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Hydrochemistry Assessment of Surface and Groundwater Quality Using GIS and a Heavy Metal Pollution Index (HMPI) Model in a Hawija area, Kirkuk, north Iraq

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Abstract

The Heavy Metal Pollution Index (HMPI) has been used to assess the quality of surface and groundwater drinking water in the Hawija region, where residents use groundwater for drinking. Forty groundwater samples were collected from the Hawija region's wells and analyzed in the Acme Laboratories in Canada. The results of this study were compared with the Environmental Protection Agency's (EPA) and the World Health Organization's (WHO) classification of water quality and its suitability for different uses. Five samples (12.5%) had low pollution levels during the low flow season, 26 samples (65%) had medium levels, and nine samples (22.5%) had high levels. Thirty samples, a mean of 75% of the total groundwater samples obtained during the high flow season, were rated as having low pollution, while ten samples (25%) were rated as having medium pollution. This shows that a large portion of the groundwater samples in the study area are impermissible for human consumption. In the low-flow season, the HMPI values ranged from 8.38 to 148.68, with a mean of 32.43 in the high-flow season, they ranged from 3.55 to 29.23, with a mean of 8.54. The HMPI values of surface water ranged from 3.75 to 77.64 and had a mean of 26.101 during the low-flow season, whereas they varied from 4.19 to 26.35 and had a mean of 11.25 during the high-flow season.

Keywords: Surface and Groundwater, HMPI, GIS, Kirkuk, Iraq.

التقييم الهيدروكيميائي لجودة المياه السطحية والجوفية باستخدام نظم المعلومات الجغرافية ونموذج *(HMPI)* مؤشر التلوث بالمعادن الثقيلة في منطقة الحويجة كركوك، شمال العراق

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الخلاصة

تم تقييم جودة مياه الشرب للمياه السطحية والجوفية في منطقة الحويجة باستخدام نظم المعلومات الجغرافية ومؤشر التلوث بالمعادن الثقيلة (HMPI). حيث يستخدم بعض السكان المياه الجوفية للشرب. استخدم (40) بئر لجمع عينات من المياه الجوفية الموجودة في منطقة الحويجة. تم ارسال هذه العينات إلى (Acme Lab) في كندا لتحليلها. كما تم مقارنه النتائج مع تصنيف منظمة الصحة العالمية (WHO) ووكالة حماية البيئة (EPA) لجودة المياه ومدى ملاءمتها للاستخدامات المتنوعة ، بينت النتائج أنه خلال موسم التدفق المنخفض، كانت 5 عينات (12.5%) ذات مستويات تلوث منخفضة، و26 عينة (65%) ذات مستويات تلوث متوسطة، و9 عينات (22.5%) ذات مستويات تلوث عالية. اما في موسم التدفق العالي تم تصنيف 30 عينة (أو 75%) من عينات المياه الجوفية التي تم الحصول عليها خلال موسم التدفق العالي على أنها ذات تلوث منخفض، في حين تم تصنيف 10 عينات (أو 25%) على أنها ذات تلوث متوسط. وهذا يدل على أن نسبة كبيرة من عينات المياه الجوفية في منطقة الدراسة غير صالحة للاستهلاك البشري. في موسم التدفق المنخفض، كما تراوحت قيم HMPI من 8.38 إلى 148.68، بمتوسط 32.43، وفي موسم التدفق العالي، وتراوحت من 3.55 إلى 29.23، بمتوسط 8.54. اما قيم HMPI للمياه السطحية تراوحت من 3.75 إلى 77.64 وكان متوسطها 26.101 خلال موسم التدفق المنخفض، في حين تراوحت من 4.19 إلى 26.35 وكان متوسطها 11.25 خلال موسم التدفق العالي.

1. Introduction

Hydrochemistry is the study of water's chemical and behavior in natural systems. A category of metallic elements known as heavy metals was hazardous at low concentrations and had high densities and atomic weights. As it greatly impacts the environment and human health, the hydrochemistry of heavy metals in waterways is a crucial research topic [1][2]. Both natural processes, such as the weathering and erosion of rocks, and human activity, such as mining and industrial operations, may introduce heavy metals into the water cycle[3][4]. Heavy metals may change their behavior and movement once they interact with other chemical elements such as dissolved oxygen, pH, and other ions [5][6]. Heavy metal concentrations in water are often stated in parts per billion (ppb) or parts per million (ppm). Heavy metal concentrations in the natural waterways are typically relatively low, but human activity has the potential to raise them considerably, posing risks to both the environment and human health [7][5][8].

Numerous factors, such as pH, temperature, dissolved oxygen, and the presence of other chemical components like ions and organic matter influence the hydrogeochemistry of heavy metals in water. There are two types of heavy metal behavior in water, dissolved and particulate. Heavy metals dissolved in water are typically connected to the water-dissolved mineral composition [9][8]. For instance, copper and zinc are more soluble at higher pH levels than iron and manganese, which are more soluble at lower pH levels [10]. Heavy metals suspended in the water linked to the silt, organic materials, and other minerals are known as particulate heavy metals. Heavy metal particles are often greater in size and more difficult to remove from water [10][11]. Because of the potential risks to human health and the environment, the hydrogeochemistry of heavy metals in water is an important research topic. Heavy metals can accumulate throughout the food chain and cause a variety of health problems in both humans and animals. Monitoring the content and behavior of heavy metals in water is important to ensure both environmental sustainability and human health. The most important heavy elements in the water of the study area were reviewed. The calculation of the Heavy Metal Pollution Index (HMPI) for water using several equations developed by the US Environmental Protection Agency provides insight into the assessment of water pollution with heavy metals (USEPA)[12]. The present research aims to assess the level of heavy metal pollution in the surface and groundwater in the study area. Many researchers studied the study area; for example, Al-Obaidi [13] investigated the water quality and found that Hawija's drinking water had a higher content of heavy elements such as chromium, iron, zinc, lead, and nickel in the industrial areas. This increase was attributed to water transport pipe corrosion. After conducting a general hydrological analysis, Awadh [14] concluded that the Hawija region had poor irrigation water.

