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Assessment of heavy metals and ecological risk in the sediments of Thi Oar and Basrah governorates - Southern Iraq

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Abstract. The distribution of heavy metals in surface sediment in the four sites of Thi Qar governorate and one site in the eastern part of Basrah governorate were investigated in order to detect the environmental characteristics in these areas. The texture of sandysilt, silt and sandymud are dominant in the study area. The distribution of heavy metals follows the pattern Fe>Ti>Mn>V>Cr>Zn>Pb>Ni>Cu > Co> As. The heavy metals content was reduced in the sandy sediments and low TOC. The heavy metals had a positive correlation with the silt fraction in the sediments of the study area. Sediments alkalinity found with a positive relationship with TOC content. The values of Fe, Zn, Pb, V, and Co were lower than their content in the world wild sedimentary rocks, while Ti, Mn, Ni, Cr, Cu, and As were higher than their content in the world wide sedimentary rocks. The spatial distribution of heavy metals is higher in the Majnoon oil field compared with the other areas. An approach utilizes various contamination indices (Enrichment Factor EF, Geoaccumulation index Igeo, Contamination Factor CF, and Ecological risks Er) were used to evaluate a contamination degree. The values of the contamination indices showed no/low sediment contamination with Co, Zn, Pb, Cu, V, Fe, and Mn in the Chibayish, Nasiriyah city center, and Tal Abu Dahab. Moderate contamination with Ti and Cr in the Suq Al-Shuyukh , Majnoon oil field and Chibayish, while considerable contamination with Ni and As in the Majnoon oil field. The results of Er showed low heavy metals ecological risks.

Keywords: Majnnon, Iraq, Thi Qar, Basrah, Heavy metals, Tal Abu Dahab

1. Introduction

Heavy metals are referred to those metals which possess a specific density of more than 5 g/cm³ and adversely affect the living organisms and environment [11]. There is a high probability of contamination by heavy metals, due to the availability of sources of pollution. Pollution can be considered as the main and most dangerous factor of anthropogenic impact on the hydrosphere [4].



Heavy metals contamination in soil is a major concern because of their toxicity and threat to human life and the environment [3]. The heavy metals coming in the ecosystems may lead to bioaccumulation, geo- accumulation, and bio- magnification. Geochemical partitioning of trace metals in soils with different land-use groups is important to understand behavior of metals, which derived from the anthropogenic activity and directly affected to human and animal health [8,6, and 9]. The fixation of heavy metals are controlled in organic matter, iron, clay minerals, manganese oxides and hydroxides by adsorption and in poorly soluble sulfide, phosphate, and carbonate minerals by precipitation [5]. Oil trash burning from oil refining, exhaust emissions from vehicles under actual traffic conditions, and private electrical generators, all of these represent as important sources of air pollutants that precipitate on the soil surface as an aerosol thin layer [2]. heavy metals are considered environmental pollutants and their toxicity is a problem of increasing importance for ecological, evolutionary, nutritional and environmental reasons [10 and 17]. The most commonly found heavy metals in waste water include cadmium, arsenic, copper, chromium, nickel, lead, and zinc, all of these cause risks for the environments and human health [13]. Majnoon oil field is a super-giant oil field located 60 km from Basrah in southern Iraq. Majnoon is one of the richest oil fields in the world with an estimated 38 billion barrels of oil in place. The field was named Majnoon which means crazy in Arabic in reference to an excessive amount of oil in a dense area. The study area was chosen on the basis of the impact of large oil production and the licensing rounds in the Majnoon oil field and its impact on neighboring areas (Suq Al-Shuyukh, Chibayish, Nasiriyah city center, and Tal Abu Dahab area) in the Dhi Qar governorate through the concentration of heavy elements and their environmental assessment.

