Temporal Analysis of Physicochemical Parameters and Heavy Metal Contamination in the Water of Derbendikhan Reservoir: A Six-Year Study

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Abstract

The rapid expansion of industrial activities, extensive use of chemicals, and discharge of untreated waste in many developing regions have become a major threat to environmental quality, ecosystem stability, and human well-being. This research aimed to assess the variation of physicochemical properties and heavy metal contamination in the waters of Derbendikhan Reservoir. Monthly samples were collected from the upstream area of the reservoir in Sulaimani, Kurdistan Region of Iraq, between 2013 and 2018. The analyzed physicochemical indicators included pH, nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}), hydrogen peroxide (H_2O_2), fluoride (F^-), bromide (Br^-), free and total chloride (Cl^-), potassium (K^+), sodium molybdate (Na_2MoO_4), molybdate (MoO_4^{2-}), cyanuric acid, hardness, alkalinity, and acidified chloride. In addition, trace metals such as copper (Cu), magnesium (Mg), manganese (Mn), molybdenum (Mo), and iron (Fe) were determined using atomic absorption spectrophotometry. All analyses followed the standard procedures of the American Public Health Association (APHA). Data were statistically evaluated on a monthly, seasonal, and annual basis using SPSS v22, applying one-way ANOVA followed by Duncan's test. The findings revealed that concentrations of Cu, Mg, Mo, and Fe, along with NO_3^-, NO_2^-, and F^-, frequently exceeded or approached permissible limits and exhibited increasing trends during the study period. In conclusion, urgent measures are required from all stakeholders, including regulatory authorities, to enforce discharge standards, while industries must adopt proper treatment systems to reduce pollution.

Keywords: Water Quality, Surface Water, Physicochemical, Heavy metals

Introduction

پوختە

فراوانبوونی ئەم دواییەی پیشەسازییەکان، زیادبوونی بەکارهێنانی مادده کیمیاییەکان و پاشماوە/دەردانی چارەسەرنەکراو لە زۆربەی بەشەکانی وڵاتانی تازەپێگەیشتودا، خەریکە دەبێتە نیگەرانییەکی گرینگ بۆ ژینگە، بەردەوامیی ئیکۆسیستەم و تەندروستی مرۆڤ. ئەم توێژینەوەیە بە ئامانجی لێکۆڵینەوە بوو لە شێوازەکانی پارامێتەرەکانی فیزیکی و کیمیایی و پیسبوونی کانزا قورسەکان لە ئاوی خەزنەی دەربەندیخان. لە ماوەی ساڵی ٢٠١٣ تا ٢٠١٨ مانگانە نمونە لە سەرەوەی خەزانەکەی دەربەندیخان، سلێمانی، هەرێمی کوردستانی عێراق وەرگیراوە. تایبەتمەندییە فیزیکی و کیمیاییەکانی ئاو لەوانە pH، نیترات (No3-)، نیترات (No2-)، سەلفات ((So4 2-)، H2O2، فلۆرین (F)، برۆمین (Br)، بێ کلۆرید Cl، کۆی گشتی Cl کلۆرید، پۆتاسیۆم (K)، مۆلیبدەیتی سۆدیۆم (Na2MoO4)، مۆلیبدەیت (MoO4)، ترشی سیانوریک، ڕەقیی، ئەلکالی و... ترشی کلۆرید بوون پێوەر. کانزا قورسەکان لەوانە مس (Cu)، مەگنیسیۆم (Mg)، مەنگەنیز (Mn)، مۆلیبدینیۆم (Mo) و ئاسن (Fe) بە بەکارهێنانی سپێکترۆفۆتۆمێتری مژینی ئەتۆمی شیکرانەوە. هەموو تاقیکردنەوەکان بە بەکارهێنانی شێوازە ستانداردەکانی کۆمەڵەی تەندروستی گشتی ئەمریکی (APHA) لێکۆڵینەوەیان لەسەر کرا. داتاکان مانگانە، وەرزی و ساڵانە بە بەکارهێنانی SPSS v22 شیکرانەوە؛ شیکاری یەکلایەنەی جیاوازی (ANOVA) و دواتر تاقیکردنەوەی دانکان. ئەنجامەکان دەریانخست کە بڕی کانزا قورسەکانی Cu، Mg، Mo و Fe و پارامێتەرەکانی NO3-، NO2- و F لە ئاوی خەزنەی دەربێندیخان پێویستیان بە گرنگیدانی تایبەت هەیە چونکە لە سەرووی (یان نزیک) ئاستەنگە ڕێگەپێدراوەکانن یان ڕەوتێکی زیادبوونیان نیشانداوە لە ماوەی ساڵی ٢٠١٣ تا ٢٠١٨. لە کۆتاییدا، پێویستی بە کردەوەی جددی هەیە لەلایەن هەموو لایەنە پەیوەندیدارەکانەوە، لەوانەش ڕێکخراوەیی ئۆرگانەکان، بۆ جێبەجێکردنی یاسا و ڕێساکانی پەیوەست بە دەردانی ڕێگەپێدراو، و بۆ پیشەسازییەکان کە پیسبوونەکانیان بە سیستەمی چارەسەرکردنی گونجاو کۆنترۆڵ بکەن.