2. Study area

2.1 Location of the Study Area

The Hawija city is situated in the Kirkuk Governorate, northern Iraq, between the longitudes (34^o 55' 59.99″ - 35^o 27' 39.26″ N) (44^o 07' 58.55″ - 43^o 15' 37.58″ L), at an altitude of 193 m above sea level, 65 km southwest of the governorate center. Hawija, the largest district in Kirkuk Governorate in northern Iraq, has 215,000 residents. It is Iraq's second-largest agricultural area and a source of vegetables[15], with about 200 villages and three administrative districts, Al-Riyad, Al-Abbasi, and Al-Zab (Figure 1). Therefore, it is important to study the health effects and environmental pollution with heavy metals in the soil and drinking water due to industrial and agricultural activities and military waste that were present due to previous military operations. The present study gives a complete picture of the environmental and health situation and its effects on the region's population. The study area is made up of the Quaternary sediments that are characterized by thick, highly permeable sand and gravel layers. These sediments are harder to characterize than layers of the Bai-Hassan Formation below them. The Recent Quaternary sediments that are composed of silt, clay, and sand and have little thickness are injected with water through shallow well drilling [16]. The conglomerates that make up the Bai-Hasan Formation are interbedded with sandstone, siltstone, and claystone. The Bai-Hassan Formation was regarded as a separate formation primarily due to the predominance of conglomerates [17]. The study area's northern boundaries are the Al-Fatha and Injana Formations, which symbolize the Kirkuk structure—one of the province's most significant structures that splits the Kirkuk region into two primary hydrogeological basins. The study area's northwest boundaries are formed by the Hamrin and Makhoul Mountains [18].

2.2 Hydrogeology of the study area

The groundwater springs from formations of thick sediments of the Muqdadiya Formation (mainly gravel and gravel with silt, clay, and sand, which partly serve as cement). The groundwater depth increases from less than (10 m) to more than (300 m) in the upper parts of the plain. In general, the movement of groundwater is from the recharge zone in the northeast to the southwest, with a tendency to converge towards the Tigris River. Most deep-drilled wells penetrated the Muqdadiyah Formation and produced water from Muqdadiyah and alluvial deposits.

As for the surface water, the region includes four rivers: Tigris River (TR), Lesser Zab River (LZR), Hawija Canal (HC), and Wadi Alnaft (WA), in addition to many drains. TR, which borders the study area from the northeast, is one of the largest rivers in the study area. The LZR flows into the Tigris River, which enters the study area from the northeast and extends towards the southwest, dividing the region into two main parts.

The region also contains an irrigation canal that passes through the city center of Hawija and from north to south, with a length of 1.8 km inside the city only. It is called the Hawija Canal (Hawija Irrigation Project). It takes its water from the area west of the LZR, specifically in the village of Al-Batmeh. This canal extends into the Hawija region through agricultural lands. In addition to the Hawija irrigation canal, the WA (a polluted site) extends from the oil fields of the North Oil Company located northwest of Kirkuk Governorate. Wadi Alnaft enters the study area from the northeast and continues until it changes its course towards the southeast, where all trowels flow into this valley. The study area also contains a group of tributaries on the eastern side of the study area (Figure 1).

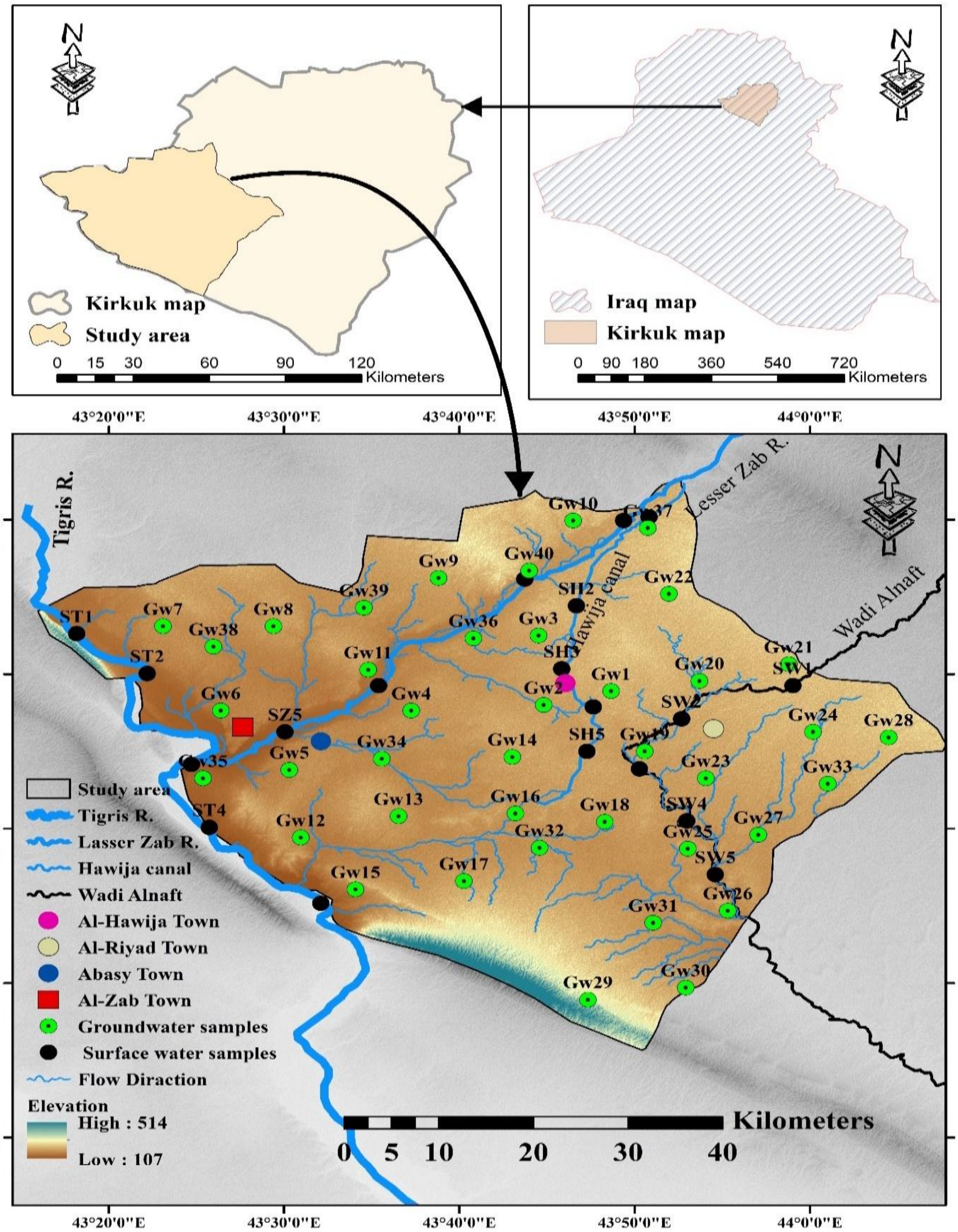

Figure 1: Study area and sample sites for surface and groundwater.

3. Materials and method

3.1 Water sampling

Twenty surface water samples were collected from (TR, LZR, HC and WA), each with five samples (Figure 1 and Table 1) in polyethelene bottles and stored in a cool box at 4°C in the field. Water sampling was conducted for two seasons, October 2021 and May 2022.

Groundwater samples were collected from forty shallow groundwater wells. Figure 1 illustrates the location of the samples. 100 ml of each water sample (groundwater and surface water) was filtered through acid-treated millipore filters (0.45 µm mesh) to remove any remaining suspensions, into polyethylene terephthalate (PET) bottles, then acidified with (HNO_3) nitric acid to reduce the pH <2. The low pH reduced the deposition, uptake and microbial decomposition of heavy metals on container surfaces [19], and these samples were then transferred to (Acme Lab) in Canada for heavy metal analysis.

