



Concentration of heavy metals in soil contaminated with crude oil at two Iraqi sites according to environmental indices of pollution

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Submitted on: 10/25/2023; Accepted on: 12/15/2023; Published on: 12/31/2023.

ABSTRACT: Contaminated soil samples were collected from the Al-Kasak refinery and Al-Qayyarah refinery in western and southern Nineveh, at specific distances in six dimensions (0, 50, 100, 150, 200, 300) meters from the source of pollution, to study the concentrations of heavy metals Pb, Mn, Ni, Cd and the effect of oil refinery pollutants on some soil pollution standards, in addition to some physical and chemical properties of the soil and their concentrations. The results showed an increase in the concentration of heavy metals in the soil near the sources of pollution, with cadmium significantly superior to the Al-Qayyarah site over Al-Kasak site (491.744 mg kg⁻¹) and lead, nickel and manganese recorded a higher concentration at Al-Kasak site compared to Al-Qayyarah site (166.356, 114.687, 36.487 mg kg⁻¹), respectively. The order of mineral elements in the two study sites was Cd>Pb>Ni>Mn. As for the Contamination Factor (CF), it was Cd > Pb > Ni > Mn with values of 684.50, 9.91, 5.13, and 0.1701, where the concentration factor was highly polluted for cadmium and lead, and with significant contamination for nickel, while manganese was low in contamination, cadmium recorded severe pollution at Al-Qayyarah site compared to Al-Kasak site. In contrast, lead, nickel, and manganese were significantly contaminated at the Al-Kasak site compared to Al-Qayyarah. In addition, the pollution load index (PLI) was at the level of 5.81, 4.67, highly polluted at D1 and D2, while the rest of the percentages were at the level of 2, moderate pollution, Al-Kasak site had the highest pollution (PLI) value of (6.28). At the same time, the ecological risk (ER) averaged (20534.88, 16896.71, 19867.11, 19063.14, 18721.07, 18888.61), which indicates that all the sites had very high pollution. The ecological risk index was also within the limits of very high pollution, with the highest value on D1 recorded (20568.45). The potential ecological risk of cadmium was very high at the Al-Qayyarah site, with a value of (19410.95) compared to the Al-Kasak site, where the ecological risk of lead, nickel, and manganese was very high. The ecological risk indices for the Al-Qayyarah site were higher than the Al-Kasak site. The study aims to estimate the concentration of heavy metals according to environmental indices and the impact of oil refineries on the ecosystem in raising the level of heavy metal concentration.

Keywords: soil pollution; contamination factor; pollution load index; ecological risk.

Concentração de metais pesados em solo contaminado com petróleo bruto em duas localidades iraquianas de acordo com índices ambientais de poluição

RESUMO: Amostras de solo contaminado foram coletadas da refinaria Al-Kasak e da refinaria Al-Qayyarah no oeste e sul de Nínive, nas distâncias específicas de 0, 50, 100, 150, 200 e 300 metros da fonte de poluição. Estudou-se as concentrações dos metais pesados Pb, Mn, Ni, Cd e os seus efeitos em alguns padrões de poluição do solo e em propriedades físicas e químicas do solo. Os resultados mostraram um aumento na concentração de metais pesados no solo próximo às fontes de poluição, com cádmio significativamente superior em Al-Qayyarah quando comparado com Al-Kasak (491.744 mg kg⁻¹); chumbo, níquel e manganês apresentaram concentrações mais elevadas em Al-Kasak (166,356, 114,687, 36,487 mg kg⁻¹, respectivamente). A ordem dos elementos minerais nos dois locais de estudo foi Cd>Pb>Ni>Mn. Quanto ao Fator de Contaminação (FC), a ordem observada foi Cd > Pb > Ni > Mn com valores de 684,50, 9,91, 5,13 e 0,1701; o fator de concentração indica alta poluição para cádmio e chumbo, e com contaminação significativa para níquel; manganês apresentou baixos fatores de contaminação, e, cádmio gerou o grau de poluição severa em Al-Qayyarah quando comparado com Al-Kasak. Em contraste, chumbo, níquel e manganês foram significativamente contaminados no local de Al-Kasak em comparação com Al-Qayyarah. Além disso, o índice de carga poluente (PLI) ficou no nível 5,81, 4,67, altamente poluído em D1 e D2, enquanto o restante dos percentuais ficou no nível 2, poluição moderada, o local de Al-Kasak teve a maior poluição (PLI) valor de (6,28). Ao mesmo tempo, o risco ecológico (ER) foi médio (20.534,88, 16.896,71, 19.867,11, 19.063,14, 18.721,07, 18.888,61), o que indica que todos os locais apresentavam poluição muito elevada. O índice de risco ecológico também esteve dentro dos limites de poluição muito elevada, tendo sido registrado o valor mais elevado no D1 (20568,45). O risco ecológico potencial do cádmio era muito elevado no local de Al-Qayyarah, com um valor de (19410,95) em comparação com o local de Al-Kasak, onde o risco ecológico de chumbo,

