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Concentration of heavy metals in some springs in the Shaqlawa district, Erbil Governorate, Kurdistan Region of Iraq

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ABSTRACT

The study deals with determining the concentrations of heavy metals—silver (Ag), aluminum (Al), arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), lithium (Li), manganese (Mn), nickel (Ni), chromium (Cr), lead (Pb), selenium (Se) and zinc (Zn)—in 8 springs within the Shaqlawa district in the Erbil Governorate, Kurdistan Region of Iraq. The samples were collected during two seasons: the first in summer 15-8-2024 and the other in winter 15-1-2025. The values of Ag, Al, As, Ba, Cd, CO, Cr, Cu, Fe, Li, Mn, Ni, Cr, Pb, Se and Zn as µg/L ranged between 0.617 and 0.843, 4.92 and 10.70, 0.305 and 1.01, 30.20 and 49.30, 0.10 and 0.324, 0.13 and 1.49, 3.97 and 9.85, 0.992 and 1.35, 0.43 and 1.100, 57.4 and 73.30, 1.00 and 1.00, 0.20 and 1.140, 1.63 and 2.69, 1.26 and 2.30, and 54.5 and 123.0 µg/L, respectively. The results indicated that, according to WHO guidelines, the concentrations of all heavy metals were within allowable levels for drinking water, except for lithium, which was recorded at high levels at all sites. The heavy metal pollution index (HPI) ranged from 76.455 to 88.213 in the summer season and 77.045 to 96.585, below the critical limit of 100, indicating that the water sources were generally not contaminated with heavy metals. Nevertheless, the single-factor contamination index (SFPI) indicated a high lithium concentration at all sites and considered them contaminated. At the same time, other metals recorded low levels at all sites, indicating that they were not contaminated.

Keywords: Heavy, Metals, Spring, Shaqlawa, Erbil

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تركيز المعادن الثقيلة في بعض ينابيع قضاء شقلاوة، محافظة أربيل، إقليم كردستان العراق

سازان سيروان ياسين، جنان جبار توما

قسم علوم الصحة البيئية، كلية العلوم، جامعة صلاح الدين–اربيل–أقليم كردستان العراق

الملخص

تتناول الدراسة تحديد تراكيز المعادن الثقيلة – الفضة **(Ag)**، الألمنيوم **(Al)**، الزرنيخ **(As)**، الباريوم **(Ba)**، الكادميوم **(Cd)**، الكوبالت **(CO)**، الكروم **(Cr)**، النحاس **(Cu)**، الحديد **(Fe)**، الليثيوم **(Li)**، المنغنيز **(Mn)**، النيكل **(Ni)**، الكروم **(Cr)**، الرصاص **(Pb)**، السيلينيوم **(Se)** والزنك **(Zn)** في 8 ينابيع ضمن قضاء شقلاوة في محافظة أربيل، إقليم كردستان العراق. تم أخذ العينات في موسمين، الأول في الصيف 15−8−2024 والآخر في الشتاء 15−1−2025. قيم كل من Ag, Al, As, Ba, Cd, CO, Cr, Cu, Fe, Li, Mn, Ni, Cr, Pb, Se وZn تباينت بين 0.843−0.617, 10.70−4.92, 1.01−0.305, 49.30−30.20, 0.324−0.10, 1.49−0.13, −3.97 9.85, 1.35−0.992, 1.100−0.43 −0.43, 57.4− 1.00, 73.30−1.00, 1.140−0.20, 2.69−1.63, 2.30−1.26, 54.5-123.0 على التوالي. أشارت النتائج إلى أنه وفقًا لإرشادات منظمة الصحة العالمية فإن تركيز جميع المعادن الثقيلة كان ضمن المستويات المسموح بها لمياه الشرب باستثناء الليثيوم الذي سجل مستوى مرتفعًا في جميع المواقع. تراوح مؤشر التلوث بالمعادن الثقيلة **(HPI)** بين 76.455 و88.213 في فصل الصيف وبين 77.045 و في الشتاء على التوالي96.585 وهو أقل من الحد الحرج البالغ 100، مما يشير إلى أن مصادر المياه لم تكن عمومًا ملوثة بالمعادن الثقيلة. ومع ذلك، أشار مؤشر التلوث أحادي العامل **(SFPI)** إلى ارتفاع تركيز الليثيوم في جميع المواقع، مما يُشير إلى تلوثها، بينما سجلت معادن أخرى مستويات منخفضة في جميع المواقع، مما يشير إلى عدم تلوثها.

