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Evaluation of the Impact of Different Land Use Types on Shallow Groundwater and Discussion on Water Chemistry Genesis A Case Study of the Middle Reach of the Beijiaolai River

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Main point 1: The hydrochemical characteristics of shallow groundwater in the middle reaches of the Beijiaolai River are dominated by a dual-driver mechanism of "natural weathering–anthropogenic input".;

Main point 2: Multi-method coupled analysis reveals the synergistic effects of fluoride enrichment and anthropogenic pollution.

Abstract: To determine the hydrochemical distribution characteristics of shallow groundwater used for agriculture and construction in the middle reaches of the Beijiaolai River, as well as to accurately analyze its natural and anthropogenic driving mechanisms, we conducted a study. Methodology: Qingdao Liaolan was selected as the research area, where 41 sets of shallow groundwater samples were collected and tested. A comprehensive approach combining multivariate statistical analysis, Piper trilinear diagrams, ion source and control factor discrimination, and mineral saturation indices was employed to identify groundwater chemical types, key controlling processes, and anthropogenic contributions. Results: (1) The overall groundwater in the study area is slightly alkaline, predominantly exhibiting HCO₃⁻-Ca²⁺ and Cl⁻-Na⁺ chemical types. The mineralization level (average TDS of 1140 mg/L) and Na⁺ content in construction land are significantly higher than those in cultivated land, reflecting the differentiated impacts of domestic sewage input and agricultural fertilization; (2) Weathering of silicate and carbonate rocks is the main natural driving factor, accounting for 73.2%. The mineral saturation index confirms that calcite (SI: -0.48 to 0.88), dolomite (SI: -0.97 to 2.44), and fluorite (SI: -1.51 to 0.43) are in a state of dynamic equilibrium between dissolution and precipitation; (3) The undersaturation characteristics of high fluoride areas (F⁻ > 10 mg/L) observed in 85% of the samples reveal that the dissolution of calcium fluoride dominates the fluoride enrichment mechanism. Cation exchange effects are weak (CAI ≈ 0), highlighting the core role of water-rock interactions; (4) Agricultural non-point source pollution and domestic sewage discharge are the primary anthropogenic factors, with significant contributions from livestock manure application. Conclusion: The "natural weathering-anthropogenic input" dual driving mechanism of shallow groundwater chemical evolution in this region indicates that different land use types directly reshape hydrochemical characteristics by altering the types of pollution source inputs (domestic sewage vs. agricultural non-point sources). The findings provide scientific references for ecological restoration of groundwater and land planning in the watershed.

Keywords: Beijiao River; Water-rock interaction; Hydrogeochemical evolution; Land use type; Driving

mechanism.

0 Introduction

Groundwater is an important strategic water resource in China, especially critical in northern regions, supplying approximately two-thirds of drinking water, half of industrial water, and one-third of agricultural irrigation water (Bei et al., 2019). As a fundamental resource that maintains ecological balance and supports socio-economic development (M. H. Zhang et al., 2024), shallow groundwater plays an irreplaceable role in residential life, agricultural production, and industrial development (2020; Wen et al., 2020). However, with the rapid industrialization and urbanization processes in China, groundwater systems (particularly shallow aquifers) are facing unprecedented environmental pressures (Li et al., 2022; Ma et al.; Choudhary et al., 2024). These pressures manifest primarily in three ways: (1) agricultural areas experiencing non-point source pollution from pesticides and fertilizers, leading to nitrate and organic contamination (Das et al., 2023); (2) urban areas suffering from point source pollution due to industrial and domestic wastewater, resulting in heavy metals and organic micro-pollutants (B. et al., 2022); and (3) widespread regional over-extraction issues (Lall et al., 2020; Mei Shijie, 2023), which accelerate the renewal of shallow aquifer groundwater (Cheng et al., 2024). Research indicates that the formation of hydrochemical characteristics in groundwater is controlled by dual mechanisms: on one hand, natural factors such as regional geological structures and aquifer characteristics impose constraints (Hu Shuang et al., 2023; Jiang Feng et al., 2023; Kou Yahui et al., 2023); on the other hand, land use practices significantly influence groundwater quality through differentiated hydrological processes and pollution input pathways (Aktar et al., 2025; An Lesheng et al., 2012). Therefore, systematically studying the hydrochemical characteristics and formation mechanisms of shallow groundwater under different land use types not only aids in elucidating the evolution of water quality under the coupling of natural and anthropogenic forces (N. et al., 2022) but also provides theoretical support for implementing regionally tailored groundwater management strategies. This has significant scientific implications for achieving the sustainable use and protection of groundwater resources.

As the world's largest developing country and an important agricultural producer, China faces increasingly severe groundwater environmental challenges amid rapid industrialization and urbanization. The dual compounding effects of agricultural non-point source pollution and industrial point source pollution have subjected the national groundwater system (especially shallow aquifers) to unprecedented pollution pressures (Li et al., 2022; Ma et al.). In response to groundwater environmental pollution issues, the international academic community has gradually established a comprehensive research framework that includes fundamental hydrochemical analysis methods (e.g., ion ratio method, mineral saturation index analysis), visualization techniques (such as Gibbs diagrams, Durov plots, and Piper trilinear diagrams), isotope tracing

technologies, and multivariate statistical methods (e.g., principal component analysis, cluster analysis, and factor analysis) (A. et al., 2012; Kammoun et al., 2018; Moussa et al., 2011; Sacks & Tihansky, 1996; Yong-Hong et al., 2007; Liu Wenjie et al., 2009; Wang Jihua et al., 2023). The integrated application of these methods provides essential technical support for revealing the hydrochemical characteristics and formation mechanisms of groundwater under different land use types. For instance, M. H. Zhang et al. (2024) systematically analyzed the hydrochemical characteristics and controlling factors of the lower Oujiang River by integrating ion ratio methods, salinity index methods, and multivariate statistical approaches. Su Huimeng et al. (2024) utilized isotope tracing, hydrochemical methods, and principal component analysis to reveal the hydrogeochemical mechanisms in mining areas. Laouni Benadela et al. (2022) explored the hydrochemical characteristics of shallow aquifers in semi-arid regions using multivariate statistical analysis combined with the ion ratio method. Du Qianqian et al. (2024) examined the impact of land use patterns on the hydrochemical characteristics of surface water and groundwater in Tianjin based on hydrochemical analysis methods. These research findings quantitatively identify the key factors controlling groundwater chemical components and their causative mechanisms (Sun Yanling et al., 2024; Zhang Jianmang et al., 2024; Chen Huaxiong et al., 2024), providing more precise scientific evidence for groundwater pollution prevention and control. This study selects the main vegetable production area in Pingdu City, Shandong Province, as a typical research subject. The shallow groundwater in this region serves as the primary source for agricultural irrigation and faces intense developmental pressure.

To clarify the impact of human activities on groundwater, the study strictly categorizes the research area into two major land use types based on surface functions: agricultural production areas and village construction areas (Meng Chunxia et al., 2019). In recent years, the expansion of facility agriculture and the increase in domestic sewage discharge have significantly disturbed the groundwater flow and chemical fields due to these distinctly different surface utilization methods, posing potential threats to vegetable yield, quality, and the health of regional residents. Although some scholars have conducted relevant research on the groundwater environment in this area, most studies focus on the hydrochemical characteristics of high-fluoride groundwater and their geological causative mechanisms (Meng Chunxia et al., 2019b; Xu Lirong et al., 2012). Existing studies often emphasize the identification of single pollution indicators or treat the aquifer system as a purely natural unit controlled by geological background, lacking a systematic characterization of the spatial heterogeneity of groundwater chemical components between agricultural production and construction land. Moreover, there is little research that quantitatively separates the contributions of natural weathering processes and various anthropogenic inputs to the evolution of water chemistry.