níquel e manganês era muito elevado. Os índices de risco ecológico para o sítio Al-Qayyarah foram mais elevados do que para o sítio Al-Kasak. O estudo tem como objetivo estimar a concentração de metais pesados de acordo com índices ambientais e o impacto das refinarias de petróleo no ecossistema na elevação do nível de concentração de metais pesados.

Palavras-chave: poluição do solo; fator de contaminação; índice de carga poluente; risco ecológico.

1. INTRODUCTION

Heavy metals have a relatively high density and are considered toxic at low concentrations. For example, Cd and Pb do not have basic biological functions for living organisms. Some elements, such as (Ni and Mn) have an important role in the functions and systems of enzymes at small concentrations. Still, they become toxic and highly dangerous when they exceed the limits of natural concentrations (HASAN et al., 2019).

Heavy metal pollution is one of the most common environmental problems that threaten ecosystems because heavy metals accumulate in the human body and cause organ failure or cancer. They also have toxic effects on animals and plants. These environmental and health effects are long-term because these materials cannot decompose biologically. Knowledge about the characteristics of plants and animals that contain them can generate new phytoremediation technologies that can help treat sites (soils) contaminated with heavy metals and reduce their toxicity to the ecosystem (HUANG et al., 2020). Among the studies that emerged in this regard, Thongyuan et al. (2021) found that the contamination factor (FC) for the elements cadmium and nickel was very high in the soil of a solid waste landfill in an area in central Thailand; in this case, the contamination factor (FC) value for lead was 4.58 mg kg⁻¹ and according to the classification of Tomlinson et al. (1980). Other recent studies also show these same concerns for soil contamination with heavy metals, associating them with environmental pollution indices (KADHIM et al., 2017; AZIZI et al., 2020; QUIN et al., 2022; DONG et al., 2023; MOHAMMED; SALEH, 2023).

In this case, this study evaluates whether crude oil changes the physical and chemical properties of the soil depending on the distance from the source of contamination generation and evaluates the concentrations of some heavy metals (TAHER; SAEED, 2023).

2. MATERIALS AND METHODS

2.1. Soil samples collection

Oil-contaminated soil samples were collected at specific distances 0, 50, 100, 150, 200 and 300 meters, from sites contaminated with crude oil and oil spills from the Al-Kasak refinery located west of Nineveh Governorate, about 40 kilometers from the city center of Mosul, and Al-Qayyarah refinery, which is located in the south of Nineveh Governorate, which is about 60 kilometers from the city center of Mosul in Nineveh Governorate. To estimate the heavy metals in them, the samples were placed in sterile poly bags with the required information written on them (sample number, date, weight) and then transported to the laboratory and stored at a temperature of 4.0 °C in the refrigerator until use.

2.2. Soil tests - Chemical analysis

2.2.1. Measurement of pH

50 g of air-dry soil was weighed, 50 g of soil was placed in a 250 mL conical flask, and 50 mL of distilled water was added to it, according to the suspension method (soil: solution), (1:1) according to the method of Mclean (1982).

2.2.2. Measurement of electrical conductivity (EC)

The electrical conductivity of the soil was read using the suspension method (soil: water - 1:1). Then, the solution was filtered using filter papers and a Buchner funnel until the filtrate became completely clear. We transferred the filtrate for measurement using an electrical conductivity device for three readings, then we found the average of the readings to avoid the error rate, by calibrating the device with its standard solution (RICHARDS, 1954).

2.2.3. Cation exchange capacity (CEC)

We weigh 4 grams of air-dry soil and place it in centrifuge tubes, adding 33 mL of sodium acetate trihydrate 1N and shaking for 5 minutes. We repeat this process 4 times, filtering the liquid each time. Then, add 33 mL of 95% ethyl alcohol, shake for 5 minutes, and place it in the centrifuge until we obtain a clear liquid. The process is repeated with 95% ethanol 3 times, and the liquid is filtered each time until the electrical conductivity of the clear liquid is less than 400 cm μS^{-1} . The anion is removed with an excess amount of ammonium ions through the solution resulting from the removal, replacing all the cations absorbed on the soil colloidal with sodium ions. The samples are estimated by taking spectrometer readings using a flame photometer with a wavelength of 767 nm. The sodium was concentrated according to what was described by Gelderman et al. (1987) and Rhoades (1982).