INTRODUCTION

Water is an important resource for humans, agricultural production, and animals. With the ongoing development of human society and the economy, human activities have caused serious pollution of water resources [(1).] Moreover, water needs for drinking water, agriculture, industry and recreation [(2)]. Many heavy metals that enter water bodies, directly or indirectly, affect human health and pose a threat to the aquatic ecosystem [(3)]. The availability of heavy metals to organisms depends on many physical variables, such as adsorption and temperature [(4)]. There are two important types of heavy metals; the first are the essential elements that have an important role in the activity of living organisms, such as Cu, Cr, Fe, Mn, Mo, Ni, Se, and Zn, which are called microelements or essential trace elements because they are necessary for various functions such as physiological and biochemical functions, and do not cause disease sufficiently. High levels of these metals are toxic to living organisms [(5)]. The second type of heavy metal is that whose function is unknown (6), and even in small quantities, such as lead and cadmium, is extremely harmful [(7)]. Heavy metals enter the environment naturally or through geological processes, such as the erosion of soil, rocks, and sediments, and volcanic activity [(8)]. These processes cause pollution through acid rain, which carries heavy metals, and also erodes the Earth's crust. Heavy metals then enter the water system. Household and industrial wastes, urban wastewater, pesticides, fertilizers, and other factors are also attributable to anthropogenic activities[(9)]. The evaluation of potable water using indicators is an extremely useful tool for addressing related water quality problems [(10)]. Some previous studies have

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examined current levels of heavy metals in Erbil Province [1, 10-12]. This study aimed to estimate heavy metal concentrations in some springs in the Shaqlawa sub-district and determine their suitability for drinking use by using the heavy metal pollution index and the single-factor pollution index.

MATERIALS AND METHODS

Description of the area studied.

In this study, eight spring sites were selected in the Shaqlawa area: the first is Kani, located in Chneran village and called "Chneran Spring"; the second is located in Aquban Saru and called "Aquban Upper Spring." At the same time, in Aquban Lower, four springs were found: Sard, Piawan, Zhnan, and Mena. Finally, two springs are located in Punchena village. In general, residents of the studied areas use spring water for many purposes, including irrigation, livestock, and domestic use (Table 1 and Figure 1).

Table 1: Explain the kind and site of the studied area in the Shaqlawa sub-district

Site	Latitude	Longitude	Location	Name of Village
1	36°22'07.3"N	44° 23' 11.5" E	Chneran Spring	Chernan
2	36° 20' 41.3" N	44° 24' 37.1" E	Aquban Upper Spring	
3	36° 21' 08.7" N	44°25'17.9"E	Sard Spring	
4	36° 21' 16.3" N	44° 25' 28.1" E	Piawan Spring	Aquban
5	36° 21' 17.4" N	44°25'28.9"E	Zhnan Spring	
6	36° 21' 46.3" N	44° 26' 01.1" E	Aquban Lower Spring	
7	36° 19' 57.1" N	44° 25' 18.9" E	Pungina	Pungina
8	36° 20' 21.9" N	44° 25' 01.3" E	Mewraka Spring	