In light of this, the current study aims to transcend the limitations of traditional

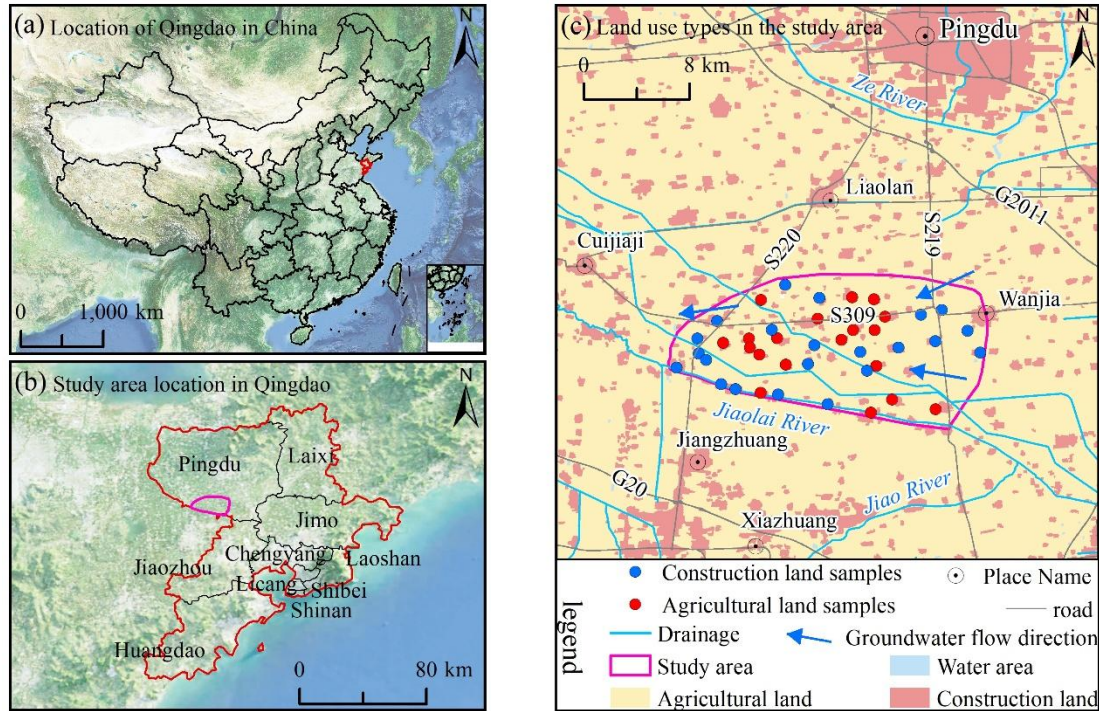
singular indicator research by adopting a coupling perspective of "land use-water quality response." It clearly defines agricultural land and construction land as two research objects and seeks to address the following scientific questions: (1) Identify the hydrochemical fingerprint characteristics under different functional zones: Reveal the specific impacts of agricultural cultivation and village life activities on the spatial differentiation of shallow groundwater chemical components; (2) Construct a quantitative analysis model driven by natural and anthropogenic factors: Utilize multivariate statistical and ion chemometric methods to analyze the relative contributions of water-rock interactions and specific human activities; (3) Elucidate the mechanisms of hydrochemical evolution in complex habitats: Establish a conceptual model for the hydrochemical evolution of shallow groundwater in this region, providing scientific evidence for the formulation of targeted groundwater management strategies and optimizing agricultural land use patterns, ultimately achieving a collaborative guarantee for sustainable agricultural development and ecological environmental protection.

1 Study Area Overview

The study area is located in Qingdao City, Shandong Province, positioned in the middle reaches of the Beijiaolai River (Figure 1), within the central-western part of the Jiaolai Basin, characterized as a Late Mesozoic terrestrial sedimentary volcanic rock basin (Wang Lijuan et al., 2024). A complete depositional sequence consisting of fluvial, lacustrine, deltaic, and riverine facies develops within the area, with a gradual transition from lacustrine to riverine facies from east to west (Ren Tianlong, 2019). The stratigraphy of the working area primarily comprises the Quaternary Holocene Yihe Formation (Qhy) and the Heitu Lake Formation (Qhh) (Figure 2). According to data from eleven hydrogeological boreholes, the stratigraphic thickness increases progressively from the southeast to the northwest. The Yihe Formation mainly occurs in the floodplain and riverbed areas of the Jiaolai River Valley, characterized by fine sand and medium-coarse sand with a thickness of 1-2 meters. The Heitu Lake Formation is widely developed across the region and is typical of marsh depression deposits, with a thickness ranging from 10 to 25 meters (locally exceeding 30 meters). It exhibits distinct tripartite features: the upper section consists of gray-black to brown silty clay rich in aquatic mollusks; the middle section contains calcareous nodules and gravelly silty clay; and the bottom section consists of a medium-coarse sand layer with a thickness of 0-2 meters. The spatial distribution of sand layers is uneven, with the northwest predominantly consisting of medium-coarse sand with a thickness of 5-8 meters, while the southern and eastern areas are primarily composed of fine sand with a thickness of 1-3 meters, and the southwestern area lacks sand layers.

In the Quaternary loose rock formations of the study area, pore water is extensively developed, with the aquifer lithology mainly comprising fine sand and medium-coarse sand, overlain by silt and gravelly silty clay (containing calcareous nodules) (Figure 2).

The main sources of recharge are atmospheric precipitation infiltration and lateral runoff, supplemented by irrigation return flow; the primary mode of discharge is artificial extraction, with natural discharge predominantly occurring as downstream flow. The groundwater level dynamics exhibit significant seasonal variation: during the flood period from July to September, the water level rises, while a low water level occurs during the spring irrigation period from April to July. Long-term dynamics are controlled by precipitation cycles and require comprehensive assessment in conjunction with regional hydrometeorological data.



The map is based on the standard map with drawing review No. GS(2024)0650, and the base map remains unaltered.

Figure 1: Schematic Diagram of Land Use in the Study Area and Sampling Locations

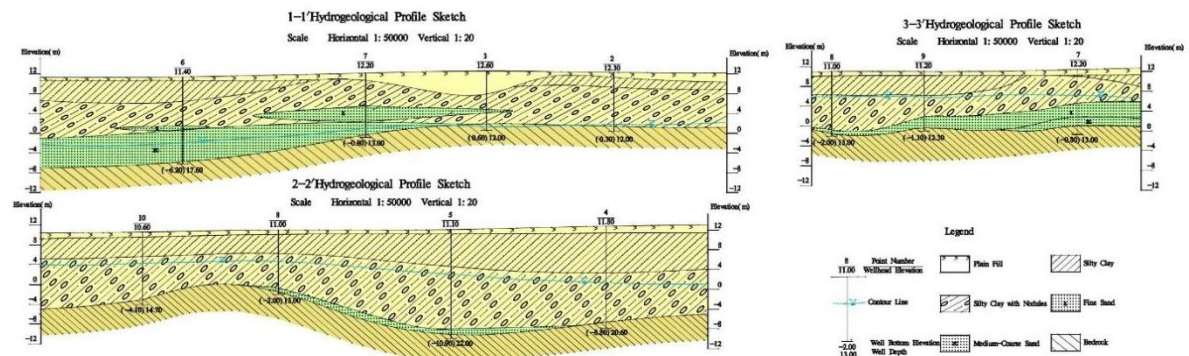


Figure 2 Profile of the study area

2 Sample Collection and Research Methods

2.1 Groundwater Sample Collection Method

To accurately reflect the characteristics of shallow groundwater in the study area, this research considered land use types (urban land and agricultural land), urban

distribution patterns, as well as hydrogeological and geological topographical conditions when establishing sampling points. Based on these principles, a total of 41 groundwater sampling points were set up, including 22 in urban areas and 19 in agricultural areas. The sampling points primarily originated from domestic wells, irrigation wells, and hydrogeological exploration boreholes, with sampling depths ranging from 10 to 20 meters. Sampling was conducted in August 2022, chosen for the summer period following the peak agricultural irrigation season to minimize the effects of irrigation disturbances, thereby ensuring that the collected samples could more accurately reflect the hydrochemical status of shallow groundwater in the Liaolan region.

Groundwater sampling must strictly follow standardized procedures. For routine physicochemical parameters (pH, TDS, conductivity, etc.), acid-washed polyethylene or glass bottles should be used, rinsed three times before sampling to avoid headspace preservation. pH should be measured on-site or samples should be refrigerated at 4°C and analyzed within 6 hours. Cation samples (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , etc.) must be acidified with nitric acid to a pH < 2 and refrigerated, with a validity period of 30 days. Anion samples (Cl^- , SO_4^{2-} , NO_3^- , etc.) must be filtered (0.45 μm membrane) and stored at 4°C, to be analyzed within 7 days. Total alkalinity should be collected in full bottles and titrated within 24 hours. During sampling, field parameters such as water temperature, turbidity, and dissolved oxygen should be recorded simultaneously to avoid sample aeration or precipitation interference.

