. while Zn and Cr were observed to show significant enrichment.

Table (3): Enrichment Factor of heavy metals

Elements	Enrichment Factor (EF)
Cd	227.49
Cr	16.97
Cu	4.11
Ni	31.97
Pb	96.54
Zn	17.37

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