

Research Paper

Temporal and spatial variations hydrochemical components and driving factors in Baiyangdian Lake in the Northern Plain of China

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Abstract: Understanding the temporal and spatial variation of hydrochemical components in large freshwater lakes is crucial for effective management and conservation. In this study, we identify the temporal-spatial characteristics and driving factors of the hydrochemical components in Baiyangdian Lake using geochemical methods (Gibbs diagram, Piper diagram and End-element diagram of ion ratio) and multivariate statistical techniques (Principal component analysis and Correlation analysis). 16 sets of samples were collected from Baiyangdian Lake in May (normal season), July (flood season), and December (dry season) of 2022. Results indicate significant spatial variation in Na^+ , Cl^- , SO_4^{2-} and NO_3^- , suggesting a strong influence of human activities. Cation concentrations exhibit greater seasonal variation in the dry season compared to the flood season, while the concentrations of the four anions show inconsistent seasonal changes due to the combined effects of river water chemical composition and human activities. The hydrochemical type of Baiyangdian Lake is primarily $\text{HCO}_3\text{-Cl-Na}\cdot\text{Ca}^{2+}$, Mg^{2+} and HCO_3^- originate mainly from silicate and carbonate rock dissolution, while K^+ , Na^+ and Cl^- originate mainly from sewage and salt dissolution in sediments. SO_4^{2-} may mainly stem from industrial wastewater, while NO_3^- primarily originates from animal feces and domestic sewage. Through the use of Principal Component Analysis, it is identified that water-rock interaction (silicate and carbonate rocks dissolution, and dissolution of salt in sediments), carbonate sedimentation, sewage, agricultural fertilizer and manure, and nitrification are the main driving factors of the variation of hydrochemical components of Baiyangdian Lake across three hydrological seasons. These findings suggest the need for effective control of substandard domestic sewage discharge, optimization of agricultural fertilization strategies, and proper management of animal manure to comprehensively improve the water environment in Baiyangdian Lake.

Keywords: Hydrochemical variation; Sources; Human activities; Water-rock interaction; Multivariate statistical techniques.

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Introduction

Lakes serves as crucial water resources, playing an irreplaceable role in regional environmental dyna-

mics, cycling of source factors, maintenance of ecological functions, ensuring water supply safety, flood control, drought resistance, and fostering economic and social development in river basins (Downing et al. 2006; Dearing et al. 2012; Mendona et al. 2017). However, human activities have increasingly disrupted lakes, resulting in the influx of nutrients and pollutants into lake water. This has led to a decline in water quality and alterations in the evolution of hydrochemical components, seriously impacting the ecological functions and utility of lakes (Han et al. 2020). Therefore, studying the spatiotemporal variation characteristics and driving factors of lake hydrochemical

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components holds vital importance for addressing lake water environmental pollution (Wan et al. 2017; Ren et al. 2020).

The evolution of lake hydrochemical components is influenced by both natural factors and human activities (Ren et al. 2023). Natural factors encompass various elements such as stratigraphic lithology, water rock interaction, and rainfall within the watershed (Lin et al. 2012), while human activities mainly involve the substandard discharge of sewage, excessive use of pesticides, fertilizers, and manure, as well as improper waste disposal (Ren et al. 2022). In recent years, scholars have extensively investigated the characteristics of lake hydrochemical evolution and pollution sources (Li et al. 2021; Ren et al. 2022; Shaw et al. 2013). For instance, Mbaye et al. studied the spatiotemporal changes in the hydrochemical characteristics of Senegal Lake, revealing higher concentrations of hydrochemical indicators in densely populated areas compared to upstream regions of the lake (Mbaye et al. 2016). Lu et al. (2010) identified that the hydrochemical characteristics of lakes in the Badajilin Desert are primarily influenced by regional climate disparities and fluctuations. Xu et al. (2023) discovered that the hydrochemical characteristics of Sha lakes in arid and semiarid regions are significantly impacted by elevated temperatures, intensified human activity during tourist season, and surface runoff during the rainy season. Additionally, some scholars have explored the correlation between the evolution of hydrochemical components in basins and the level of socio-economic development (Ma et al. 2014; Wang et al. 2023). However, the mechanism underlying lake hydrochemical variation and its driving forces remain unclear.

Baiyangdian Lake, situated at the heart of the Xiong'an New Area, stands as the largest lake and one of the few lake wetland ecosystems in the North China Plain. Its significance extends to flood control, transportation, fisheries, and climate regulation, rendering essential ecological protection for the development of the Xiong'an New Area. However, in recent years, industrial and agricultural development, coupled with escalating water demands in the basin, have led to water pollution issues in Baiyangdian Lake, posing a significant challenge to the region's sustainable development (Han et al. 2020). Scholars have conducted extensive research on water quality, biodiversity loss, and heavy metal pollution in the Baiyangdian River basin (Li et al. 2018; Wang et al. 2021; Xue et al. 2018; Zhou et al. 2020). Nevertheless, research on the driving mechanism behind the

evolution of the chemical composition of Baiyangdian Lake water remains limited, thereby hindering efforts in environmental remediation work for the lake.

In this study, we focused on identifying the variation characteristics and driving mechanisms of the chemical composition of Baiyangdian Lake based on the hydrochemical data from three hydrologic seasons. The main objectives of this study were to: (1) elucidate the patterns of variation in the chemical composition of Baiyangdian Lake water; (2) uncover the driving mechanisms behind the variation of the chemical composition of Baiyangdian Lake; (3) explore the primary sources of the chemical composition of Baiyangdian Lake. These findings can serve as a scientific foundation for the comprehensive improvement of the water environment in Baiyangdian Lake and the preservation of the water environments in lakes across China.

1 Study area

Baiyangdian Lake (115°38'–116°07'E, 38°43'–39°02'N) is mainly located in Anxin County, Baoding City, Hebei Province (Fig. 1). It falls within the tributary system of the Daqing River in the Hai River basin, covering a total drainage area of 366 km². The area comprises 143 lakes, with an average depth of 2.3 m, making it the largest wetland ecosystem in the North China Plain. Baiyangdian Lake experiences a temperate semi-humid continental monsoon climate characterized by distinct four seasons. Springs are dry, windy, and rainy, while summers are hot and wet, with precipitation mostly concentrated from July to September. The long-term average temperature is 12.2°C, and the mean annual precipitation is 529.7 mm. Soil types in the watershed mainly include tidal soil, swamp soil, brown soil, and paddy soil. Land use types encompass forest land, farmland, construction land, grassland, and water bodies. The sedimentary facies of Baiyangdian mainly consist of lacustrine and fluvial facies, with sediment containing high salt content. Surface exposed strata primarily comprise Quaternary alluvial-proluvial loose strata, mainly composed of loam, sandy soil, fine sand, and silty-fine sand. In certain areas, a peat layer is present, with its mineral composition predominantly comprising silicate and carbonate rocks.