Table 1: Information on water sampling sites in the study area.

Sample Types		Site N.	Northing	Easting	Depth of W. (m)	Land Cover Description
Groundwater		Gw1	43.811	35.315	150	Agricultural land
		Gw2	43.747	35.3	-	Agricultural land
		Gw3	43.742	35.375	90	Agricultural land
		Gw4	43.621	35.294	120	Agricultural land
		Gw5	43.505	35.23	30	Barren land
		Gw6	43.44	35.294	20	Barren land
		Gw7	43.385	35.385	25	Agricultural land
		Gw8	43.49	35.385	100	Agricultural land
		Gw9	43.647	35.437	200	Barren land
		Gw10	43.776	35.498	180	Agricultural land
		Gw11	43.58	35.338	120	Agricultural land
		Gw12	43.516	35.157	110	Agricultural land
		Gw13	43.609	35.18	-	Agricultural land
		Gw14	43.717	35.244	-	Agricultural land
		Gw15	43.568	35.101	60	Agricultural land
		Gw16	43.72	35.183	155	Agricultural land
		Gw17	43.671	35.11	-	Agricultural land
		Gw18	43.805	35.174	107	Agricultural land
		Gw19	43.843	35.25	95	Agricultural land
		Gw20	43.895	35.326	80	Agricultural land
		Gw21	43.98	35.344	125	Agricultural land
		Gw22	43.866	35.42	163	Barren land
		Gw23	43.901	35.221	-	Agricultural land
		Gw24	44.003	35.271	-	Agricultural land
		Gw25	43.884	35.145	-	Agricultural land
		Gw26	43.922	35.078	117	Agricultural land
		Gw27	43.951	35.16	100	Barren land
		Gw28	44.076	35.268	123	Agricultural land
		Gw29	43.789	34.983	139	Agricultural land
		Gw30	43.882	34.996	156	Agricultural land
		Gw31	43.851	35.065	-	Agricultural land
		Gw32	43.743	35.146	-	Agricultural land
		Gw33	44.017	35.215	-	Agricultural land
		Gw34	43.593	35.242	143	Agricultural land
		Gw35	43.423	35.221	109	Agricultural land
		Gw36	43.68	35.372	85	Agricultural land
		Gw37	43.846	35.491	122	Agricultural land
		Gw38	43.433	35.363	-	Agricultural land
		Gw39	43.576	35.405	225	Agricultural land
		Gw40	43.733	35.445	-	Agricultural land
Surfaces water	Tigris river	ST1	43.303	35.377	-	Water
		ST2	43.37	35.334	-	Water
		ST3	43.412	35.236	-	Water

	ST4	43.429	35.168	-	Water
	ST5	43.535	35.086	-	Water
Lesser Zab River	SZ1	43.823	35.499	-	Water
	SZ2	43.59	35.321	-	Water
	SZ3	43.823	35.499	-	Water
	SZ4	43.729	35.436	-	Water
	SZ5	43.501	35.271	-	Water
Hawija canal	SH1	43.847	35.503	-	Water
	SH2	43.778	35.407	-	Water
	SH3	43.764	35.339	-	Water
	SH3	43.794	35.298	-	Water
	SH5	43.788	35.25	-	Water
Wadi Alnaft	SW1	43.984	35.321	-	Water
	SW2	43.851	35.269	-	Water
	SW3	43.838	35.231	-	Water
	SW4	43.883	35.175	-	Water
	SW5	43.908	35.157	-	Water

3.2 Heavy Metal Pollution Index (HMPI)

Heavy metals' total impact on water quality was evaluated using the heavy metal pollution index (HMPI). The following equations (1,2,3,4) are used to determine the HMPI [7] :

$$\boldsymbol{HMPI} = \frac{\sum_{i=1}^{n} \mathrm{Wi} \times \mathrm{Qi}}{\sum_{i=i}^{n} Wi} \qquad (1)$$

$$\boldsymbol{Qi} = \sum_{i=1}^{n} \frac{\mathrm{Mi} - \mathrm{Ii}}{Si - Ii} \qquad (2)$$

$$\boldsymbol{K} = \frac{1}{\sum_{i=1}^{n} \frac{1}{si}} \qquad (3)$$

$$\boldsymbol{Wi} = \frac{K}{\mathrm{Si}} \qquad (4)$$

Where *Wi* is the heavy metal's unit weight, *K* is the proportionality constant, *n* is the number of heavy metals taken into consideration (Table 2), Qi is the ith heavy metal's sub-index, Mi, Ii, and Si are the ith heavy metal's monitored value, ideal value, and standard value, respectively, for drinking water, the heavy metals pollution index (HMPI) critical threshold is (100). (Mohan et al., 1996).

Table 2: Unit Weightage of heavy metals and standard values [20] used in HPI calculation.

Elements	Si*	1/si	k= (1/sum 1/si)	Wi
As (ppb)	10	0.1	3.69	0.36941
Cu(ppb)	2000	0.0005		0.00185
Cr(ppb)	50	0.02		0.07388
Ni(ppb)	20	0.05		0.18471
Pb(ppb)	10	0.1		0.36941
Zn(ppb)	5000	0.0002		0.00074
Total		0.2707		1

*Standard of WHO 2021

Table 3: Water pollution levels and the Heavy Metal Pollution Index (HMPI) [21].

HMPI	Pollution Level
< 15	Low pollution
15 – 30	Medium pollution
>30	High pollution

4. Results and Discussion

4.1 Assessment of Surface and Groundwater Quality by GIS

Water-heavy metal content and behavior must be monitored for environmental sustainability and human health. The study area's most important heavy metals were reviewed**:**

Arsenic (As): Arsenic is a toxic element that enters water via natural and human causes, including weathering, corrosion, oil refining processes, pesticides used in agriculture, paints, and other industrial operations [22]**.** The mean and rates of arsenic concentrations in groundwater and surface waters are shown in Table 4. The mean value of arsenic content in the water wells throughout the low flow and high flow seasons was, (5.08-1.85 ppb) respectively, with a range in surface water of Wadi Alnaft samples (9.7 - 2.04 ppb), (Table 4 and Figure 2). The concentration of arsenic in the study wells was compared in Table 4 with Iraq standard [23], WHO [20], EPA [24] and local Iraqi research studies [25][13]. The mean level of arsenic in the study area groundwater was lower than the Iraqi standard [23], WHO [20], and [24].

Table 4: Concentrations of some heavy metals in water samples (in ppb) of the study area and comparing them with local studies and with the WHO [20] and QIS [23].