2.2 Groundwater Sample Preservation Methods.

Different water quality parameters require specific preservation methods: pH samples should be refrigerated at 4°C and measured within 6 hours. Cation samples need to be acidified with nitric acid (pH < 2) and refrigerated, with analysis by atomic absorption or ICP within 30 days. Anion samples should be filtered and stored at 4°C, with analysis by ion chromatography or titration within 7 days. Total alkalinity samples require full-bottle storage in the dark and refrigeration, with titration completed within 24 hours. For F^- , add TISAB buffer to eliminate interference, and for sulfides, add $Zn(Ac)_2$ for fixation. All samples should be protected from shock and light during transportation.

2.3 Sample Testing Methods

In this study, groundwater samples were preserved in polyethylene bottles and subjected to pretreatment according to the analytical requirements for various indicators. The determination of cations Na^+ , K^+ , Ca^{2+} , and Mg^{2+} was conducted following the standard "HJ 812-2016 Water Quality – Determination of Soluble Cations (Li^+ , Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) Using Ion Chromatography," with concentration measurements performed using a flame atomic absorption spectrometer (contrAA 300, Jena, Germany). Anions F^- , Cl^- , NO_3^- , and SO_4^{2-} were analyzed based on the standard "HJ 84-2016 Water Quality – Determination of Inorganic Anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- ,

PO₄³⁻, SO₄²⁻) Using Ion Chromatography," utilizing an ion chromatograph (IC883, Metrohm, Switzerland) for analysis. HCO₃⁻ was measured according to the standard "DZ/T 0064.49-2021 Methods for Analyzing Groundwater Quality – Part 49: Determination of Carbonate, Bicarbonate, and Hydroxide Ions by Titration," employing an acid-base indicator titration method. After testing all water samples, the charge balance error (CBE) for cations and anions was maintained within ±5%, ensuring the reliability of the data.

2.4 Data Processing Methods

The data processing and map preparation in this study primarily utilized the geostatistical analysis module of ArcGIS 10.8 to create a regional location map of the study area. Additionally, the Kriging spatial interpolation method was employed to depict the spatial distribution of conventional ion elements in groundwater. IBM SPSS Statistics 26 was used, along with Pearson correlation coefficients, to conduct statistical analyses, cluster analyses, and correlation analyses of element concentrations in groundwater samples. Furthermore, Origin 2022 was applied to generate related visualizations, including ion ratio charts, Gibbs diagrams, end-member ion ratio plots, mineral saturation index graphs, and cation exchange ratio plots alongside chloride alkalinity index distribution maps. Moreover, analysis of variance (ANOVA) was conducted to examine differences in groundwater experimental results between urban land and agricultural land types, thereby verifying the variability in groundwater characteristics associated with these two land use types.

3 3 Results and Discussion

3.1 Statistical Characteristics of Water Chemical Components

3.1.1 Statistical Analysis of Mathematical and Physical Characteristics

The groundwater in the study area exhibits significant regional pollution characteristics, particularly with respect to nitrate (NO₃⁻) concentrations in urban and agricultural land, which have average values of 175.12 mg/L and 205.92 mg/L, respectively—both of which far exceed national standards for drinking water quality and groundwater quality limits. This widespread phenomenon of exceeding thresholds transcends the boundaries of individual land use types, revealing a strong “source-sink” coupling and pollution accumulation effect beneath both land categories. Although the nitrate concentration in agricultural land is slightly higher, indicating a direct contribution from agricultural nitrogen fertilizer application, the levels in urban land remain exceptionally elevated. This suggests that at the scale of towns and villages, decentralized rural domestic wastewater discharge, livestock waste, and surrounding farmland infiltration runoff have created a regional, inseparable mixed pollution source. This high degree of similarity implies that the evolution of groundwater in the study area has entered a stage of anthropogenic interference characterized by nitrogen enrichment, with the physical boundaries of land use types becoming increasingly blurred in the face of groundwater circulation and the transport of pollutants.

A deeper analysis of the enrichment mechanisms of groundwater components reveals that the overall increase in total dissolved solids (TDS) and total hardness (TH) in urban land is not merely a result of ion accumulation but reflects complex geochemical dynamic processes. The average concentration of bicarbonate (HCO_3^-) in urban land is significantly higher than that in agricultural land, closely related to the oxidation and decomposition of large amounts of organic matter in rural wastewater, which releases CO_2 and drives the dissolution of carbonate minerals in the aquifer. At the same time, the concentrations of Na^+ and Cl^- in urban land are also higher than those in agricultural land. Since there are no industrial discharges in this area, these components are typically considered tracers of human excreta and domestic wastewater. The rise in groundwater mineralization due to domestic sources interacts with the mineralization processes occurring in agricultural land as a result of irrigation return flow and fertilizer leaching. Together, they form the chemical signature of groundwater evolution in the study area, wherein a profound anthropogenic "water chemistry fingerprint" overlays the natural geological background..

3.1.2 Spatial Variability Characteristics

An in-depth interpretation of the spatial variability characteristics further reveals the arrangement patterns and migration features of pollution sources. The extreme variability of K^+ ($\text{CV}=168.32\%$) and F^- ($\text{CV}=108.84\%$) in urban land serves as key evidence for identifying heterogeneous pollution inputs. In the context of no industrial emissions, the occurrence of locally extreme high values of F^- (maximum value of 16.37 mg/L) in urban land is likely derived from local enrichment of fluorine minerals in the geological background, which may have been concentrated and released due to changes in flow patterns caused by groundwater extraction near villages or the alkaline conditions induced by domestic wastewater (He Jin et al., 2010; Wang Xiaoyan et al.). The significant fluctuations of potassium ions (K^+) in residential areas of towns directly point to highly discrete point sources such as rural dry toilets and domestic waste dumping sites (Qingling et al.; Wen et al., 2012; Wagh et al., 2025). In contrast, the coefficients of variation for various ions in agricultural land are relatively low, indicating that agricultural non-point source pollution has formed a more uniform pollution landscape through prolonged irrigation and leaching processes over an extensive cultivation history (Y. Zhang et al., 2024; Yang et al., 2023). This "point-surface combination" structure of pollution presents significant challenges for groundwater remediation in the study area, as it necessitates not only the management of regional non-point source nitrates but also the precise identification and mitigation of highly random, dispersed point sources within the villages and towns.

Table 1 Numerical and Statistical Table of Groundwater Geochemical Parameters in Different Land Use Types in the Study Area

Project	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	F^-	TDS	TH
Minimum	6.35	0.32	53.77	12.95	20.39	111.32	49.16	276.93	13.43	0.42	772.94	227.10

Construction Land	Maximum	8.55	14.73	524.83	261.00	121.74	486.64	280.17	656.21	324.94	16.37	1791.31	572.69
	Mean	7.38	2.36	211.50	96.72	53.29	224.60	125.08	491.74	175.12	3.45	1140.01	405.50
	Standard Deviation	0.59	3.98	112.26	68.99	24.45	106.83	61.57	124.36	65.91	3.76	288.65	104.98
	Coefficient of Variation	7.96	168.32	53.08	71.33	45.89	47.56	49.22	25.29	37.64	108.84	25.32	25.89
Farmland	Minimum	6.60	0.42	71.78	18.72	20.86	81.83	23.70	258.87	39.64	0.70	702.88	212.29
	Maximum	8.55	6.09	373.51	168.70	81.82	471.90	268.94	583.96	307.28	5.06	1573.94	478.88
	Mean	7.42	1.56	166.52	98.13	51.29	192.04	92.15	414.13	205.92	2.24	1018.46	341.17
	Standard Deviation	0.38	1.57	80.63	37.40	15.09	88.13	55.45	113.90	72.31	1.27	211.66	94.96
	Coefficient of Variation	5.10	100.85	48.42	38.11	29.43	45.89	60.17	27.50	35.12	56.76	20.78	27.83

Note: pH is dimensionless, the coefficient of variation is in %, and the units of other parameters are in mg/L.

3.1.3 Comparison of Land Use Types

The chemical components of shallow groundwater in the study area exhibit significant spatial heterogeneity (Figure 3), demonstrating marked anthropogenic driving characteristics, with their biogeochemical processes being influenced by high external nitrogen loads. The observed spatial coupling of low pH and high NO_3^- in the northeastern and central regions indicates a transformation of the groundwater system from a natural evolutionary model to one dominated by intense nitrification processes (Gong Shifei et al., 2025). This reflects the strong conversion potential and proton release capacity of the unsaturated zone and shallow aquifers in response to surface inputs of ammonia nitrogen. Simultaneously, the co-enrichment characteristics of HCO_3^- with typical domestic tracer ions (Na^+ , Cl^-) reveal a deep coupling mechanism of "organic mineralization-water-rock interaction": the biodegradation of exogenous organic carbon significantly alters the acid-base buffering system of the aquifer, inducing the non-natural dynamic dissolution of carbonate minerals. This results in a compensatory increase in mineralization triggered by anthropogenic activities superimposed on natural components.

