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Evaluation of Vanadium Contamination in Some Soils of the East Baghdad Oil Field

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Abstract
Since oil is the primary source of vanadium in the environment and crude oil has a correspondingly high percentage of vanadium. Vanadium is crucial as a sign of oil contamination. Twenty soil samples were taken from various locations surrounding the East Baghdad oil field in Iraq during February 2022 and then analyzed to determine the effects of industrialization along with urbanization-related pollutants. The soil samples were analyzed using spectrophotometry analysis. In soil samples taken from the research area, vanadium concentrations range from (0.26 to 1.2 ppm). The contamination (CF), geoaccumulation (Igeo) and Enrichment factors (EF) indicated that all the soil samples are uncontaminated.

Keywords: Vanadium, East Baghdad oil field, Soil, Contamination; Spatial distribution

تقييم تلوث عنصر الفاناديوم في بعض ترب حقل شرق بغداد النفطي

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قسم علم الارض, كلية العلوم, جامعة بغداد, بغداد, العراق

الخلاصة
نظرًا لأن النفط هو المصدر الأساسي للفاناديوم في البيئة ، وبما أن النفط الخام يحتوي على نسبة عالية من الفاناديوم ، فإن الفاناديوم أمر بالغ الأهمية كعلامة على التلوث النفطي ، فقد تم أخذ ثمانية عشر عينة تربة من مواقع مختلفة تحيط بحقل نفط شرق بغداد في العراق خلال شهر شباط 2022 وتحليلها لتحديد اثار التصنيع والتحضر ذات الصلة الملوثات. تم تحليل عينات التربة باستخدام التحليل الطيفي. في عينات التربة المأخوذة من منطقة البحث ، تتراوح تركيزات الفاناديوم من (0.26 إلى 1.2 مغ/كغ). تشير عوامل التلوث (CF) و التراكم الجغرافي (Igeo) و الاثراء (EF) إلى أن جميع عينات التربة غير ملوثة.

1. Introduction

The marketing and distribution, transportation, refining, and exploration and production of crude oil and natural gas are the primary segments that make up the petroleum industry [1]. Exploration and production activities in oil field locations can have very detrimental impacts because of their harmful consequences, the effects of oil spills, drilling mud and fluid, formation waters, and effluent discharge are of significant concern for the environment [2].

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Vanadium is widely distributed in the earth's crust at an average concentration of 100 ppm (approximately 100 mg/kg), similar to that of zinc and nickel [3].

As oil is among the major sources of vanadium in the environment and because most crude oil has relatively high vanadium contents, vanadium is crucial as a sign of oil pollution that vanadium enrichment in the sediment may be seen if the oil has dropped to the bottom and biodegradation has occurred. Unlike many environmental pollutants [4]. Vanadium, like the majority of heavy metal elements, may be dangerous at high doses but is completely safe at low doses. Vanadium has been demonstrated to have detrimental effects on the cardiovascular and immune systems, kidneys, liver, skin, and even the respiratory and digestive systems when exposed for an extended time [5].

1.1 Location and Geological Setting of the study area

Baghdad is the largest city in Iraq and the second largest capital in the Arab World region according to the density of inhabitancy [6]. The East Baghdad oil field is located in the area between latitudes 44.31877 and 44.3504 and longitudes 33.50312 and 33.48871 (Figure 1).

The East Baghdad field has a north-south length of more than 100 km and a width of more than 10 km in some areas. It occupies the northeastern part of the Mesopotamian plain. The Mesopotamian plain is primarily covered by Holocene deposits, which constitute a complicated and overlapping sequence of sand, clay, silt, and gravel. Baghdad Region is situated on the Unstable Shelf of the Arabian Plate, primarily in the Tigris Subzone of the Mesopotamian Zone [7]. The pollutants can travel over a large distance and settle on sediment or water, as a result of wet and dry deposition. The distribution and deposition of pollutants through air largely depend on climatic factors [8].