2.2.4. Determination of calcium carbonate

We weigh 1 gram of the soil sample in a 250 mL beaker, then add standard hydrochloric acid (1N) to it, heat it to a temperature of 50-60 °C, or leave it overnight. After that, the remaining hydrochloric acid is estimated after titration with a standard sodium hydroxide solution 1N, using the Phenolphthalein index to estimate calcium carbonate in the soil, according to Jackson (2005).

2.2.5. Determination of chlorides

Using a pipette, a certain amount of soil extract sample was withdrawn, then adding drops of potassium chromate solution to it, and by adding silver nitrate (AgNO₃) solution, the soil suspension was titrated (1:1). The appearance of a reddish-brown color indicates the determination of chlorine according to the description of Richards (1954).

2.2.6. Determination of phosphorus

A solution containing ammonium molybdate and a small amount of antimony with ascorbic acid was used to develop color in soil extracts. The developed sodium bicarbonate method was modified by neglecting the use of black coal. Available phosphorus was determined by Watanabe et al. (1965) and Olsen et al. (1954).

2.2.7. Determination of calcium and magnesium

I am using saturated soil extracted in a 250 mL beaker by preparing a suspension (soil: water) using Eriochrome black, then titrating with 0.01N (Ethylene Diamine Tetraacetic acid) EDTA solution as an index for determining (calcium + magnesium) (RICHARDS, 1954).

2.2.8. Determination of total organic matter

We weigh 1.0 grams of air-dry soil in a 250 mL beaker, add 10 mL of potassium dichromate solution 1N; then add (20) mL of concentrated sulfuric acid 98%, with continuous stirring to mix the suspension; leave the suspension for 30 minutes, then add 200 mL of distilled water; add 10 mL of concentrated phosphoric acid and leave the mixture to cool, then add 10-15 drops of phenylamine index while stirring on a magnetic shaker. The solution is titrated with ferrous and ammonium sulfate 0.5N, where the color changes from blue-violet to green to determine potassium dichromate. Thus, the organic matter content in the soil is estimated according to Walkley-Black's method (1934).

2.2.9. Determination of total nitrogen

Colorimetric method using the Nessler reagent (total nitrogen by the Nessler method) Nitrogen is determined after digestion of the soil. All forms of nitrogen are transformed into NH_4^+ , where the Nessler solution $K_2[HgI_4]$ reacts with the ion NH_4^+ , which gives the yellow color that was read at the wavelength of 425 nm (PEECH et al., 1947).

2.3. Soil tests - Physical examinations

2.3.1. Determine soil texture

20 grams of soil samples collected from the study areas were weighed, then dried and sieved (using sieves with 2 mm holes). The samples were placed in a 600 mL beaker with 60 ml distilled water. After that, the samples were taken and placed on a surface (hot plate) for 40 minutes, then transfer the mixture was in the blender and add 25 mL of distilled water and 10 mL of the dispersion solution that was previously prepared from (dissolving 40 g of sodium hexametaphosphate and 10 g of sodium carbonate in one liter of distilled water. The mixture was stirred with a blender at high speed for 5 minutes. Then, we transferred the mixture and poured it into a graduated glass cylinder with a one-liter capacity, completing the volume with distilled water. The cylinder with the mixture was placed in a water bath at a temperature of 20 °C and the first reading was taken using a 25 mL pipette after 30 minutes and 44 seconds at a depth of 10 cm, then placed inside the evaporating dish with a known weight and at a temperature of 110 °C for 45 minutes for drying. The next day, we weigh the evaporating dish, and this represents the difference in weight, the weight of the clay and silt, then take a second reading after 30 minutes and 15 seconds from a depth of 20 cm as in the previous step, the difference in weight here represents clay only. As for the weight of the silt, we obtain it by subtracting the weight of the clay from the sum of the silt and clay, while we extract the weight of the sand by subtracting the total weight of the silt and clay from 100, and by knowing the proportions of the soil components (clay, silt and sand), the soil texture is determined by soil texture triangle, from which the soil type can be known (BLAKE et al., 1986).

2.4. Heavy metals experiments - Soil sample digestion

The process of soil digestion was carried out in the Department of Soil and Water Resources, College of Agriculture, Tikrit University, in which 5.0 grams of air-dried soil were weighed and placed in a clean glass beaker with a capacity of (250 mL) and then a solution (1:1:3) of each of concentrated sulfuric acid, concentrated nitric acid, and perchloric acid. The beaker is covered with glass for an hour to prevent the concentrated acids of the samples from evaporating. Then, they are heated on the surface of a heat plate at a temperature of 105 °C for an hour and a half or

until they evaporate. We obtain dry soil by placing it on the (electric heating plate), then adding 20 mL of nitric acid to the dry soil sample. Then, we transfer the beaker's contents to a 100 mL volumetric beaker after filtering the liquid with filter paper to prevent clogging of the capillary tube of the Atomic Absorption Spectrometer (A.A.S.). We carry out the dilution process by adding distilled water to 50 mL, according to Jackson (1958).