The spatial decoupling and overlapping relationships of the water chemistry components finely characterize the complex pollution source architecture of the study area. The localized high values of F^- in the southwest show significant independence from the nitrogen pollution-dominated patterns in the central and eastern regions, providing clear spatial evidence for distinguishing geological native backgrounds from subsequent anthropogenic disturbances. In contrast, the banded synergistic distribution of Ca^{2+} and NO_3^- along transportation corridors further confirms that linear infrastructure alters component inputs not only through the application of de-icing agents and leaching of construction materials (Fay & Shi, 2012) but also by reconstructing local recharge pathways, thereby implementing directed reshaping of

groundwater chemical fields. This spatial pattern of randomly distributed point sources, directionally guided line sources, and broadly permeated area sources signifies that the groundwater environment in the study area has entered a highly differentiated stage under the profound intervention of an "urban-rural continuum."

In summary, the chemical characteristics of shallow groundwater in the study area profoundly reveal the composite driving effects of multi-source activities on the water environment in rural towns. The ubiquitous exceedance of NO_3^- in both urban and agricultural land, along with their spatial convergence, indicates that the region has entered a stage of "anthropogenic nitrogen enrichment," where the physical boundaries of land use have become increasingly blurred under strong hydraulic connectivity. Geochemical evolution analysis shows that the organic oxidation induced by domestic wastewater and mineral dissolution have raised the levels of HCO_3^- and mineralization in urban land, while the strong variability of K^+ and F^- intricately characterizes the pollution structure of discrete point sources combined with non-point agricultural sources. Spatially, the nitrification driven by localized high nitrogen loads has led to acidification trends in groundwater around provincial roads, with pathway flow, application of de-icing agents, and lateral recharge from agricultural fields creating a typical Ca^{2+} - NO_3^- superimposition zone within transportation corridors.

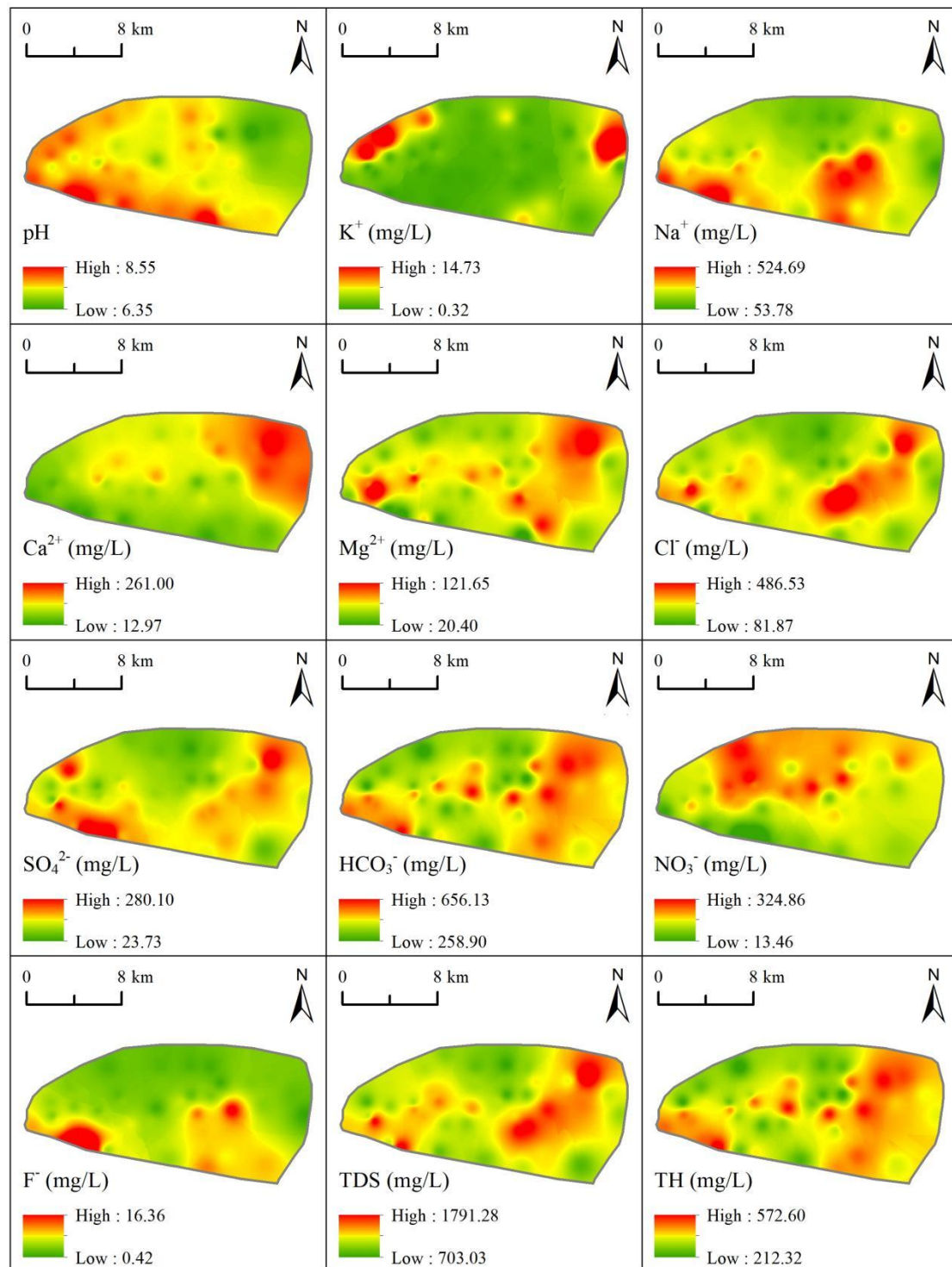


Figure 3: Spatial Distribution Maps of Various Indicators in the Study Area

3.2 Hydrochemical Type

3.2.1 Statistical Differentiation Characteristics of Water Chemical Types

Based on the Shukarev classification method, the statistical results of 41 groundwater samples from the study area reveal a significant shaping effect of land use patterns on water chemical types. In construction areas (22 samples), the water chemical types exhibit a pronounced trend towards "chlorination and sodiumization," with chloride-sodium types represented by $\text{HCO}_3\text{-Cl-Na}$ and $\text{Cl-HCO}_3\text{-Na-Mg}$

dominating (11 samples, accounting for 50%). This region almost exclusively contains high-mineralization Cl^- -Na end-member types. In contrast, the water chemical types in agricultural areas (19 samples) display "mixed and transitional" characteristics. While there are some chloride-type waters, they are more reflective of the sustained dominance of Ca^{2+} and Mg^{2+} ; particularly, among the 9 contaminated water samples where NO_3^- exceeds 25% of milliequivalents, 7 samples (77.8%) are from arable land, forming a unique $\text{NO}_3\text{-Cl-Ca-Mg}$ agricultural leaching type series. The statistics indicate that only one sample of the $\text{HCO}_3\text{-Ca}$ type remains under the original background, suggesting that regional groundwater has generally transitioned away from a single-component phase to a complex mixed system with multiple ion coexistence.

3.2.2 Water Chemical Evolution Trajectories from Piper Trilinear Diagram

The Piper trilinear diagram (Figure 4) visually illustrates the evolution path of groundwater components from their natural background to anthropogenically influenced types (Mandal et al., 2022) (Li Xiaobo & Li Jing) (Piper, 1984). In the cation triangle area, the agricultural samples are primarily concentrated in the transitional zone between Area A (calcium type) and Area B (mixed type), indicating that Ca^{2+} and Mg^{2+} remain predominant. Meanwhile, samples from construction areas have significantly drifted towards the lower right area C (sodium type), accompanied by a notable increase in the diameter of the TDS circles (generally >1000 mg/L). In the anion triangle area, sample points fan out along the HCO_3^- axis towards the Cl^- (and SO_4^{2-}) axis, with construction area samples exhibiting a stronger characteristic of aggregation towards the Cl^- end-member (Area F). When projected onto the central diamond area, it is evident that the water sample points are not limited to the common freshwater Area 1 ($\text{HCO}_3\text{-Ca}$), but are widely distributed across Area 2 (mixed type) and extend into Area 3 (Cl^- -Na type). Notably, samples from construction areas prominently occupy the right side of the diamond diagram, indicative of high salinity, long residence time, or significant anthropogenic inputs, creating a clear spatial separation from the relatively concentrated left and central areas represented by agricultural samples.