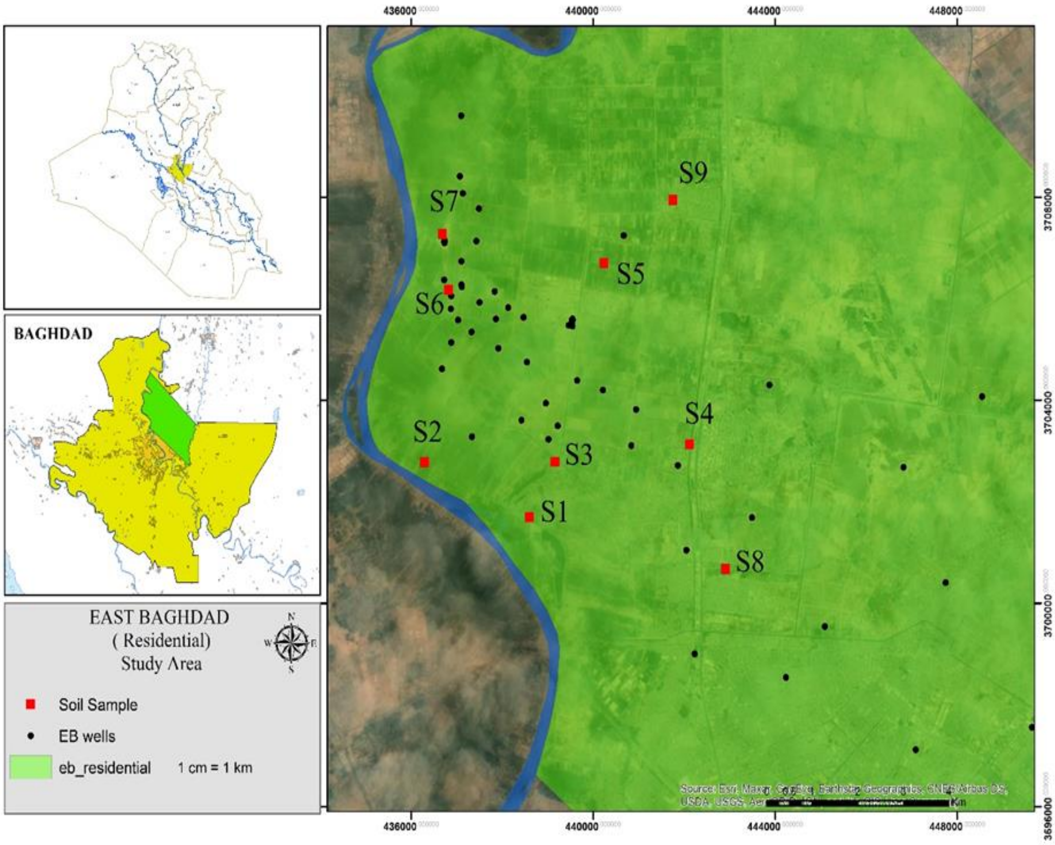

Figure 1: Map of the study area shows the location of soil samples.

2. Materials and methods

In the investigation that was done on 12/2/2022, 18 soil samples were obtained at (9) sites, each site was sampled at two depths. Every sample has a depth component (0 to 20 cm (A) and 20 to 40 cm (B). Samples are located around 5 km east of Baghdad oil. All samples were stored for later examination in airtight Ziploc polyethene bags and labelled, and the precise position was identified using GPS readings as shown in Table 1.

Table 1: Coordinates the soil sampling sites.

Sample		location	Coordination	
			Longitude	latitude
S1	A1	Near the water liquefaction station	33.452929	44.339363
	B1			
S2	A2	3 km away from S1	33.462535	44.314518
	B2			
S3	A3	Near the residential area south of the field (qumira)	33.462797	44.345319
	B3			
S4	A4	Near the trocar site, June 1st, facing Bob Al-Sham	33.0466106	44.0377149
	B4			
S5	A5	Near Al Quds Electricity Station	33.498168	44.356684
	B5			
S6	A6	Abu Dali village near the drilling company	33.477385	44.319885
	B6			
S7	A7	1 km away from smart option store	33.477385	44.350144
	B7			
S8	A8	Near Mrs. Narjs Mosque	33.477385	44.350144
	B98			
S9	A9	Near Al-Entisar clinic	33.469615	44.345880
	B9			

Each sample was then processed in a lab so that it could be used for the required analysis. The moist samples were separated for enough time to allow for full drying. After that, remove any large debris, gravel, plant matter, and other impurities before sieving the material through a 2 mm sieve. UV-Visible spectrophotometer analysis is one technique used in the College of Science, Department of Biology at University of Baghdad to evaluate the soil's V concentration in the samples. Additionally, the pH value was examined in a lab at the Ministry of Science and Technology's Directorate of Environmental and Water Research and Technology.

2.2 Soil pollution indicators

Different methodologies were utilized to evaluate the soil pollution, and different indices were employed for the evaluation of (V) contamination in some soils surrounding the East Baghdad oil field. Three indicators were utilized: Geoaccumulation Index (I_{geo}), Contamination Factor (CF) and Enrichment factor (EF).