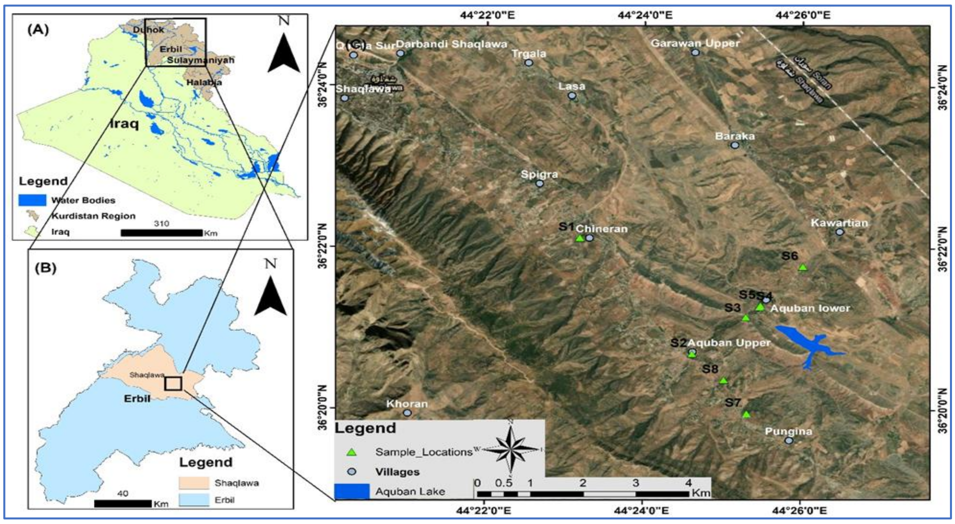

Fig. 1: Shown are A- A map of Iraq and Erbil province, shaded; B- A map of Erbil; C- Chneran village, Aquban village, and Pungina village (shows selected study sites)

Samples Collection

In the current study, water samples were collected from eight springs over two seasons: the first in winter (15-8-2024), with three replications and the second in winter (15-1-2025), with three replications per site. Water samples were collected in prewashed polypropylene bottles. Samples were brought to the laboratory in a chilled icebox (4°C) and filtered through filter paper of the same size as a Whatman 0.45 μm filter. Nitric acid was used to lower the sample's pH to less than 2.0 to reduce sedimentation and adsorption to the container walls. [1].

Sample Analysis

Analyzed samples that were collected for heavy metal concentrations, including Ag, Al, As, Ba, Cd,

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CO, Cr, Cu, Fe, Li, Mn, Ni, Cr, Pb, Se, and Zn, by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), depending on the standard method for the examination of water and wastewater, where sample analysis is done in the College of Sciences, University of Salahaddin, Erbil, Iraq[13]. All equipment, chemical materials and instruments were obtained from the College of Sciences, University of Salahaddin, Erbil, Iraq.

Heavy Metal Contamination Indices

Heavy metal contamination indices are assessment mechanisms that quantify the combined impact of all heavy metals on water quality. The value rating ranges from 0 to 1 and reflects the importance of an individual's quality. Wi is inversely proportional to the maximum permissible value stated in the standard. Recommended standard (Si) proportionally inversely for every factor[14].

For estimating the HPI index, the following steps were included:

1. Estimating the weight unit for all factors.
2. Determining the values of the sub-index.
3. Total of sub-index.

The weight of every factor can be estimated by utilizing Equation (1):

$$W_i = K \ / \ S_i \_\_\_\_\_\_\_\_ (1)$$

Where the sub-indices are named Qi for the ith variable, the control value is named Vi, which is for the ith variable, and the standard "v" value is named Si, which is the allowable or standard limit for the ith factor.

$$Q_i = 100 \ V_i / S_i \_\_\_\_\_\_\_\_ (2)$$

Where Wi is the weight of the unit, Si is the permissible level mentioned in the standard for every factor, and k is the fit constant. The expression indicates the quality of an individual's rating.