2.5. Determination of heavy metals in soil

The heavy metals of soil samples were estimated in the central laboratory at the College of Agriculture/University of Mosul, which included soil digestion and after dilution with distilled water, the absorption of each of the heavy metals in the soil samples was estimated using an A.A.S atomic absorption device, of the Perkin Elmer type. The wavelength and current used for each heavy metal were determined. The absorbance was converted to concentration units using the regression equations for the standard curves for the heavy metals under study. The results were expressed in units of micrograms of metal and per gram of dry weight of the soil according to what was stated in the method by Jackson (1958).

2.6. Statistical analysis

The data were analyzed according to the factorial experiment system of a completely randomized block design, and the averages of the coefficients were compared using Duncan's multiple range method using the least significant difference test ($LSD \leq 0.05$), where the different coefficients were distinguished significantly by different letters of the alphabet using SPSS (PRESCOTT et al., 2005)

2.7. Environmental indices of pollution

Data for soil samples were analyzed according to environmental indices as shown:

2.7.1. The contamination factor (CF):

Soil pollution was evaluated using the contamination factor (CF) proposed by Hakanson (1980), as in the following Equation:

$$CF = \frac{C_{\text{metal}}}{C_{\text{background}}} \quad (01)$$

where: C_{metal} : heavy metal concentration in soil; $C_{\text{background}}$: heavy metal concentration in the natural state. The following terms describe the contamination factor according to Hakanson (1980) (Table 1).

2.7.2. Pollution load index (PLI):

It is calculated from the contamination factor (CF), (C_f^i) . According to the method of Tomlinson et al. (1980), where n is the number of elements:

$$PLI = (CF_1 * CF_2 * CF_3 * \dots * CF_n)^{1/n} \quad (02)$$

The following terms are used to describe the state of pollution (TOMLINSON et al., 1980) (Table 1).

2.5.3. Ecological Risk Index (RI):

This index was used by Hakanson (1980) to measure the rate of heavy metal content in soil and can be calculated according to the equation:

$$RI = \sum_{i=1}^n Er^i \sum_{i=1}^n Tr^i C_r^i / C_n^i \quad (03)$$

Regarding RI is a comprehensive ecological risk index that summarizes the effects of the accumulation of elements, ER^i is the potential ecological risk index, Er^i is the toxic

response coefficient, C_r^i is the measured error for each element, and C_b^i is the background concentration in soil for which this value serves as a reference.

Table 1. Description of the pollution state for the contamination factor and the pollution load.

Tabela 1. Descrição do estado de poluição para o fator de contaminação e a carga poluente.

Pollution condition	Pollution load index (PLI)	Pollution condition	contamination (CF) factor	n
Is polluted	PLI > 1	low contamination factor	1 > CF	.1
Indicates no pollution	1 > PLI	moderate contamination factor	1 < CF ≤ 3	.2
		considerable contamination factor	3 < CF ≤ 6	.3
		very high contamination factor	CF > 3	.4

Table 2. The following terms are used to express the ecological risk index and the potential ecological hazard.

Tabela 2. Os termos a seguir são usados para expressar o índice de risco ecológico e o perigo ecológico potencial.

Pollution degree	Valuable E_r^i	Category values	Risk degree	Valuable RI	Category values
Slight	$E_r^i < 30$	0	Slight	$RI < 40$	0
Medium	$30 \leq E_r^i < 60$	1	Medium	$40 \leq RI < 80$	1
Strong	$60 \leq E_r^i < 120$	2	Strong	$80 \leq RI < 160$	2
Very strong	$120 \leq E_r^i < 240$	3	Very strong	$160 \leq RI < 320$	3
Extremely strong	$240 \leq E_r^i$		-	$RI \geq 320$	4

3. RESULTS

Table 3 shows the chemical and physical characteristics of the soil at the Kasak and Qayyarah sites.

Table 3. Soil Samples Properties.

Tabela 3. Propriedades das Amostras de Solo.