2.2.1 Index of Geoaccumulation (I_{geo})

Several researchers have employed the Geo-accumulation Index (Igeo), which was developed by [9] to calculate the level of metal accumulation in sediments. The mathematical formula for I_{geo} according to [9] is:

$$Igeo = log2\,[Cn/1.5Bn] \quad (1)$$

Where Cn is the element concentration in the sediment and Bn is the geochemical background value. To account for any variations in background data caused by the lithogenic effect, the connection includes factor 1.5. There are seven classes (0–6) on the geo-accumulation index (Igeo) scale, ranging from severely contaminated to unpolluted.

Table 2 : Geoaccumulation index (I_{geo}) for soil pollution levels **[6]**.

I_{geo} Class	I_{geo} value	Pollution level
0	<0	practically unpolluted
1	0-1	unpolluted to moderately polluted
2	1-2	moderately polluted
3	2-3	moderately to strongly polluted
4	3-4	strongly polluted
5	4-5	strongly to extremely polluted
6	>5	extremely polluted

2.3.2 Contamination Factor (CF)

This factor can be calculated with the formula established by [10] as follows:

$$CF = C\ Heavy\ metal\ /\ C\ Background \quad (2)$$

Where C heavy metal is the measured concentration of heavy metal in a sample, according to [10]. and C background is the average concentration of the corresponding heavy metal in the background samples according to [3] background for vanadium is 100 ppm. There are four types of contamination factors, as shown in Table 3:

Table 3: Soil pollution classifications depending on the level of contamination (CF)

CF Value	contamination Level
CF<1	Low contamination
1<CF<3	Moderate contamination
3<CF<6	Considerable contamination
CF>6	Very high contamination

2.2.3 Enrichment Factor (EF)

The enrichment factor measures how abundant a chemical element is in the soil concerning the bedrock [11]. EF was computed by comparing the concentration of each tested metal with that of a reference metal [12].

$$EF = (\ Cn\ /\ Cref\ )\ sample\ /(\ Bn\ /\ Bref\ )\ background \quad (3)$$

where Cn is the trace element's concentration in the topsoil (n), Cref is the reference element's concentration in the topsoil sample, Bn is the trace element's value in the geochemical background of the topsoil (background value), and Bref is the value of the reference element in the geochemical background of the topsoil sample. Using this index makes it possible to evaluate how a potentially harmful ingredient differs from a standard ingredient. An element is referred to as a reference element if it is exceptionally stable in the soil and shows no signs of vertical movement or degradation. Aluminium, iron, manganese, rubidium, and scandium are the often-used reference elements [13].

Iron was used in this study to maintain differences between natural and anthropogenic components, following the hypothesis that states that "the content components in the earth crust have not been troubled or disturbed by anthropogenic activity affect" and "natural sources and natural process is approximated equal to (98%) of the all process that the earth evolved, so the natural sources greatly dominate its coevolution" [14]. Generally, the soils can be classified as shown in Table 4.

Table 4 : Categories of EF.

EF value	Enrichment category
EF≤2	Minimal enrichment
2<EF≤5	Moderate enrichment
5<EF≤20	Significant enrichment
20<EF≤40	Very high enrichment
EF>40	Extremely enrichment

3. Results and Discussion

3.1. Content and spatial distribution of V in the study soil

Vanadium is widely distributed in the earth's crust at an average concentration of 100 ppm (approximately 100 mg/kg) [3]. The vanadium concentration in soil samples obtained from the study region was a range between 0.26 – 1.2 ppm as displayed in Table 5. The GIS technique uses spatial analyst extension in Arc Map to prepare the map to predict the spatial distribution of the element [15]. spatial distributions of vanadium in soil are displayed in Figure 2.

Table 5: Vanadium concentrations in the study area.

Sample		V (ppm)	location
S1	A1	0.31	Near the water liquefaction station
	B1	0.37	
S2	A2	0.3	3 km away from S1
	B2	0.35	
S3	A3	0.34	Near the residential area south of the field (Qumira)
	B3	0.38	
S4	A4	1.2	Near the trocar site, June 1st, facing Bob Al-Sham
	B4	0.71	
S5	A5	0.28	Near Al Quds Electricity Station
	B5	0.37	
S6	A6	0.26	Abu Dali village near the drilling company
	B6	0.36	
S7	A7	0.35	1 km away from the smart option store
	B7	0.39	
S8	A8	0.33	Near Mrs. Narjs Mosque
	B8	0.37	
S9	A9	0.39	Near Al-Entisar clinic

	B9	0.3
Range	0.26 ppm in S6A to 1.2 ppm in S4A	
Average	0.408.	
Geochemical Background value	V 100 ppm [3]	

