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Pollution Assessment and Source Identification of Heavy Metals in Groundwater on Mosul's Left Bank, Iraq.

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Abstract

The occupation of Mosul by the terrorist organization ISIS and the subsequent military operations to liberate the city forced residents to resort to dig wells randomly and rely on the water from these wells for various uses, without conducting any tests to determine their suitability. Some of these wells are still used in some situations. The current study aims to determine the content and sources of trace elements in groundwater on the left bank of the city and to assess the risks associated with using this water for drinking purposes. Sixteen trace elements (Al, As, B, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, U, and Zn) were analyzed in well water using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Fe, Mn, and Al had concentrations above the recommended limits at two locations among all the trace elements analyzed and assessed. The results of the pollution indices showed that the groundwater under investigation, excluding one sample (M5), isn't polluted by heavy metals. For the M5 sample, the pollution indices yielded different classifications: the sample was classified as highly polluted, non-polluting, and moderately polluted according to the Contamination Index, Heavy-Metal Evaluation Index, and Nemerow Pollution Index, respectively. Factor analysis and cluster analysis findings generally agree that redox reactions, mineral composition of reservoir materials, geochemical behavior, and anthropogenic influences are all involved in controlling the groundwater content of heavy metals. Overall, the Nemerow Pollution Index was the best way to express the state of groundwater pollution by heavy metals, and the source of these heavy metals is primarily geogenic and secondary anthropogenic.

Keywords: *pollution indices, heavy metals, trace elements, Mosul, Groundwater*

1. Introduction

Groundwater is a major source of drinking water globally and the only source in arid regions. In Iraq, given the growing environmental pressures on freshwater, particularly in recent years, water resources have been under considerable stress in terms of both water quality and quantity for various reasons. This stress is due to dams constructed on the Tigris and Euphrates in the riparian countries, global climate change, a significant local decline in annual precipitation rates, and inappropriate planning of water use in Iraq (Adamo et al., 2018; Al-Ansari et al., 2018; Alobaidy et al., 2010; Jones et al., 2008; M. J. Trondalen, 2009; Rahi & Halihan, 2010) Kurdistan region, Iraq using ten water quality pa-rameters (pH, Dissolved Oxygen, Turbidity, Conductivity, Hardness, Alkalinity, Sodium, Biochemical Oxy-gen Demand, Nitrate and Nitrite. As a result, groundwater has been used as the most convenient and easiest option to supply freshwater in many areas, and it is the only option in arid regions. In fact, it is the only refuge in some cases and emergency conditions, as happened in the city of Mosul during the terrorist organization ISIS,s occupation of the city and the difficult periods that followed during the liberation operations and the accompanying military operations that led to the cessation or destruction of water treatment plants and water supply lines in almost all Mosul areas(Khattab et al., 2021; Lead IG, 2017). Most groundwater is of phenomenal natural microbiological quality and has the appropriate chemical quality for most applications. Indeed, many people buy bottled water from natural groundwater sources at considerable cost in preference to public tap water, which may be sourced from treated river water (Smith et al., 2016). This is because groundwater is less susceptible to pollution than surface water, but this does not mean that groundwater can be used for particular purposes without assessing its appropriateness of use. It is therefore important to evaluate its quality characteristics and compare them with international determinants and standards in order to consider the possibility of using it for different uses. One of the essential criteria for assessing groundwater is the contamination of groundwater with trace elements, especially heavy metals, as they pose a direct risk to human health and are difficult to handle when they occur.

Based on the above, groundwater samples were collected from some wells on the left side of Mosul City to examine and evaluate their heavy metal content and other trace elements. Mosul is Iraq›s second-largest city, located in the northwest of Iraq and is the main commercial city in the country›s northwestern part (Augustin et al., 2019). The city of Mosul is divided into two sides by the Tigris River: right and left sides, with an approximate population of 1.5 million inhabitants, more than half of who live on the left bank (Al-Sabawi, 2008; UNAMI, 2017). During the ISIS occupation and the ten-month military operations to retake

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the city, citizens suffered from water shortages. To address this situation, the residents of the city dug wells in each area and used the water from wells for different purposes without any testing.

Accordingly, the current study focuses on groundwater on Mosul›s left bank, as the city relied on well water for various purposes during the emergency period of city life, and some of these wells are still used for domestic and irrigation purposes. Therefore, the objectives of this study are to: (i) determine the concentrations of trace elements in groundwater and compare them with international drinking-water guideline values, (ii) assess the potential human health risks associated with heavy-metal contamination, and (iii) identify the sources of these elements and evaluate the influence of anthropogenic activities on groundwater quality using multivariate statistical methods.

2. Materials and methods

2.1. Study area

Mosul is located approximately 465 kilometers northwest of Baghdad in the northwestern part of Iraq (Figure 1). It is situated at 36.3388° N latitude, 43.1349° E longitude, and 228 m altitude (AtlasWorld, 2019). The Tigris River divides Mosul into two sides, with the left side being the northeastern side of the city and the right side the southwestern side. The left side covers approximately 140 square kilometers and is divided into 51 residential neighborhoods, with a population of over 750000 (UN-Habitat, 2016).