The water flow in Baiyangdian Lake basin flows from west to northeast, primarily sourced from nine rivers (Zhulong River, Xiaoyi River, Tang River, Qingshui River, Baohe River, Fuhe River,

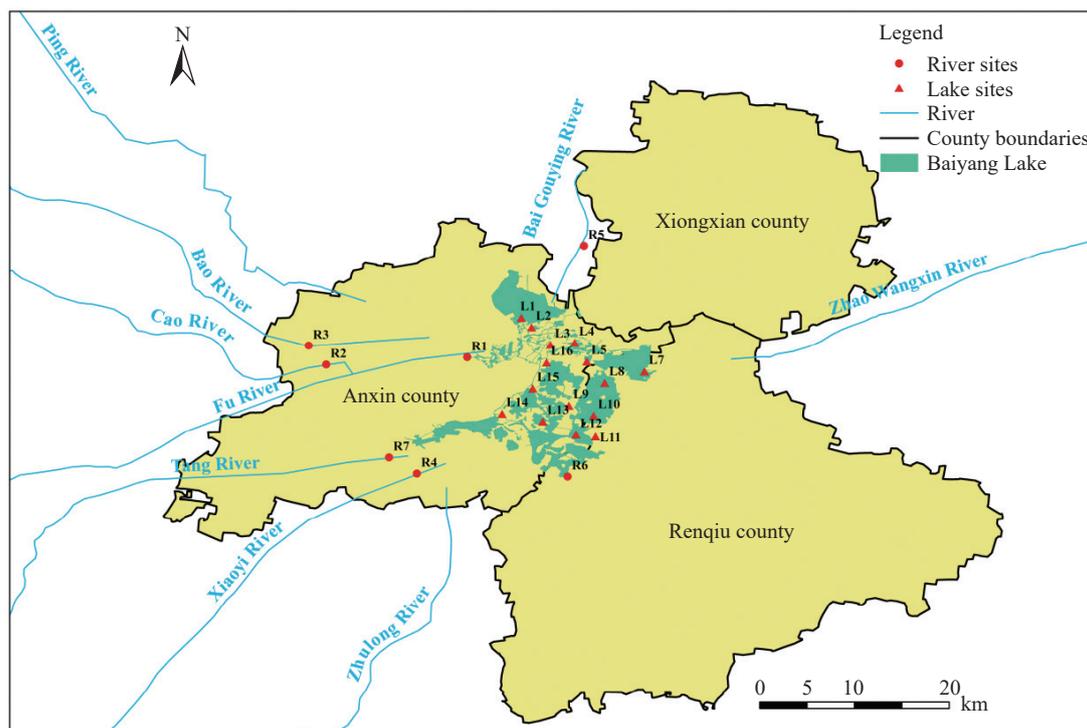


Fig. 1 Distribution of sampling sites in Baiyangdian Lake basin

Ping River, Caohe River and Baigou River Diversion) and ecological water, such as water diversion from the Yellow River to the lake, and South-to-North Water Diversion projects. Groundwater does not contribute significantly to Baiyangdian Lake's water supply due to the depth of the water table (>10 m) (Chi et al. 2022). The water environment in Baiyangdian faces relatively high pressure from pollution, stemming from both external sources and within the lake area. Notably, numerous industrial enterprises with high water consumption and heavy pollution, including chemical fiber, papermaking, batteries, and film production, are concentrated upstream of the Fuhe River. Additionally, the sewage treatment plant pipeline network is incomplete, leading to untreated sewage flowing directly into the Fuhe River and ultimately into the lake. Pollution sources within the lake area include domestic sewage, fecal matter, and garbage from residents, as well as pollution from aquaculture bait.

Further details of the sites are provided in Supplementary Table S1.

2 Sample collection and analysis

2.1 Sample collection

This study established 16 sampling points in Baiyangdian Lake and conducted sampling in mid-

May (normal season), July (flood season), and December (dry season, during the frozen period) of 2022. Samples were collected using 2.5 L polyethylene bottles, which were rinsed with water three times prior to sampling. A surface water sampler was utilized to collect samples at a distance of 0.5 m from the river surface. After collection, the bottle was sealed and transported to the laboratory in a refrigerated box. Upon arrival, the samples were filtered using a 0.45 μ m fiber-glass filter membrane and stored at 4°C until analysis, which was completed within 48 hours. On-site measurements of pH, Dissolved Oxygen (DO), and Electrical Conductance (EC) of the water were conducted using a pre-calibrated portable water quality parameter meter (HQ40D).

2.2 Sample analysis

The test parameters mainly include pH, Electrical Conductivity (EC), Dissolved Oxygen (DO), potassium ions (K^+), calcium ions (Ca^+), sodium ions (Na^+), magnesium ions (Mg^+), bicarbonate ions (HCO_3^-), sulfate ions (SO_4^{2-}), chloride ions (Cl^-), and nitrate ions (NO_3^-). Analysis of hydrochemical indicators involved the following methods: pH, EC, and DO were measured using a glass electrode method (Hash HQ40D portable multi-parameter measuring instrument). Anions (Cl^- , NO_3^- , and SO_4^{2-}) were determined using an ion

chromatograph (ICS-1000), while HCO_3^- was measured using a standard dilute hydrochloric acid titration method. Cations (K^+ , Ca^+ , Na^+ and Mg^+) were analyzed using an inductively coupled plasma emission spectrometer. Further details regarding the analytical parameters, methods and detection limits can be found in Supplementary Table S2.

2.3 Data analysis

Data analysis in this study involved several approaches. Firstly, the hydrochemical types of Baiyangdian Lake were identified using the Piper Diagram. Secondly, the controlling factors influencing the evolution of hydrochemical components were determined through the construction of Gibbs Diagram. Thirdly, the origin of the hydrochemical components in Baiyangdian Lake was assessed using ion Ratio Diagrams. Additionally, correlation analysis and principal component analysis were employed to identify the sources and driving factors of hydrochemical components. Data analysis was conducted using R (version 4.3.0), Origin (2022), and ArcGIS (version 10.8).

3 Results

3.1 The spatiotemporal variation characteristics of basic physical and chemical indicators

Table 1 summarizes the basic characteristics of the

chemical components of Baiyangdian Lake. The pH of Baiyangdian Lake ranges from 7.31 to 10.2, with an average of 8.16. Specifically, during the normal season, flood season, and dry season, pH ranges from 8.17 to 10.2, 7.73 to 8.87, and 7.31 to 7.54, respectively, with average values of 8.68, 8.41, and 7.41. The lake's water environment is characterized as neutral to weakly alkaline. Seasonal variation in pH follows the pattern of dry season < flood season < normal season, with relatively small spatial variation across different seasons (coefficient of variation < 7%), indicating stability in water acidity and alkalinity.

The Electrical Conductivity (EC) values range from 704 $\mu\text{s}/\text{cm}$ to 1,199 $\mu\text{s}/\text{cm}$, with an average of 837 $\mu\text{s}/\text{cm}$. Seasonal variation in EC is observed as normal season > dry season > flood season, primarily influenced by rainfall dilution effects (Njuguna et al. 2020). Significant spatial variation of EC is evident across the three hydrological seasons. Specifically, during normal and flood seasons, higher EC values are observed in the eastern region (L6-L12) compared to other areas. Conversely, during the dry season, higher EC value is recorded in the southeast (L10-L12) compared to the West (L13-L16) and near the eastern discharge outlet (L5-L8).