2. Methods and materials

Sediment samples were collected from four sites in the Dhi Qar governorate (Suq Al-Shuyukh, Chibayish, Nasiriyah city center, and Tal Abu Dahab area) and one site in Majnon oil field in the eastern part of Basrah governorate (Fig 1). The samples were carried by a polythene bag. After collection, some portion of sediment samples were dried in a vacuum oven at 105°C until constant weight, lightly ground in an agate mortar for homogenization and prepared for analysis of heavy metal and some portion of samples were prepared for sieve analysis, and organic content test. Mineral identification of the specimens took place with X-ray diffraction patterns obtained by means of a D-5000 X-ray diffractometer, using CuK α sources in wavelength, v being 1.54056Å at 40 kV and 30 mA between 5-65°. Geochemical analyses for Fe ,Mn, Ti, Cr , Co, Ni, Cu, Zn, As, Pb, and V calculated by Inductively Coupled Plasma – Mass Spectrometry (ICPMS) at the ALS Laboratories in Spain. Grain size analyses achieved by Master Sizer Instrument in Geology departments of Basrah University. Total organic method (TOC) results are calculated by combustion at different temperature degrees. Use ArcGIS version 10.6 program for the distribution of heavy metals in the study area.

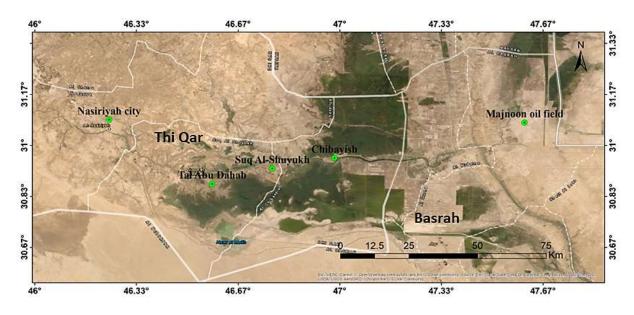


Fig 1. Map of study area

3. Grain size analyses

Grain size analyses and texture sediments are presented in the Table 1. Sand fractions were increased gradually from Majnnon oil filed towards the other sites in the study area, whereas silt decreased. The sediment texture varied from silt, sandysilt, and sandymud. The TOC recorded higher in the silt texture than sandysilt and sandymud textures. Sediments alkalinity found with a positive relationship with TOC content.

Table 1. Grain size, texture, TOC, and pH of the sediments in the study area

Site No.	TOC	pН	Sand	Silt	Clay	Texture
	%		%	%	%	
Majnoon oil field	0.71	7.7	7	86	7	Silt
Chibayish	0.67	7.5	11	80	9	Sandy Silt
Suq Al-Shuyukh	0.62	7.45	13	75	12	Sandy Mud
Tal Abu Dahab	0.6	7.32	26	68	6	Sandy Silt
Nasiriyah city center	0.5	7.25	25	67	8	Sandy Silt

4. Heavy metal concentrations

Concentration of heavy metals for each site was present in Table 2. The concentrations were ranging over following intervals; Ti: 3500-4490 mg/kg, Mn: 525-697 mg/kg, Zn: 61-69.24 mg/kg, Ni: 115-174.9 mg/kg, Pb: 8.9-9.93 mg/kg, V: 75.62-108.6 mg/kg, Cr: 145-383.16 mg/kg, Cu: 28.35-32.11mg/kg, Co: 3.01-7.62mg/kg, As: 4.1-4.75 mg/kg and Fe: 27654-35446 mg/kg. Allowing to arrange of heavy metals from higher to lower mean content as following: Fe > Ti >Mn > Cr > Ni > V > Zn > Cu > Pb > Co > As.

Site No.	Ti	Mn	Zn	Ni	Pb	V	Cr	Cu	Со	As	Fe
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Majnoon oil field	4499	697	69.24	174.9	9.93	108.6	383.16	32.11	7.62	4.75	35446
Chibayish	3900	610	63	147	9.2	98	310	31	6.7	4.4	31210
Suq Al-Shuyukh	3500	550	62.3	120	9.08	81	163	30.5	3.3	4.2	29230
Tal Abu Dahab	3525	525	61	115	8.9	78	159	29.7	3.1	4.1	27980
Nasiriyah city center	3777	537	61.5	117.3	8.91	75.62	145	28.35	3.06	4.16	27654
Range	3500-	525-	61-	115-	8.9-	75.62-	145-	28.35-	3.01-	4.1-	27654-
-	4490	697	69.24	174.9	9.93	108.6	383.16	32.11	7.62	4.75	35446
Average	3840.2	583.8	63.4	140.2	9.2	88.2	232	30.33	4.75	4.32	30304

Table 2. Heavy metal concentrations in the surface sediments

5. Assessment of heavy metals

5.1. Assessment according to Contamination Factor:

Contamination Factor (CF) is an indication of the anthropogenic inputs of heavy metals in the soils [1]. It was calculated by following the equation given by [21]. The level of contamination by metals was established by applying the CF that can be calculated as follows: CF= Cm Sample/ Cm Background. In this study world surface rock average proposed by [20] is considered as background concentration; CF < 1: low contamination factor; $1 \le CF < 3$: moderate contamination factor; $3 \le CF < 6$: considerable contamination factor; CF = 6: very high contamination factor.