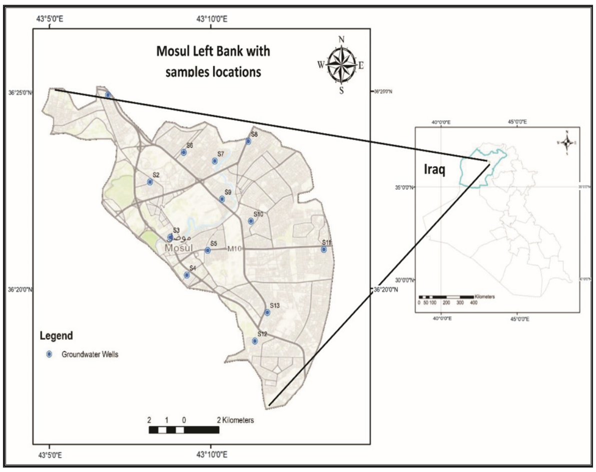

Figure 1. Study area location map with current study wells locations.

2.2. Geological and hydrogeological setting

The study area is situated in a semi-arid region, with hot, dry, sunny summers, and cold and partly cloudy winters. The climate in Mosul is classified as warm and temperate, with an average annual rainfall of approximately 370.4 mm. Temperatures peak in July, reaching up to 46°C, while January is the coldest month, with average lows of 3.3°C and highs of 12.2°C (Climate-Data.Org, 2024; WeatherSpark, 2024).

Geologically, the study area is predominantly characterized by sedimentary deposits ranging in age from the Late Miocene to the Recent (Figure 2). These deposits are stratigraphically arranged in the following order, from oldest to youngest as follows: Fat'ha Formation (Late Miocene), composed of layers of anhydrite, gypsum, limestone, marl, sandstone, and mudstone, often overlain by recent sedimentary layers (Al-Naqib et al., 2018; Mahder-Bashi & Khattab, 2009). Injana Formation, located in the northern part of the study area, is primarily composed of sandstone, siltstone, and mudstone, with evidence of fluvial and deltaic depositional environments. The clastic sediments of the Fat'ha and Injana Formations contain a variety of minerals, including feldspar, pyroxene, quartz, magnetite, chromite, rutile, titanite, and clay minerals. These minerals are derived from the weathering of exposed igneous, metamorphic, and older sedimentary rocks located in the northern and northeastern regions of Iraq. Although these sediments include heavy minerals, such as magnetite, chromite, rutile, and titanite, their overall mineral composition is diverse and reflects the complex processes of sedimentation and transport from the source rocks (Al-Nuaimi & Al-Sayegh, 2004). The Quaternary deposits, which include river terraces and alluvial sediments, are also rich in a diverse array of clasts and minerals, including feldspar, mica, rutile, magnetite, almandite, chromite, and various clay minerals. These deposits, primarily covering the left bank of the Mosul region, consist of conglomerates, gravel, sand, silt lenses, and residual soils, reflecting a dynamic fluvial environment. The floodplain areas along the Al-Khoser and Tigris Rivers further highlight the role of modern hydrological processes, which continue to shape the sedimentary landscape through periodic flooding and sediment deposition. Groundwater movement in the region predominantly follows a flow pattern from the north and northeast toward the south and southwest, particularly to the east of the Tigris River, with some localized exceptions (Al-Jiburi & Al-Basrawi, 2015).

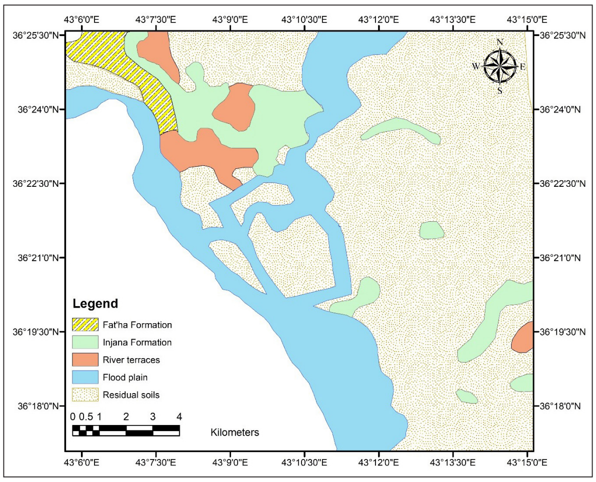

Figure 2. Geological map of the study area (modified from Sissakian et al., 1995)

2.3. Sampling and analytical procedure

Thirteen wells, distributed across the left side of Mosul city, were carefully selected for water sample collection (Figure 1). Samples were collected in November 2019, and well locations were determined using GPS. The depths of the wells examined ranged from 12 to 60 m. Electrical conductivity (EC) was measured in the field using a portable Hanna EC meter. After pumping, samples were collected once EC had stabilized. Samples were collected in 60 ml pre-washed polyethylene bottles, filtered in situ through a

0.2 µm membrane filter, and then acidified with ultrapure HNO_3. Trace elements (Al, As, B, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, U, and Zn) were determined by ICP-MS at TU Bergakademie Freiberg in Germany. To confirm the accuracy of the results, an internal standard containing three elements was added to the samples. Measurements were performed in direct, interaction, or collision mode, depending on the element being measured.