Dissolved Oxygen (DO) values range from 4.59 mg/L to 11.8 mg/L, with an average of 8.03 mg/L. During the normal, wet, and dry seasons, DO concentrations range from 4.99 mg/L to 11.0 mg/L, 4.59 mg/L to 11.7 mg/L, and 4.25 mg/L to 9.27 mg/L, respectively, with average values of 8.03 mg/L, 8.41 mg/L, and 7.72 mg/L. The lake's

Table 1 Statistical table of chemical components of Baiyangdian Lake

Parameter	Mean value			Range			Variable coefficient(%)			National standard
	NS	FS	DS	NS	FS	DS	NS	FS	DS	
pH	8.67	8.41	7.41	8.17–10.2	7.73–8.87	7.31–7.54	6.51	4.58	0.856	6.0–9.0
EC	945	719	848	704–1199	540–984	706–1089	15.2	21.3	12.9	–
DO	8.03	8.41	7.72	4.99–11.0	4.59–11.7	4.25–9.27	25.6	29.8	26.1	5.0
K^+	6.30	6.39	8.33	5.45–8.62	4.12–8.95	5.15–10.1	12.7	26.9	16.8	–
Na^+	103	72.7	75.5	59.4–175	32.6–141	34.9–113	31.2	55.4	31.5	–
Ca^{2+}	50.8	41.1	56.4	22.3–69.5	32.9–49.9	47.5–63.3	25.9	12.4	8.39	–
Mg^{2+}	26.2	23.1	24.8	19.8–31.4	19.9–29.2	20.0–29.2	14.6	13.6	9.36	–
HCO_3^-	197	206	243	134–285	178–227	216–266	21.0	7.10	5.51	–
Cl^-	116	72.8	86.0	82.8–153	40.3–124	28.8–144	16.1	40.9	42.3	250
SO_4^{2-}	73.3	93.0	92.5	33.8–137	39.9–149	24.4–202	34.4	34.3	50.3	250
NO_3^-	2.36	1.68	2.34	0.050–5.98	0.574–4.73	0.448–8.91	58.0	67.4	98.9	44.3

Note: pH is dimensionless. EC unit is $\mu\text{s}/\text{cm}$. The unit of other indicators is mg/L. NS: Normal season; FS: Flood season; DS: Dry season; National standard: Class III standard of the national surface water quality standard, Chinese (GB 3838—2002).

water environment is oxygen-rich. Seasonal variation in DO concentration follows the pattern of flood season > normal season > dry season, with spatial variation observed as flood season > normal season > dry season. This indicates that DO concentration in the Baiyangdian Lake is significantly influenced by rainfall runoff during the rainy season, which carries organic pollutants into the lake, leading to organic matter decomposition and decreased DO concentration during the flood season (Zhang et al. 2015).

Table 2 summarizes the basic characteristics of the chemical components of the rivers flowing into the Baiyangdian Lake. The pH of the river ranges from 7.51 to 9.39, with an average of 8.53, indicating neutral to weak alkaline water. Compared to Baiyangdian Lake, the mean pH of the rivers is higher. Seasonal variation in pH follows the pattern of flood season < dry season < normal season, with relatively small spatial variation observed across different seasons (coefficient of variation ranging from 1.66% to 8.71%).

The EC values range from 331 $\mu\text{S}/\text{cm}$ to 2,270 $\mu\text{S}/\text{cm}$, with an average of 877 $\mu\text{S}/\text{cm}$. Seasonal variation in EC is observed as dry season > normal season > flood season. Spatial variation in EC in the rivers (coefficient of variation ranging from 47.2% to 64.7%) is significant higher than in Baiyangdian Lake. The Xiaoyihe River exhibits the highest EC value (mean value of 1,658 $\mu\text{S}/\text{cm}$), while the Baohe River has the lowest EC value (mean value of 353 $\mu\text{S}/\text{cm}$).

The DO values range from 5.11 mg/L to 8.81 mg/L, with an average of 7.56 mg/L. Seasonal variation in DO in rivers is similar to Baiyangdian Lake, but spatial variation in DO is less pronounced compared to the lake.

3.2 The spatiotemporal variation characteristics of hydrochemical components

The concentrations of K^+ , Mg^{2+} , Ca^{2+} and Na^+ in the Baiyangdian Lake range from 4.10 mg/L to 10.1 mg/L, 19.8 mg/L to 31.3 mg/L, 22.3 mg/L to 69.5 mg/L, and 32.6 mg/L to 175 mg/L, respectively, with an average of 7.00 mg/L, 24.7 mg/L, 49.4 mg/L, and 83.8 mg/L, respectively (Table 1). The order of cation concentration across the three hydrological seasons is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. Overall, the spatial variation of Ca^{2+} , Mg^{2+} , and K^+ concentrations is smaller than that of Na^+ , as indicated by the smaller coefficient of variation for Ca^{2+} , Mg^{2+} , and K^+ compared to Na^+ . The spatial variability of Na^+ concentration suggests that the eastern sites (L4-L11) exhibit higher concentrations compared to other sites. Seasonal variation in cation concentration shows that concentrations are greater during the dry season compared to the flood season, indicating a dilution effect from rainfall on cation concentrations in Baiyangdian Lake.

The concentrations of HCO_3^- , Cl^- , SO_4^{2-} , and NO_3^- in Baiyangdian Lake range from 134 mg/L to 286 mg/L, 28.8 mg/L to 144 mg/L, 24.4 mg/L to 203 mg/L, and 0.050 mg/L to 8.91 mg/L, respectively, with an average of 217 mg/L, 91.8 mg/L, 82.3 mg/L, and 2.13 mg/L, respectively (Table 1). The overall concentration order of anions in the lake water is $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$. The spatial variation of HCO_3^- is relatively small across the three seasons, while Cl^- , SO_4^{2-} , and NO_3^- show greater variability, reflecting the significant influence of human activities on these hydrochemical components (Zhang et al. 2019). The seasonal

Table 2 Statistical table of chemical components of the river flows into Baiyangdian Lake

Parameter	Mean value			Range			Variable coefficient (%)			National standard
	NS	FS	DS	NS	FS	DS	NS	FS	DS	
pH	8.66	8.38	8.59	8.42–8.76	7.65–8.46	7.51–9.39	1.66	4.48	8.71	6.0–9.0
EC	721	661	1188	357–1324	331–1379	370–2270	47.2	64.7	52.5	–
DO	7.11	7.99	7.33	5.22–8.81	5.55–8.77	5.11–8.49	17.4	18.0	15.8	5.0
K^+	6.64	5.86	9.97	2.18–14.0	2.80–13.0	2.80–25.4	82.4	52.7	77.2	–
Na^+	73.1	68.8	151	8.28–233	13.0–212	13.8–413	136	104	91.9	–
Ca^{2+}	45.4	41.3	52.9	44.6–45.9	32.1–52.7	35.2–80.3	1.39	19.2	29.3	–
Mg^{2+}	20.4	16.8	21.8	11.5–26.9	13.5–24.9	11.5–36.9	39.4	22.7	41.4	–
HCO_3^-	192	191	272	149–303	137–259	161–471	33.1	22.2	44.7	–
Cl^-	76.4	61.1	120	16.3–173	7.17–162	13.9–234	77.0	104	67.6	250
SO_4^{2-}	55.4	91.1	96.8	30.8–98.5	34.1–181	21.0–212	52.0	65.6	82.7	250
NO_3^-	7.13	6.80	12.7	3.20–10.6	1.20–11.8	8.02–20.5	34.9	65.0	37.9	44.3

changes in these four anions are inconsistent. Specifically, Cl^- and NO_3^- concentrations exhibit a pattern of normal season (116 mg/L and 2.36 mg/L) > dry season (86.0 mg/L and 2.34 mg/L) > flood season (72.8 mg/L and 1.68 mg/L), while HCO_3^- concentrations follow a sequence of dry season (243 mg/L) > flood season (206 mg/L) > normal season (197 mg/L). SO_4^{2-} concentration shows a pattern of flood season (93.0 mg/L) and dry season (92.5 mg/L) > normal season (73.3 mg/L). This complex seasonal variation may be attributed to the diverse sources of water in Baiyangdian Lake, which includes inflow from nine rivers and ecological replenishment. The seasonal changes in the chemical composition of these inflowing rivers, along with variations in human activity levels, contribute to the complexity of hydrochemical changes in Baiyangdian Lake (Güler et al. 2012).

Overall, the mean concentrations of water chemistry indicators in the rivers entering Baiyangdian Lake are generally similar to those in the lake itself, except for NO_3^- , which show higher average concentrations in the lake. The temporal variation of hydrochemical indices of the rivers entering the lake exhibit the same seasonal variation pattern as Baiyangdian Lake, with higher mean concentrations observed during the dry season compared to the normal and flood seasons due to the dilution effect of rainfall. In addition, the spatial variation degree of hydrochemical indices in the rivers entering the lake is generally greater than that in Baiyangdian Lake, except for Ca^{2+} and NO_3^- , which could be attributed to differences in geological background and human activity intensity among these rivers.