The heavy metal index (HPI) is then estimated as follows:

$$HPI = \sum_{i=1}^{n} Q_i W_i \ / \sum_{i=1}^{n} Wi$$

The level of the critical pollution indicators is 100. This study uses the WHO drinking water guidelines to determine the Si value.

Single-factor pollution index method

The single-factor pollution index method is determined by the environmental quality criteria used to assess the contamination.

Advantages include easy operation and simple application; however, it is only used to reflect the contamination level of each heavy metal element in the studied area. In addition, it cannot reflect all contamination values resulting from the combination of different contamination factors.[15]. See equation (3) for the calculation.

$$P_i = \frac{Ci}{S_i} \ \_\_\_\_\_\_\_\_ (3)$$

"Pi" means the single factor indices of heavy metal "i"; "Ci" means the freely valued level of heavy metal "i" in water sources, and "Si" represents the standard concentration utilized for heavy metals in ground and surface water. The single-factor pollution index classification criterion is explained in Table 2.

Table 2: Single-factor contamination index

Indice	Range	Contamination Degree
single factor index	$Pi \leq 1$	Uncontaminated
	$1 < Pi \leq 2$	Light pollution
	$2 < Pi \leq 3$	Moderately polluted
	$Pi > 3$	Heavy pollution

RESULTS AND DISCUSSION

The values for all heavy metals in this study are shown in Tables 3 and 4 for the summer and winter seasons, respectively. The values of Ag, Al, As, Ba, Cd, CO, Cr, Cu, Fe, Li, Mn, Ni, Cr, Pb, Se, and Zn, which lower than the permissible level for drinking purposes according to WHO guidelines, except the lithium concentration was higher than the allowable level for drinking purposes in all sites; a similar conclusion was obtained by (10-12). Many researchers have reported the harmful effects of metalloids and heavy metals, especially when their concentrations exceed allowable levels [16, 17]. Heavy metal content in the environment varies depending on the geological composition of the wells, as well as human activities such as factories,

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pesticides, agricultural fertilizers, fossil fuels, land construction activities, and soil erosion caused by rainfall [18]. Higher lithium concentrations recorded in the studied area exceed the WHO drinking water guideline [19]. This may be due to environmental contamination by Li arising from geological or human activity, which can be split into determined and non-determined resources, depending on the precise site. Li that enters the Eco-friendly cabins (i.e., air, water, and soil). Determined resources are when contamination comes from a specific area, and non-determined resources are when contamination comes from various areas [20]. Additionally, the risk of health assessment in various age groups was calculated utilizing the Target Hazard Quotient (THQ). The Target risk ratio for lithium in water sources for consumers in Iraq, Mexico, South Africa, Afghanistan, Bolivia, Portugal, Malawi, South Korea, Nepal, Argentina, and the United States was greater than 1. So, these countries need continuous monitoring of lithium levels in water resources, reduction of lithium levels, particularly in spring water, and the use of new treatment methods [21]. The HPI levels in the current investigation for water samples from eight sites ranged from 76.455 to 88.213 at Punchena spring. Aquban Khwaru Springs in summer seasons, and 77.045 to 96.585 in Punchena spring and Zhnan spring, respectively, which are less than 100, the standard level for potable water use (Table 5), indicating that the water is not seriously contaminated with the heavy elements studied (21). Spring water at the current study sites was not contaminated with heavy metals. The HPI data in the present study are consistent with the conclusions [22, 23]. The single-factor index for all heavy metals in this study was less than 1 at many sites considered uncontaminated, except for lithium in all spring sites, which was calculated to be more than 3 and considered heavily contaminated, as shown in Tables 6 and 7. The lithium concentration varied between 57.40µg/L in site 7 to73.30µg/L in the Piawan spring. Lithium enters the water during the weathering of lithium-containing minerals like lepidolite, spodumene, and petalite. The lithium concentration in groundwater can be much higher than in surface water, especially in areas with lithium-rich rocks or geothermal activity [24]. Studies suggest that lithium concentrations in groundwater range from 0.01 to more than 1 mg/L, with some hot springs and deep aquifers containing up to 10 mg/L. Lithium levels in groundwater are affected by rock-water interactions, residence time, and hydrogeochemical processes such as ion exchange and evaporation [25].