Variable	Al-Kasak	Al-Qayyarah
PH	6.4	6.2
EC (μ Siemens cm^{-1})	1.00	4.40
CEC (Cmole kg^{-1})	42.8	73.6
P (mg kg^{-1})	3.4	3.5
N (mg kg^{-1})	940	780
Ca (mg kg^{-1})	150	250
Mg (mg kg^{-1})	54	10
Cl (mg kg^{-1})	63	12
Organic Total (%)	3.17	3.86
CaCo3 (%)	35	24
Clay (%)	64.95	47.45
Silt (%)	28.25	25.75
Sand (%)	6.8	26.8
Soil Texture	Clay	Clay

We note from Table 4 and Figure 1 that the cadmium element was significantly superior to the rest of the concentrations of lead, nickel, and manganese (36.487, 114.687, 166.356, 470.678) mg/kg, respectively. The order of the elements was as follows (Cd > Pb > Ni > Mn) At the Al-Kasak site. In contrast, at the Al-Qayyarah site, cadmium was superior to lead, nickel, and manganese at concentrations of (14.457, 72.008, 139.605, 491.744) mg kg^{-1} according to the following order (Cd > Pb > Ni > Mn). The reason may be attributed to the proximity of the study site to the source of oil pollution, which Kubier et al. (2019) indicated that cadmium enters the soil through combustion emissions, sewage sludge, industry and mining.

The results of Table 4 and Figure 1 also showed that the cadmium element at the Al-Qayyarah site was significantly superior to the Al-Kasak site at a concentration of 491.744 mg kg^{-1} . At the same time, lead, nickel, and manganese were more polluted in the Al-Kasak site than in the Al-Qayyarah site. These results are consistent with the findings of Kadhim et al. (2017), Azizi et al. (2020), Taher; Saeed (2021) and Dong et al. (2023).

Table 4. Average concentrations of heavy metals in the Kasak and Qayyarah sites.

Tabela 4. Concentrações médias de metais pesados em Kasak e Qayyarah.

Sites	Cd	Pb	Mn	Ni
S1	470.678	166.356	36.487	114.687
S2	491.744	139.605	14.457	72.008
LSD (0.05)	4.568	14.760	15.818	17.017

S1 and S2* represent the sites of Kasak and Al-Qayyarah, respectively.

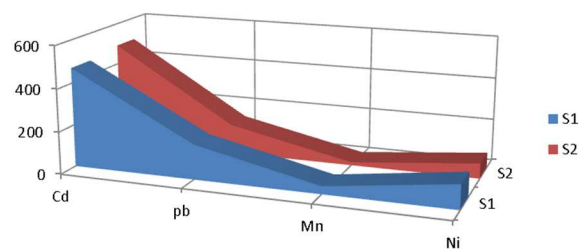


Figure 1. Difference between the concentrations of heavy metals between the Al-Kasak and Al-Qayyarah sites.

Figura 1. Diferença entre as concentrações de metais pesados entre Al-Kasak e Al-Qayyarah.

In Table 5 and Figure 2, we note that D1 recorded the highest value for the element cadmium compared to the rest of the dimensions (D2, D3, D4, D5, D6) with a concentration of 684.50 mg kg^{-1} , which is highly polluted, due to the location of the studied site being located in an oil pool. Lead recorded the highest concentration of D4, amounting to 9.91 mg kg^{-1} , with a severe degree of contamination compared to other dimensions, perhaps due to the lack of plants on the site and its proximity to refining furnaces. At the same time, the elements manganese and nickel were higher in the degree of pollution in the dimensions (D2, D6) with an average of 0.1701 and 5.13 mg kg^{-1} with low and highly polluted, respectively, compared to the rest of the dimensions; this may be due to the acidity of the soil, and its proximity to oil reservoirs. According to the classification of Hakanson (1980), the order of the heavy metals was as mentioned above: $Mn < Ni < Pb < Cd$. As for the Pollution Load Index (PLI), according to the classification of Tomlinson et al. (1980), for Al-Kasak and Al-Qayyarah sites, the highest concentration was recorded at 5.81 mg kg^{-1} ,

meaning that $PLI > 1$; and this is an indication of the presence of pollution in the dimensions studied (Figure 3), corroborating with Thongyuan et al. (2021) and Shi et al. (2023).

Table 5. The degree of pollution and the ecological risk index for the study soil according to the dimensions.

Tabela 5. Grau de poluição e índice de risco ecológico do solo em estudo segundo as dimensões.

Distances	Cf				PLI
	Cd	Pb	Mn	Ni	
D1	684.50	3.40	0.1645	2.98	5.81
D2	563.22	6.84	0.1701	0.73	4.67
D3	662.24	7.22	0.0013	2.98	2.09
D4	635.44	9.91	0.0020	3.94	2.64
D5	624.04	7.93	0.0014	3.57	2.21
D6	629.61	7.60	0.0019	5.13	2.61

*(D1, D2, D3, D4, D5, D6) represents the soil of the Kasak and Qayyarah sites for dimensions (0, 10, 40, 80, 150, 300), respectively.