3.3 Seasonal variation of hydrochemical types

The analysis of hydrochemical types is crucial for understanding the formation and evolution of water bodies (Li et al. 2019). Fig. 2a illustrates that the primary cations in Baiyangdian Lake are Na^+ and Ca^{2+} , and the average milligram equivalent percentage of each cation follows the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. Regarding anions, HCO_3^- predominates, followed by Cl^- and SO_4^{2-} . The main hydrochemical type in Baiyangdian Lake is $\text{HCO}_3\text{-Cl-Na}$ type (72.9%). However, hydrochemical types vary across different hydrological seasons. During the normal season, the dominant type is $\text{HCO}_3\text{-Cl-Na}$ (100%). In the flood season, the prevailing type shifts to $\text{HCO}_3\text{-SO}_4\text{-Na}$

(75.0%), with chlorine ions comprising a significant portion (56.3%) of the nomenclature. Conversely, during the dry season, the main type reverts to $\text{HCO}_3\text{-Cl-Na}$ type (62.5%), with a notable proportion of SO_4 (37.5%) in the nomenclature. Overall, chlorine-type and sodium-type waters are predominant in Baiyangdian Lake, indicating a significant influence of evaporation and human activities on the lake's chemical composition (Yan et al. 2021).

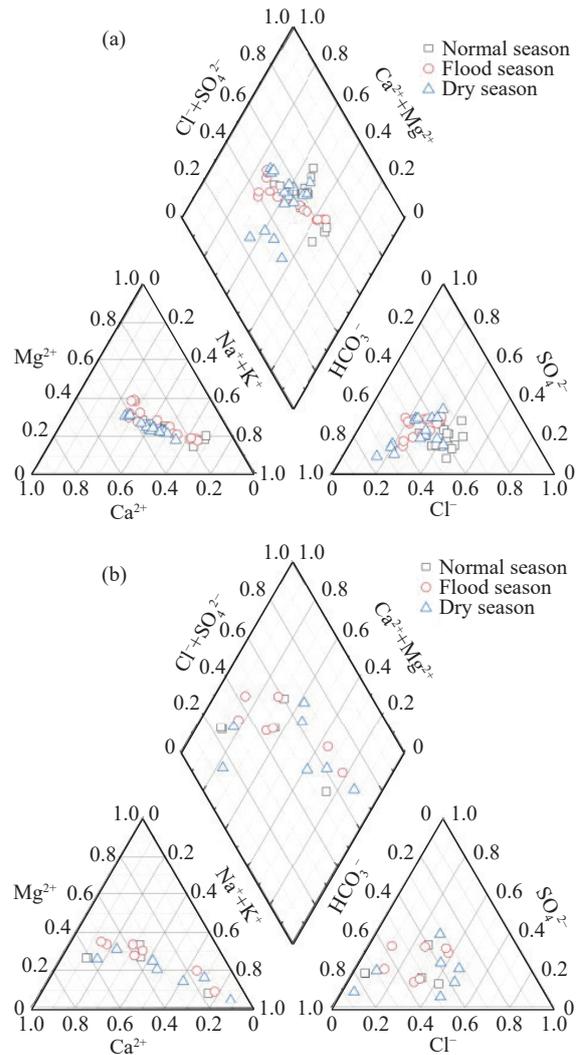


Fig. 2 Piper diagram of Baiyangdian Lake in different seasons (a) Lake water; (b) River water

The main cations and anions in the rivers entering the lake are consistent with those in Baiyangdian Lake (Fig. 2b). The hydrochemistry types of the rivers are diverse. Among them, the proportion of Cl-Na type water and SO_4 type water is as high as 68% and 32%, respectively. The hydrochemical type of Baohe River is consistently $\text{HCO}_3\text{-Ca-Mg}$ in all three seasons. However, for Fuhe River, Xiaoyihe River, and Baigouyinhe River, Cl and SO_4 are both involved in naming in all three

seasons, indicating that the hydrochemistry of these rivers is significantly influenced by human activity.

4 Discussion

4.1 Control factors of hydrochemistry

Gibbs plots can help identify the influence of atmospheric precipitation, rock weathering, and evaporation on the chemical compositions of lake water (Li et al. 2013). Fig. 3 illustrates the Gibbs diagram of the Baiyangdian Lake water for three hydrological seasons. The TDS of the overall water samples ranges from 360 mg/L to 799 mg/L, and the ratio $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ranges from 0.11 to 0.48. All sample points are situated in the upper part of the rock weathering control area, indicating that the chemical composition of Baiyangdian Lake water is primarily influenced by rock weathering, with a weak effect from evaporative crystallization. The $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ranges from 0.39 to 0.86, with most points exceeding the boundaries controlled by natural factors. This suggests that the hydrochemical characteristics of Baiyangdian Lake water are also influenced by other factors such as human activities and the recharge of river water, as well as the occurrence of calcium carbonate sedimentation, resulting in a decrease in Ca^{2+} concen-

tration and an increase in $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ value. In addition, according to the distribution of points in the Gibbs diagram for the three hydrological seasons, points in the dry and normal seasons are predominantly located in the upper right position, indicating that the evaporation and crystallization control during these seasons are more significant compared to the flood season.

4.2 Hydrochemical process

The hydrochemical lithologic endmember diagram uses the influence of different minerals on HCO_3^- , Na^+ , Mg^{2+} and Ca^{2+} in the water body. It takes the ratio of HCO_3^- to Na^+ and Mg^{2+} to Na^+ as the ordinate, and the ratio of Ca^{2+} to Na^+ as the abscissa, to determine the position of each mineral dissolution area in the diagram, allowing for the judgement of the main lithologic role of water hydrochemistry based on the relative position of the sampling point and the lithologic end element (Li et al. 2013).

Upon calculation, $\text{Ca}^{2+} / \text{Na}^+$ is 50, 0.35, 0.17, $\text{Mg}^{2+} / \text{Na}^+$ is 20, 0.24, 0.02, and $\text{HCO}_3^- / \text{Na}^+$ is 120, 2, and 0.3, respectively. By examining the relationships between $\text{HCO}_3^- / \text{Na}^+$, $\text{Mg}^{2+} / \text{Na}^+$, and $\text{Ca}^{2+} / \text{Na}^+$ in the water bodies of Baiyangdian during three sampling seasons, it becomes evident (Fig. 4a, b) that the sample points of Baiyangdian Lake in three seasons are located near the end element of