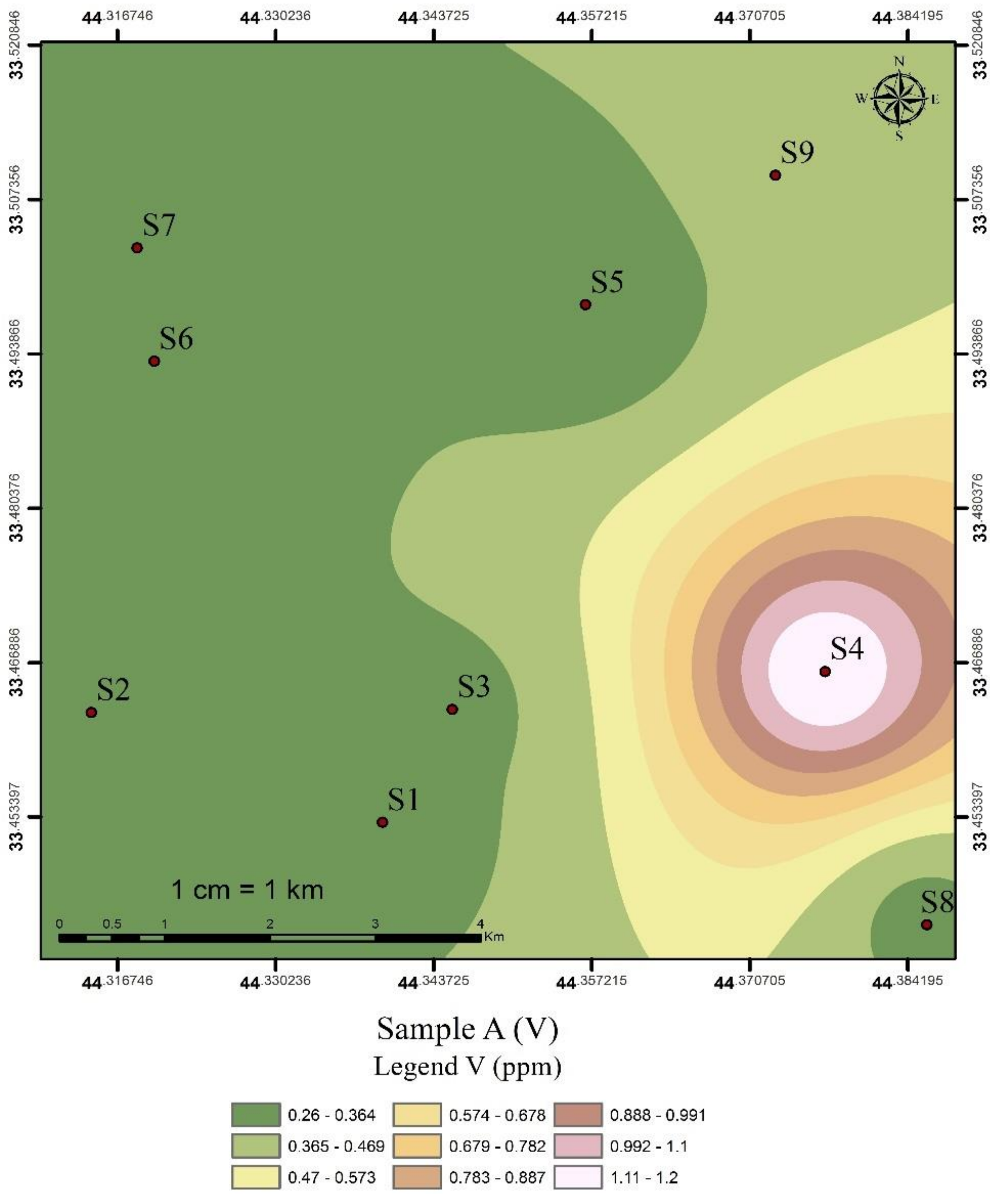

Figure 2: The spatial distribution map of vanadium (V) in the soil of the study area for samples (A)