وشەی سەرەکی: کوالیتی ئاو، ئاوی ڕووکار، فیزیکی کیمیایی، کانزا قورسەکان

ملخص

أصبح التوسع الصناعي الأخير، وزيادة استخدام المواد الكيميائية، والنفايات/التصريفات غير المعالجة في معظم أنحاء الدول النامية، مصدر قلق بالغ على البيئة واستدامة النظام البيئي وصحة الإنسان. هدفت هذه الدراسة إلى دراسة أنماط المعاملات الفيزيائية والكيميائية وتلوث المعادنالثقيلة في مياه خزان دربنديخان. جُمعت عينات من أعلى خزان دربنديخان، السليمانية، إقليم كردستان العراق، شهريًا خلال الفترة من ٢٠١٣ إلى ٢٠١٨. تم قياس الخصائص الفيزيائية والكيميائية للمياه، بما في ذلك الرقم الهيدروجيني(pH) ، والنترات(No3-) ، والنتريت(No2-) ، والكبريتات (So42-)، وH2O2، والفلور(F) ، والبروم(Br) ، وكلوريد الكلور الحر، وكلوريد الكلور الكلي، والبوتاسيوم(K) ، وموليبدات الصوديوم(Na2MoO4) ، والموليبدات .(MoO4) كما تم تحليل المعادن الثقيلة، بما في ذلك النحاس

(Cu)، والمغنيسيوم(Mg) ، والمنغنيز(Mn) ، والموليبدينوم(Mo) ، والحديد(Fe) ، باستخدام مطياف الامتصاص الذري. اُجريت جميع التجارب باستخدام الطرق القياسية للجمعية الأمريكية للصحة العامة (APHA). حُللت البيانات شهريًا وموسميًا وسنويًا باستخدام برنامج SPSS الإصدار ٢٢؛ وتحليل التباين أحادي الاتجاه (ANOVA) متبوعًا باختبار دنكان. أظهرت النتائج أن كمية المعادن الثقيلة (النحاس، والمغنيسيوم، والموليبدينوم، والحديد)، ومعايير NO3- وNO2- وF في مياه خزان دربنديخان، تحتاج إلى اهتمام خاص، نظرًا لتجاوزها (أو اقترابها) من الحدود المسموح بها، أو لتزايدها خلال عام ٢٠١٣، وذلك للجهات المعنية، ولتطبيق القواعد واللوائح المتعلقة بالتصريفات المسموح بها، ولمساعدة الصناعات على ضبط تلوثها باستخدام أنظمة معالجة مناسبة.

الكلمات المفتاحية: جودة المياه، المياه السطحية، فيزيائية وكيميائية، المعادن الثقيلة

Water is essential not only for aquatic life and biodiversity but also for human activities such as drinking, bathing, food production, agriculture, and various industries. However, concerns regarding both the **quantity and quality** of freshwater are intensifying due to rising per capita consumption, driven by continuous population growth, urbanization, industrialization, climate change, and pollution, all of which negatively affect its use (Ayeku et al., 2020). Although water is the most abundant substance on Earth, less than 3% (approximately 2.53%) is freshwater, of which only about 0.3% is accessible in rivers, lakes, and reservoirs, with the remainder stored in glaciers, permanent snow, and groundwater aquifers.

Freshwater resources, particularly surface waters, are highly vulnerable to contamination. Combined with spatial and temporal variations in availability, this makes water scarcity an increasingly urgent issue that may lead to severe crises (Pimentel et al., 2004; Rasul, 2019). Consequently, studies in this field are vital for assessing water quality, identifying potential pollutants, understanding their consequences, evaluating current protection measures, and proposing corrective actions.

Pollutants enter aquatic systems through both natural and anthropogenic pathways, such as rainfall, erosion, wastewater discharges (domestic and industrial), and agricultural inputs like fertilizers and pesticides (Pimentel et al., 2004; Gupta et al., 2016; Ayeku et al., 2020). Physicochemical parameters can exert short- and long-term impacts—either beneficial or harmful depending on their source—on the ecosystem as a whole. Among chemical contaminants, heavy metals are of particular concern, as they may cause toxicity and chronic poisoning in aquatic organisms and have harmful effects on human, animal, and plant health. These include soil contamination, bioaccumulation of heavy metals in algae, fish, and crops, transmission to humans through the food chain, and disruption of ecological balance (Khezri et al., 2016; Rasheed & Saleh, 2016; Ma et al., 2020).

Heavy metals have also been linked to various health disorders in terrestrial and aquatic wildlife worldwide, such as cancers, Alzheimer's disease, Parkinson's disease, tissue damage, mental decline, and muscular dystrophy. These effects may occur through direct exposure (oral or dermal contact) or indirectly via consumption of contaminated aquatic organisms or livestock (Mohod & Dhote, 2013; Rasheed & Saleh, 2016; Sacdal et al., 2022). Additionally, some non-sporulating bacteria, including *Escherichia*, *Salmonella*, *Vibrio*, and *Listeria*, may enter a viable but non-culturable (VBNC) state when exposed to environmental stressors such as pH shifts, temperature changes, salinity, or osmotic stress, posing further risks to human health (Khezri et al., 2020).

For these reasons, analyzing the physicochemical properties and heavy metal concentrations of water is crucial for understanding pollutant levels, their potential impacts, and strategies for water quality protection.

The Derbendikhan Reservoir, constructed between 1956 and 1961 in the southeast of Sulaimani (35°06′35″ N, 45°41′20″ E), is the second largest reservoir in the Kurdistan Region of Iraq, covering approximately 114.30 km² with a maximum depth of 75 m at an altitude of 485 m above sea level (Rasheed, 2022). It provides drinking water for the Darbandikhan district, supports fisheries, tourism, irrigation, and hydropower generation (Rasul, 2019). This study investigates the patterns of physicochemical parameters and heavy metal contamination in the water of Derbendikhan Reservoir during the period 2013–2021.