2.4. Groundwater pollution assessment

To evaluate heavy-metal contamination in groundwater in the study area, three heavy-metal pollution assessment models were applied, as indicated below:

2.4.1. Contamination index (Cd)

The Cd accounts for both the sum of parameters exceeding the acceptable upper limits or guideline values of potentially hazardous elements and the concentrations above those limits (Backman et al., 1998). It is calculated separately for each water sample analyzed as the sum of the water contaminant factor for the individual components that exceed the upper permissible limits.

Generally, the Cd summarizes the cumulative effects or degree of pollution across several parameters considered potentially harmful to household water. It is calculated using the following equation:

$$C_d = \sum_{i=1}^{n} C_{fi}$$

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

Where:

C_{fi}= contamination factor for the *i*th component, C_{Ai} = analytical value for the *i*th component and C_{Ni}= upper permissible concentration of the ith component.

The Cd values are classified as follows into three categories: low (Cd < 1), medium (1 < Cd < 3), and high (Cd > 3)(Backman et al., 1998; Edet & Offiong, 2002; Prasad Ahirvar et al., 2023)

2.4.2. Heavy metal evaluation index (HEI)

The Heavy Metal Evaluation Index (HEI) is a quantitative tool used to assess the overall contamination level of heavy metals in water, soil, or sediment. It provides a single value that represents the cumulative impact of multiple heavy metals, making it easier to evaluate pollution levels and compare different samples or sites. This approach provides an overall water quality concerning heavy metals (Bhuiyan et al., 2010; Edet & Offiong, 2002; Singh Brraich & Jangu, 2015) and is measured using the following equation:

$$HEI = \sum_{i=1}^{n} \frac{H_c}{H_{mac}}$$

where H_c and H_{mac} are the measured value and the maximum allowable concentration of the *i*th parameter, respectively.

The level of the heavy metal evaluation index is divided into three categories, as follows: low (HEI < 10), medium (10 < HEI < 20), and high (HEI >20) (Bodrud-Doza et al., 2016; Edet & Offiong, 2002).

2.4.3. Nemerow Pollution Index (NI).

This index is used to assess the extent of contamination of groundwater by several heavy metals at a given sampling location. It considers the average and maximum values of the single-factor pollution index and focuses on pollutants with high pollution rates (Zhong et al., 2015). It is calculated as follows:

$$NI = \sqrt{\frac{\left[\left(\frac{1}{n}\right)\Sigma\left(\frac{Ci}{Si}\right)\right]^2 + \left[\max\left(\frac{Ci}{Si}\right)\right]^2}{2}}$$

Where:

n = the number of indices; *Ci* = the measured content of heavy metal *i*; *Ci* = the standard value. The groundwater is divided by Nemerow Pollution Index into six degrees (Li et al., 2001) (Table1).

Table 1. Classification of Nemerow Pollution Index (NI).

Class	Pollution degree	NI
1	No pollution	≤0.5
2	Clean	0.5–0.7
3	Warm	0.7–1.0
4	Polluted	1.0–2.0
5	Medium pollution	2.0–3.0
6	Severe pollution	>3.0

2.5. Multivariate statistical analysis:

Multivariate statistical techniques, such as factor analysis (FA) and cluster analysis (CA), are effective ways of manipulating, interpreting, and representing data concerning groundwater pollutants and geochemistry and are often used to distinguish groundwater quality(Alaarajy et al., 2023; Chen et al., 2007a; Dmitrijeva et al., 2020; Liu et al., 2003).

2.5.1. Factor analysis

Factor analysis was used to identify and interpret the underlying structure of the data set by reducing it it to smaller set of new orthogonal (uncorrelated) variables (principal components), ordered by decreasingimportance. In addition to significant data reduction, principal components can capture the full variability of the multidimensional data set without losing much of the original information(Dhannoun & Mahmood, 2019). Factor analysis with Varimax rotation of standardized component loadings for extracting and deriving factors, respectively, were carried out and those principal components with eigenvalues greater than 1 were retained(Belkhiri et al., 2018; Li & Zhang, 2010).

2.5.2. Hierarchical cluster analysis

Cluster analysis is one an important multivariate method used to identify correlated data sets. Objects are grouped into clusters so that related objects fall into the same class (Chen et al., 2007a; Danielsson et al., 1999; Xu et al., 2020). Hierarchical clustering combines the most similar observations, followed by the next most similar observations. A dendrogram is constructed based on the degree of similarity at which observations are combined. In this study, cluster analysis was carried out on the standardized data set using Euclidean distances as a measure of similarity and Ward›s linkage method to obtain a dendrogram.