5.2. Assessment according to Enrichment Factor (EF)

EF is the enrichment of heavy metals against the content of the background of heavy metals [18]. Geochemically, heavy metals differentiating with elevated content in the ecosystem and not competent in presenting antagonism or synergism toward the evaluated heavy metals are used as background heavy metals [7]. The EF is widely used to calculate the ratio between uncontaminated background levels and contaminated sediment layers [25]. In the calculations of EFs, the normalization against Al is widely applied, mainly because it has a minor anthropogenic input and it is not significantly influenced by changes in the redox potential as compared with Fe. The EFs were calculated as follows :

EF = C sample / N sample $\div C$ Al/ N Al, where C and N refer to the concentrations of the elements (e.g. Cu) and normalizers (e.g. Al) in the sample of surface sediments (sample) and the Earth's shale (shale), respectively. According to [15], The EF is categorized into seven types such as (EF < 1; no enrichment), ($1 \le EF < 3$; less enrichment), ($3 \le EF < 5$; moderate enrichment), ($5 \le EF < 10$; moderately enrichment), ($10 \le EF < 25$; high enrichment), ($25 \le EF < 50$; very high enrichment), and (EF > 50; exceptionally high enrichment).

5.3. Assessment according to the geoaccumulation index (I geo)

I geo is assessments of the sediment pollution with metals [25]: I geo = log2 (Cn/ 1.5 Bn). Where Cn is the concentration of the element in the enriched samples, and the Bn is the background or pristine value of the element. The constant 1.5 signifies changes in concentrations of heavy metals in the environment [24]. On the basis of I geo values, it is grouped as I geo ≤ 0 , no pollution; I geo (0–1), moderate pollution; I geo (1–2), strong pollution; I geo (2– 3), high pollution; I geo (3–4), very high pollution; I geo (4–5), severe pollution; and I geo ≤ 5 , extreme pollution [14].

5.4. Assessment according to Ecological risk assessment (Er)

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Er is computation to evaluate of ecological risk assessment of heavy metals in the agricultural soils. It is defined as the multiplication of CF of each heavy metal and toxicological response factor (Tr) of individual heavy metals, viz., Cu (5), Zn, and Mn (1) [12]. It was determined by the following equation: Er = CF × Tr, where CF and Tr are the CF and toxicological response factors of individual heavy metals, respectively. The grades used for risk assessment are as follows: Er < 40 (low risk), 40–80 (moderate risk), 80–160 (considerable risk), 160–320 (high risk), and >320 (very high risk).