Material and methods

Physicochemical Measurements

- **pH**: Determined using a HI 3222 PH/ORP/ISE meter (HANNA) (Rasheed & HamaKarim, 2017).
- **Nitrate (NO□$^{-}$)**: Quantified by ultraviolet spectrophotometric screening at 220 nm using a CECIL 2021 spectrophotometer (APHA, 2005; Rasheed & HamaKarim, 2017).
- **Sulfate (SO_4^{2-})**: Measured by the turbidimetric method with barium chloride, absorbance recorded at 420 nm, and concentrations determined against a standard curve ranging from 0 to 40 mg L^{-1} (Gupta et al., 2016; Amedi et al., 2021).
- **Chloride (Cl^-)**: Determined by argentometric titration (Mohr's method), using $AgNO_3$ as titrant and K_2CrO_4 as indicator. Chloride concentration (mg L^{-1}) was calculated as:

Cl^- (mg L^{-1})=(V1−V2)×N×35.45Sample volume×1000\text{Cl^- (mg L^{-1})} = \frac{(V_1 - V_2) \times N \times 35.45}{\text{Sample volume} \times 1000}Cl^- (mg L^{-1})=Sample volume×1000(V1−V2)×N×35.45

where V_1 = $AgNO_3$ volume for the sample (mL), V_2 = $AgNO_3$ volume for the blank (mL), N = normality of $AgNO_3$, and 35.45 = molar mass of Cl^- (Rasheed & HamaKarim, 2017).

- **Potassium (K^+)**: Measured using a Flame Photometer (Jenway, Model FFP7) (Amedi et al., 2021).
- **Total Hardness**: Assessed by EDTA titration, following APHA guidelines (APHA, 2005; Rasheed & HamaKarim, 2017).
- **Alkalinity**: Determined by titration with H_2SO_4 (0.01 N) after adding methyl orange indicator. Results were expressed as mg L^{-1} $CaCO_3$ using:

Alkalinity (mg L^{-1} $CaCO_3$)=A×B×50,000Sample volume\text{Alkalinity (mg L^{-1} $CaCO_3$)} = \frac{A \times B \times 50,000}{\text{Sample volume}}Alkalinity (mg L^{-1} $CaCO_3$)=Sample volumeA×B×50,000

where A = volume of H_2SO_4 titrant (mL), B = normality of H_2SO_4 (Gupta et al., 2016).

Heavy Metals

Cu, Mg, Mn, Mo, and Fe were analyzed using a Shimadzu 7000 Atomic Absorption Spectrophotometer (Flame model), according to APHA methods (APHA, 2005; Rasheed & HamaKarim, 2017).

Statistical Analysis

The data were processed using SPSS software (version 22). Normality of the variables was examined with the Kolmogorov–Smirnov test, while Levene's test was employed to assess variance homogeneity. As the datasets met both assumptions of normal distribution and equal variance, a one-way ANOVA was performed. Post hoc comparisons were carried out using Duncan's multiple range test, with statistical significance determined at $p < 0.05$.

Results and discussion

In this study, the physicochemical properties and heavy metals contents in water of Derbendikhan reservoir, Sulaimani, Iraqi Kurdistan region were investigated during a 6 year period from 2013 to 2018. The monthly, seasonally and annually measurements and comparisons are shown in Tables 1, 2 and 3, respectively.

Table 1. Monthly levels of physicochemical properties and heavy metals contents in water of Derbendikhan reservoir, Sulaimani, Iraqi Kurdistan region during 2013-2018

Variable	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	
pH	7.8±0.1^{cd}	7.9±0.3^{abcd}	7.9±0.3^{abcd}	8.2±0.1^{abc}	8.2±0.4^{abc}	8.4±0.3^{a}	8.3±0.3^{ab}	8.2±0.1^{abc}	8.0±0.2^{abcd}	7.8±0.1^{bcd}	7.7±0.2^{d}	.2^{abcd}
No$_3^-$(mg.L^{-1})	19.05±9.61^{a}	13.63±10.81^{a}	18.08±7.33^{a}	15.47±10.44^{a}	15.44±8.66^{a}	15.32±10.71^{a}	21.36±1.16^{a}	8.71±11.54^{a}	8.00±10.02^{a}	3.10±0.72^{a}	14.16±12.19^{a}	±12.57^{a}
No$_2^-$ (mg.L^{-1})	0.021±0.008^{a}	0.062±0.035^{a}	0.054±0.024^{a}	0.255±0.310^{a}	0.057±0.015^{a}	0.110±0.144^{a}	0.038±0.008^{a}	0.005±0.007^{a}	0.039±0.040^{a}	0.094±0.060a	0.061±0.079a	±0.002
Sulphate (SO$_4^-$) (mg.L^{-1})	58.36±4.35^{a}	56.75±3.09^{a}	58.00±3.91^{a}	61.33±17.09^{a}	50.25±3.59^{a}	51.33±5.03^{a}	56.00±6.24^{a}	48.00±15.58^{a}	61.66±28.91^{a}	66.97±12.39a	57.66±7.57a	±19.79
H$_2$O$_2$ (mg.L^{-1})	0.056±0.018^{a}	0.046±0.013^{a}	0.068±0.057^{a}	0.050±0.018^{a}	0.098±0.121^{a}	0.072±0.020^{a}	0.072±0.053^{a}	0.040±0.060^{a}	0.307±0.528^{a}	0.083±0.092a	0.074±0.077a	±0.049
F (mg.L^{-1})	0.89±0.37^{a}	1.11±0.61^{a}	1.06±0.44^{a}	0.93±0.65^{a}	0.67±0.21^{a}	0.77±0.21^{a}	0.77±0.56^{a}	0.98±0.38^{a}	1.01±0.43^{a}	0.97±0.30a	0.99±0.42a	0.17a
Br$_2$ total (mg.L^{-1})	0.25±0.10^{a}	ND	0.22±0.02^{a}	ND	0.31±0.17^{a}	ND	0.23±0.11^{a}	ND	0.14±0.19^{a}	ND	ND	