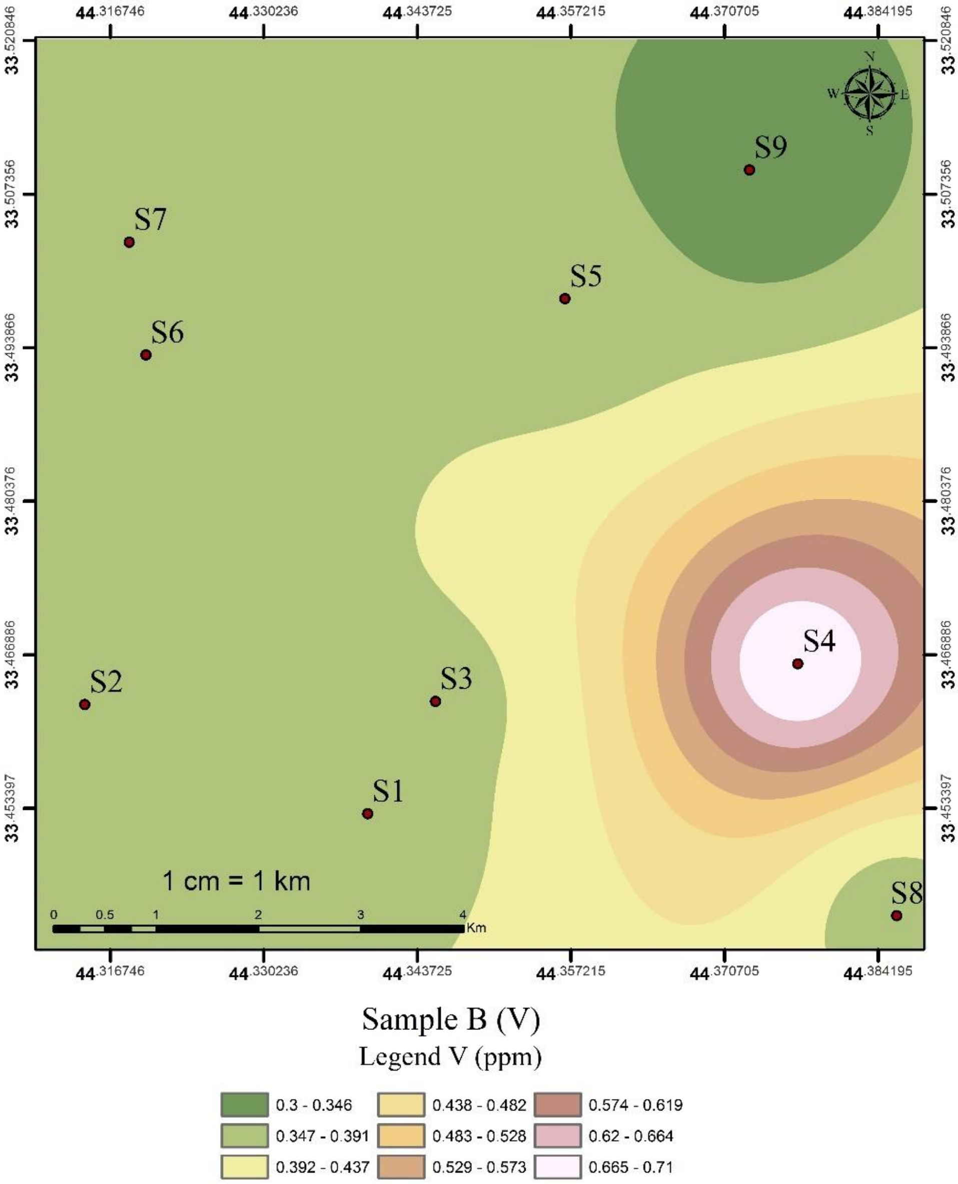

Figure 3: The spatial distribution map of vanadium (V) in the soil of the study area for samples (B)

3.2. Effect of pH on the Valence State of Vanadium in Soil

The net charge of the soil is negative whenever the pH is higher than (7), and positive whenever the pH is lower than (pH 7). There are two different types of charges present in soil colloids, such as metal oxides, organic matter, and clay minerals. The first charge is constant and independent of pH, while the other is changeable and dependent on pH [16]. As a result, soil pH plays a key role in regulating the presence of heavy metals in the soil. These substances may be collected from the soil and bind to it, with the potential for subsequent activation and transfer whenever the pH shifts [17]. Most cation heavy metals become more soluble and transportable at low pH levels, and due to electrostatic repulsion and competition for adsorption sites with anions such as $CO3^{-}$, $SO4^{2}$-, $PO4^{2-}$, and Cl^{-}, their adsorption decreases [18]. Vanadium exhibits various geochemical behaviors due to its capacity to create cations and anions depending on the pH of the soil [19]. The pentavalent cation type predominates at pH levels (pH> 8) while the tetravalent V(IV) cation type predominates at pH 4 and in reduction conditions. Tetravalent V(IV) eventually converts to pentavalent V(V) in anion form when rising pH values and/or increasing oxygen [20].

The present study indicated the pH levels in some of the soils surrounding the East Baghdad oil field ranged from 7.44 to 7.87 with an average of 7.63 (Table 6). This indicates that the city's soil is alkaline and that pentavalent vanadium V(V) is present there, which poses more health risks than V(IV) due to its solubility, mobility, and bioavailability [21].
This could be a result of electrostatic attraction between the negative charges of vanadium and the adsorbent substance [22] or due to competition between the soil's available surface sites for vanadium anions and the hydroxyl ion (OH^-) [23].