3. Results and discussion

Table 2 presents the statistical summary of trace element concentrations in the groundwater samples from the current study, including key statistical metrics such as the maximum, minimum, standard deviation, mean, and median values. Additionally, it includes the maximum permissible limits (MPL) for these elements in drinking water, as specified by the World Health Organization (WHO, 2011). Table 3 provides a detailed list of the analytical results for the trace element concentrations in each groundwater sample. All pollution indices and statistical analyses were based on this dataset.

Table 2. Statistical summary of trace element concentrations in the current study samples and their maximum permissible limits(MPL)

Element	Mean	Median	Minimum	Maximum	St. Dev.	MPL (WHO, 2011).
Al	62.69	41.57	26.35	271.50	65.22	200
As	0.30	0.28	0.04	0.72	0.18	10
B	538.37	418.20	278.50	1314.00	283.77	500
Ba	32.05	24.35	12.08	108.50	26.12	700
Cd	0.05	0.05	0.01	0.12	0.03	3
Cr	5.12	4.90	2.81	10.66	2.41	50
Cu	9.35	8.95	7.50	16.49	2.32	2000
Fe	156.04	44.29	20.36	1109.00	298.60	300
Mn	113.24	10.70	0.99	971.80	266.34	400
Mo	5.08	5.22	1.82	10.87	2.91	70
Ni	3.92	2.91	0.93	12.72	3.06	70
Pb	0.70	0.65	0.33	1.66	0.38	10
Sb	0.11	0.10	0.08	0.17	0.03	20
Se	0.63	0.47	0.18	1.58	0.47	40
U	10.83	11.61	2.49	18.97	5.45	30
Zn	29.43	15.95	8.30	145.80	36.67	3000

Table 3. EC (µmhos/cm) and trace element (ppb) of studied groundwater samples

Parameters	Sample No.												
	1M	2M	3M	4M	5M	6M	7M	8M	9M	10M	11M	12M	13M
EC	2922	2116	1310	1814	2721	1612	1814	2015	3829	1612	1008	1310	1914
Al	50.93	36.35	48.22	33.96	60.89	271.5	35	40.04	44.54	41.57	95.99	29.61	26.35
As	0.336	0.382	0.18	0.721	0.043	0.496	0.168	0.256	0.28	0.15	0.45	0.313	0.165
B	418.20	720.50	302.50	365.70	670.40	516.90	359.20	733.30	1314	616.70	278.50	344	358.90
Ba	14.40	14.73	37.00	24.35	108.50	29.27	16.60	17.76	12.08	29.4	58.48	31.40	22.62
Cd	0.049	0.048	0.076	0.117	0.081	0.081	0.007	0.044	0.037	0.065	0.069	0.012	0.016
Cr	5.927	5.275	3.072	2.812	3.722	7.296	3.084	3.119	5.865	10.66	4.902	2.857	8.016
Cu	7.676	7.499	9.559	8.551	9.514	9.27	7.853	8.706	8.949	9.181	10.5	16.49	7.856
Fe	44.24	115.6	44.29	26.85	1109	341.8	34.91	42.66	69.22	48.01	101.5	30.11	20.36
Mn	0.994	227	22.06	131.2	971.8	7.1	13.33	6.981	61.66	10.7	3.561	9.211	6.544
Mo	5.723	10.87	5.338	2.484	2.179	3.314	10.14	5.265	6.847	5.216	1.974	4.91	1.82
Ni	2.925	6.115	2.627	2.906	12.72	3.528	2.362	6.604	2.772	2.647	2.911	0.925	1.92
Pb	0.421	0.361	0.707	1.005	0.92	0.78	0.374	0.483	0.654	1.004	1.659	0.429	0.326
Sb	0.131	0.098	0.144	0.142	0.171	0.104	0.115	0.083	0.123	0.077	0.088	0.089	0.081
Se	1.580	0.190	0.469	0.444	0.176	0.501	0.237	1.022	1.495	0.394	0.35	0.796	0.598
U	9.034	9.301	2.494	5.94	16.83	12.4	11.61	17.46	4.442	15.97	11.83	4.505	18.97
Zn	8.299	145.8	12.04	9.981	43.97	15.83	8.719	13.25	23.08	29.36	19.36	36.98	15.95

3.1 pollution assessment

The computed results for the pollution evaluation indices (Cd, HEI, and NI) are presented in Tables 4 and 5. The study considered the following trace elements (Al, As, B, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, U, and Zn). The calculated contamination factor (*Cfi*) values indicate that the analytical values for almost all trace elements are below the maximum permissible concentration (WHO, 2011), except for iron and manganese in a single sample (5M). Thus, considering only analytical values that exceed the maximum permissible limit for the pollution index (Cd) calculation (Backman et al., 1998; Edet & Offiong, 2002), all samples in the current study, except sample 5M, fall within the low contamination field (Cd < 1). Sample 5M, with a Cd value of 4.13, falls within the high contamination field (Cd > 3).