Water Type				As	Cu	Co	Cr	Ni	V	Pb	Zn	S
Groundwater		Low flow Season	Min.	0.7	0.4	0.02	1.4	0.1	1.5	0.1	11.2	2
			Max.	14.9	11.39	1.7	9.6	2.3	10.4	5.94	500.8	300
			Mean	5.08	2.98	0.21	3.27	0.71	4.82	1.82	135.24	59.68
		High flow Season	Min.	0.4	0.5	0.03	1.1	0.1	1.1	0.02	2.6	10
			Max.	5.1	8.31	2.6	22.3	21.6	7.8	3.71	309.8	1125
			Mean	1.84	2.87	0.22	3.53	1.76	3.3	0.98	83.61	250.08
Surface water	Tigris River	Low flow Season	Min.	0.2	2.4	0.8	2.4	0.1	1.2	1.7	96	3
			Max.	5.6	4.05	1.02	5.5	1.3	4.9	3.5	815.6	20
			Mean	2.04	3.3	0.86	3.68	0.8	2.74	2.562	364.36	8
		High flow Season	Min.	0.8	1.3	0.05	1.8	0.5	0.57	0.21	3.3	23
			Max.	1.4	4	5.8	5.8	2	1.7	0.78	59.5	899
			Mean	1	1.92	1.37	3.38	0.88	1.234	0.514	33.06	203.8
	Lesser Zab River	Low flow Season	Min.	0.1	1	0.4	1.5	0.8	4.7	2.1	197.3	7
			Max.	5.4	4.16	0.9	3.5	1.5	5.4	3.3	501.9	132
			Mean	1.4	2.77	0.68	2.2	1.16	5.08	2.722	329.96	37
		High flow Season	Min.	0.4	0.6	0.02	1.3	0.3	1.4	0.2	0.5	65
			Max.	1.4	1.1	0.3	4.6	0.9	1.7	0.5	19.3	1430
			Mean	0.98	0.92	0.14	2.38	0.64	1.54	0.3	6.26	744.4
	Wadi Alnaft	Low flow Season	Min.	2.1	7.2	1.7	4.3	1.5	3.4	5.3	34	12
			Max.	20.3	20.87	16.9	11.5	4.3	45.6	19.27	527.5	476
			Mean	9.7	13.75	5.98	6.88	2.5	24.36	10.78	257.62	272.2

	High flow Season	Min.	1.3	0.8	1	2.6	1.3	1.3	0.8	7.2	21
		Max.	3.6	13.7	16.9	132.7	2.8	89.1	1.5	12.8	306
		Mean	2.04	4.12	4.32	36.6	2.12	49.47	1.08	10.98	102.6
Hawija Canal	Low flow Season	Min.	0.2	3.1	0.1	2.8	1.1	2	1.25	225	7
		Max.	7.1	6.85	1.6	4.1	3.8	4.7	3.66	648.3	116
		Mean	2.24	4.7	0.84	3.54	2.06	3.1	2.69	327.84	40.2
	High flow Season	Min.	0.8	1.3	0.4	1	0.5	0.52	0.22	2	21
		Max.	1.3	2.88	2.8	2.9	0.9	2.1	0.54	68.3	76
		Mean	1.02	1.89	1.48	2.1	0.74	1.182	0.32	18.02	36.8
[23]			10	1000	-	50	20	-	10	3000	#60
[20]			10	2000	-	50	20	*10	10	5000	250
[24]			10	1300	-	100	-	-	15	-	-
Surface water		Iraq[1]	1.5	2.3	-	8.8	4.7	-	1.8	36.2	
		Iraq[2]	-	0.73	0.1	0.27	0.74	-	0.25	3.45	-
Groundwater		Iraq[2]	-	16.24	0.07	4.24	0.52	-	13.88	82.75	-

(1) concentration of Heavy metals in Iraq (Hawija area) [13], **(2)** concentration of Heavy metals in surface water in Iraq (Lasser Zab Valley) [6], (*) concentration of Vanadium in drinking water (WHO,1988) , (#)[26]

Copper (Cu): The concentration of copper in water grows with rising temperatures and pH levels and with the concentration of carbonate minerals in the water. Copper is one of the important components of living things [27]. The concentration of copper in groundwater and surface water is shown in Table 4, along with comparisons to local research, Iraqi standards, and international standards (WHO and EPA). (Table 4, and Figure 2) the concentration of copper in the groundwater during the low flow and high flow seasons was (2.98-2.87ppb) respectively. Surface water samples from Wadi Alnaft had the most significant concentrations of copper, which were greater than those from the TR, LZR, and HC (13.75 - 4.12 ppb) in the low-flow and high-flow seasons, respectively. This result of Cu is definitely because oil pollution has spread over the valley. It was also discovered that the copper element concentration was lower than that of Al-Saady [6] for the ZRB and groundwater. In contrast, the surface water represented by the TR, LZR, HC, and WA conflicted with the study of Al-Obeidi [13].

Cobalt (Co): Cobalt is mobile in the earth's atmosphere. Yet, it is quickly absorbed by suspended organic matter in aquatic settings when soluble species are present [28]. (Table 4) shows cobalt concentrations in surface and groundwater. Cobalt levels in groundwater were (0.21-0.22 ppb) in the low and high flow seasons, respectively. The samples taken from Wadi Alnaft showed their most significant possible concentration in the surface water, with a mean of (5.98-4.32ppb) during the low and high flow seasons, respectively. The concentration of a copper element in groundwater and surface water was higher than that of Al-Saady [6] for LZRB (Table 4 and Figure 3).