Total hardness (mg.L^{-1})	189.00±16.73^{a}	180.00±15.81^{a}	180.00±10.80^{a}	166.66±14.43^{a}	142.50±32.78^{a}	131.66±10.40^{a}	130.00±18.02^{a}	136.66±34.03^{a}	155.00±43.30^{a}	216.25±84.39^{a}	163.33±5.77^{a}	0±10.6
Ca hardness (mg.L-1)	53.70±8.09abc	53.00±12.52abc	56.33±9.77ab	52.50±8.81abc	38.80±20.09bcd	22.50±6.55d	34.00±11.76cd	21.66±2.51d	45.80±13.70abc	58.90±20.87a	43.60±6.18abc	±4.94a
Total alkalinity CaCO3 (mg.L-1)	145.00±14.14abc	155.00±13.69a	135.83±24.16abcd	142.50±23.97abc	90.00±16.95cde	94.75±50.76bcde	103.00±48.16abcde	65.00±56.78e	80.00±59.58de	130.75±31.44abcd	156.00±48.39a	0±10.6
Total alkalinity HCO3 (mg.L-1)	179.16±9.70a	186.00±25.83a	165.83±29.39abc	173.75±28.68ab	109.00±21.03cde	112.50±59.51bcde	98.00±18.23de	76.66±67.14e	97.00±72.59de	158.75±38.59abcd	186.00±51.76a	0±14.1
Total alkalinity CO3 (mg.L-1)	86.66±6.83ab	93.00±11.51a	81.66±13.66abc	86.25±15.47ab	56.00±9.61bcde	55.00±30.00cde	49.00±9.61de	38.33±33.29e	48.00±35.46de	77.50±18.48abcd	90.00±25.00a	±7.70a
Acidify Chloride salt Cl (mg.L-1)	13.78±8.11a	13.40±8.23a	13.78±9.53a	18.72±13.47a	16.68±12.03a	18.12±12.01a	10.16±4.15a	7.66±5.39a	13.20±7.52a	27.62±10.76a	7.82±2.89a	±6.01a
Acidify Chloride salt CaCO3 (mg.L-1)	15.92±9.35a	18.46±12.39a	19.13±13.10a	26.62±19.12a	23.52±16.98a	25.87±17.56a	14.44±5.91a	10.86±7.69a	19.46±11.73a	37.83±18.60a	10.94±3.93a	±8.48a
Acidify Chloride salt (mg.L-1)NaCl	18.96±10.97a	22.42±13.64a	22.35±15.62a	30.92±21.78a	27.52±19.82a	30.25±20.02a	17.20±7.27a	12.66±8.89a	23.02±13.24a	45.50±22.46a	28.22±37.39a	±9.89a
Cu total (mg.L-1)	1.64±1.09a	1.27±0.55a	1.73±0.78a	.98±0.43a	1.08±0.91a	1.25±0.90a	0.93±0.67a	1.25±0.93a	1.13±0.76a	0.93±0.63a	1.47±1.04a	1.58a
Mg (mg.L-1)	74.84±38.58a	80.50±19.00a	85.25±20.59a	103.00±1.00a	73.33±15.27a	78.66±20.74a	78.33±7.63a	82.66±30.43a	88.33±28.86a	78.85±35.42a	68.33±7.63a	90 1.65a
Mn (mg.L-1)	0.007±0.002a	0.004±0.001a	0.005±0.002a	0.007±0.004a	0.009±0.004a	0.009±0.004a	0.011±0.005a	0.004±0.007a	0.006±0.001a	0.006±0.002a	0.009±0.004a	0.).001a
Mo (mg.L-1)	0.35±0.32a	0.36±0.24a	0.39±0.25a	0.65±0.34a	0.21±0.12a	0.50±0.27a	0.36±0.06a	0.49±0.51a	0.40±0.29a	0.63±0.33a	0.51±0.24a	0. 26a

Different letters a, b, c, … indicate significant difference for each parameters among different months.

ND indicate not detected.**able 2. Seasonally levels of physicochemical properties and heavy metals contents in water of Derbendikhan reservoir, Sulaimani, Iraqi Kurdistan region during 2013-2018**