The calculated heavy metal evaluation index (HEI) for the current study ranges from 1.02 to 7.87 (Table 5). The classification is based on the procedure followed in Bodrud-Doza et al. (2016) and Edet & Offiong (2002)Contamination index (Cd, which divides the Heavy Metal Evaluation Index into three categories: low (HEI < 10), medium (10 < HEI < 20) and high (HEI > 20). All samples of the current study fall under the low HEI category (HEI < 10).

The calculated values of the Nemerow Pollution Index (NI) indicated that the sample 5M was categorized as medium-polluted and the sample 6M was at warming level while the rest of the samples were all at no-pollution level (Table 5). Figure 3 illustrates that the highest value of the Nemerow Pollution Index was observed approximately in the central area of the left bank of Mosul, an old and commercial zone that is also one of the most densely populated areas in the city. This likely reflects the impact of human activities on groundwater contamination

Table 4. Contamination factors of individual components (*Cfi*) and Contamination index (Cd) of the studied samples

Heavy metals	Sample No.												
	1M	2M	3M	4M	5M	6M	7M	8M	9M	10M	11M	12M	13M
	contamination factors of individual components (*Cfi*)												
Al	-0.75	-0.82	-0.76	-0.83	-0.70	0.36	-0.83	-0.80	-0.78	-0.79	-0.52	-0.87	-0.87
As	-0.97	-0.96	-0.98	-0.93	-1.00	-0.95	-0.98	-0.97	-0.97	-0.99	-0.96	-0.98	-0.98
B	-0.83	-0.70	-0.87	-0.85	-0.72	-0.78	-0.85	-0.69	-0.45	-0.74	-0.88	-0.85	-0.85
Ba	-0.98	-0.98	-0.95	-0.97	-0.85	-0.96	-0.98	-0.97	-0.98	-0.96	-0.92	-0.97	-0.97
Cd	-0.98	-0.98	-0.97	-0.96	-0.97	-0.97	-1.00	-0.99	-0.99	-0.98	-0.98	-0.99	-0.99
Cr	-0.88	-0.89	-0.94	-0.94	-0.93	-0.85	-0.94	-0.94	-0.88	-0.79	-0.90	-0.84	-0.84
Cu	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-0.99	-1.00	-1.00
Fe	-0.85	-0.61	-0.85	-0.91	2.70	0.14	-0.88	-0.86	-0.77	-0.84	-0.66	-0.93	-0.93
Mn	-1.00	-0.43	-0.94	-0.67	1.43	-0.98	-0.97	-0.98	-0.85	-0.97	-0.99	-0.98	-0.98
Mo	-0.92	-0.84	-0.92	-0.96	-0.97	-0.95	-0.86	-0.92	-0.90	-0.93	-0.97	-0.97	-0.97
Ni	-0.96	-0.91	-0.96	-0.96	-0.82	-0.95	-0.97	-0.91	-0.96	-0.96	-0.96	-0.97	-0.97
Pb	-0.96	-0.96	-0.93	-0.90	-0.91	-0.92	-0.96	-0.95	-0.93	-0.90	-0.83	-0.97	-0.97
Sb	-0.99	-1.00	-0.99	-0.99	-0.99	-0.99	-0.99	-1.00	-0.99	-1.00	-1.00	-1.00	-1.00
Se	-0.96	-1.00	-0.99	-0.99	-1.00	-0.99	-0.99	-0.97	-0.96	-0.99	-0.99	-0.99	-0.99
U	-0.70	-0.69	-0.92	-0.80	-0.44	-0.59	-0.61	-0.42	-0.85	-0.47	-0.61	-0.37	-0.37
Zn	-1.00	-0.95	-1.00	-1.00	-0.99	-0.99	-1.00	-1.00	-0.99	-0.99	-0.99	-0.99	-0.99
Cd	< 1	< 1	< 1	< 1	4.13	0.50	< 1	< 1	< 1	< 1	< 1	< 1	< 1

Table 5. Single pollution weight (*Ci* / *Si*), Nemerow Pollution Index(NI) and Heavy metal evaluation index (HEI) of the studied samples