3.2.3 Geochemical Processes

The aforementioned statistical differentiation and graphical trajectories profoundly reflect the hydrological geochemical response mechanisms driven by various human activities. The directional evolution of groundwater in construction areas towards the Cl^- -Na type confirms the dual effects of "evaporation concentration-anthropogenic input" during the urbanization process: the coverage of impermeable layers blocks the dilution recharge from atmospheric precipitation, enhances evaporation concentration, and superimposes continuous inputs of Na^+ and Cl^- from domestic wastewater discharge, disrupting the original carbonate balance, thereby leading to rapid accumulation of soluble salt components in shallow aquifers (Kou Yawei et al., 2023). In contrast, the evolution trajectory in agricultural areas is controlled by the "agricultural leaching-cation exchange" mechanism, where long-term

application of nitrogen fertilizers converts to NO_3^- that infiltrates with irrigation water. This process creates an acidic environment that promotes the dissolution of soil carbonate minerals, resulting in the sustained enrichment of Ca^{2+} and Mg^{2+} in groundwater, thereby maintaining the characteristic of mixed cations. Overall, the evolution of groundwater in the study area has bifurcated: one branch is developing towards a high mineralization Cl^- -Na direction controlled by urban drainage, while the other is evolving towards a NO_3^- -Ca·Mg mixed direction controlled by agricultural leaching, marking the replacement of natural water-rock interactions by anthropogenic sources as the dominant factor controlling the evolution of regional water quality (Wang Changshu et al., 2025) (Du Qianqian et al., 2024).

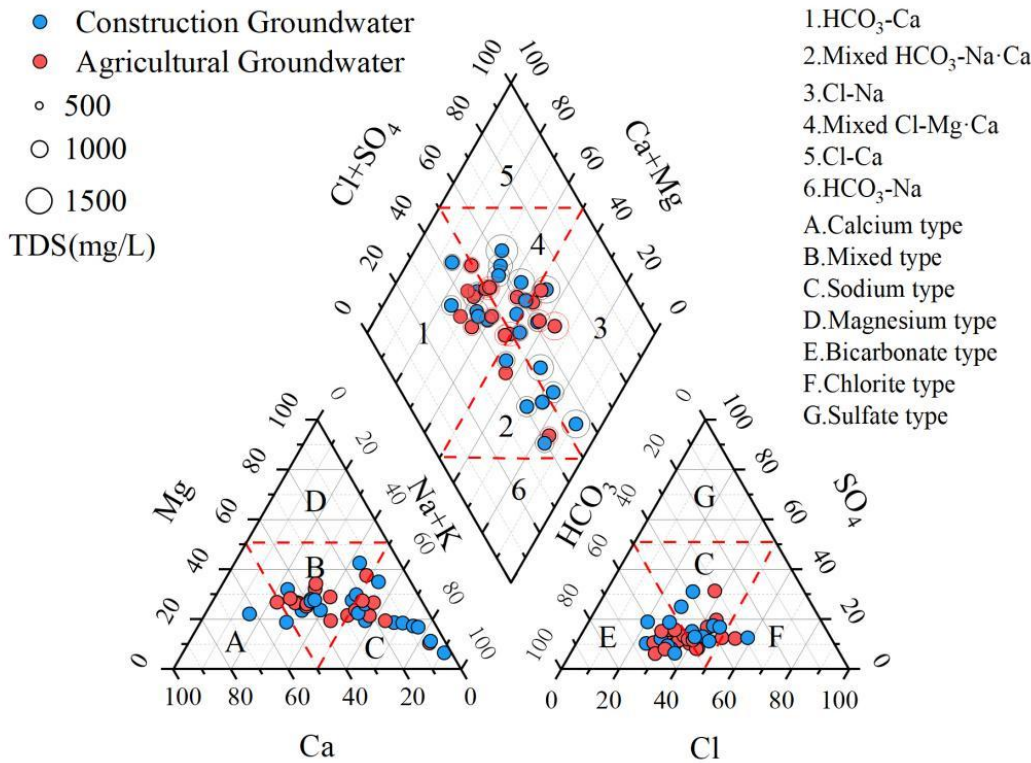


Figure 4: Piper Trilinear Diagram

3.3 Ion Source Analysis

3.3.1 Variable Cluster Analysis and Correlation Heatmap Analysis

The R-type cluster analysis (Figure 5a) divides the 12 water chemistry indicators into three main clusters, clearly depicting the dual-source evolutionary driving model of groundwater in the study area. Cluster I (bottom light blue branch): Comprised of Ca^{2+} and NO_3^- -N, which preferentially cluster with a very short Euclidean distance. This combination exhibits distinct "agricultural characteristics," revealing that the influx of exogenous nitrates into the aquifer induces the co-dissolution of carbonate minerals through nitrification acid production. Cluster II (middle deep blue major branch): Demonstrates a close coupling of Cl^- -TDS and Na^+ - F^- , further converging with SO_4^{2-} , HCO_3^- , and hardness indicators (TH, Mg^{2+}). This cluster represents a salinization process driven by both "evaporation concentration" and "anthropogenic discharge"

during urbanization. Cluster III (top independent branch): The independent clustering of pH and K^+ indicates their control by specific geochemical equilibrium environments or sporadic point source pollution.

The correlation heatmap (Figure 5b) provides quantitative statistical support for the cluster analysis. Cl^- and TDS exhibit the strongest positive correlation ($r=0.88$, $p<0.001$), and the high correlation between Na^+ and Cl^- ($r=0.84$, $p<0.001$) confirms that the accumulation of sodium chloride is a core factor in the increased mineralization of groundwater in the study area. Additionally, Ca^{2+} shows a significant positive correlation with NO_3^- -N ($r=0.50$, $p<0.01$), quantitatively affirming the role of agricultural activities in reshaping the cation composition. Furthermore, pH is significantly negatively correlated with Ca^{2+} ($r=-0.80$) and Mg^{2+} ($r=-0.65$), reflecting the biogeochemical processes where carbonate mineral dissolution releases hardness ions in a slightly acidic environment (due to H^+ produced from agricultural nitrification). Integrating the projections from the Piper trilinear diagram, multivariate statistics, and sample point distribution characteristics, the sampling points across the entire region ($N=41$) can be categorized into the following three evolutionary models, clarifying their spatial affiliations:

Category I: Urban High Salinity Chloride Evolution Type

This category is controlled by Cluster II (Cl^- -TDS and Na^+ - F^- combination) from the variable cluster analysis, with correlation analysis showing a highly significant positive correlation between Cl^- and TDS ($r=0.88$), confirming the salinity accumulation effect during urbanization. In terms of sample distribution, this category occupies 72.7% of the construction land (16/22 groups), while covering only 15.8% of the arable land (3/19 groups), demonstrating a strong spatial aggregation. The formation mechanism primarily results from the coverage of impermeable surface layers, which enhances the evaporation concentration effect of the aquifer, combined with external inputs of Na^+ and Cl^- from urban wastewater leakage, leading to a transition of groundwater from its natural state to a high mineralization "chloride-sodium" type, exhibiting distinct anthropogenic fingerprints characteristic of urbanization.

Category II: Agricultural Nitrification-Calcium Magnesium Leaching Type

The core geochemical logic of this category corresponds to Cluster I (Ca^{2+} and NO_3^- -N), which shows a significant positive correlation in the heatmap ($r=0.50$), revealing a coupled process driven by agricultural activities involving "nitrification-acid production-mineral dissolution." Statistical analysis shows that this category is predominantly occupied by arable land samples, accounting for 68.4% (13/19 groups), while construction land constitutes only 18.2% (4/22 groups, mostly distributed in urban-rural interface zones). This indicates that long-term intensive fertilizer application not only leads to the accumulation of NO_3^- -N but also accelerates the dissolution of carbonate minerals in the soil and aquifer due to the resulting acidic environment, resulting in groundwater in agricultural areas exhibiting distinct

characteristics of "hardening and nitrification."

Category III: Natural Background and Mixed Equilibrium Type

This category features relatively balanced ion indicators, generally low mineralization, and maintains a certain equivalent dominance of HCO_3^- , being the least affected by external anthropogenic disturbances. In terms of sampling distribution, this category represents the smallest proportion in the region, including only 9.1% of construction sites (2/22 groups) and 15.8% of arable sites (3/19 groups). These samples are mostly located at the recharge sources of the study area or in sparsely disturbed edge zones, maintaining a relatively pristine carbonate balance system. It represents residual background areas that have not been fully anthropogenically transformed during the evolution of regional groundwater, serving as an important reference for assessing the degree of human impact on water quality changes.