Table 6: pH values of soil samples

Sample	pH for depth (0-20) cm	pH Depth (20-40) cm
S 1	7.81	7.75
S 2	7.87	7.71
S 3	7.6	7.67
S 4	7.57	7.62
S 5	7.48	7.61
S 6	7.52	7.69
S 7	7.64	7.56
S 8	7.62	7.44
S 9	7.59	7.61
Range	7.44 -7.87	
Average	7.63	

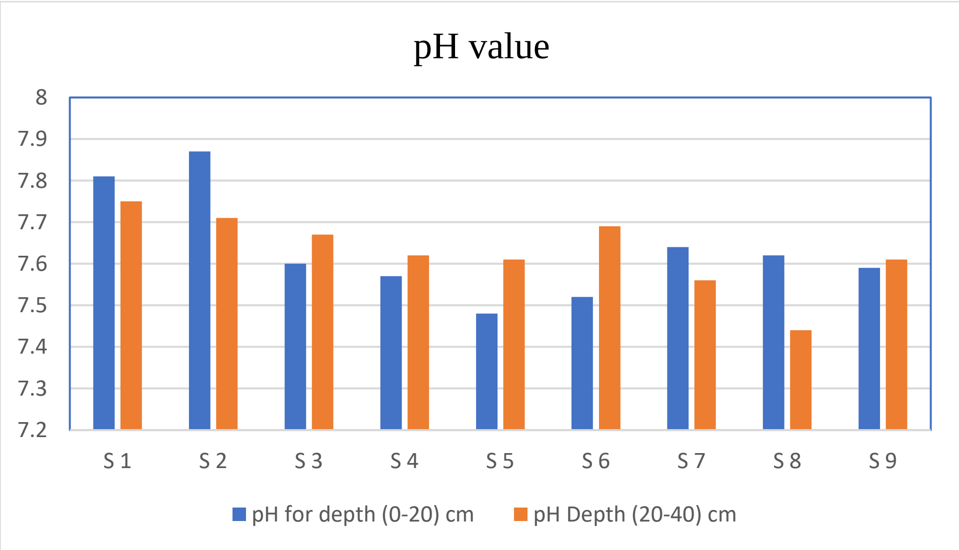

Figure 4: pH value for soil samples.

To establish the relation between pH and Vanadium concentration correlation coefficient was used in this study. The correlation coefficient often aims to study whether there is some association between 2 observed variables and to estimate the strength of this relationship by using the Pearson equation [24].

$$r_{xy} = \frac{\sum X \quad Y - \frac{(\sum X)(\sum Y)}{n}}{\sqrt{\left[\left(\sum X^2 - \frac{(\sum X)^2}{n_x}\right)\left(\sum Y^2 - \frac{(\sum Y)^2}{n_y}\right)\right]}} \quad (4)$$

Where:
X, Y = the variations (in this study vanadium concentration and pH)
r = Correlation coefficient
n = Number of observations

Table 7: correlation coefficient results

X	X^2	Y	Y^2	$X \quad Y$
0.335	0.112225	**7.81**	60.9961	2.61635
0.325	0.105625	**7.87**	61.9369	2.55775
0.36	0.1296	**7.6**	57.76	2.736
0.955	0.912025	**7.57**	57.3049	7.22935
0.325	0.105625	**7.48**	55.9504	2.431
0.31	0.0961	**7.52**	56.5504	2.3312
0.37	0.1369	**7.64**	58.3696	2.8268
0.35	0.1225	**7.62**	58.0644	2.667
0.345	0.119025	**7.59**	57.6081	2.61855
$\sum X$ = 3.675	$\sum X^2$= 1.839625	$\sum Y$= 68.7	$\sum Y^2$= 524.5408	$\sum X \quad Y$= 28.014
Result	-0.18283			

The result of the equation indicates that there is a negative or inverse relationship between Vanadium concentration and pH value in the study area.

3.3. Assessment of soil pollution

Table 8 : Mean value (A and B) of Geoaccumulation I_{geo}

Stations	location	Igeo value	Igeo Class	Pollution level
S1	Near the water liquefaction station	-8.785	0	practically unpolluted
S2	3 km away from S1	-8.85	0	practically unpolluted
S3	Near the residential area south of the field (qumira)	-8.702	0	practically unpolluted
S4	Near the trocar site, June 1st, facing Bob Al-Sham	-7.295	0	practically unpolluted
S5	Near Al Quds Electricity Station	-8.85	0	practically unpolluted