6. Results and discussion

The descriptive of heavy metals analyses of Fe, As, Co, Cu, Cr, V, Pb, Ni, Zn, Ti, and Mn in addition, TOC and pH are present in the Tables 1 and 2. The pH detected in the range of 7.25 to 7.7. The sediment alkalinity nature of pH is responsible for reducing the mobility of heavy metals [22]. The TOC was recorded in the range of 0.5 to 0.71% in different sampling sites. [23] observed that organic matter affected the retention of heavy metals. Heavy metals in study area were found low in sandysilt and sandymud textures and high in silt texture. [16] concluded that heavy metals content higher in finer grains (silt and clay) compared in sandy soils. Table 3 presented that heavy metals decreased in sandy sediments and low TOC. Heavy metals have a positive correlation with silt fraction. In the present study, the mean value of Fe is 30304 mg/l. Fe content was found lower than their values in the world wild sedimentary rocks for Taylor and McLennan [19 and 20], except in the Majnoon oil field (Table 2). Ti concentration was recorded in the mean value of 3840.2 mg/l. This concentration is higher than world wild sedimentary rocks [19 and 20]. Mn was observed in the present study at a value of 583.8 mg/l, this is higher than world wild sedimentary rocks (542 mg/l) for Taylor and McLennan [19 and 20]. Zn content varies from 61 to 69.24 mg/l with mean value 63 mg/l. Zn content was found low as compared with world wild sedimentary rocks (71 mg/l) [19 and 20]. Ni was found in the mean value of 140.2 mg/l. Ni recorded higher than their values in the world wild sedimentary rocks (44mg/l) [19 and 20]. Cr content for the present study was found at a mean value of 232 mg/l, it found high compared with worldwide sedimentary rocks (85 mg/l) [19 and 20]. The mean value of Pb was found at 9.2 mg/l, it low compared with their content in worldwide sedimentary rocks (50 mg/l) [19 and 20]. V was recorded in the range of 75.62 to 108.6 mg/l in different sampling sites, with a mean value of 88.2 mg/l. Observable of V content was lower than worldwide sedimentary rocks (107 mg/l) [19 and 20] except in the Majnoon oil field. The mean value of Cu is 30.33 mg/l, this value was high compared with world wild sedimentary rocks (25mg/l) [19 and 20]. Co was found of a mean value of 4.75 mg/l, its low compared with worldwide sedimentary rocks (17 mg/l) [19 and 20]. As was observed in the mean value of 4.32 mg/l, this value was high compared with worldwide sedimentary rocks (1.5 mg/l) [19 and 20]. The spatial distribution maps of heavy metals are presented in Figures 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, which concluded that accumulated of heavy metals in the eastern part of study area (Majnnon oil field) than the western parts. In order to evaluate the pollution effect at the studied sites with elevated metal concentrations, the contamination indices (CF, EF, I - geo, ER) were calculated (Table 4). The state of contamination according to CF values (Table 4), showed that studied sites exhibited low contamination factor (CF<1) for Zn, Pb, and Cu for all sites, V and Fe in the Suq Al-Shuyukh, Tal Abu Dahab, and Nasiriyah city center, while Mn was in Tal Abu Dahab and Nasiriyah city center. Moderate contamination factors ($1 \le CF \le 3$) for Cu and Ti for all of the studied sites, Fe was in the Majnoon oil field and Chibayish, Mn was in the Majnoon oil field, Chibayish, and Suq Al-Shuyukh, V was in the Majnoon oil field, Cr was in stations of Suq Al-Shuyukh, Tal Abu Dahab, and Nasiriyah city center, and finally, As was moderate in the Chibayish area, Suq Al-Shuyukh, Tal Abu Dahab, and Nasiriyah city center. Sediments exhibited considerable contamination factor ($3 \le CF \le 6$) for Ni, Cr and As in the Majnoon oil field and Chibayish. In this study, EF varied between 0.4 to 9.57 (Table 4) and showed no enrichment of Co in all sites. The EF varied between 1.15 to 8.44, showed less enrichment for V, Cu, Fe, Zn, Pb, Mn in all sites, and Ti in the Suq Al-Shuyukh and Tal Abu Dahab areas. The computed EF that varied between 3.02 to 4.85 (Table 4) showed moderate enrichment for Ti in the Majnoon oil field, Chibayish, Nasiriyah city center, and Cr in sites of Suq Al-Shuyukh, Tal Abu Dahab, Nasiriyah city center and Cu in site of Nasiriyah city center. The EF varied between 5.7 to 9.57 showed moderately enrichments for Ni and As for all studied sites, while Cr just in the Majnoon oil field and Chibayish. The state of contamination based on I geo values (Table 4), showed most of the studied sites exhibited moderate pollution (I geo 0–1) for Ti, Mn, Zn, Pb, V, Cu, Co, and Fe. Strong pollution (I geo 1-2) showed for Ni in the sites of Suq Al-Shuyukh, Tal Abu Dahab, and As shown in the sites of Chibayish, Suq Al-Shuyukh, Tal Abu Dahab, and Nasiriyah city center. High pollution (I geo 2-3) showed for Ni and As in the Majnoon oil field. Ecological risk assessment (Er) was also calculated (Table 4). From the results of Er, it was found that Er values for heavy metals were found less than 40, indicating low ecological risks of these heavy metals.