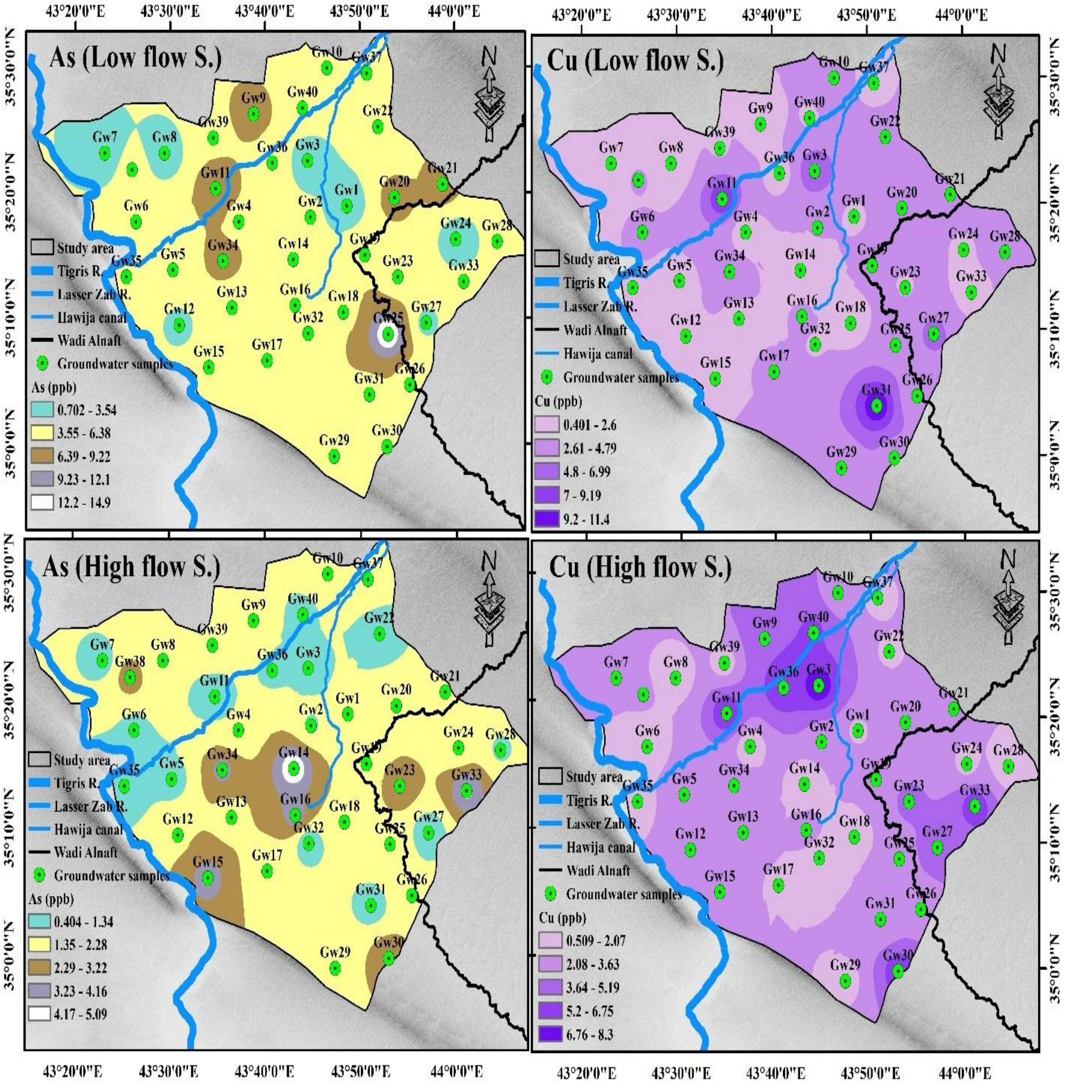

Figure 2: Spatial distribution of As and Cu in groundwater of the study area for low flow season and high flow season.

Chromium (Cr): Trivalent chromium (3) is one of the necessary elements for humans, and its deficiency may have adverse effects on glucose metabolism, elevated insulin, elevated cholesterol and triglycerides [29]. The highest concentration of chromium was found in the surface water samples of the WA samples in the low flow season and high flow season in the samples. The mean concentration of Cr in groundwater samples was (3.27 and 3.53 ppb) in low-flow and high-flow seasons, respectively (Table 4 and Figure 3). The mean concentration of Cr in groundwater samples was (3.27 and 3.53 ppb) in low-flow and high-flow seasons, respectively (Table 4). The oil pollutants contain high chromium concentrations. The mean concentration of Cr for groundwater and surface water was lower than IQS [23], WHO [20], and EPA [24], but the mean concentration of Cr in LZV for Al-Saady [6] was higher than Cr in the study area. Meanwhile, the mean concentration for surface water was lower in Al-Obeidi [13] except in WA.

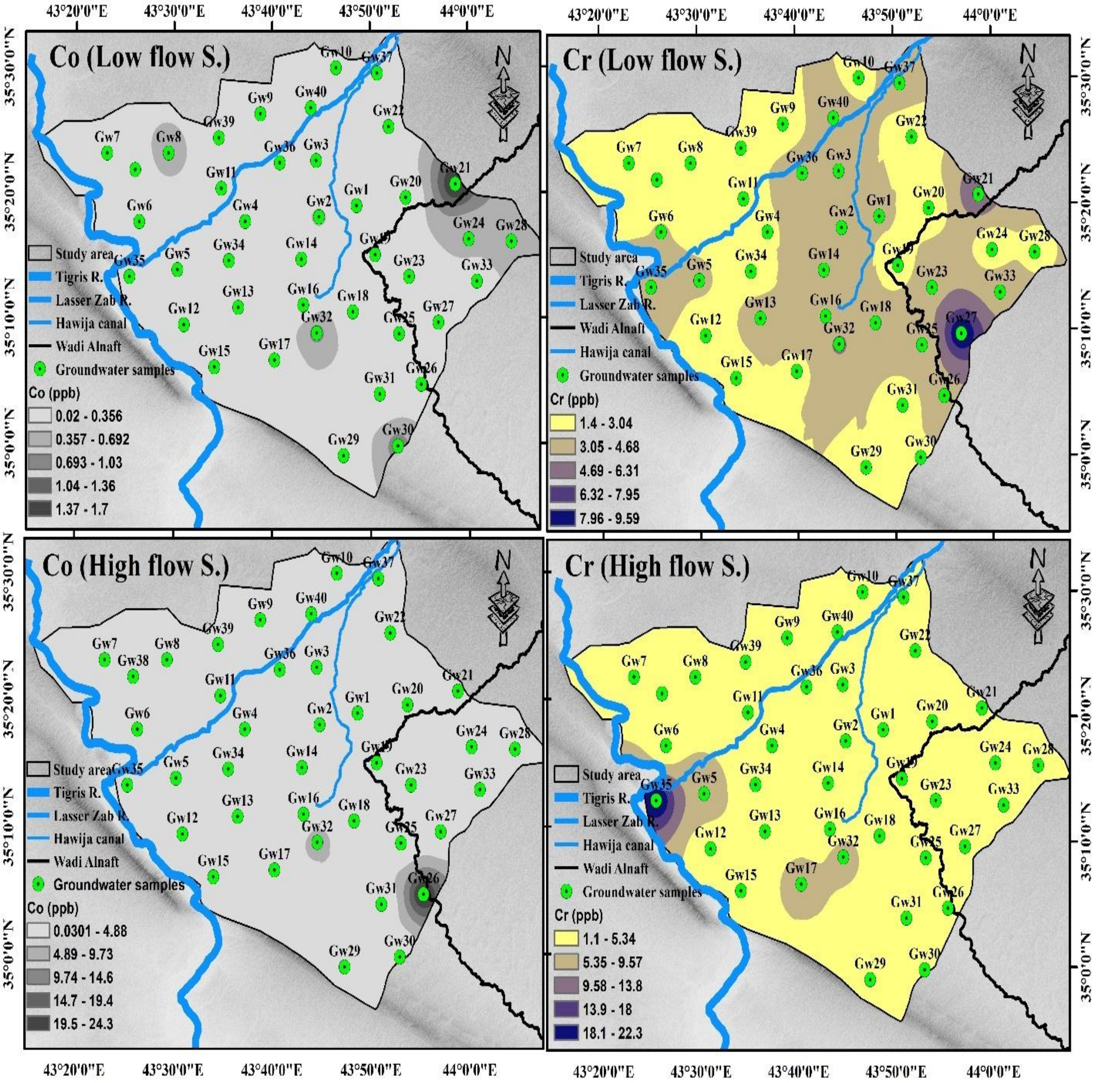

Figure 3: Spatial distribution of Co and Cr in groundwater of the study area for low flow season and high flow season.