S6	Abu Dali village near the drilling company	-8.918	0	practically unpolluted
S7	1 km away from smart option store	-8.663	0	practically unpolluted
S8	Near Mrs. Narjs Mosque	-8.743	0	practically unpolluted
S9	Near Al-Entisar clinic	-8.764	0	practically unpolluted
Average	-8.61889			
Range	-8.918 to -7.295			
geochemical background value for Vanadium	V 100 ppm [3]			

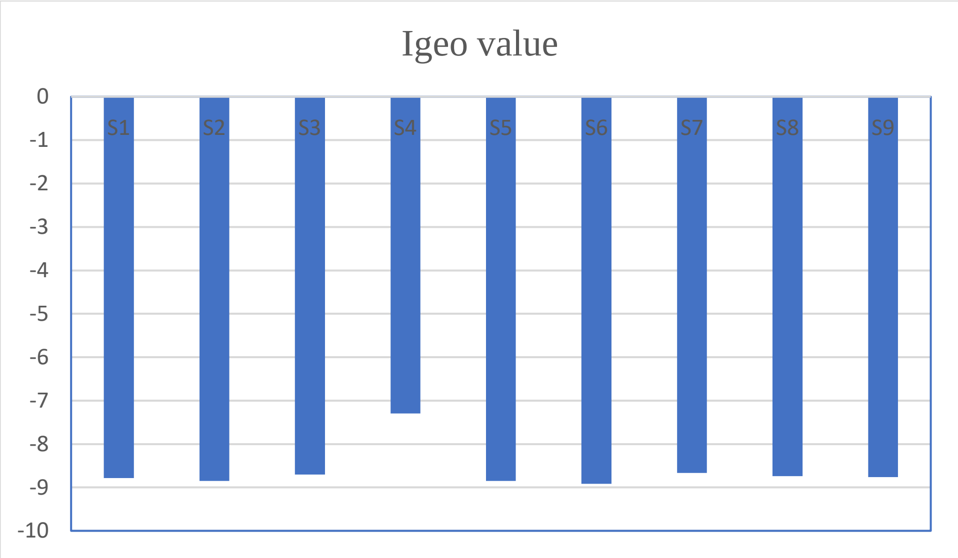

Figure 5: I_{geo} values of tested soil samples.

Table 9: Mean value (A and B) of Contamination factor for different locations.

Stations	Location	CF Value	CF Value	contamination Level
S1	Near the water liquefaction station	0.0034	0.0034	Low contamination
S2	3 km away from S1	0.0032	0.0032	Low contamination
S3	Near the residential area south of the field (qumira)	0.0036	0.0036	Low contamination
S4	Near the trocar site, June 1st, facing Bob Al-Sham	0.0095	0.0095	Low contamination
S5	Near Al Quds Electricity Station	0.0032	0.0032	Low contamination

S6	Abu Dali village near the drilling company	0.0031	0.0031	Low contamination
S7	1 km away from smart option store	0.0037	0.0037	Low contamination
S8	Near Mrs. Narjs Mosque	0.0035	0.0035	Low contamination
S9	Near Al-Entisar clinic	0.0034	0.0034	Low contamination
Average	0.004067			
Range	0.0031 to 0.0095			

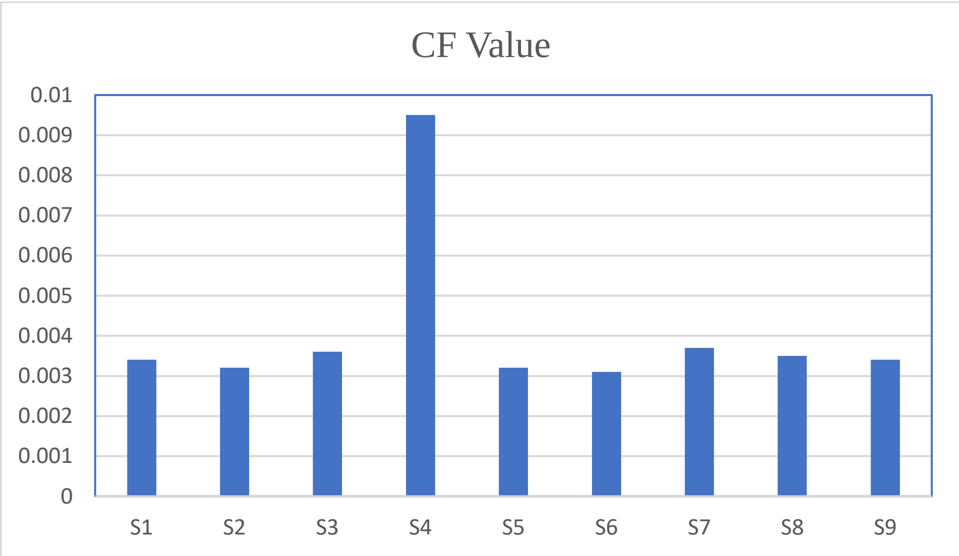

Figure 6: CF values of tested soil samples.