Heavy metals	Sample No.												
	1M	2M	3M	4M	5M	6M	7M	8M	9M	10M	11M	12M	13M
Al	0.255	0.182	0.241	0.170	0.304	1.358	0.175	0.200	0.223	0.208	0.480	0.132	0.132
As	0.034	0.038	0.018	0.072	0.004	0.050	0.017	0.026	0.028	0.015	0.045	0.017	0.017
B	0.174	0.300	0.126	0.152	0.279	0.215	0.150	0.306	0.548	0.257	0.116	0.150	0.150
Ba	0.021	0.021	0.053	0.035	0.155	0.042	0.024	0.025	0.017	0.042	0.084	0.032	0.032
Cd	0.016	0.016	0.025	0.039	0.027	0.027	0.002	0.015	0.012	0.022	0.023	0.005	0.005
Cr	0.119	0.106	0.061	0.056	0.074	0.146	0.062	0.062	0.117	0.213	0.098	0.160	0.160
Cu	0.004	0.004	0.005	0.004	0.005	0.005	0.004	0.004	0.004	0.005	0.005	0.004	0.004
Fe	0.147	0.385	0.148	0.090	3.697	1.139	0.116	0.142	0.231	0.160	0.338	0.068	0.068
Mn	0.002	0.568	0.055	0.328	2.430	0.018	0.033	0.017	0.154	0.027	0.009	0.016	0.016
Mo	0.082	0.155	0.076	0.035	0.031	0.047	0.145	0.075	0.098	0.075	0.028	0.026	0.026
Ni	0.042	0.087	0.038	0.042	0.182	0.050	0.034	0.094	0.040	0.038	0.042	0.027	0.027
Pb	0.042	0.036	0.071	0.101	0.092	0.078	0.037	0.048	0.065	0.100	0.166	0.033	0.033
Sb	0.007	0.005	0.007	0.007	0.009	0.005	0.006	0.004	0.006	0.004	0.004	0.004	0.004
Se	0.040	0.005	0.012	0.011	0.004	0.013	0.006	0.026	0.037	0.010	0.009	0.015	0.015
U	0.301	0.310	0.083	0.198	0.561	0.413	0.387	0.582	0.148	0.532	0.394	0.632	0.632
Zn	0.003	0.049	0.004	0.003	0.015	0.005	0.003	0.004	0.008	0.010	0.006	0.005	0.005
HEI	1.287	2.266	1.023	1.343	7.869	3.611	1.200	1.632	1.737	1.717	1.848	1.327	1.327
NI	0.22	0.41	0.18	0.24	2.64	0.97	0.28	0.42	0.39	0.38	0.35	0.11	0.45

3.2 Statistical analysis and trace element sources

3.2.1 Factor analysis

Factor analysis was performed on the trace elements data using the principal component analysis approach and based on the normalized varimax rotated matrix. The analysis revealed six major factors with eigenvalues >1 influencing the trace elements concentration as shown by the scree plot (Figure 4). These factors together constitute more than 88% of the variance (Table 6).

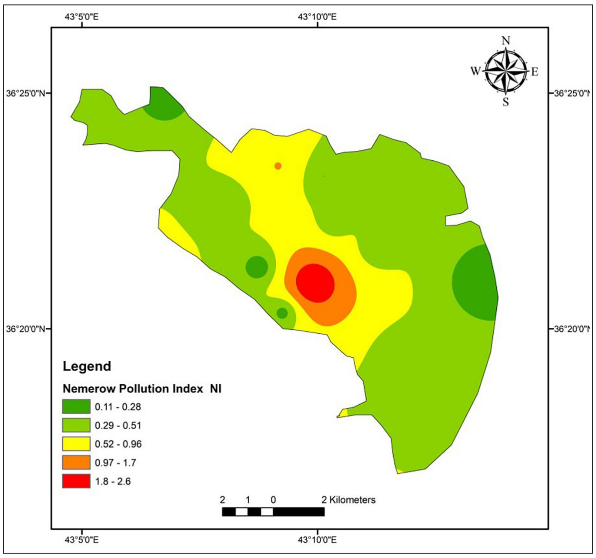

Figure 3. Spatial Distribution of the Nemerow Pollution Index in Groundwater on the Left Bank of Mosul

The first factor accounts for 28.5% of the total variance represented by the positive loadings of Fe, Mn, Co, Ni, Ba, Sn, Zn, and Sb. This factor is naturally related to redox processes that control Fe and Mn phases in the groundwater (Brown et al., 1999; Suada Luzati et al., 2016). It suggests that Fe and Mn oxy-hydroxides regulate the concentration of Co, Ni, Ba, Sn, Zn, and Sb, as these colloids can reduce the dissolved concentrations of heavy metals by adsorption (Mary Ugwu & Anthony Igbokwe, 2019; Wołowiec et al., 2019). With 19.4% of the total variance, the second factor high loaded with Br, B, Li, Se, and EC. The variables loaded on this factor suggest a geogenic source, particularly evaporite rocks commonly found in the study area (Khattab et al., 2023). This is further supported by the fact that the elements with the highest loadings on this factor are highly soluble in water (Kabata-Pendias & Pendias, 2001), along with the positive loading of electrical conductivity (EC) on this factor. The third and fifth factors, which account for 17.7% and 7.8% of the total variance, respectively, show positive loadings on elements such as Cr, Si, U, Al, Ti, V, and Y. These factors also indicate a geogenic origin. However, unlike the elements loaded on the second factor, the elements associated with the third and fifth factors are among the least soluble. Their source is silicate minerals found in sand and sandstone (Kabata-Pendias & Pendias, 2001; Mahmood, 2021). The fourth and sixth factors account for 10.3% and 5% of the variance, respectively, and are represented by the positive loading of the following elements (Cd, Pb, and As on the fourth factor and Cu, Zn on the sixth factor). The trace elements loaded ontp the last two factors are typically influenced by both natural and anthropogenic sources from groundwater of urban areas (Huang et al., 2020; Mohammed et al., 2024; Ou et al., 2024; Rivera-Rivera et al., 2020; Souza et al., 2016). These two factors are therefore likely to reflect the combined effect of natural and anthropogenic sources within the city on the concentrations of these elements, particularly since they are widely used in the various fields of industry, agriculture, and transport. Given Mosul's history as a conflict zone, it is plausible that military activities, including the use of explosives and ammunition during the conflict with ISIS, could have contributed to the contamination of groundwater. Elements such as lead, cadmium, and copper, potentially from explosive residues or the destruction of infrastructure, might have leached into the environment (Hantoush & Hassen, 2023). While the statistical results point to a combination of natural and anthropogenic sources, the potential impact of military operations remains an important consideration when interpreting these findings.