Nickel (Ni): The life cycle of plants depends on nickel; hence, vegetable fertilizers often include it [30]. Nickel is extensively distributed in aquatic habitats. However, large concentrations in specific places may be caused by human pollution, which in turn causes an increase in its concentration in living animals' bodies, which may cause poisoning of those organisms, particularly humans [31] as they consume it mainly via water. To examine the surface water and well water in the research region, tainted drinking water is required to determine the extent of nickel concentrations [32]. The mean concentration of Ni was (0.71-1.76ppb), respectively (Table 4 and Figure 4). Since the region is an agricultural one and fertilizers were widely utilized, it is possible that washing the soil and pouring it into the groundwater are the reasons for the rising nickel concentrations in the high flow season compared to the low flow season. According to the Iraqi standards [23] and the WHO [20], the mean concentration of the nickel element was less than that of IQS [23] and WHO.

Vanadium (V): Vanadium is found in most aquatic environments, and the most important factor affecting its concentration is the weathering of the original rocks [33]. Rainwater also contributes to increasing its rates by filtering soil contaminated with Vanadium into the groundwater [34]**.** The average groundwater vanadium concentration in low-flow and high-flow seasons was (4.82 - 3.3ppb), respectively (Table 4 and Figure 4). The highest mean concentration of vanadium in surface water in Wadi Alnaft samples was (24.36 – 49.47 ppb) in low-flow and high-flow seasons, respectively. This high concentration of vanadium was due to oil pollutants, which confirms that the oil industry in the study area contributed mainly to the rising concentration of V. It is higher than the concentration recommended by the World Health Organization (10ppb) [35] (Table 4).

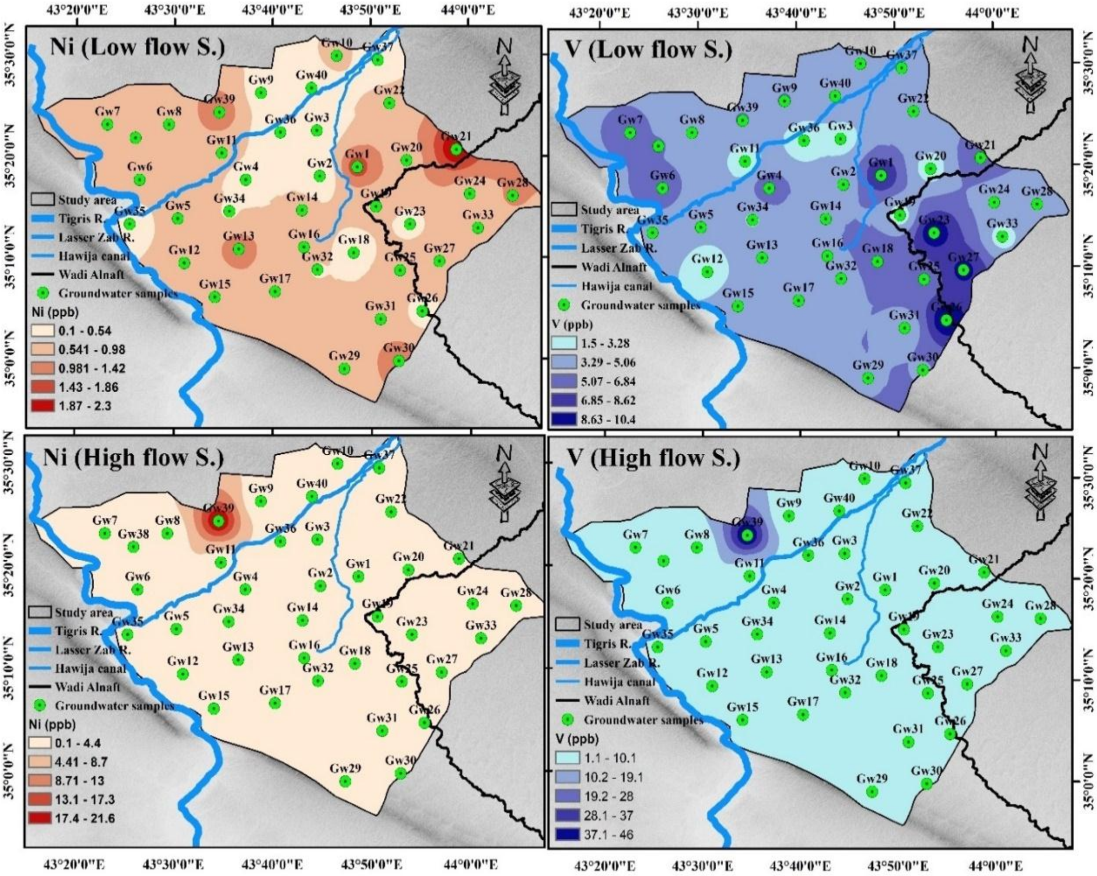

Figure 4: Spatial distribution of Ni and V in groundwater of the study area for low flow season and high flow season.

Lead (Pb): The lead concentration in groundwater increases through its natural or industrial sources and is affected by complex geochemical and biological factors [36]. However, its danger increases in groundwater when the water is acidic, even if only slightly because it becomes more conducive to plants and humans [37]. The mean lead concentration in groundwater samples in the low-flow and high-flow seasons was from 0.98 to 1.82 ppb (Table 4 and Figure 5). The highest mean lead concentration in surface water was found in WA samples, as the lead rate varies from 1.08 to 10.78 ppb in the low-flow and high-flow seasons, respectively. When comparing lead concentration with local studies and standard specifications, its concentration was higher than that of Al-Obeidi for surface water. As for groundwater, it was lower than the groundwater of Al-Saady [6] for LZRB, IQS, 2009 and WHO.

Zinc (Zn): The movement and transfer of zinc in the terrestrial environments (the hydrosphere and the lithosphere) depends on its environmental characteristics and the forms of its presence. The acidity index is one of the most important factors that control its solubility [38]. The concentration of zinc in groundwater was at a mean of (135.24 - 83.61ppb) in the low-flow and high-flow seasons, respectively (Table 4 and Figure 5). In surface waters, the highest concentration of zinc in the LZR water samples reached (33.06 - 364.36 ppb) in the low flow and high flow seasons, as shown in (Table 4), which is less than the permissible limits according to the WHO [20] and IQS [23] the amount (3000 ppb), are the high concentration of zinc in the groundwater of the northern regions and the center of the study area compared to that toward the south, east and western part of the area (Figure 5), and this may be due to the variation in weathering of zinc-containing rocks, such as zinc sulphide, or due to the presence of sulfur springs scattered in this area, which eventually flow into the LZR.