Variable	winter	spring	summer	fall
pH	7.91±0.29^{b}	8.29±0.31^{a}	8.21±0.30^{a}	7.810.20^{b}
No$_3^-$(mg.L^{-1})	17.22±8.71^{a}	15.42±8.65^{a}	14.33±9.68^{a}	10.43±10.49^{a}
No$_2^-$(mg.L^{-1})	0.045±0.029^{a}	0.134±0.192^{a}	0.033±0.028^{a}	.065±0.064^{a}
Sulphate (SO$_4^-$) (mg.L^{-1})	57.75±3.61^{a}	53.90±10.07^{a}	55.22±17.74^{a}	64.54±12.21^{a}
H$_2$O$_2$ (mg.L^{-1})	0.056±0.034^{a}	0.075±0.074^{a}	0.142±0.304^{a}	0.075±0.070^{a}
F (mg.L^{-1})	1.01±0.44^{a}	0.77±0.35^{a}	0.91±0.44^{a}	0.90±0.32^{a}
Br$_2$ total (mg.L^{-1})	0.28±0.12^{a}	0.31±0.13^{a}	0.16±0.14^{a}	0.31±0.08^{a}
Chloride Cl free (mg.L^{-1})	0.080±0.036	0.113±0.056	0.110±0.098	ND
Chloride Cl total (mg.L^{-1})	0.083±0.020	0.090±0.026	0.700±0.056	ND
K (mg.L^{-1})	9.36±2.44	ND	ND	ND
Na$_2$MoO$_4$ (mg.L^{-1})	1.14±0.63	1.29±0.66	1.09±0.20	ND
MoO$_4$ (mg.L^{-1})	1.01±0.66	1.21±0.60	0.84±0.15	ND
Cyanuric acid (mg.L^{-1})	1.00±0.00	1.66±0.57	0.5±0.70	ND
Total hardness (mg.L^{-1})	183.46±14.34^{a}	146.50±25.39^{b}	140.55±31.06^{b}	187.77±58.52^{a}
Ca hardness (mg.L^{-1})	54.42±9.57^{a}	38.00±17.75^{bc}	35.69±14.23^{c}	48.41±14.83^{ab}
Total Alkalinity CaCO$_3$ (mg.L^{-1})	144.70±18.83^{a}	107.61±38.39^{b}	85.38±52.33^{b}	146.18±37.36^{a}
Total Alkalinity HCO$_3$ (mg.L^{-1})	176.47±23.23^{a}	130.00±46.50^{b}	92.69±51.98^{c}	175.90±41.52^{a}
Total Alkalinity CO$_3$ (mg.L^{-1})	86.76±11.31^{a}	65.00±23.09^{b}	46.15±25.58^{c}	85.45±19.93^{a}
Acidify Chloride salt Cl (mg.L^{-1})	13.67±8.11^{a}	17.75±11.42^{a}	10.75±5.87^{a}	16.37±11.36^{a}
Acidify Chloride salt CaCO$_3$ (mg.L^{-1})	17.91±11.11^{a}	25.20±16.32^{a}	15.54±8.93^{a}	21.12±15.57^{a}
Acidify Chloride salt NaCl (mg.L^{-1})	21.31±12.87^{a}	29.40±18.77^{a}	18.39±10.34^{a}	32.86±28.67^{a}
Cu total (mg.L^{-1})	1.54±0.78^{a}	1.11±0.73^{a}	1.10±0.73^{a}	1.33±1.08^{a}
Mg (mg.L^{-1})	79.78±26.69^{a}	85.00±18.80^{a}	83.11±21.75^{a}	79.04±24.77^{a}
Mn (mg.L^{-1})	0.005±0.002^{a}	0.009±0.004^{a}	0.008±0.005^{a}	0.007±0.003^{a}
Mo (mg.L^{-1})	0.36±0.25^{a}	0.43±0.30^{a}	0.40±0.27^{a}	0.52±0.26^{a}
Fe (mg.L^{-1})	0.003±0.005	0.040±0.052	ND	ND

Different letters a, b, c, … indicate significant difference for each parameters among different seasons.

ND indicate not detected.

Variable	2013	2014	2015	2016	2017	2018

pH	8.28±0.39^{a}	8.23±0.19^{ab}	8.02±0.24^{abc}	7.73±0.12^{c}	7.94±0.51^{bc}	7.86±0.25^{c}
No$_3^-$ (mg.L^{-1})	8.29±8.84^{a}	16.28±9.61^{a}	15.63±9.64^{a}	19.30±7.30^{a}	12.88±9.99^{a}	20.10±0.00^{a}
No$_2^-$ (mg.L^{-1})	0.120±0.20^{a}	0.056±0.03^{a}	0.047±0.04^{a}	0.038±0.02^{a}	0.030±0.01^{a}	0.137±0.12^{a}
Sulphate (SO_4^-) (mg.L^{-1})	48.36±8.95^{a}	60.50±10.86^{a}	63.08±11.98^{a}	57.25±5.31^{a}	ND	61.85±14.21^{a}
H_2O_2 (mg.L^{-1})	0.031±0.014^{b}	0.038±0.024^{b}	0.094±0.059^{b}	0.265±0.378^{a}	0.064±0.039^{b}	0.056±0.015^{b}
F (mg.L^{-1})	0.84±0.34^{a}	0.85±0.39^{a}	0.93±0.39^{a}	1.020.54^{a}	0.99±0.44^{a}	ND
Br_2 total (mg.L^{-1})	0.26±0.14^{a}	ND	ND	0.28±0.18^{a}	0.20±0.09^{a}	ND
Chloride Cl free (mg.L^{-1})	ND	ND	ND	ND	0.06±0.02	0.14±0.03
Chloride Cl total (mg.L^{-1})	ND	ND	ND	ND	0.068±0.027	0.102±0.009
K (mg.L^{-1})	ND	ND	ND	ND	5.32±2.56	7.05±7.14
Na_2MoO_4 (mg.L^{-1})	ND	ND	ND	ND	0.92±0.52	1.45±0.36
MoO_4 (mg.L^{-1})	ND	ND	ND	ND	0.65±0.30	1.43±0.32
Cyanuric acid (mg.L^{-1})	ND	ND	ND	ND	1.25±0.50	1.00±0.81
Total hardness (mg.L^{-1})	152.72±27.69^{b}	165.41±18.27^{b}	162.08±31.43^{b}	166.25±44.97^{b}	ND	265.00±106.06^{a}
Ca hardness (mg.L^{-1})	39.18±11.69^{bc}	40.33±14.19^{bc}	46.08±17.31^{abc}	35.71±7.97^{c}	54.00±13.49^{ab}	61.11±17.40^{a}
Total alkalinity $CaCO_3$ (mg.L^{-1})	87.27±53.86^{b}	115.41±30.78^{ab}	135.00±37.29^{a}	125.00±33.16^{ab}	135.00±64.61^{a}	151.71±27.59^{a}
Total alkalinity HCO_3 (mg.L^{-1})	105.00±65.07^{b}	142.08±39.39^{ab}	153.33±45.24^{ab}	148.57±40.59^{ab}	160.00±72.19^{ab}	184.28±33.84^{a}
Total alkalinity CO_3 (mg.L^{-1})	51.36±32.25^{b}	69.58±18.76^{ab}	75.83±22.13^{ab}	75.71±15.92^{ab}	77.00±35.10^{ab}	90.71±16.18^{a}
Acidify Chloride salt Cl (mg.L^{-1})	11.03±11.20^{a}	15.74±10.61^{a}	18.70±9.34^{a}	11.54±3.29^{a}	10.02±5.49^{a}	16.77±9.08^{a}
Acidify Chloride salt $CaCO_3$ (mg.L^{-1})	15.32±16.20^{a}	22.18±14.87^{a}	26.41±13.29^{a}	16.44±4.68^{a}	13.74±7.55^{a}	18.40±10.37^{a}
Acidify Chloride	18.51±19.04^{a}	26.12±17.19^{a}	37.29±23.70^{a}	19.28±5.55^{a}	16.92±9.13^{a}	21.34±11.82^{a}