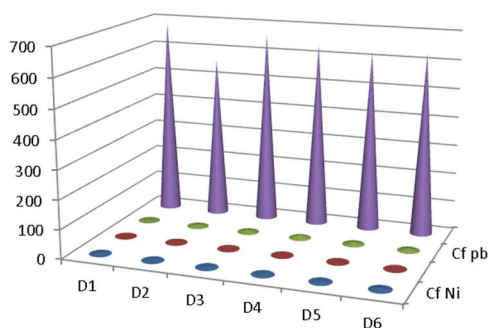


Figure 2. Degree of soil contamination for the Kasak and Qayyarah sites, according to dimensions.

Figura 2. Grau de contaminação do solo em Kasak e Qayyarah, de acordo com as distâncias da fonte contaminante.

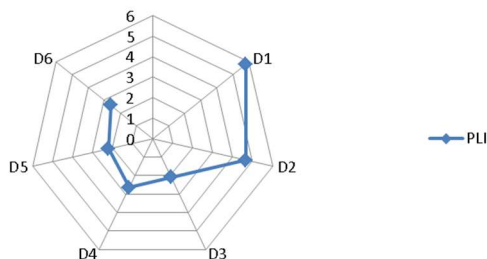


Figure 3. Ecological risk index for the soil of the Kasak and Qayyarah sites.

Figura 3. Índice de risco ecológico para o solo dos sítios Kasak e Qayyarah.

We note from Table 6 and Figure 4 that the index of potential ecological risks (ER) according to the classification of Hakanson (1980) that cadmium (20534.88 mg kg⁻¹) on D1 recorded the highest value compared to the rest of the dimensions, which has a very high level of pollution. As for lead, it was 49.53 mg kg⁻¹ for dimension D4, which is the most concentrated with a moderate ecological risk index, and the elements nickel and manganese recorded the following values (25.66 and 1.70 mg kg⁻¹) for dimensions D6, D2, as they are considered to have low potential ecological risks. Therefore, the order of the heavy metals for potential ecological risks was Cd>Pb>Ni>Mn. The ecological risk for site D1 was very high compared to sites (D2, D3, D4, D5, and D6) with a concentration of (20568.45 mg kg⁻¹), (Figure 5). However, all study sites were of very high ecological risk

for each heavy metal due to oil tanks and pools and the combustion of petroleum products and wastewater contaminated with heavy metals. These results are consistent with Salem et al. (2022) and Saberi et al. (2023).

Table 6. Ecological risk index and the potential environmental risk for the soil of the Kasak and Qayyarah sites for different dimensions.

Tabela 6. Índice de risco ecológico e risco ambiental potencial para o solo em Kasak e Qayyarah para diferentes dimensões.

Distances	ER				RI
	Cd	Pb	Mn	Ni	
D1	20534.88	17.00	1.64	14.92	20568.45
D2	16896.71	34.22	1.70	3.63	16936.26
D3	19867.11	36.10	0.01	14.88	19918.10
D4	19063.14	49.53	0.02	19.71	19132.40
D5	18721.07	39.65	0.01	17.84	18778.57
D6	18888.16	37.98	0.02	25.66	18951.81

*(D1, D2, D3, D4, D5, D6) represents the soil of the Kasak and Qayyarah sites for dimensions (0, 10, 40, 80, 150, 300) respectively.

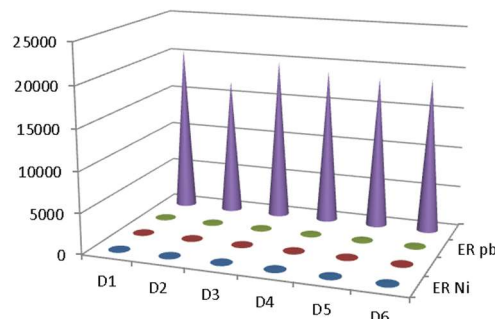


Figure 4. Potential ecological risks of the soil of Kasak and Qayyarah.

Figura 4. Potenciais riscos ecológicos do solo de Kasak e Qayyarah.

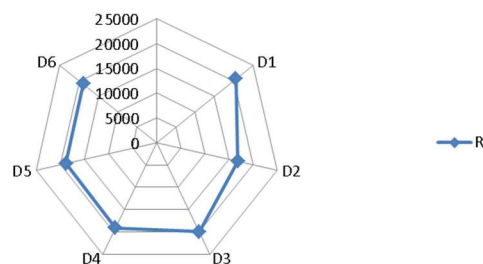


Figure 5. Ecological risk index for the soil of Kasak and Qayyarah.