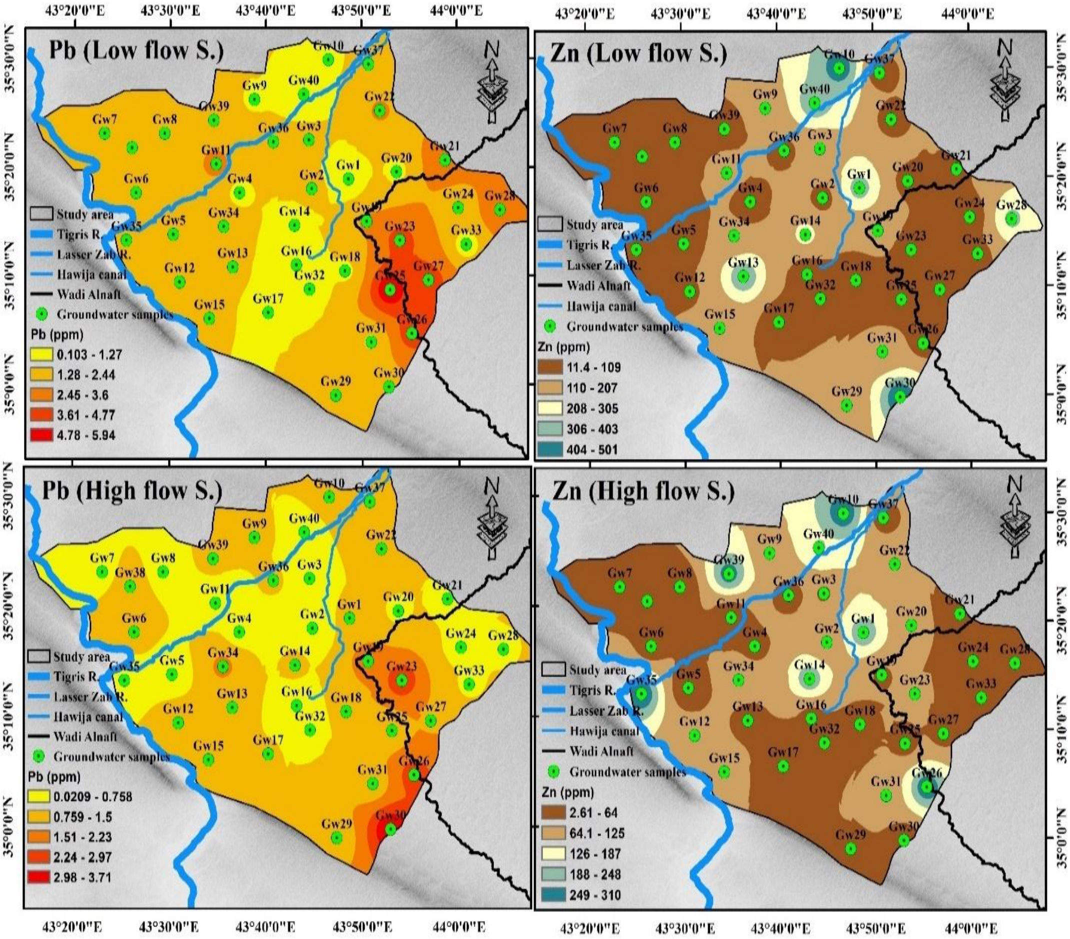

Figure 5: Spatial distribution of Pb and Zn in groundwater of the study area for low flow and high flow seasons.

Sulfur (S): The TR, from the hydrological point of view, is a natural drainage area for groundwater present in the Fatha formation and the study area due to the hydraulic connection of the study area with the (TR and LZR) due to its height above the level of the two rivers [39]. In some regions, groundwater appears as springs stemming from the upper part of the Fatha formation, which contains large amounts of sulfur. The reason is due to the tectonic conditions that the region went through, which led to the presence of many faults. (Table 4) presents the concentrations of sulfur in well groundwater and surface water. It is noted from (Table 4 and Figure 6) that the mean sulfur concentration in groundwater of the low flow and high flow seasons was (59.68-250.08ppm) respectively, and this may be due to the process of washing the soil in the high flow seasons and feeding the groundwater with water containing high concentrations of sulfur. Figure 6 shows an increase in sulfur concentrations in the high-flow season compared to the low-flow season, especially in the northern part of the study area. This is due to the spread of sulfur springs in the study area. As for the surface water, the highest mean concentration of sulfur in the Tigris River samples reached (37-744.4ppb) (Table 4).

The reason may be due to the valley drainages towards the Tigris River during the high-flow season and the influence of the Mishraq Sulfur Mine [39], when comparing the concentration of sulfur from the Iraqi standard [26] and the World Health Organization [20].