Table 3: Spatial difference of heavy metals as µg/L in the studied area during August 2024

Sites / Element	Standard values	1	2	3	4	5	6		8
Ag	100	0.843	0.796	0.755	0.825	0.702	0.694	0.672	0.709
Al	100	7.160	6.920	4.92	8.25	5.77	5.78	6.18	6.03
As	10	0.724	0.619	0.584	0.335	0.305	0.537	0.387	0.988
Ba	1000	33.40	33.80	31.60	39.9	31.30	35.10	32.2	34.40
Cd	3	0.222	0.195	0.128	0.145	0.10	0.118	0.03	0.241
CO	2000	1.190	0.780	0.41	1.00	1.00	0.13	1.00	1.49
Cr	50	8.92	8.06	6.63	6.45	3.97	6.34	4.58	8.88
Cu	2000	1.200	1.17	1.10	1.09	0.975	1.09	1.01	1.22
Fe	300	1.100	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Li	10	60.800	59.4	61.8	63.6	61.7	65.2	57.5	60.20
Mn	80	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ni	70	1.140	0.40	0.20	0.20	0.20	0.20	0.20	0.50
Pb	10	2.440	2.30	2.14	2.12	1.63	2.04	1.72	2.47
Se	10	1.700	1.82	1.66	1.68	1.26	1.65	1.39	2.03
Zn	3000	78.100	62.20	59.90	63.10	54.5	59.8	60.10	68.40

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Table 4: Spatial variation of heavy metals as µg/L in the studied area during January 2025

Element \ Sites	Standard values	1	2	3	4	5	6	7	8
Ag	100	0.702	0.713	0.689	0.882	0.763	0.669	0.617	0.713
Al	100	7.100	7.570	5.990	10.70	7.970	5.630	5.620	7.05
As	10	0.911	0.735	0.853	0.672	0.579	0.592	0.305	1.01
Ba	1000	37.40	37.60	35.70	49.30	41.10	32.80	30.20	36.00
Cd	3	0.251	0.222	0.204	0.324	0.210	0.111	0.021	0.275
CO	2000	1.420	0.960	1.210	1.30	0.61	0.280	1.00	1.85
Cr	50	8.99	8.64	8.200	9.85	7.80	6.43	4.43	9.66
Cu	2000	1.35	1.19	1.25	1.24	1.13	1.12	0.992	1.24
Fe	300	1.00	1.00	1.00	1.00	1.00	1.00	0.43	1.00
Li	10	61.4	59.6	63.4	73.30	70.20	64.4	57.40	60.00
Mn	80	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ni	70	0.80	0.20	0.20	0.40	0.20	0.20	0.20	0.71
Pb	10	2.51	2.37	2.36	2.69	2.33	2.05	2.47	2.61
Se	10	2.11	2.05	1.97	2.30	1.96	1.67	1.41	2.26
Zn	3000	123.0	67.60	76.50	75.30	67.90	61.30	53.90	67.60

Table 5: Heavy Metals Pollution Indices in the Studied Location Through the Studied Period

Sites	Name of site	Value of HPI index (15-8-2024)	Value of HPI index (15-1-2025)	Status
1	Chneran Spring	86.165	87.114	Not seriously polluted
2	Aquban Upper Spring	83.789	83.986	Not seriously polluted
3	Sard Spring	84.344	88.447	Not seriously polluted
4	Piawan Spring	86.524	87.406	Not seriously polluted
5	Zhnan Spring	82.161	96.585	Not seriously polluted
6	Aquban Lower Spring	88.213	89.232	Not seriously polluted
7	Pungina	76.455	77.045	Not seriously polluted
8	Mewraka Spring	85.406	86.170	Not seriously polluted