salt NaCl (mg.L^{-1})						
Cu total (mg.L^{-1})	1.38±0.73^{a}	1.72±0.56^{a}	1.60±0.73^{a}	0.31±0.56^{b}	ND	ND
Mg (mg.L^{-1})	87.33±19.53^{a}	84.16±17.26^{a}	86.25±19.52^{a}	70.00±5.00^{a}	ND	18.81±13.59^{b}
Mn (mg.L^{-1})	0.008±0.005^{a}	0.007±0.004^{a}	0.007±0.003^{a}	0.006±0.003^{a}	0.005±0.002^{a}	
Mo (mg.L^{-1})	0.28±0.18^{a}	0.39±0.30^{a}	0.51±0.30^{a}	0.37±0.18^{a}	0.51±0.30^{a}	0.70±0.16^{a}
Fe (mg.L^{-1})	ND	ND	ND	ND	0.004±0.005	0.043±0.049

Table 3. annual levels of physicochemical properties and heavy metals contents in water of Derbendikhan reservoir, Sulaimani, Iraqi Kurdistan region during 2013-2018

Different letters a, b, c, … indicate significant difference for each parameter among different years.

ND indicate not detected.

The **hydrogen ion concentration (pH)** of water plays a crucial role in **regulating aquatic ecosystem productivity, determining metal solubility, and influencing corrosion in pipelines** (particularly in wastewater treatment facilities) (Getachew et al. 2021; Dessie et al. 2022). In this study, **maximum pH values occurred during the warmer periods (spring and summer).** Monthly variation revealed a gradual increase from January, peaking in June at 8.40, followed by a decline to its lowest value of 7.72 in November. **Across the six-year monitoring period, a general decline was recorded, with pH decreasing from 8.28 in 2013 to 7.86 in 2018.** Consistent with these findings, Atique and An (2019) reported **higher pH values in September and October** in the Chungju Reservoir, South Korea. Similarly, Gupta et al. (2016) observed **elevated pH in Jaipur drainage, India, during spring and summer, attributing this to algal blooms and CO□ uptake from carbonic acid.** Al-Taani (2014) also identified a **seasonal cycle in pH at Al-Wehda Dam, Jordan, with the highest values in spring.** The author explained that although winter inflows supply significant amounts of base cations (Ca, HCO□, Mg), lower pH values were detected in that season, probably due to reduced photosynthesis at low temperatures, dilution from inflows, slightly acidic rainfall, and agricultural runoff carrying ammonium fertilizers and organic matter into the reservoir. However, some research indicated that nutrient release from decomposing vegetation may elevate pH levels, partly explaining the increases seen in spring and summer (Howard-Williams and Howard-Williams 1978; Al-Taani 2014). For comparison, pH in Malaysia's Bakun Reservoir ranged from 4.93 ± 0.06 to 8.06 ± 0.05 during the wet season, while remaining stable in the dry season with a mean of 7.30 (Ling et al. 2017). Since the upper pH threshold for fish health is 8.7 (Water Quality Criteria 1963), and values above 9 can trigger phosphorus release from sediments and the mobilization of metals, ammonia, and salts—conditions unsuitable for aquatic organisms (Zhao et al. 2013; Al-Taani 2014)—regular monitoring is strongly recommended, particularly as this study recorded a high of 8.40. In line with our results, Rasul (2019) also documented pH values between 7.3 and 8.7 in Derbendikhan Reservoir.

The WHO recommended threshold of 3 mg.L^{-1} for NO$_2^-$, while ISWTL does not allow any NO$_2^-$. In the present study, the NO$_2^-$ showed a decreasing trend from 2013 to 2017, but a sudden increase was observed in 2018. The trend of seasonal and monthly changes showed that the highest amount of NO$_2^-$ was observed in spring and the lowest levels were observed in summer and winter, so that an increase peak in NO_2^- was observed in April (0.25) and in other months of the year the values were below 0.11. The lowest values were observed in August and January. A decreasing trend in the amount of NO_3^- was observed from winter to autumn, so that the amount of NO_3^- from about 19.05 - 21.36 during the months of January to July showed a decreasing trend to October (minimum monthly of 3.10). In addition, No_3 level showed an increase from 8.29 in 2013 to 20.10 in 2018. NO_3^- levels were always lower than the WHO recommended threshold of 50, but with the exception of August, September and October in other cases the levels were even higher than the ISWTL recommended level of 15. The surface NO_2^- concentration was low in the Bakun Reservoir with a mean of 0.003 $mg.L^{-1}$ during wet season and 0.002 – 0.008 $mg.L^{-1}$ during dry seasons (Ling *et al.* 2017).Similar monthly trend for NO_3^- was observed by Atique and An (2019) in water of Chungju Reservoir (Atique and An 2019). Also, Al-Taani (2014) observed peaks in NO_3 in water of AlWehda Dam, Jordan in winter and strongly associated it with agricultural runoff, animal waste, inputs from sewage, soil erosion, and domestic waste from cesspools as well as nitrogen fixation microbes (specially, in spring). The researcher observed the lowest amount in fall, may be it can removed either by algal uptake and sedimentation or through denitrification (Al-Taani 2014). Moreover, positive correlation was observed between NO3–N and TP (r=0.63) suggesting that both are associated with agricultural runoff (Al-Taani 2014). The surface NO_2 concentration was low in the Bakun Reservoir with a mean of 0.003 $mg.L^{-1}$ during wet season and 0.002 – 0.008 $mg.L^{-1}$ during dry seasons (Ling *et al.* 2017).