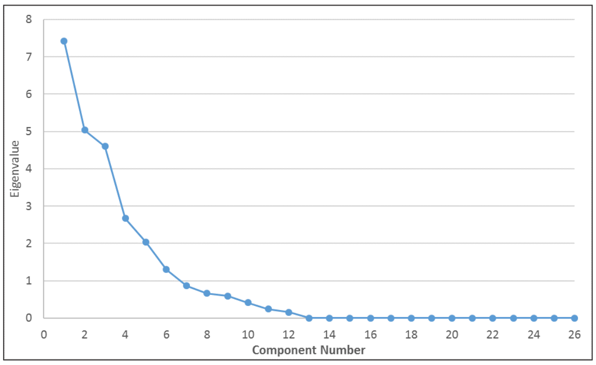

Figure 4. Scree plot showing that the data has six major factors with eigenvalues>1

3.2.2 Cluster analysis

The Hierarchical Cluster Analysis (HCA) results were presented as a dendrogram (Figure 5), revealing four distinct groups. Variables within a given group (cluster) are likely to be derived from the same source, exhibit a similar geochemical behavior, or are influenced by particular factors unrelated to the element's geochemical behavior (Chen et al., 2007b; Danielsson et al., 1999; Dhannoun & Mahmood, 2019)

The HCA results broadly match the FA results, as the clustering of trace elements in the four groups is largely compatible with the factor analysis findings, as seen below:

Cluster 1 consists of Fe, Mn, Co, Ni, Ba, Sn, and Sb. It appears that the elements of this group were aggregated in the same group by the impact of the natural factor represented by the Redox reactions and their effect on the iron and manganese phases and the rest of the group elements. It suggests that Fe and Mn oxy-hydroxides regulate the concentrations of Co, Ni, Ba, Sn, and Sb, as these colloids can reduce the dissolved concentrations of heavy metals through adsorption (Mary Ugwu & Anthony Igbokwe, 2019; Wołowiec et al., 2019).

Cluster 2 consists of B, Br, Li, Se, Mo, Sr, and EC. This cluster contains a group of trace elements that are distinguished by a high ability to move in dissolved form in the aquatic environment, as evidenced by the presence of EC in this group. Such elements are usually present at substantial concentrations in evaporites and carbonate rocks that are highly abundant in the study area (Kabata-Pendias and Pendias, 2001; Khattab et al., 2023).

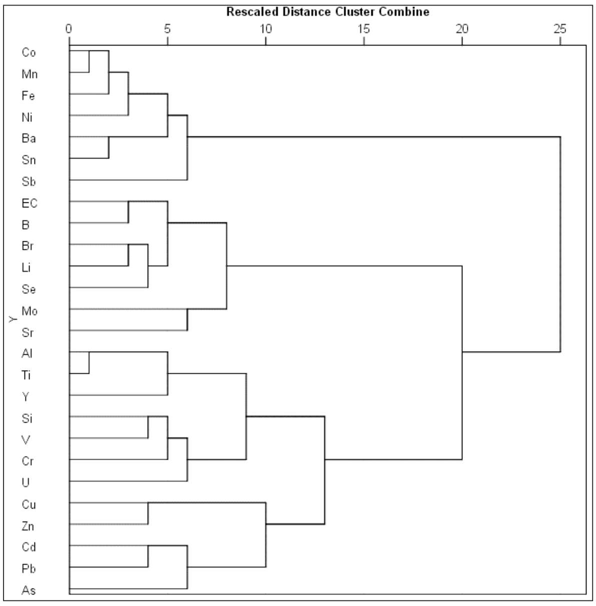

Figure 5. Dendrogram using ward's linkage showing results of hierarchical clustering

Cluster 3 consists of Al, Ti, Y, Si, V, Cr, and U. It seems that the grouping of the elements in this group is the consequence of the influence of similar geochemical behavior and common sources. this group includes several lithophilic trace elements, which are characterized by low mobility in the aquatic environment (White, 2013). These elements are found in igneous and metamorphic silicate minerals such as feldspar, mica, and amphiboles, which are commonly present in sand and sandstone in the study area (Mahmood, 2021).