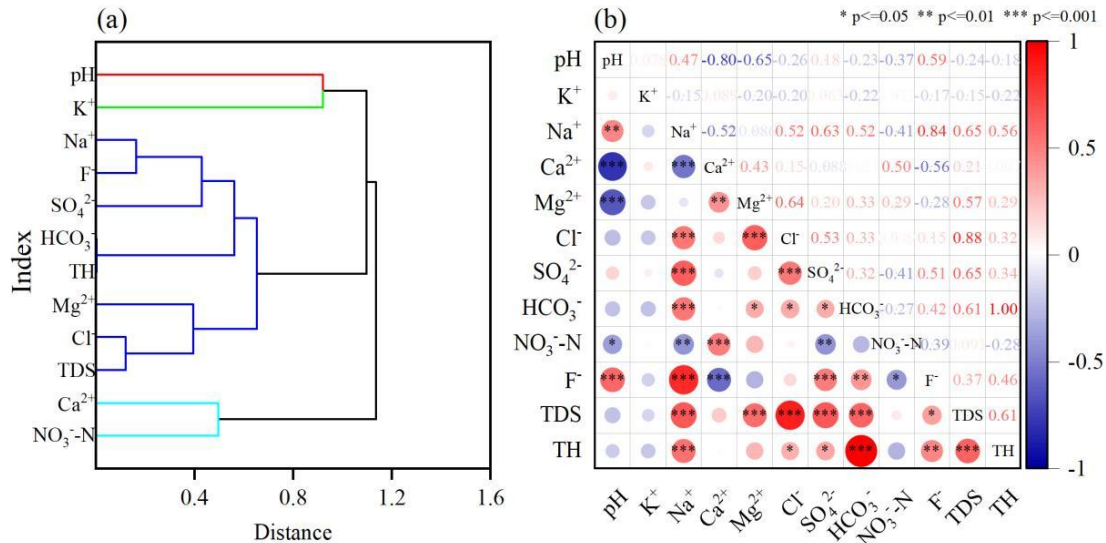


Figure 5 Results of cluster analysis and correlation analysis.

3.3.2 Leaching

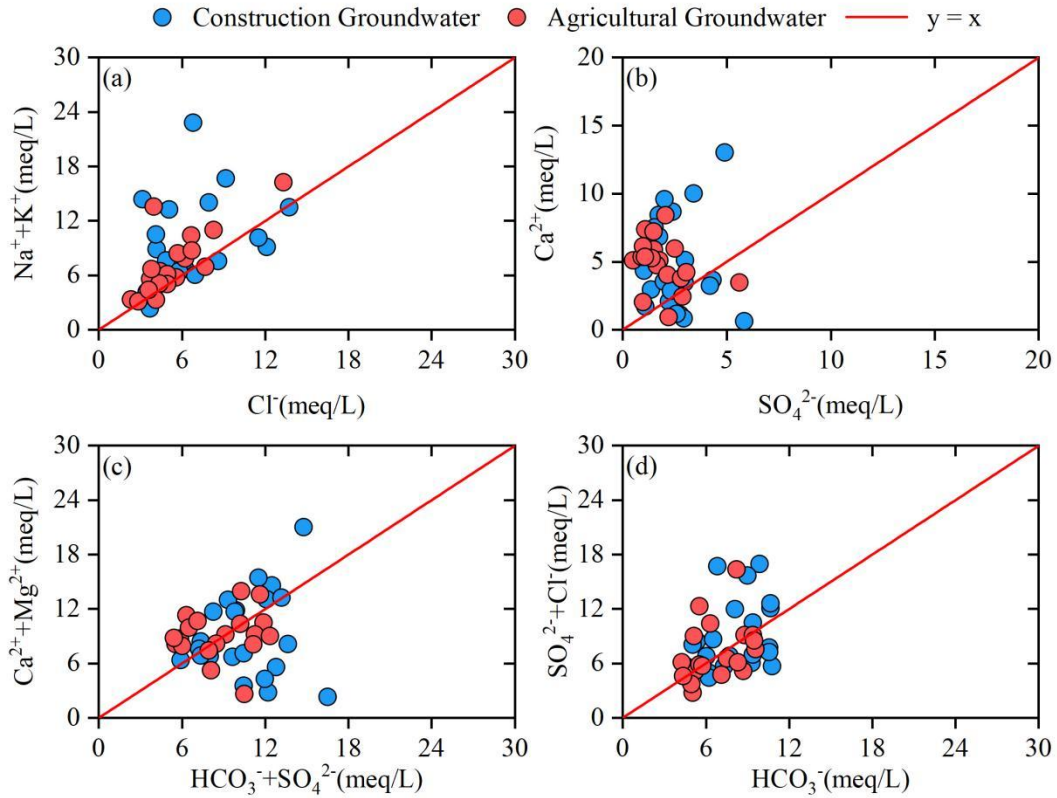


Figure 6: Ion Ratio Plots

Groundwater is hosted in aquifers, where water-rock interactions occur, leading to various physicochemical processes such as the dissolution and hydrolysis of soluble salts and ions in the rocks. The major ion ratio relationships in groundwater can effectively reveal the sources of ions in the water (Mukherjee & Fryar, 2008; Rezaei & Saatsaz, 2021; He Jin et al., 2019). Typically, Na^+ , K^+ , and Cl^- in water bodies primarily originate from the dissolution of rock salt and silicate minerals. By calculating the mg-equivalent concentration ratio of $\gamma(\text{Na}^+ + \text{K}^+)/\gamma(\text{Cl}^-)$, the sources of these ions can be effectively distinguished: when the ratio equals 1, it indicates that the ions mainly derive from the dissolution of rock salt; when the ratio exceeds 1, it suggests the presence of an additional source of Na^+ , usually related to the weathering and dissolution of silicate minerals; conversely, when the ratio is less than 1, it implies an alternative source of Cl^- , often associated with industrial discharges or domestic wastewater inputs (Li Zeyan et al., 2022; Liu Yuanqing et al., 2023). As shown in Figure 5(a), the $\gamma(\text{Na}^+ + \text{K}^+)/\gamma(\text{Cl}^-)$ ratios at 41 monitoring points in the study area exhibit significant spatial differentiation. Among them, 13 points (7 in constructed land and 6 in arable land) have ratios ranging from 0.8 to 1.2, indicating these areas are primarily controlled by water-rock interactions; 2 points (both in constructed land) have ratios less than 0.8, reflecting a dominant input of additional Na^+ ; and 26 points (13 in constructed land and 13 in arable land) have ratios greater than 1.0, indicating an input of exogenous Cl^- . Comprehensive analysis shows that the chemical characteristics of pore water in the study area are not only influenced by the weathering and dissolution of silicate minerals

but more significantly affected by external Cl^- inputs.

The $\gamma(\text{Ca}^{2+})/\gamma(\text{SO}_4^{2-})$ ratio (expressed in mg-equivalent concentrations) is a commonly used ionic ratio indicator in groundwater chemical analysis to reveal the chemical characteristics and genesis mechanisms of water. A ratio close to 1 indicates that Ca^{2+} and SO_4^{2-} mainly originate from the dissolution of gypsum (Zheng Tao et al., 2021; Zou Jiawen et al., 2022). A ratio less than 1 may result from the dissolution of other sulfate minerals or anthropogenic inputs, while a ratio greater than 1 may indicate contributions from the dissolution of calcite or dolomite or the adsorption of Na^+ by clay minerals, releasing Ca^{2+} (Zhou Zhongfa et al., 2018). Figure 5(b) displays significant spatial differentiation in the $\gamma(\text{Ca}^{2+})/\gamma(\text{SO}_4^{2-})$ ratios in the study area: 9.8% (4/41) of sampling points have ratios of 0.8-1.2 (3 in constructed land, 1 in arable land), dominated by gypsum dissolution; 73.2% (32/41) have ratios > 1.2 (14 in constructed land, 16 in arable land), reflecting significant contributions from carbonate dissolution or cation exchange to Ca^{2+} ; and 17.1% (7/41) have ratios < 0.8 (5 in constructed land, 2 in arable land), indicating the dissolution of other sulfate minerals or anthropogenic SO_4^{2-} inputs. The results suggest that the chemical evolution of groundwater is primarily controlled by carbonate dissolution and cation exchange, with gypsum dissolution as a fundamental influence, and local disturbances from human activities.