Nitrate pollution negatively impacts water quality by promoting eutrophication and algal blooms. Elevated nitrate concentrations in drinking water pose risks to both humans and animals, being linked to disorders such as methemoglobinemia, diabetes, spontaneous abortion, thyroid dysfunction, and certain cancers. The primary pathway of nitrate toxicity in humans involves its reduction to nitrite, which oxidizes the ferrous ion in hemoglobin to ferric form, thereby reducing oxygen transport. Another toxic route is its transformation into nitric oxide, a compound with mutagenic and carcinogenic potential, formed through bacterial activity in the oral cavity and subsequent reactions with ascorbic acid in gastric fluids. Infants are particularly vulnerable, as ingestion of water with nitrate levels as low as 10 $mg{\cdot}L^{-1}$ N may cause methemoglobinemia, commonly known as “blue baby syndrome” (Knobeloch et al. 2000; Dessie et al. 2022)

The permissible threshold of 200 for sulfate ($SO_4{}^{-2}$) has been reported by the ISWTL. In the present study, the amount of sulfate was always below this threshold. The highest amount of sulfate was observed in autumn and then winter and the lowest amount was observed in spring and summer. The monthly changes showed a slightly decreasing trend from January to August (the minimum value of 48) and then increased until the end of December and reached its maximum value of 70. Moreover, the annual changes showed and slightly increasing trend from 2013 to 2018. **Elevated concentrations of $SO_4{}^{2-}$ impart a bitter or medicinal taste to water and may exert laxative effects. Individuals unaccustomed to sulfate-rich water are at risk of diarrhea and dehydration, with infants being particularly vulnerable. Excessive sulfate can also adversely affect both aquatic and terrestrial organisms. In young animals, prolonged exposure to high levels has been linked to persistent diarrhea and, in severe cases, mortality (Dessie et al. 2022).**

In the present study, it was observed that the lowest level of H_2O_2 was related to winter and then it showed an increasing trend until it reached its maximum value in summer (0.3 in September) and then a downward trend was observed again. Moreover, an increasing trend in the amount of H_2O_2 was observed from 2013 to 2016, but lower levels were observed during 2017 and 2018.

WHO and ISWTL recommended the thresholds of 1.5 and 0.2 for F, respectively. The F values were always below the WHO recommended level but it levels were always above the ISWTL recommended value. The monthly changes in levels of F showed that the lowest value of F was related to Spring in May (0.67) and then showed a gradual increase trend reached its highest value in winter and February (1.1). The annual change trend showed a slight and gradual increase in F level from 2013 to 2016, but it showed a slight reduction in 2017. The monthly changes in total Br showed a decreasing trend from the beginning of winter to the end of summer, and then it showed again an increasing trend during autumn. The measured values for K indicated that the highest values were observed during winter and in February, and lower values were observed during other seasons of spring, summer and autumn. However, in contrast to our results, Al-Taani (2014) reported lower levels for K in winter which is likely attributed to mixing and dilution processes following heavy rainfall events and the highest levels observed in fall seasons are related to precipitation of carbonate minerals and subsequent prevalence of Na, K, and Cl salts (Al-Taani 2014). The Acidify Chloride salt based on Cl, NaCl and $CaCO_3$ showed similar pattern to each other. This amount sowed an increase from 2013 to 2015, then it decreased until 2017 and it increased again in 2018. Seasonal variations indicated an increasing trend during winter and spring, followed by a reduction during summer and again an increase in autumn. The amount of Chloride Cl free gradually increased from the lowest level in late autumn and early winter to its highest level in summer. Chloride (Cl^-) levels displayed a nearly stable pattern across all seasons. Consistent with this observation, Gupta et al. (2016) found that chloride concentrations in the Jamawa Ramgarh reservoir peaked during the summer months. The perception of salinity from chloride is largely influenced by the overall ionic composition of the water, particularly its association with sodium. Concentrations of chloride exceeding permissible limits in aquatic systems are often considered an indicator of domestic sewage contamination (Gupta et al. 2016). Furthermore, chloride is an important component of industrial effluents, where elevated levels can negatively impact agricultural productivity, disrupt microbial communities and aquatic food webs, enhance water corrosivity, and pose health risks to humans—especially those with impaired sodium chloride metabolism, such as individuals suffering from congestive heart failure (Dessie et al. 2022).

The level of Na_2MoO_4 and MoO_4 as well as Cyanuric acid showed an almost constant trend during different seasons, although slightly higher amount was observed in spring.