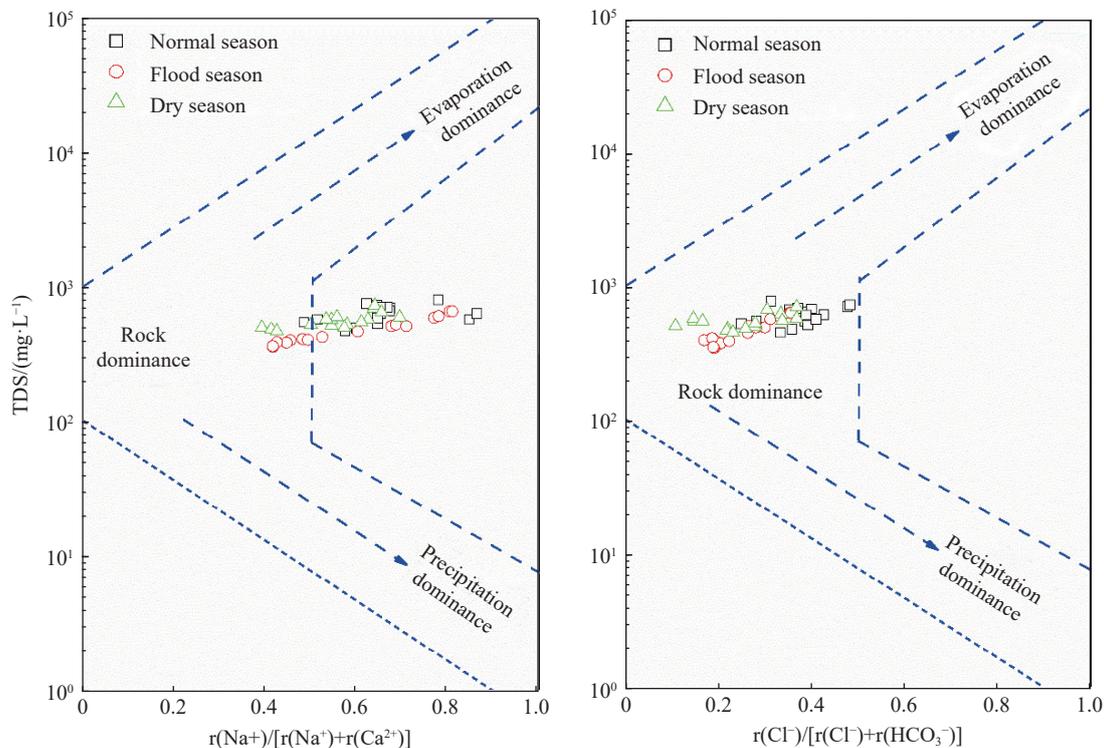


Fig. 3 Gibbs diagram of Baiyangdian Lake

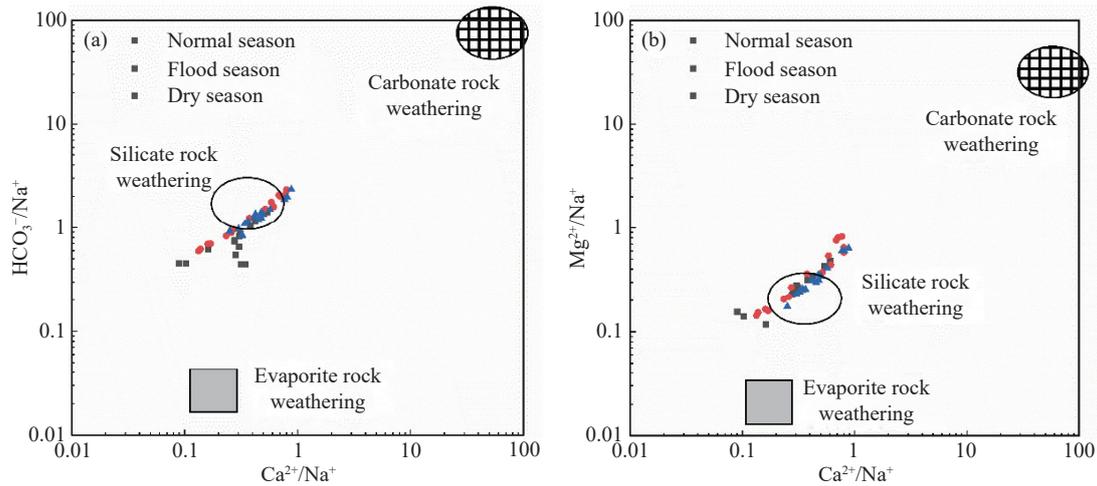


Fig. 4 Relationship between $\text{HCO}_3^-/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ (a), $\text{Mg}^{2+}/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ (b) in Baiyangdian Lake

silicate rock. Consequently, the primary lithologic action controlling the water chemical characteristics of Baiyangdian Lake is the weathering and dissolution of silicate rock.

To further determine the main sources of Ca^{2+} and Mg^{2+} in the Baiyangdian Lake, we applied the milligram equivalent ratio diagram of $\gamma(\text{Ca}^{2+} + \text{Mg}^{2+})$ to $\gamma(\text{HCO}_3^- + \text{SO}_4^{2-})$ for deeper exploration (Fig. 5). In the diagram of $\gamma(\text{HCO}_3^- + \text{SO}_4^{2-})/\gamma(\text{Ca}^{2+} + \text{Mg}^{2+})$, most of the points lie below the $y=x$ line, indicating that Ca^{2+} and Mg^{2+} in the water primarily originate from the dissolution of silicate minerals. However, some points are positioned near or above the $y=x$ line, indicating that carbonate mineral dissolution also contributes to the presence of Ca^{2+} and Mg^{2+} in the water.

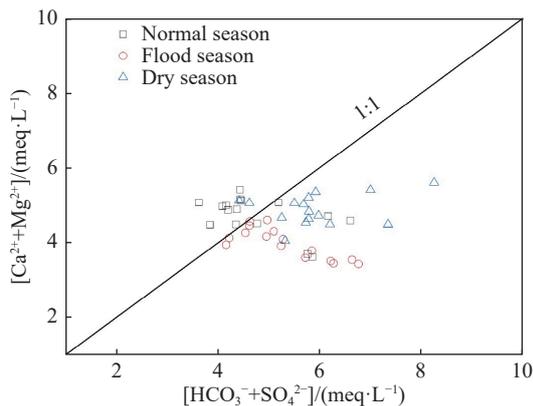


Fig. 5 Baiyangdian Lake $\gamma[\text{Ca}^{2+} + \text{Mg}^{2+}]$ and $\gamma[\text{HCO}_3^- + \text{SO}_4^{2-}]$ relationship

4.3 Impact of human activities

Human activities exert a significant impact on the hydrochemical characteristics of lake water bodies. Water bodies affected by human activities tend to

exhibit higher concentrations of SO_4^{2-} , Cl^- , and NO_3^- . Specifically, SO_4^{2-} primarily originates from industrial wastewater and mining activities, while Cl^- and NO_3^- stem from artificial fertilizers, animal manure, and domestic sewage (Li et al. 2019). By calculating the values of $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ and $[\text{NO}_3^-]/[\text{Ca}^{2+}]$, it becomes possible to further differentiate which human activities affect the hydrochemistry of Baiyangdian Lake. Previous studies have shown that water bodies greatly affected by industry tend to have higher $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ values, while those affected by agricultural activities and municipal sewage exhibit higher $[\text{NO}_3^-]/[\text{Ca}^{2+}]$ values (Fan et al. 2012). From Fig. 6a, it is evident that the $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ values in Baiyangdian Lake water range from 0.17 and 1.89, with average values of 0.64, 0.99, and 0.68 during the normal, flood and dry seasons, respectively. Significant seasonal differences in $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ values are observed, with the highest ratio occurring during the flood season, indicating substantial influence from industrial activities. Considering that the factories around Baiyangdian have been shut down, the SO_4^{2-} in Baiyangdian Lake may primarily originate from industrial activities along the river. Notably, the Xiaoyi River and Baigouyin River exhibit higher concentrations of SO_4^{2-} , with the mean values of 95.9 mg/L and 96.2 mg/L, respectively.