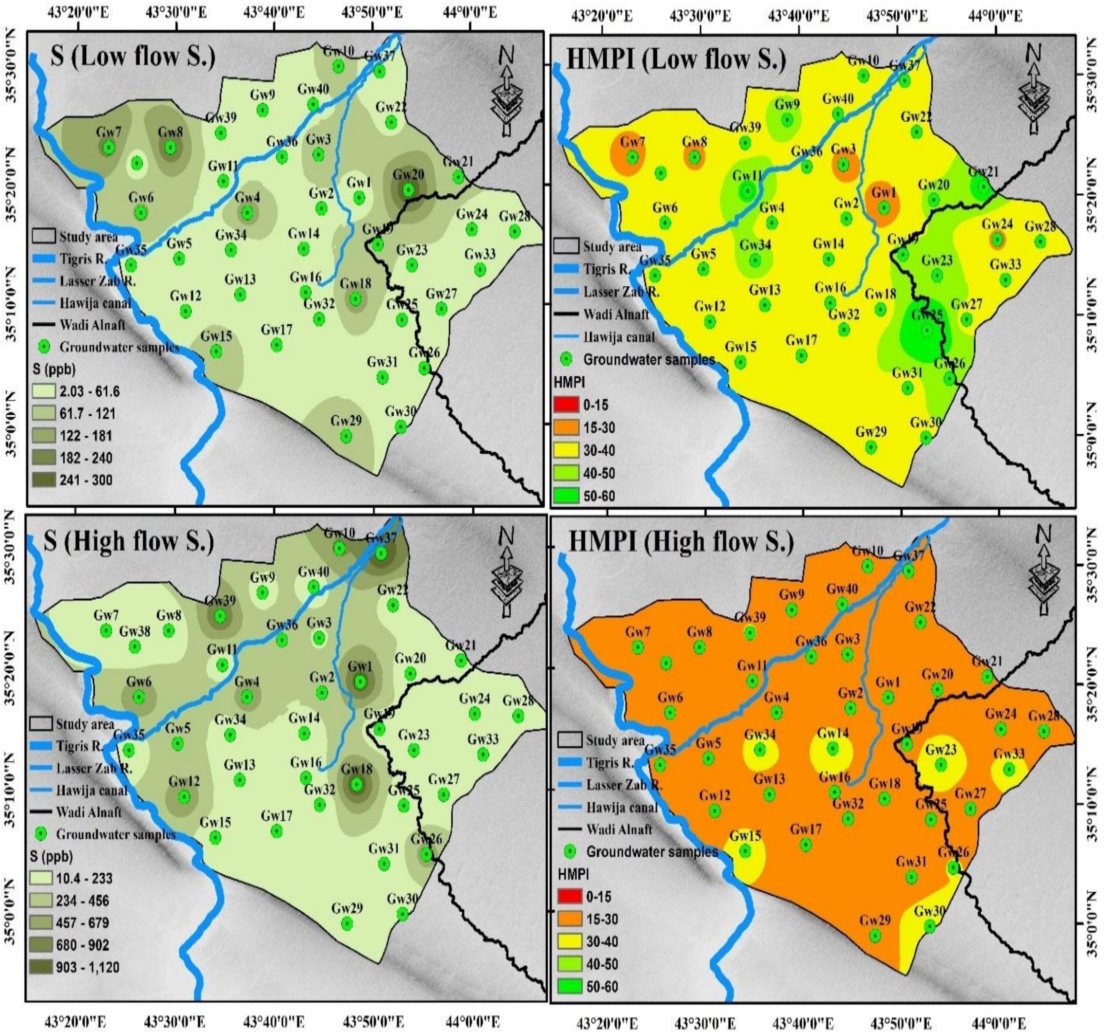

Figure 6: Spatial distribution of S and HMPI in groundwater of the study area for low flow and high flow seasons.

4.2 Heavy Metal Pollution Index (HMPI)

For the two seasons (high flow and low flow), the computed HMPI values of ground and surface water are shown in Table 5.

Table 5: Heavy metals pollution index (HMPI) of the surface and groundwater of the study area.

Groundwater						Surface water		
Site Name	low flow	high flow	Site Name	low flow	high flow	Site Name	low flow	high flow
Gw1	3.75	8.88	**Gw21**	46.02	7.61	**SZ1**	11.69	7.56
Gw2	21.01	5.61	**Gw22**	23.65	8.25	**SZ2**	28.98	7.8
Gw3	9.2	4.43	**Gw23**	33.49	23.16	**SZ3**	22.76	6.47
Gw4	25.21	7.04	**Gw24**	11.82	7.31	**SZ4**	14.19	4.13
Gw5	26.54	5.16	**Gw25**	77.64	12.6	**SZ5**	10.87	5.31
Gw6	28.13	8.5	**Gw26**	33.49	15.36	**ST1**	13.73	5.55

Gw7	9.56	6.07	**Gw27**	26.21	8.12	**ST2**	13.08	6.27
Gw8	10.83	6.72	**Gw28**	27.17	8.11	**ST3**	31.26	6.31
Gw9	33.79	11.38	**Gw29**	23.78	11.22	**ST4**	10.77	3.55
Gw10	20.85	12.17	**Gw30**	28.98	26.35	**ST5**	10.01	4.31
Gw11	43.71	4.34	**Gw31**	24.43	7	**SH1**	40.46	6.59
Gw12	16.03	13.31	**Gw32**	21.7	4.19	**SH2**	8.38	6.21
Gw13	23.22	10.9	**Gw33**	16.98	19.36	**SH3**	24.18	5.15
Gw14	26.04	22.62	**Gw34**	35.35	20.81	**SH4**	12.79	4.79
Gw15	23.78	18.15	**Gw35**	24.7	6.98	**SH5**	9.79	4.25
Gw16	20.14	15.15	**Gw36**	27.93	8.07	**SW1**	83.6	29.23
Gw17	22.21	9.89	**Gw37**	28.06	13.26	**SW2**	88.08	16.85
Gw18	25.21	10.36	**Gw38**	25	15.76	**SW3**	148.68	20.08
Gw19	32.71	13.88	**Gw39**	28.56	15.77	**SW4**	37.23	11.05
Gw20	33.23	10.28	**Gw40**	23.93	6.21	**SW5**	28.25	9.49
Min.				3.75	4.19	Min.	8.38	3.55
Max.				77.64	26.35	Max.	148.68	29.23
Mean				26.101	11.25	Mean	32.439	8.5475

*Low pollution * Medium Pollution * High Pollution

The HMPI values varied from 8.38 to 148.68, with a mean of 32.43. In high flow season, the values ranged from 3.55 to 29.23, with a mean of 8.54. During the low-flow season. Five of these samples (12.5%) were found to have low levels of pollution, 26 of these samples (65%) were found to have medium levels, and nine of these samples (22.5%) were found to have high levels of pollution (Table 5 and Figure 6). It was determined that 30 of the groundwater samples collected during the high flow season had low levels of contamination, making up 75% of the total, while 10 of the samples, representing 25% of the total, were determined to have medium pollution levels. This demonstrates that a significant proportion of the groundwater samples in the research area are unsuitable for human ingestion. In the season with low flow, All wells were found to have low to medium levels of heavy metal contamination during the wet and dry seasons, except for wells (GW9, GW11, GW19, GW20, GW21, GW23, GW25, and GW26) that have high pollution index where the degree of pollution was significant (Table 5 and figure 6). The HMPI values of surface water varied from 3.75 to 77.64, with a mean of 26.101. However, during the high-flow season, the values ranged from 4.19 to 26.35, with a mean of 11.25. Due to the oil pollutants dispersed in the valley, the WA will affect the contamination of these wells. Except for the samples (ST3, SH1, SW1, SW2, SW3, and SW4), the majority of the samples of surface water had minimal levels of heavy metal pollution in the surface water (Table 5).

5. Conclusion

Heavy metals (As, Cu, Co, Cr, V, Ni, Pb, Zn, and S) were found in the WA in concentrations beyond the permissible limits defined by IQS and WHO. The maps showing the spatial distribution of these elements show that the largest concentrations of heavy metals (As, Cu, Co, Cr, Ni, V, and Pb) may be found in samples collected close to the Wadi Alnaft. In terms of heavy metals, the concentrations of these elements were higher in locations adjacent to oil activity, specifically in regions bordering the WA. This was due in part to the region's geological features and the agricultural operations that take place there, both of which are considered variables that affect the area.

HMPI values of ground and surface water were found to have low to medium levels of heavy metals during the low flow and high flow seasons, except for wells (GW9, GW11, GW19, GW20, GW21, GW23, GW25, and GW26) which have had high pollution index where the degree of pollution was significant. For surface water, most samples had minimal heavy metal levels except for the samples (ST3, SH1, SW1, SW2, SW3, and SW4).

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