Figura 5. Índice de risco ecológico para o solo de Kasak e Qayyarah.

The results of Table 7 and Figure 6 showed that lead's Contamination Factor (CF) was 7.77 mg kg⁻¹ with severe contamination, while nickel was highly polluted (3.95 mg kg⁻¹). The lowest value was recorded for manganese at the Al-Kasak site, with a concentration of 0.08 mg kg⁻¹ compared to the Al-Qayyarah site. The value of the cadmium recorded severe pollution in the Al-Qayyarah site with a concentration of 647.03 mg kg⁻¹, while the Pollution Load Index (PLI) was 6.28 mg kg⁻¹, which is $PLI > 1$. This indicates pollution of the Al-Kasak site compared to the Al-Qayyarah site; this may be due to the acidity of the soil and the fact that the studied site is close to ponds contaminated with crude oil (THONGYUAN et al., 2021; SABERI et al., 2023).

Table 8 and Figure 7 shows that the potential ecological risk index at the Al-Qayyarah site was very high (19410.95 mg kg⁻¹) for cadmium compared to the Al-Kasak site for

cadmium (18579.39 mg kg⁻¹) and lead recorded (38.87 mg kg⁻¹) medium ecological risk. In contrast, the value of nickel and manganese (19.77 and 0.81 mg kg⁻¹) was low ecological risk in the Al-Kasak site, which is higher than in the Al-Qayyarah site. The ecological risks of the Al-Qayyarah site were higher compared to the Al-Kasak site, with a value of (19456.30 mg kg⁻¹), due to the possibility of soil contamination of the studied sites by oil spills and the percentage of excess salts that prevent ion exchange between soil particles and heavy metals. These results are consistent with many Abbas (2020) and Qin et al. (2022) studies.

Table 7. Difference between the degree of pollution and the pollution load index for the Kasak and Qayyarah sites.

Tabela 7. Diferença entre o grau de poluição e o índice de carga poluente para Kasak e Qayyarah.

Sites	Cf				PLI
	Cd	Pb	Mn	Ni	
S1	619.31	<u>7.77</u>	<u>0.08</u>	<u>3.95</u>	<u>6.28</u>
S2	<u>647.03</u>	6.52	0.03	2.48	4.29

S1 and S2* represent the sites of Kasak and Al-Qayyarah, respectively.

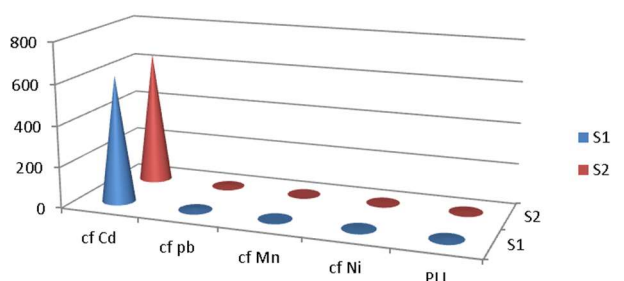


Figure 6. Difference between the degree of pollution and the ecological load index for Kasak and Qayyarah soils.

Figura 6. Diferença entre o grau de poluição e o índice de carga ecológica para os solos Kasak e Qayyarah.

Table 8. Difference between the potential environmental risks and the ecological risk index for the Kasak and Qayyarah sites.

Tabela 8. Diferença entre os potenciais riscos ambientais e o índice de risco ecológico para Kasak e Qayyarah.

Sites	ER				RI
	Cd	Pb	Mn	Ni	
S1	18579.39	<u>38.87</u>	<u>0.81</u>	<u>19.77</u>	18638.85
S2	<u>19410.95</u>	32.62	0.32	12.42	<u>19456.30</u>

S1 and S2* represent the sites of Kasak and Al-Qayyarah, respectively.

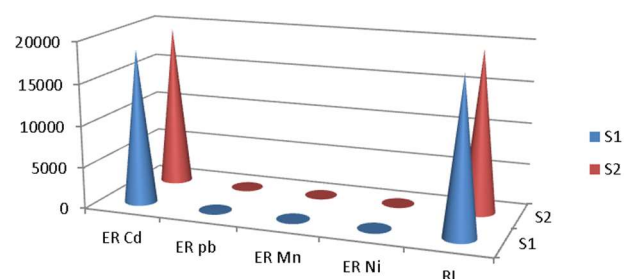


Figure 7. Difference between potential environmental risks and the ecological risk index for the soil of Kasak and Qayyarah.

Figura 7. Diferença entre os riscos ambientais potenciais e o índice de risco ecológico para o solo de Kasak e Qayyarah.