Chloride ions (Cl^-) have strong inertness and are not easily influenced by physical, chemical, and biological processes in water bodies, making them useful for characterizing the impact of human activities on the chemical components of water bodies (Zhang and Wang, 2020). High concentrations of $[\text{Cl}^-]$ and low concentrations of $[\text{NO}_3^-]/[\text{Cl}^-]$ indicate that the main sources of NO_3^- are domestic sewage and feces. Conversely, low

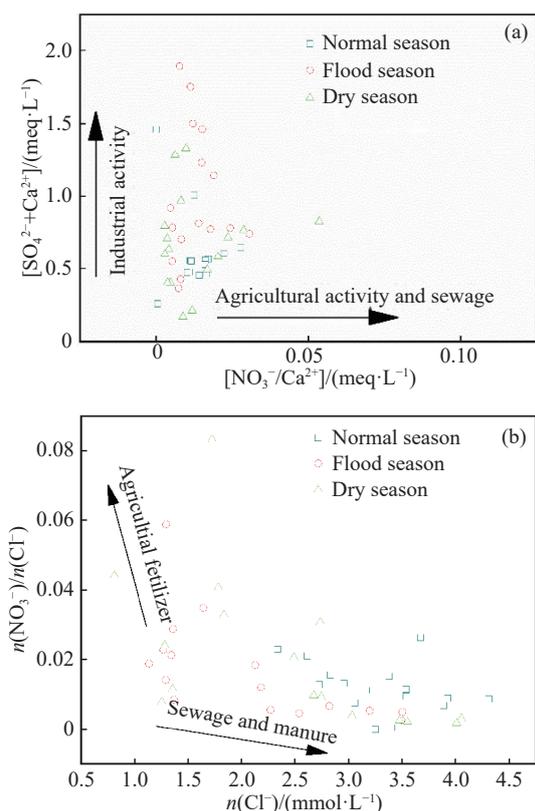


Fig. 6 Baiyangdian Lake $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ and $[\text{NO}_3^-]/[\text{Ca}^{2+}]$ (a), $[\text{Cl}^-]$ and $[\text{NO}_3^-]/[\text{Cl}^-]$ (b) relationship

concentrations of $[\text{Cl}^-]$ and high concentrations of $[\text{NO}_3^-]/[\text{Cl}^-]$ suggest that agricultural activities are the primary source of NO_3^- . If both $[\text{NO}_3^-]/[\text{Cl}^-]$ and $[\text{Cl}^-]$ values are low, it indicates that NO_3^- mainly originates from soil organic nitrogen. This study utilized the relationship between $[\text{NO}_3^-]/[\text{Cl}^-]$ and $[\text{Cl}^-]$ to further identify the impact of human activities on the hydrochemical components of the Baiyangdian Lake (Fig. 6b).

The average concentrations of Cl^- measured in Baiyangdian Lake during the normal, flood and dry seasons are relatively high, at 117 mg/L, 72.8 mg/L and 86.0 mg/L, respectively, while the $[\text{NO}_3^-]/[\text{Cl}^-]$ values range from 0 to 0.080. The average values during the normal, flood and dry seasons are relatively low, at 0.013, 0.017, and 0.019, respectively, indicating that NO_3^- in the Baiyangdian Lake is primarily influenced by domestic sewage and animal feces. Seasonal variation shows a $[\text{NO}_3^-]/[\text{Cl}^-]$ ratio characterized by dry season > flood season > normal season. The $[\text{Cl}^-]$ value varies greatly among different sampling seasons, with the highest Cl^- concentration during the normal season and the lowest during the flood season, indicating more severe pollution from domestic sewage and feces during the normal season. Spatial variation indicates that the varia-

tion coefficients of $[\text{NO}_3^-]/[\text{Cl}^-]$ values during the normal, flood and dry seasons are 51%, 100% and 114%, respectively, while the variation coefficients of Cl^- concentration are 16%, 41%, and 42%, respectively. The distribution of samples during the flood and dry seasons is relatively dispersed. During the flood season, the $[\text{NO}_3^-]/[\text{Cl}^-]$ values of L14 and L15 in the southeast region are relatively high, with Cl^- concentration lower than 1.4 mmol/L. This may be due to the presence of arable land on the southeast bank of Baiyangdian Lake, with fewer artificial buildings and abundant rainfall in July, resulting in strong soil leaching. During the dry season, the $[\text{NO}_3^-]/[\text{Cl}^-]$ values of L1, L2, and L4 in the northern region of the study area are relatively high, with Cl^- concentrations ranging from 1.73 mmol/L to 1.84 mmol/L. This may be attributed to the concentrated distribution of farmland in the northern region of the study area, where water from the Baigouyin River flows through the farmland along the line and enters Baiyangdian Lake.

4.4 Sources of hydrochemical components in Baiyangdian Lake

Based on the correlation analysis between the chemical components of water, it is possible to determine whether ions share the same source. Generally, K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and HCO_3^- in water primarily originate from mineral rock dissolution, while Cl^- , NO_3^- and SO_4^{2-} may also result from pollution caused by human activities. For example, domestic sewage and agricultural fertilization can elevate Na^+ , K^+ , Cl^- , and NO_3^- concentrations in water bodies. Combustion of fossil fuels, application of sulfur-containing fertilizers, and industrial activities may raise SO_4^{2-} levels in water bodies. To ascertain the sources of various water chemical components in Baiyangdian Lake, Pearson correlation analysis was conducted on pH, DO, and major ions in Baiyangdian Lake (Fig. 7a, 7b, and 7c).

As depicted in Fig. 7a, 7b, and 7c, significant positive correlations were observed between Na^+ and K^+ during the three hydrological seasons (correlation coefficient of 0.87, 0.98 and 0.80 for normal, flood and dry seasons, respectively), as well as between Ca^{2+} and Mg^{2+} in the normal and dry seasons (correlation coefficient of 0.84 and 0.83 for normal and dry seasons, respectively), indicating shared sources. K^+ and Na^+ primarily originate from salt dissolution in sediments, while Ca^{2+} and Mg^{2+} mainly derive from silicate and carbonate rock dissolution. A weak positive corre-