The threshold of 500 is recommended for total hardness by WHO and ISWT. In the present study, the total hardness value was always below 265. The highest value of total hardness was observed in autumn and winter and then it showed a decreasing trend during spring and summer and reached its lowest value in summer (140). From 2013 to 2016, an almost constant trend was reported, but a sudden increase in the total hardness was observed in 2018. The trend of seasonal and monthly changes indicated that the highest amount of calcium hardness was observed in winter and autumn, but it showed a decreasing trend during spring and summer to reach the lowest amount in summer. The annual trend of calcium hardness showed an increasing trend, increased from about 30.18 in 2013 to about 61.11 in 2018. In line with our results, Rasul (2019) reported total hardness between 129.84 – 223.92 mg/L for water samples of Derbendikhan reservoir (Rasul 2019). Al-Taani (2014) also observed elevated levels of Ca, Mg, and HCO_3 in winter periods in response to leaching and decreased concurrent with the drier months. The researcher stated that the lower values measured in summer seasons are attributed to precipitation of carbonate minerals following an increase in temperatures and evaporation. It is documented that Ca, Mg, and HCO_3 have been derived from limestone, dolomite and apatite mineral sources (Al-Taani 2014). The highest amount of total alkalinity was recorded during the autumn and winter seasons and then showed a decreasing trend during the spring and summer to reach its lowest value in August. Moreover, the annual trend of total alkalinity showed an increasing trend from 2013 to 2018. In a study by Gupta et al. (2016) it was observed that the highest and the lowest values of alkalinity of Jamawa Ramgarh reservoir's water was recorded in May and October, respectively (Gupta *et al.* 2016). In the natural water the alkalinity is due to the salts of carbonate, borate, silicate, and phosphate along with hydroxyl ions in the Free State (Gupta *et al.* 2016).

In the present study, the highest amount of total Cu was observed during winter and autumn (maximum monthly value of 1.73 in March) and the lowest amount was observed in spring and summer (minimum monthly value of 0.93 in July). From 2013 to 2015, the amount of total Cu showed an increasing trend but it showed a reduction in in 2016. Total Cu was throughout the study period above the limit of 0.05 recommended by the ISWTL 1967, However, it was within the maximum permissible (100 $mg.L^{-1}$) levels of the Iraqi standards for inland natural water (Aziz and Rasheed 2017). The highest amount of magnesium (Mg) was observed in spring and in April (monthly average 103) and then showed a downward trend and reached its lowest level in November (68.33) and then re-entered the increasing cycle. Also, during the 6-year period, Mg level showed a decreasing trend reached from 87.33 in 2013 to 18.81 in 2018. Overall, the Mg level during the study period, except for 2018, was above the allowable limit of 30-50 recommended by WHO. The highest Mn was observed during spring and early summer (maximum monthly average of 0.112 in July) and then showed a downward trend to its lowest monthly value in February (0.004), however, a smaller peak was also observed from August to November. A decreasing trend was observed for Mn since 2013 to 2018. In the present study the Mn level was always less than 0.012, which was always below the threshold recommended by WHO (0.4) and ISWTL 1967 (0.1). Our results are in line with those reported by Aziz and Rasheed (2017), who observed the higher levels of Mn in water of Derbendikhan reservoir in summer and lower levels in winter (Aziz and Rasheed 2017). Abdullah (1996) reported also similar results in drinking water of Erbil city, Iraq (Abdulla 1996). Abaychi and Mustafa (1988) reported the level of 0.05 to 0.13 $mg.L^{-1}$ in water of Shatt Al-Arab river, Iraq which is close to the minimum and maximum levels observed in our study (Abaychi and Douabul 1985; Abaychi and Al-Saad 1988). The allowable limit recommended by WHO for Mo is 0.07, however, in the present study the level of Mo was always above this range. An increasing trend was observed for Mo from winter to autumn. However, in the monthly trend review, the lowest amount was observed in May (0.216), followed by an upward trend until October (0.636) and after a subsequent downward trend again an upward peak was observed until April (0.657). In the annual trend review, an upward trend was observed for Mo from 2013 to 2018. The recommended limits for iron (Fe) by WHO and ISWTL are 0.1 and 0.3, respectively. In the present study, the highest amount of Fe was observed in June (0.1) but it was always below 0.02 during the other months. Also, the Fe level was increased in 2018 compared to 2017. These result on maximum level of Fe in water of Derbendikhan reservoir are in contradictory with the results of Aziz and Rasheed (2017), who reported the high values of 11.268 $mg.L^{-1}$ for Fe in the same water body but at different station. However, the researchers reported the highest Fe level in summer and the lowest level in winter, which is in harmony with our results(Aziz and Rasheed 2017). It is reported that he higher value of Fe in summer and low value in winter may be due to the temperature, rain fall and erosion of rock and soil (Aziz and Rasheed 2017). Also, Abaychi and Mustafa (1988) reported the highest value (0.13 mg.L^{-1}) in summer and the lowest value (0.06 mg.L^{-1}) in winter (Abaychi and Douabul 1985; Abaychi and Al-Saad 1988), that is in harmony with our results. These trace metals are toxic when they are ingested into living organisms in a relatively high concentration or bio-accumulate in the human organ system (Dessie *et al.* 2022). So, serious monitoring and corrective actions are suggested.

Conclusion

This investigation demonstrated that the concentrations of Cu, Mg, Mo, Fe, NO_3^-, NO_2^-, and F in the waters of Derbendikhan Reservoir warrant close attention, as they were found to exceed or approach recommended thresholds and showed an upward trend during 2013–2018. Such contaminants pose threats to ecosystem stability, as they may bioaccumulate in fish, livestock, and other fauna, ultimately transferring through the food chain and causing chronic health effects in humans. Additional studies are essential to trace pollutant pathways within the food web and evaluate their ecological and health consequences. The outcomes of this study call for immediate interventions by both regulatory agencies and industries, including stricter enforcement of effluent standards and the adoption of effective treatment systems. Furthermore, continuous monitoring and systematic sampling of surface waters are required to quantify pollution levels and support evidence-based management and mitigation strategies.

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Statements and Declarations

The authors declare no conflict of interest.

Ethical standards

The authors declare that all the experiments comply with the current laws of Iraq.

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