	Fe	As	Со	Cu	Cr	V	pb	Ni	Zn	Mn	Ti	TOC	Clay	Silt	Sand
Fe	1	.991**	.930*	.903*	.959*	.972**	.985**	.985**	.969**	.992**	.909*	0.857	-0.132	.959 [*]	-0.862
As	.99**	1	.936*	0.840	.959**	.965**	.981**	.993**	.972**	.999**	.953*	0.787	-0.162	.934*	-0.831
Со	.930*	.936*	1	0.842	.995**	.989**	0.863	.969**	0.832	.950*	0.869	0.836	-0.168	.929 [*]	-0.825
Cu	.903*	0.840	0.842	1	0.867	.900*	0.852	0.851	0.805	0.853	0.647	.987**	0.064	.951 [*]	908-*
Cr	.959*	.959**	.995**	0.867	1	.997**	.904*	.986**	0.877	.971**	.893*	0.855	-0.204	.939*	-0.824
V	.97**	.965**	.989**	.900*	.997**	1	.920*	.986**	.891*	.976**	.879*	.882*	-0.144	.963**	-0.863
pb	.98**	.981**	0.863	0.852	.904*	.920*	1	.958*	.996**	.975**	.922*	0.78	-0.158	.911*	-0.811
Ni	.98**	.993**	.969**	0.851	.986**	.986**	.958*	1	.942*	.997**	.943*	0.815	-0.200	.938*	-0.825
Zn	.96**	.972**	0.832	0.805	0.877	.891*	.996**	.942*	1	.962**	.935*	0.732	-0.190	0.875	-0.768
Mn	.99**	.999**	.950*	0.853	.971**	.976**	.975**	.997**	.962**	1	.945*	0.806	-0.159	.944*	-0.841
Ti	.909*	.953*	0.869	0.647	.893*	.879*	.922*	.943*	.935*	.945*	1	0.590	-0.356	0.787	-0.641
TOC	0.857	0.787	0.836	.987**	0.855	.882*	0.787	0.815	0.732	0.806	0.590	1	0.000	.913*	-0.855
Clay	-0.13	-0.162	-0.168	0.064	-0.20	-0.14	-0.15	-0.20	-0.19	-0.15	-0.35	0.00	1	0.103	-0.364
Silt	.959*	.934*	.929*	.951*	.939*	.963**	.911*	.938*	0.875	.944*	0.787	.913*	0.103	1	964-**
Sand	-0.86	-0.831	-0.82	908*	-0.82	-0.86	-0.81	-0.82	-0.76	-0.84	-0.64	-0.85	-0.364	964**	1
**. Co	rrelation	is significa	ant at the 0.0	01 level (2-	tailed)	1		1	1		1	1	1		
		2	nt at the 0.05		,										

Table 3. Correlation coefficient of heavy metals with sand, silt, clay and TOC

Table 4. contamination indices of heavy metals in the studied sites

Site No.												
		Ti	Mn	Zn	Ni	pb	V	Cr	Cu	Co	As	Fe
Majnoon	CF	1.5	1.28	0.97	3.97	0.58	1.01	4.5	1.28	0.44	3.16	1.18
oil field	EF	3.19	2.73	2.06	8.44	1.23	2.14	9.57	2.73	0.93	6.72	2.5
	I-geo	1	0.608	0.65	2.63	0.38	0.68	3	0.85	0.29	2.11	0.78
	Er	1.5	1.28	0.97	19.85	2.9	2.02	9	6.4	2.2	31.6	
Chibayish	CF	1.3	1.12	0.88	3.34	0.54	0.91	3.64	1.24	0.39	2.9	1.04
	EF	3.02	2.6	2.04	7.76	1.25	2.11	8.4	2.88	0.9	6.74	2.41
	I-geo	0.86	0.74	0.59	2.21	0.36	0.61	2.43	0.82	0.26	1.95	0.69
	Er	1.3	1.12	0.88	16.7	2.7	1.28	7.28	6.2	1.95	29	
Suq Al-	CF	1.16	1.01	0.87	2.72	0.53	0.75	1.91	1.22	0.19	2.8	0.97
Shuyukh	EF	2.82	2.46	2.12	6.63	1.29	1.82	4.44	2.97	0.44	6.82	2.3
	I-geo	0.77	0.67	0.58	1.8	0.35	0.5	1.27	0.81	0.12	1.86	0.64
	Er	1.16	1.01	0.87	13.6	2.65	1.5	3.82	6.1	0.95	28	
Tal Abu	CF	1.17	0.96	0.85	2.6	0.52	0.72	1.87	1.18	0.18	2.7	0.93
Dahab	EF	2.6	2.13	1.88	5.7	1.15	1.6	4.15	2.62	0.4	6	2.06