Cluster 4 consists of Cu, Zn, Cd, Pb, and As. These heavy metals are commonly associated with urban and agricultural activities and often originate from both geogenic and anthropogenic sources (Boateng et al., 2015, 2019; Galitskaya et al., 2017; Leung & Jiao, 2006). The clustering of these elements suggests that contamination from various anthropogenic activities, including urban waste, emissions from auto repair workshops and power generators, and the use of fertilizers and pesticides in agricultural practices, alongside the impacts of military operations during the city›s liberation from terrorist groups, contribute to the observed concentrations in the studied groundwater.

Table 6. Varimax rotated principal component analysis for the groundwater samples

Variables	PC1	PC2	PC3	PC4	PC5	PC6	Communalities
EC	0.269	0.856	-0.193	-0.167	-0.100	-0.237	0.926
Al	0.088	-0.019	0.956	0.190	0.049	-0.041	0.965
As	-0.417	-0.070	0.308	0.521	-0.357	-0.215	0.728
B	0.200	0.855	-0.007	-0.119	0.052	-0.079	0.818
Ba	0.853	-0.235	0.002	0.294	0.027	0.307	0.975
Br	-0.208	0.937	0.112	-0.038	-0.012	-0.023	0.935
Cd	0.305	-0.100	0.180	0.800	-0.212	-0.302	0.921
Co	0.980	0.018	-0.109	0.056	-0.102	0.036	0.987
Cr	-0.128	0.181	0.151	0.106	0.773	-0.062	0.689
Cu	-0.087	-0.163	0.056	0.012	-0.280	0.924	0.984
Fe	0.974	0.016	0.164	0.047	-0.020	0.079	0.937
Li	-0.010	0.796	0.263	-0.340	0.335	0.056	0.981
Mn	0.969	0.000	-0.156	0.026	-0.107	-0.006	0.711
Mo	-0.208	0.085	-0.054	-0.701	-0.199	-0.325	0.895
Ni	0.908	0.082	-0.023	-0.019	0.018	-0.181	0.798
Pb	0.191	-0.147	0.183	0.804	0.154	0.174	0.844
Sb	0.593	0.111	-0.127	0.169	-0.627	-0.239	0.808
Se	-0.386	0.785	-0.080	-0.018	-0.131	0.090	0.960
Si	-0.379	-0.025	0.453	0.122	0.688	-0.341	0.923
Sn	0.882	-0.052	0.184	0.304	0.063	0.108	0.831
Sr	0.055	0.489	-0.132	-0.662	0.206	0.289	0.944
Ti	-0.028	-0.007	0.959	0.121	0.083	-0.042	0.829
U	0.356	-0.086	0.050	-0.121	0.822	-0.110	0.943
V	-0.301	-0.068	0.776	0.105	0.427	0.209	0.963
Y	0.423	0.524	0.694	0.132	0.105	-0.016	0.832
Zn	0.602	0.085	-0.092	0.018	0.116	0.723	
Eigen values	7.418	5.035	4.602	2.67	2.03	1.298	
Variance(%)	28.531	19.366	17.702	10.268	7.808	4.994	
Cumulative(%)	28.531	47.896	65.598	75.866	83.674	88.667	

4. Conclusions

Groundwater was analyzed and assessed in terms of trace element content and heavy metal pollution status in the left bank of Mosul city. Of all the trace elements analyzed and evaluated, Fe, Mn, and Al had a concentration above the acceptable limits at two locations for Fe and one of the two locations for each of Mn and Al. The results of the pollution indices showed that the groundwater under investigation, excluding one sample (M5), is not polluted by heavy elements. For the M5 sample, the findings of the pollution indices varied as they were highly polluted, non-polluting, and moderately polluted according to the Contamination index, Heavy metal evaluation index and Nemerow Pollution Index, respectively. Among the three indices used, the Nemerow Pollution Index was the most sensitive and representative of the water quality status in the current study, as its findings were in complete agreement with any exceedance of WHO guideline values.

Statistical techniques (factor analysis and cluster analysis) have shown that the main source of trace elements originates from geogenic sources, with a secondary influence of the city activities on the concentrations of certain heavy elements represented by copper, zinc, cadmium, lead and arsenic. After it became obvious that there is evidence of the city›s influence on the concentrations of certain heavy metals in groundwater, it is advised that both residents and the government take preventive measures to reduce heavy metal emissions and their impact on the urban environment, as well as an urbanization plan.

Declarations

- The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.
- The authors have no relevant financial or non-financial interests to disclose.
- Both authors contributed to the conception, design, and writing of the manuscript. Both authors read and approved the final manuscript.
- This research includes water hydrochemistry analysis. This study does not include any animal experiments or analyses.
- The data used in this research are data analyzed by the authors, and they have the full right to publish.

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