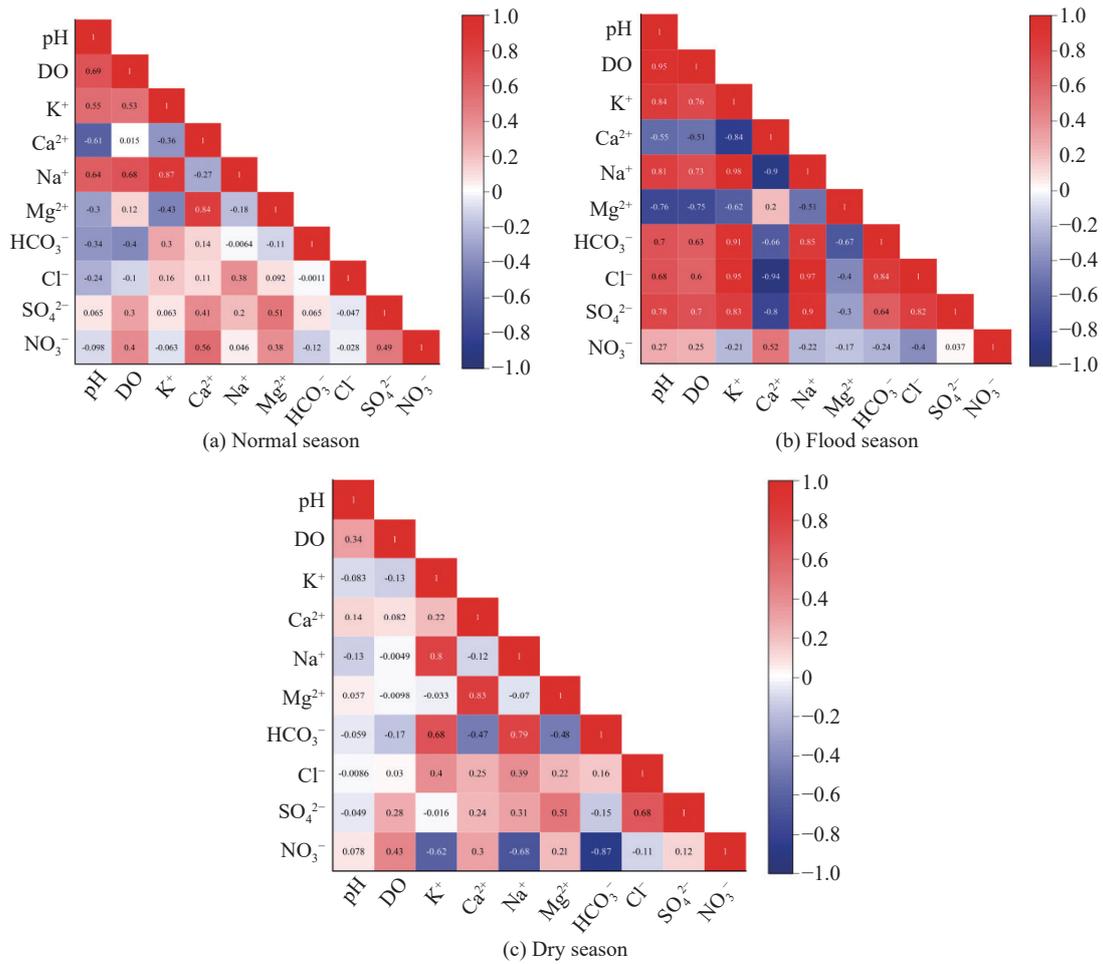


Fig. 7 Correlation analysis of Baiyangdian Lake in normal, flood and dry seasons

lation between NO₃⁻ and Ca²⁺ in all three seasons suggests common sources such as agricultural fertilizers and domestic sewage (Xue et al. 2009). During the flood season, Na⁺ and K⁺ show a significant positive correlation with Cl⁻, suggesting influence from human activities like municipal sewage and livestock manure (Jin et al. 2015). During the dry season, a weak negative correlation between Ca²⁺ and Mg²⁺ and HCO₃⁻ (Fig. 7c) indicates carbonate sedimentation in Baiyangdian Lake. Overall, correlations between hydrochemical components are weak during normal and dry seasons, but significantly enhanced during flood season due to increased water flow velocity and hydraulic connections between various stations caused by river inflow.

4.5 The driving factors of variations in hydrochemical components in Baiyangdian Lake

This study employed Principal Component Analysis (PCA) to identify the driving factors behind hydrochemical evolution in Baiyangdian Lake

across three hydrological seasons. Ten water quality parameters (pH, DO, Na⁺, K⁺, Ca²⁺, Mg²⁺, HCO₃⁻, SO₄²⁻, NO₃⁻, and Cl⁻) were selected for analysis. Before incorporating the data into the PCA model, Kaiser-Meyer-Olkin and Barlett spherical tests were conducted on the research data. The results indicate that during the normal, flood and dry seasons, the KMO values are 0.517, 0.624, and 0.545, respectively, and the Barlett spherical test values are 119, 310, and 149 (P<0.001), signifying that the hydrochemical data of Baiyangdian Lake during the three hydrological seasons have met the requirements for PCA. Based on eigenvalues >1, five, two and four main factors controlling the hydrochemical evolution of Baiyangdian Lake during normal, flood and dry seasons were identified. These factors explain 94.9%, 87.2%, and 86.4% of all variables, respectively, and could represent all information of the ten hydrochemical indicators (Table 3).

(1) The principal factor 1 (PC1) during the normal season account for 33.9% of the total variability. Strong positive correlations with PC1 are observed for pH, DO, Na⁺, and K⁺. Typically, Na⁺

Table 3 Driving factors of chemical components in Baiyangdian Lake water

Parameter	Normal season					Flood season		Dry season			
	PC1	PC2	PC3	PC4	PC5	PC1	PC2	PC1	PC2	PC3	PC4
pH	0.798	-0.179	-0.306	-0.107	-0.327	0.945	0.284	0.026	0.163	-0.200	0.846
DO	0.817	0.242	-0.374	-0.135	-0.119	0.927	0.219	-0.229	-0.132	0.335	0.767
K ⁺	0.879	-0.241	0.341	0.102	0.120	0.670	0.733	0.907	0.184	0.113	-0.011
Na ⁺	0.933	-0.029	0.040	0.012	0.330	0.629	0.765	0.857	-0.113	0.395	-0.010
Ca ²⁺	0.329	0.689	-0.404	0.397	0.175	-0.296	-0.906	-0.050	0.957	0.108	0.109
Mg ²⁺	-0.203	0.895	-0.148	-0.262	0.150	-0.797	-0.087	-0.148	0.889	0.270	-0.048
HCO ₃ ⁻	-0.043	0.021	0.994	0.011	0.003	0.578	0.675	0.881	-0.430	-0.004	-0.028
Cl ⁻	0.060	-0.009	-0.002	0.078	0.985	0.454	0.881	0.274	0.183	0.792	-0.004
NO ₃ ⁻	-0.121	-0.081	0.018	0.964	0.090	0.434	-0.783	-0.887	0.118	0.187	0.318
SO ₄ ²⁻	0.266	0.816	0.052	0.439	-0.106	0.654	0.566	-0.075	0.199	0.927	0.037
Eigenvalue	3.39	2.09	1.58	1.33	1.10	6.97	1.76	3.56	2.57	1.38	1.14
Variance contribution rate (%)	33.9	20.9	15.8	13.3	11.0	69.7	17.6	35.6	25.7	13.8	11.4
Driving factor	Dissolution of salt in sediments	Dissolution of silicate and carbonate	Carbonate sedimentation	Fertilizer Manure	Sewage	Lixivation	Sewage, manure, fertilizers, and carbonate sedimentation	Dissolution of salt, fertilizers, and manure	Silicate and carbonate dissolution	Sewage sedimentation	Nitrification

and K⁺ are predominantly influenced by water-rock interaction within the watershed (Zhou et al. 2021). As demonstrated in section 5.1.2, Na⁺ in the Baiyangdian Lake is mainly controlled by salt dissolution in sediments. Additionally, pH and DO reflect the physical and chemical characteristics of water bodies, influenced by various factors. Therefore, PC1 suggests that the chemical composition of Baiyangdian Lake water is influenced by salt dissolution in sediments (natural factors). Principal factor 2 (PC2) explains 20.9% of the total variability, showing strong positive correlations with Mg²⁺ and SO₄²⁻, while Ca²⁺ exhibits a moderate negative correlation. As described in Section 5.1.2, Ca²⁺ and Mg²⁺ in Baiyangdian Lake mainly originate from the dissolution of silicate and carbonate rocks. Therefore, PC2 indicates that the chemical composition of Baiyangdian Lake water is influenced by the dissolution of silicate and carbonate rocks (natural factor). Principal factor 3 (PC3) accounts for 15.8% of the total variability, exhibiting strong positive correlation with HCO₃⁻, while Ca²⁺ and Mg²⁺ show moderate to weak negative correlations. This indicates that an increase in HCO₃⁻ concentration can lead to a decrease in Ca²⁺ and Mg²⁺ concentration, resulting in carbonate sedimentation. Therefore, PC3 implies that carbon-

ate sedimentation influences the chemical composition of Baiyangdian Lake (natural factors). Principal factor 4 (PC4) explains 13.3% of the total variability. It showed a strong positive correlation with NO₃⁻, while SO₄²⁻ exhibits a weak positive correlation. Principal factor 5 (PC5) explains 11.0% of the total variability, showing a strong positive correlation with Cl⁻, and a weak positive correlation with Na⁺. Typically, NO₃⁻ in the water environment originates from human activities such as agricultural fertilizer, manure, soil nitrogen, sewage, and atmospheric deposition (Jin et al. 2015). Similarly, SO₄²⁻ is sourced from fertilizer, sewage, evaporite dissolution, industrial emissions, etc (Torres-Martínez et al. 2020). While Cl⁻ shares similar sources, including domestic sewage, fertilizer, manure, road snow salt and natural minerals dissolution (Zhang and Wang, 2020). Given the relatively independent nature of PC4 and PC5, and the weak positive correlation between Na⁺ and PC5, which is consistent with findings indicating the presence of Na⁺ in domestic sewage (Sun et al. 2014), PC5 suggests that the chemical composition of Baiyangdian Lake is influenced by domestic sewage (human factors), while PC4 suggests that the chemical composition is influenced by agricultural fertilizers and manure.