Ca^{2+} , Mg^{2+} , HCO_3^- , and SO_4^{2-} in groundwater typically stem from the weathering and dissolution processes of carbonate, silicate, and evaporitic minerals (Ekwere et al., 2023). The $\gamma(\text{Ca}^{2+}+\text{Mg}^{2+})/\gamma(\text{HCO}_3^-+\text{SO}_4^{2-})$ ratio can indicate the primary sources of Ca^{2+} and Mg^{2+} . When the ratio is approximately equal to 1, it signifies that calcium and magnesium ions mainly come from the weathering and dissolution of carbonate rocks (Guo Qiaoling et al., 2016). If the ratio exceeds 1, it implies that the calcium and magnesium ions in groundwater are predominantly influenced by the weathering of silicate rocks or the dissolution of evaporites (Zhang et al., 2023). Conversely, if the ratio is less than 1, it indicates that cation exchange or anthropogenic inputs are the main contributing factors to the modified ratios in the study area (Kou et al., 2024). Figure 5(c) illustrates significant spatial differentiation in the $\gamma(\text{Ca}^{2+}+\text{Mg}^{2+})/\gamma(\text{HCO}_3^-+\text{SO}_4^{2-})$ ratios of groundwater: 39% of sampling points have ratios of 0.8-1.2 (9 in constructed land, 7 in arable land), reflecting carbonate weathering-dominated water-rock interactions; 31.7% have ratios > 1.2 (5 in constructed land, 8 in arable land), indicating enhanced contributions from silicate weathering or evaporite dissolution; and 29.3% have ratios < 0.8 , possibly influenced by cation exchange or anthropogenic inputs. This ternary distribution confirms the coexistence of various geochemical processes, including carbonate leaching, silicate weathering, and evaporite dissolution. The concentration of high ratio points in constructed land and arable land suggests that human activities (such as irrigation return flow and fertilizer leaching) indirectly promote the weathering and dissolution of silicate and evaporitic minerals by altering water-rock interaction conditions.

The $\gamma(\text{Cl}^- + \text{SO}_4^{2-})/\gamma(\text{HCO}_3^-)$ ratio can assess the chemical characteristics, genesis, and evolution processes of the water body, determining the sources of Cl^- , SO_4^{2-} , and HCO_3^- in groundwater. When this ratio exceeds 1, it indicates evaporation concentration effects or anthropogenic pollution, or that the dissolution of evaporitic rocks or sulfate minerals leads to the enrichment of Cl^- and SO_4^{2-} (Gong Yabing et al., 2022); conversely, when the ratio is less than 1, it indicates a relative dominance of HCO_3^- , signifying that carbonate dissolution is the controlling water-rock interaction process (Gong Yabing et al., 2022; Liu Bing et al., 2021). Figure 5(d) shows that approximately 36.5% of the sampling points in the study area (7 in constructed land, 8 in arable land) have ratios between 0.8 and 1.2, reflecting a relative balance between carbonate and silicate rock weathering and dissolution; whereas points with ratios greater than 1.2 (indicating silicate dissolution or anthropogenic/evaporative influences) and less than 0.8 (indicating dominance of carbonate dissolution) each account for 31.7%, with a roughly equal distribution among the two land use types (both 8 in constructed land and 5 in arable land). This statistical distribution characteristic objectively indicates that the $\gamma(\text{Cl}^- + \text{SO}_4^{2-})/\gamma(\text{HCO}_3^-)$ ratio does not effectively differentiate between constructed and agricultural land, and its spatial differentiation is not significant, suggesting that this ratio mainly reflects the spatial heterogeneity of regional hydrogeochemical processes rather than direct impacts from land use types.

In summary, constructed land is more significantly influenced by anthropogenic activities such as industrial discharge, domestic sewage, and fertilizers, manifested by characteristics such as $\gamma(\text{Na}^+ + \text{K}^+)/\gamma(\text{Cl}^-) < 0.8$, $\gamma(\text{Ca}^{2+})/\gamma(\text{SO}_4^{2-}) < 0.8$, and $\gamma(\text{Cl}^- + \text{SO}_4^{2-})/\gamma(\text{HCO}_3^-) > 1.2$, indicating anthropogenic ion inputs as the main driver of its hydrochemical evolution; while arable land is primarily characterized by natural mineral dissolution and the indirect promotion of weathering processes influenced by human activities, with ratios such as $\gamma(\text{Ca}^{2+})/\gamma(\text{SO}_4^{2-}) > 1.2$, $\gamma(\text{Ca}^{2+} + \text{Mg}^{2+})/\gamma(\text{HCO}_3^- + \text{SO}_4^{2-}) > 1.2$, and $\gamma(\text{Cl}^- + \text{SO}_4^{2-})/\gamma(\text{HCO}_3^-) < 0.8$, indicating that natural mineral dissolution and indirectly driven weathering processes from irrigation return flow and fertilizer leaching are its core characteristics. The differences between constructed land and arable land in hydrochemical characteristics fundamentally reflect the direct alteration of groundwater chemistry by human activities (in constructed land) versus the indirect influences under natural process dominance (in arable land).

3.4 Factor Controlling Analysis

3.4.1 Identification of Controlling Factors

In probabilistic graphical models, Gibbs graph analysis serves not only for estimating the posterior distributions of variables within these models but also finds application in hydrochemical analysis, where it identifies the dominant controlling factors of ionic composition in water bodies (e.g., rock weathering, evaporation concentration, or atmospheric precipitation). Typically, a ratio of less than 0.5 indicates that the water body is primarily influenced by rock weathering, while a ratio greater

than 0.5 suggests that evaporation concentration is the main influencing factor. When both the ratio and Total Dissolved Solids (TDS) levels are low, it indicates that atmospheric precipitation predominantly affects the water body (Gibbs). The results of the Gibbs graph analysis (Figure 7) indicate that the TDS concentration of groundwater in the constructed land of the study area ranges from 750 to 1800 mg/L, while the TDS concentration in agricultural land varies between 700 and 1600 mg/L, reflecting an overall moderate salinity characteristic. From the distribution of ionic ratios, there are 24 sampling points with a $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio greater than 0.5 (14 in constructed land and 10 in agricultural land) and 17 sampling points with a ratio less than 0.5 (8 in constructed land and 9 in agricultural land). These points are mainly distributed in the "rock weathering type" and "evaporation concentration type" areas, clearly deviating from the "atmospheric precipitation type" region.

The analysis of the $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ratio reveals that there are 11 sampling points with a ratio greater than 0.5 (6 in constructed land and 5 in agricultural land) and 30 sampling points with a ratio less than 0.5 (16 in constructed land and 14 in agricultural land), with most of these points located in the "rock weathering type" area. In summary, the comprehensive results from the Gibbs graph analysis indicate that the chemical characteristics of this shallow groundwater are primarily controlled by rock weathering, with some influence from evaporation concentration. Notably, the groundwater sampling points in constructed land are more concentrated in the evaporation concentration area, suggesting that human activities may have exacerbated the evaporation concentration effects. This finding aligns with research results from the midstream oasis area of the Heihe River Basin (Wang Guohua et al., 2022), underscoring the significant impact of human activities on the hydrochemical characteristics of groundwater.

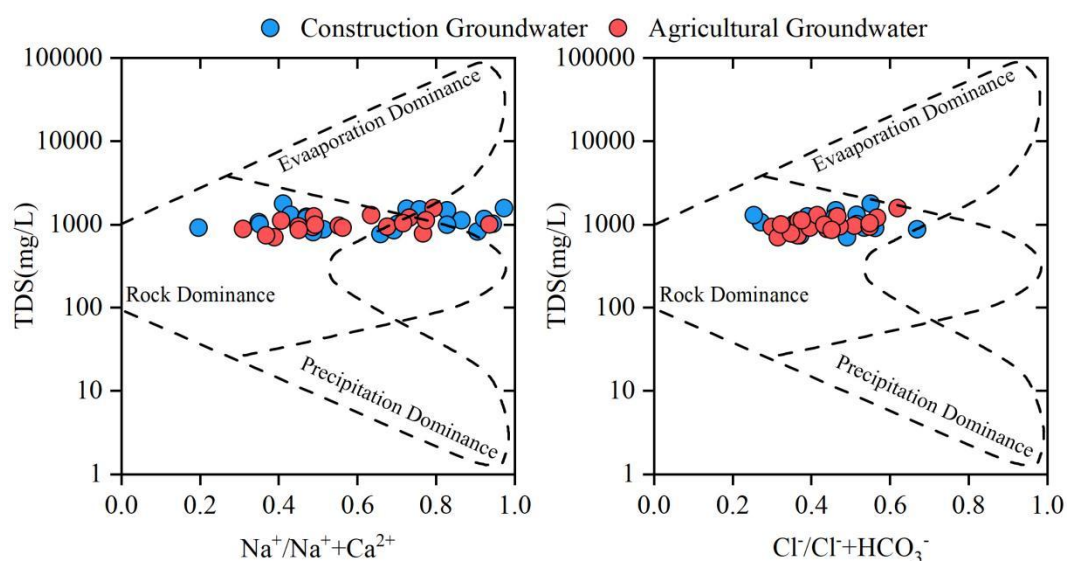


Figure 7: Gibbs Diagram of Groundwater in the Fluvial-Lacustrine Deposit Area

The ion end-member ratio plot (Figure 8) is an important tool for analyzing hydrochemical characteristics and their origins. By comparing the proportional