	I-geo	0.78	0.64	0.57	1.73	0.34	0.48	1.24	0.79	0.12	1.82	0.64
	Er	1.17	0.96	0.85	13	2.6	1.44	3.74	5.9	0.9	28	
	CF	1.25	0.99	0.86	2.66	0.52	0.7	1.7	1.13	0.18	2.77	0.92
Nasiriyah	EF	3.57	2.82	2.45	7.6	1.48	2.01	4.85	3.22	0.51	7.19	1.95
city	I-geo	0.84	0.65	0.5	1.76	0.34	0.47	1.12	0.76	0.13	1.85	0.61
center	Er	1.25	0.99	0.86	13.3	2.6	1.52	3.4	5.65	0.9	22.7	

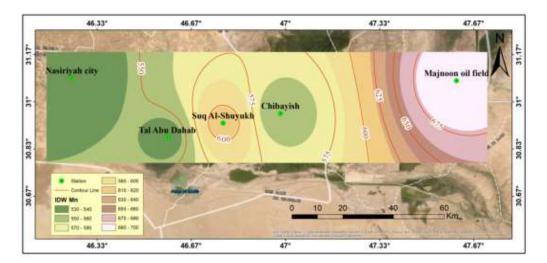


Fig 2. Distribution of Mn metal in the studied sites

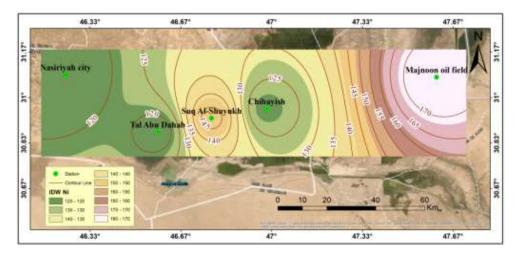


Fig 3. Distribution of Ni metal in the studied sites

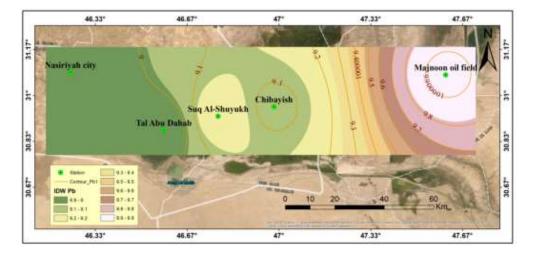


Fig 4. Distribution of Pb metal in the studied sites

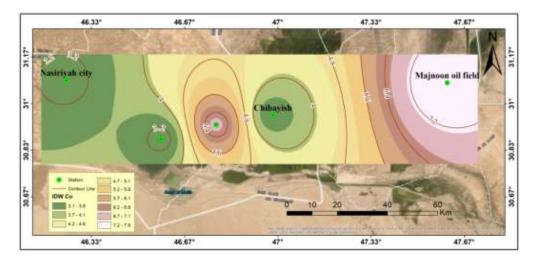


Fig 5. Distribution of Co metal in the studied sites

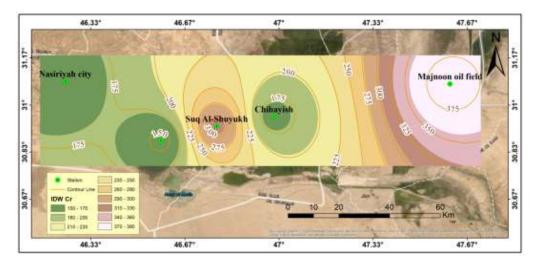


Fig 6. Distribution of Cr metal in the studied sites

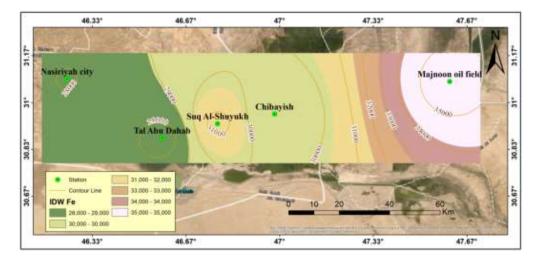


Fig 7. Distribution of Fe metal in the studied sites

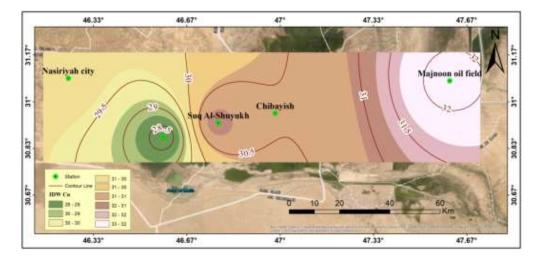


Fig 8. Distribution of Cu metal in the studied sites

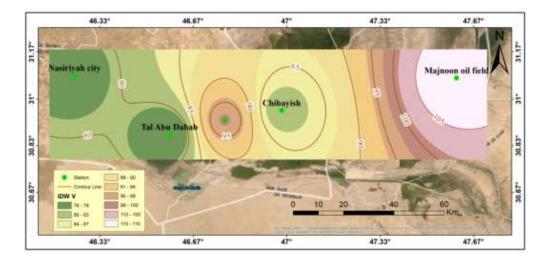


Fig 9. Distribution of V metal in the studied sites

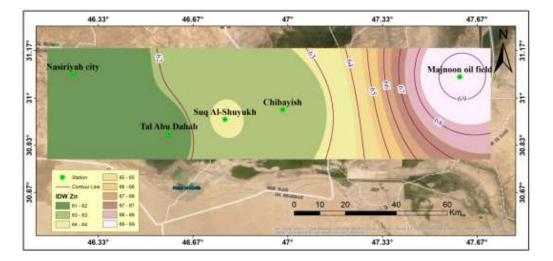


Fig 10.Distribution of Zn metal in the studied sites

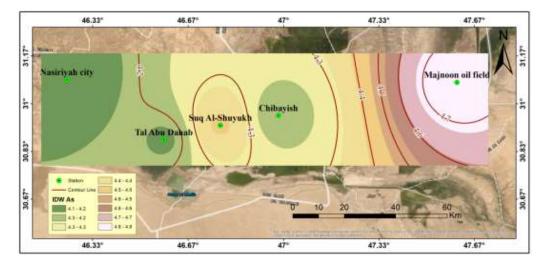