(2) Principal factor 1 (PC1) during the flood season explains 69.7% of the total variability. Strong positive correlation was observed for pH and DO, while Mg^{2+} show a strong negative correlation, and Na^+ , K^+ , Ca^{2+} , and SO_4^{2-} exhibit moderate positive correlations. As previously discussed, Na^+ , K^+ , Mg^{2+} and Ca^{2+} in Baiyangdian Lake primarily originate from the dissolution of salt in sediments, silicate, and carbonate. Thus, PC1 indicates that the hydrochemical components in Baiyangdian Lake water are affected by leaching. Principal factor 2 (PC2) explains 17.6% of the total variability, showing strong positive correlations with Na^+ and Cl^- , and strong negative correlations with Ca^{2+} and NO_3^- , while HCO_3^- , K^+ , and SO_4^{2-} exhibit moderate positive correlations. Based on the previous analysis, it can be inferred that Na^+ , Cl^- , and NO_3^- in Baiyangdian Lake mainly originate from sewage, fertilizers, and manure. Additionally, the increase in HCO_3^- concentration during the flood season led to a decrease in Ca^{2+} concentration, resulting in carbonate sedimentation. Therefore, PC2 represents the influence of sewage, manure, fertilizers, and carbonate sedimentation on the chemical composition of the Baiyangdian Lake.

(3) Principal factor 1 (PC1) during the dry season explains 35.6% of the total variability. Strong positive correlation with PC1 were observed for Na^+ , K^+ , and HCO_3^- , while a strong negative correlation was found for NO_3^- . This suggests that high nitrate concentration leads to decreased Na^+ , K^+ , and HCO_3^- concentrations, indicating a dilution effect when runoff from agricultural activities flows into Baiyangdian Lake. Moreover, Na^+ and K^+ in Baiyangdian lake water may originate from salt dissolution in sediments. Therefore, PC1 represents the salt dissolution in sediments, leaching, fertilizer, and manure on the chemical composition of Baiyangdian Lake water. Principal factor 2 (PC2) explains 25.7% of the total variability, showing strong positive correlation with Ca^{2+} and Mg^{2+} , and a moderate negative correlation with HCO_3^- , indicating that PC2 represents chemical components of Baiyangdian Lake water subjected to silicate and carbonate rock dissolution, as well as carbonate sedimentation. Principal factor 3 (PC3) explains 13.8% of the total variability, showing strong positive correlations with Cl^- and SO_4^{2-} , and a moderate or weak negative correlation with Na^+ , indicating that PC3 represents the influence of domestic sewage on hydrochemical components of the Baiyangdian Lake water. Principal factor 4 (PC4) explains 11.4% of the total variability, with strong positive correlation with pH and DO, and a weak positive correlation with

NO_3^- . pH characterizes of the comprehensive physicochemical properties of water bodies and is influenced by various factors. DO concentration indicates the redox environment of the water body, and the positive correlation between DO and NO_3^- reflects nitrification of Baiyangdian Lake water (Jiang et al. 2022). Therefore, PC4 represents the influence of nitrification on the hydrochemical components of Baiyangdian Lake.

5 Conclusion

This study utilized a combination of geochemical methods and multivariate statistical techniques to characterize the spatial-temporal variation and driving factors of the chemical composition of Baiyangdian Lake. The findings reveal that human activities exert a significant influence on the spatial variability of the chemical composition, while seasonal variation is influenced by rainfall dilution, water supply sources and human activities. Through geochemical methods, correlation analysis and principal component analysis, we identified key driving factors of hydrochemistry changes in Baiyangdian Lake, including dissolution of silicate and carbonate rocks, salt dissolution in sediments, carbonate sedimentation, sewage, agricultural fertilizers and manure, and nitrification. However, accurately pinpointing the sources of chemical components remains challenging with the current data. Future studies should incorporate high-resolution hydrogeochemical monitoring and precise source identification techniques to better discern the contributions of various sources to the variation in water chemistry in the Lake.

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Annexed Table 1 Basic information of the sampling sites

Sites	Longitude	Latitude	Land use	Potential sources of pollution
L1	115°58'26.96"	38°56'33.15"	Scenic areas, Farmland,	Sewage
L2	115°59'1.98"	38°56'0.07"	Tourist Area	Sewage
L3	116°0'6.68"	38°54'59.17"	Distribution of rural farmland	Agricultural non-point pollution
L4	116°1'29.46"	38°55'6.33"	Near the Observation Deck	—
L5	116°2'11.14"	38°54'0.71"	Village	Sewage
L6	116°3'38.26"	38°54'50.44"	Village	Sewage
L7	116°5'28.23"	38°53'25.56"	Village, near the Farmland	Agricultural non-point pollution and sewage
L8	116°3'12.39"	38°52'46.14"	Village	Sewage
L9	116°1'9.94"	38°51'27.40"	Village	Sewage
L10	116°2'34.59"	38°50'52.66"	Aquaculture intensive area	Feeding fodder and animal excrements
L11	116°2'40.78"	38°49'39.59"	Village, Aquaculture area	Sewage
L12	116°1'33.95"	38°49'46.12"	Village, Large number of aquatic plant distribution	Sewage
L13	115°59'40.70"	38°50'32.51"	Village	Sewage
L14	115°57'21.19"	38°50'59.41"	Village, Farmland	Agricultural non-point pollution and sewage
L15	115°59'6.09"	38°52'26.80"	Village	Sewage
L16	115°59'53.59"	38°53'57.37"	Village	Sewage
R1	115°55'22.3"	38°54'15.75"	Village, Farmland	Undertake domestic sewage and industrial wastewater
R2	115°47'20.12"	38°53'50.23"	Villages along the route, Farmland	Agricultural non-point pollution and sewage
R3	115°46'19.88"	38°54'56.44"	Close to Villages, Farmland, Fishing Sites	Agricultural non-point pollution and sewage
R4	115°52'29.83"	38°47'30.89"	Close to Villages, Farmland	Agricultural non-point pollution and sewage
R5	116°02'1.15"	39°00'44.03"	Village, Farmland	Agricultural non-point pollution and sewage
R6	116°01'5.21"	38°47'20.45"	Farmland along the route, Fewer villages	Agricultural non-point pollution and sewage
R7	115°50'55.11"	38°48'26.68"	Village, Farmland	Agricultural non-point pollution and sewage

Annexed Table 2 Hydrochemical parameters, analytical method, equipment and detection limits

Parameters	Analytical method	Analytical equipment	Detection limit
pH	Electrode method	HQ40D, HACH, United States	0.01
EC(μ S/cm)			0.01
DO(mg/L)			0.05
Nitrate [NO_3^-](mg/L)	Spectrophotometry	Perkin-Elmer Lambda 35, United States	0.664
Chloride [Cl^-](mg/L)			1.0
Sulfate [SO_4^{2-}](mg/L)			0.75
Potassium [K^+](mg/L)	Inductively coupled plasma-mass spectrometry	Agilent 7500ce ICP-MS, Tokyo, Japan	0.05
Sodium [Na^+](mg/L)			0.01
Calcium [Ca^{2+}](mg/L)			4.0
Magnesium [Mg^{2+}](mg/L)			3.0
Bicarbonate [HCO_3^-](mg/L)	Acid–base titration	—	5.0