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Table 6: Assessment results of the Single Factor Pollution Index during August 2024

Element \ Sites	1	2	3	4	5	6	7	8
Ag	0.0084	0.0079	0.0075	0.0082	0.0070	0.0069	0.0067	0.0070
Al	0.0716	0.0692	0.0492	0.0825	0.0577	0.0578	0.0618	0.0603
As	0.0724	0.0619	0.0584	0.0335	0.0305	0.0537	0.0387	0.0988
Ba	0.0256	0.0260	0.0316	0.0399	0.0313	0.0351	0.0322	0.0344
Cd	0.0740	0.0650	0.0426	0.0483	0.0333	0.0393	0.0100	0.0803
Co	0.0005	0.0003	0.0002	0.0005	0.0005	0.0001	0.0005	0.0007
Cr	0.1784	0.1612	0.1326	0.1290	0.0794	0.1268	0.0916	0.1776
Cu	0.0006	0.0005	0.0005	0.0005	0.0004	0.0005	0.0005	0.0006
Fe	0.0470	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033
Li	6.0800	5.9400	6.1800	6.3600	6.1700	6.5200	5.7500	6.0200
Mn	0.0033	0.0033	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125
Ni	0.0162	0.0057	0.0028	0.0028	0.0028	0.0028	0.0028	0.0071
Pb	0.2440	0.2300	0.2140	0.2120	0.1630	0.2040	0.1720	0.2470
Se	0.1700	0.1820	0.1660	0.1680	0.1260	0.1650	0.1390	0.2030
Zn	0.0156	0.0124	0.0119	0.0210	0.0545	0.0199	0.0200	0.0228

Table 7: Assessment results of the Single Factor Pollution Index during January 2025

Element \ Sites	1	2	3	4	5	6	7	8
g	0.0070	0.0071	0.0068	0.0070	0.0076	0.0066	0.0061	0.0071
Al	0.0710	0.0757	0.0599	0.0603	0.0797	0.0563	0.0562	0.0705
As	0.0911	0.0735	0.0853	0.0988	0.0579	0.0592	0.0305	0.1010
Ba	0.0374	0.0376	0.0357	0.0344	0.0411	0.0328	0.0302	0.0360
Cd	0.0836	0.0740	0.0680	0.0803	0.0700	0.0370	0.0070	0.0916
Co	0.0007	0.0004	0.0006	0.0007	0.0003	0.0001	0.0005	0.0009
Cr	0.1798	0.1728	0.1640	0.1776	0.1560	0.1286	0.0886	0.1932
Cu	0.0006	0.0005	0.0006	0.0006	0.0005	0.0005	0.0004	0.0006
Fe	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0014	0.0033
Li	6.1400	5.9600	6.3400	6.0200	7.0200	6.4400	5.7400	6.0002
Mn	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125	0.0125
Ni	0.0114	0.0028	0.0028	0.0071	0.0028	0.0028	0.0028	0.0101
Pb	0.2510	0.2370	0.2360	0.2470	0.2330	0.2050	0.2470	0.2610
See	0.2110	0.2050	0.1970	0.2030	0.1960	0.1670	0.1410	0.2260
Zn	0.0410	0.0225	0.0255	0.0228	0.0226	0.0204	0.0179	0.0225

CONCLUSION

Concentrations of all heavy metals in the studied springs were within the required levels for drinking use, except for lithium, which exceeded the World Health Organization standards. Based on the Heavy Metals Pollution Index (HPI), all spring sites in this study were free of heavy metal contamination. According to the single-factor pollution index, all studied spring sites are heavily polluted with lithium.

Declaration of Interest Statement: This research is part of the requirements for obtaining a master's degree.

Authors' Contribution Statements: Both researchers participated in the design and execution of this paper, the analysis of results, and the writing of the research.

Conflict of Interest: There is no conflict of interest.

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