Table 10: Mean value (A and B) of Enrichment factor (EF) for different locations.

Stations	Location	EF value	Enrichment category
S1	Near the water liquefaction station	0.008112	Minimal enrichment
S2	3 km away from S1	0.008062	Minimal enrichment
S3	Near the residential area south of the field (qumira)	0.00877	Minimal enrichment
S4	Near the trocar site, June 1st, facing Bob Al-Sham	0.030293	Minimal enrichment
S5	Near Al Quds Electricity Station	0.00801	Minimal enrichment
S6	Abu Dali village near the drilling company	0.007977	Minimal enrichment
S7	1 km away from smart option store	0.010678	Minimal enrichment
S8	Near Mrs. Narjs Mosque	0.010145	Minimal enrichment

S9	Near Al-Entisar clinic	0.012684	Minimal enrichment
Average		0.011222	
Range		0.007 to 0.03	
background value for Fe		40000 ppm [25]	

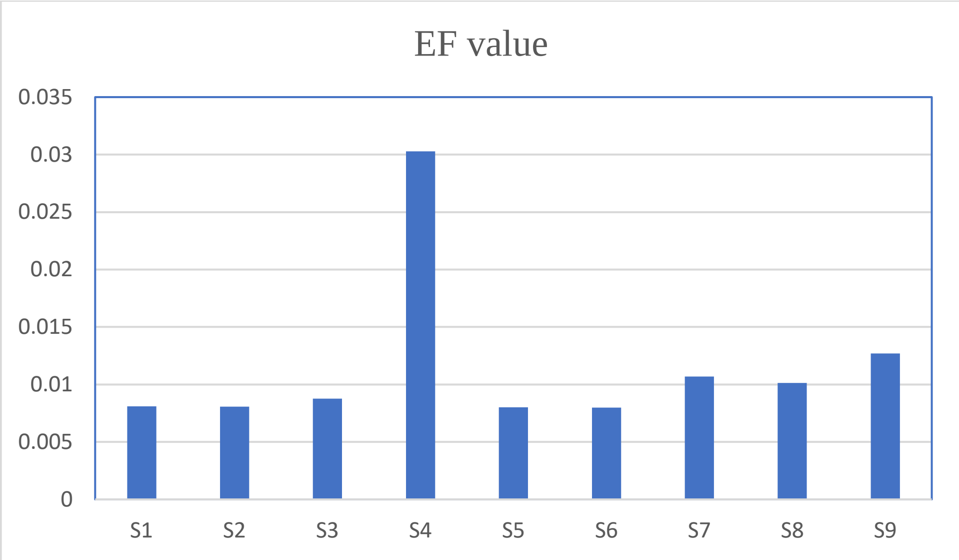

Figure 7: Er values of tested soil samples.

3.4. Discussion

Vanadium concentrations in soil samples ranged from 0.26 and 1.2 ppm. According to [11], all locations had V concentrations that were within reasonable limits (100 mg/kg). The pH value of the study soil had an average of 7.63, with a range of 7.44 to 7.87. (Table 6). Pentavalent vanadium (V), which offers more health concerns than (IV) because of higher solubility, mobility, and bioavailability, is present in the city's soil, indicating that it is alkaline.

According to Table 7, the geoaccumulation index (I_{geo}) had mean values between (-8.918 and -7.295). There were no Igeo mean values over 0 or in class 0 for any soil sample, indicating that the soil is y practically unpolluted.

The contamination factor as in Table 8 shows that the soil of the study area had a low contamination level, Where the CF value was distributed between 0.0031 and 0.0095.
Enrichment factor (EF) as shown in Table 9 indicated that the enrichment factor ranges from (0.007977 to 0.030293). which means it had minimal enrichment.

5. Conclusions

In this research, the results that had been achieved confirm that the soil pollution of the interesting zones has no toxicity because the study area is agricultural, so plants adsorb elements from the soil and obtain nutrients from photosynthesis in their leaves using the green pigment chlorophyll and water absorption with elements through their roots [26]. and may be due to the direction of the wind in these areas being northwest which can withdraw the elements far away from the study area. As well as pH has a negative relationship with Vanadium concentration, as the soil in the study area is slightly alkaline so the concentration of vanadium is not high.

that's why the vanadium concentration in the study area is very low and reaches it is height concentration near the trocar at site 4 because when the soil washes all the elements and salts it will concentrate in the trocar drainage.

3. Acknowledgements

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