Fig 11. Distribution of As metal in the studied sites

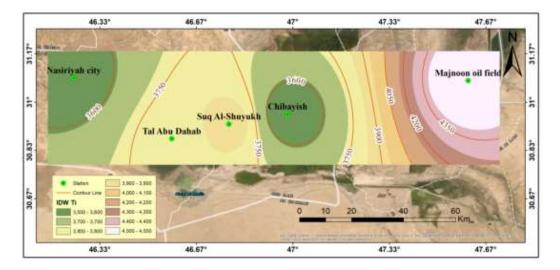


Fig 12. Distribution of Ti metal in the studied sites

7. Conclusion

Sand fractions were increased gradually from Majnnon oil filed towards the other sites in the study area, whereas silt is decrease. TOC recorded higher in the silt texture than sandysilt and sandymud textures. Sediments alkalinity found with a positive relationship with TOC content. Heavy metals were found low in sandysilt and sandymud textures and high in silt texture. The spatial distribution maps of heavy metals showed accumulated of the heavy metals in the eastern part of study area (Majnnon oil field) than the western parts. Heavy metals decreased in sandy sediments and low TOC. Heavy metals have a positive correlation with silt fraction. The values of the contamination indices showed no/low sediment contamination with Co, Zn, Pb, Cu, V, Fe, and Mn in the Chibayish, Nasiriyah city center, and Tal Abu Dahab. Moderate contamination with Ti and Cr in the Suq Al-Shuyukh ,Majnoon oil field and Chibayish, while considerable contamination with Ni and As in the Majnoon oil field. The results of Er showed low heavy metals ecological risks.

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