4. DISCUSSION

The results showed an increase in the concentration of the heavy elements Cd, Pb, Ni, and Mn in the sampled soil sites close to the source of pollution, where the cadmium

element recorded a superiority with a value of 491.744 at the Qayyarah site compared to the Al-Kasak site, where lead, nickel, and manganese recorded a higher concentration than the Qayyarah site.

In Table 4 and Figure 1, these results agree with Kubier et al. (2019), who indicated that cadmium enters the soil through combustion emissions, sewage sludge, industry and mining. Qin et al. (2022) confirmed that the average contents of the surface soil were in the order Cd > Ni > pb, where all the heavy elements exceeded the basic values of a soil layer in the site studied due to the possibility of differences in the components and quality of crude oil for the two study sites, as well as a difference in the quality of oil pollutants released for each site in Table 5 and Figure 2.

The contamination factor (CF) values for cadmium and lead were highly polluted in D1 and D4 with a concentration of 684.50 and 9.91, with high contamination for nickel in D6 with a concentration of 5.13, and low contamination for manganese in D2 with a value of 0.1701. At the same time, the pollution load index reached 5.81 in D1 with severe contamination in the form (3).

The degree of contamination of the Qayyarah site with cadmium was higher than the Al-Kasak site, which recorded higher contamination with lead, nickel and manganese (Table 7 and Figure 6). Perhaps due to the lack of plants on the site and its proximity to refining furnaces, confirmed (Thongyuan et al., 2021) that the average concentrations of the following elements and the degree of contamination Mn 1 < (CF) indicate moderate soil contamination and the degree of contamination (CF) pb was high. The Cd > Mn > Pb > Ni contamination of the soil, while the degree of contamination of both cadmium and nickel was high. Every pollution load indicator showed the presence of pollution in the area where it was < PLI 1 (KADHIM et al., 2017).

The pollution load index (PLI) higher than 1 means the area is polluted with heavy metals. The environmental risk index appears in Table 6 and Figure 4. Cadmium in D1 was very high, lead in D4 was medium, while nickel and manganese appeared at a low level in D6 and D2 with a value of 25.66 and 1.70 mg kg⁻¹, respectively. These results are consistent with Thongyuan et al. (2021), in which Mn indicates a low potential environmental risk. While Ni, Pb, and Cd indicate the presence of high risks, and cadmium is the most dangerous, while the environmental risk RI for cadmium was at a very high level in D1 compared to the rest of the dimensions with a value of 20568.45 as in Figure 5. The environmental risk for cadmium was very high at the Qayyarah site compared to the Kasak site.

Lead appeared to be moderately polluted, nickel and manganese had low contamination, and the environmental risks for the Qayyarah site were very high compared to the Kasak site. Table 8 and Figure 7 agree with Qin et al. (2022) that the environmental risks RI constituted between moderate and large environmental risks. Severe levels of the total samples and cadmium were the main controlling elements.

5. CONCLUSIONS

There was an increase in the concentration of the heavy elements Cd, Pb, Ni, and Mn in the soil sites. Cadmium outperformed by a value of 491.744 at the Qayyarah site compared to the Al-Kasak site, where lead, nickel, and

manganese had a higher concentration than at the Qayyarah site.

The values of the contamination factor (CF) for the two elements were Cadmium and lead were highly polluted in D1 and D4 with concentrations of 684.50 and 9.91, high contamination was in D6 with a concentration of 5.13, and low contamination was in manganese in D2 with a value of 0.1701.

The highly polluted pollution load index was 5.81 in D1, and the degree of contamination of the Qayyarah site with cadmium was higher than the Kasak site, which was recorded - higher contamination with lead, nickel and manganese. The environmental risk index for cadmium was on D1 at a very high level, and lead in D4 was at a medium level.

At the same time, nickel and manganese appeared at a low level on D6 and D2 with a value of 25.66 and 1.70, while the environmental risk RI for cadmium was very high in D1. Compared to the rest of the dimensions, the value of 20568.45 was 20568.45.

The environmental risk of cadmium was very high at the Qayyarah site compared to the Kasak site, which showed moderate lead contamination, nickel and manganese with low contamination. The environmental risks for the Qayyarah site were very high compared to the Kask site.

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Author Contributions: The two authors participated in all stages of the article and read and agreed to the published version of the manuscript.

Institutional Review Board Statement: *Not applicable.*

Informed Consent Statement: *Not applicable.*

Data Availability Statement: Study data/images can be obtained by request to the corresponding author or the second author via e-mail.

Conflicts of Interest: The authors declare no conflict of interest. Supporting entities had no role in the design of the study, in the collection, analysis, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.