relationships of different ions, it reveals the underlying causes of hydrochemical features, distinguishes the influences of various rock types (Zeng Jiao et al., 2024), and assesses the impact of human activities (Xu Panpan et al.), thereby guiding water resource management and conservation. Commonly used relationships such as $n(\text{HCO}_3^-)/n(\text{Na}^+) - n(\text{Ca}^{2+})/n(\text{Na}^+)$ and $n(\text{Mg}^{2+})/n(\text{Na}^+) - n(\text{Ca}^{2+})/n(\text{Na}^+)$ qualitatively identify the effects of carbonate, silicate, and evaporite weathering on groundwater solutes (Gaillardet et al., 1999; Gan et al., 2018). Results indicate that agricultural land predominantly aligns along the Carbonate arrow, exhibiting a high $\text{Ca}^{2+}/\text{Na}^+$ ratio and a moderate $\text{HCO}_3^-/\text{Na}^+$ ratio. The $\text{Mg}^{2+}/\text{Na}^+$ ratio shows a significant positive correlation with the $\text{Ca}^{2+}/\text{Na}^+$ ratio, reflecting a natural mineral dissolution process primarily driven by carbonate weathering, wherein natural factors play a dominant role (Davraz & Aksever, 2025). In contrast, constructed land deviates from the Carbonate line, displaying a low $\text{Ca}^{2+}/\text{Na}^+$ ratio and some points shifting towards the Evaporite region. The $\text{Mg}^{2+}/\text{Na}^+$ ratio is more dispersed, deviating from the natural linear relationship, indicating the combined effects of silicate or evaporite weathering and human interference, which have altered hydrological conditions and ion sources (Du Qianqian et al., 2024). In summary, the chemical characteristics of groundwater in agricultural areas maintain a consistent dominance of natural processes, while those in constructed land exhibit greater complexity due to human interference. The differing characteristics between the two are fundamentally rooted in the distinction between natural mineral weathering and the coupled evolution of anthropogenic and natural processes.

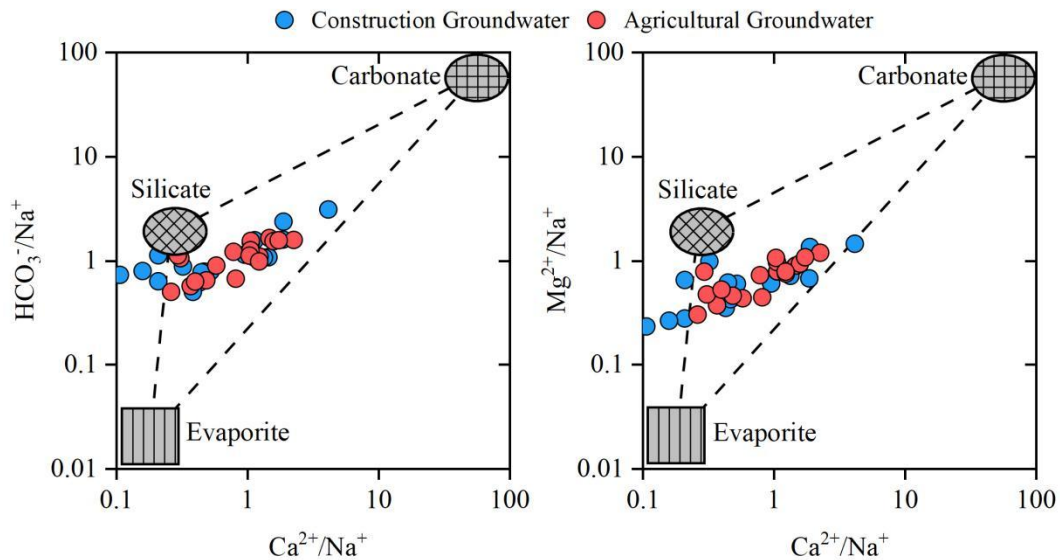


Figure 8: Ion End-Member Ratio Plots

3.4.2 Mineral Saturation Index Analysis

The Saturation Index (SI) analysis is a key method for evaluating the chemical equilibrium state between aqueous solutions and specific minerals (Zhang Yiwu et al., 2025; Promilton et al., 2025). The SI value reflects the saturation degree of groundwater concerning minerals: it is generally accepted that when $-0.5 \leq \text{SI} \leq 0.5$, the mineral is in equilibrium or near equilibrium; when $\text{SI} > 0.5$, the mineral is supersaturated and

tends to precipitate; and when $SI < -0.5$, the mineral is undersaturated and continues to dissolve (Zhao Guangshuai et al., 2024).

From the study presented in Figure 8 (a~f), significant differences in carbonate minerals (calcite, dolomite) were observed under different land use types. The SI values of groundwater in agricultural areas are predominantly greater than 0.5 (supersaturated), attributed to the enrichment of Ca^{2+} and HCO_3^- resulting from agricultural activities such as fertilization and irrigation, which significantly enhance the activity product of these ions. In contrast, SI values for constructed land tend to fall within the equilibrium range of -0.5 to 0.5 or approach undersaturation. For sulfate minerals (gypsum), the SI values in agricultural land range between -0.5 and 0.5 , indicating a near-equilibrium state, which results from the synergistic balancing effect of SO_4^{2-} provided by fertilizer decomposition and Ca^{2+} in the soil. Conversely, gypsum SI values in constructed areas are generally less than -1.0 , exhibiting strong undersaturation, primarily due to the relative reduction of Ca^{2+} concentrations caused by human activities. Regarding halide minerals (rock salt, fluorite), the SI values in agricultural areas are closer to the equilibrium range, while those in constructed land typically fall below -1.0 (strong undersaturation). Significant changes in ion composition (e.g., decreased Ca^{2+} and increased F^-) lead to a stronger tendency for dissolution of these minerals in such environments.

Analysis of the correlation between fluoride ion concentration (F^-) and fluorite saturation index (SI) in Figure 8 (g) reveals key characteristics of the fluoride chemistry behavior in the study area: (1) Fluoride concentration is significantly negatively correlated with the saturation index ($R^2 = 0.93$), indicating that high-fluoride waters are more likely to be in a significant undersaturated state, reflecting the dominant role of calcium fluoride dissolution equilibrium; (2) Over 85% of the sample points are distributed in the undersaturated zone ($SI < -0.5$), demonstrating the general potential for sustained dissolution of fluorides in these waters, possibly related to primary leaching of fluorides in the aquifer or specific geochemical environments; (3) Some highly mineralized waters ($TDS > 5$ g/L) show a trend of shifting toward equilibrium or supersaturation, suggesting that increased salinity may influence the solubility of fluorides through ionic effects. This finding provides a scientific basis for the management of high-fluoride groundwater, particularly in areas with $F^- > 10$ mg/L, where adjusting calcium ion concentrations can promote the transition of calcium fluoride to a supersaturated state ($SI > 0.5$), facilitating precipitation and effectively removing fluoride, thereby supporting the remediation of shallow high-fluoride groundwater in river-lake depositional areas.

Overall, the SI values of groundwater in agricultural areas are generally higher than those in constructed land, demonstrating a greater tendency to achieve mineral equilibrium or supersaturation ($SI > -0.5$). In contrast, minerals in constructed land are often in a state of significant undersaturation or approaching saturation, reflecting the

essential differentiation in hydrochemical processes between the two land uses. This differentiation arises from agricultural inputs reinforcing the dissolution-precipitation dynamic balance of natural minerals, leading mineral components closer to saturation, while intense human interference in constructed land disrupts the original ionic balance, causing most native minerals to remain in an undersaturated dissolved state. This difference indicates that agricultural management should consider the potential impact of mineral precipitation on soil permeability, while constructed land requires attention to prevent ongoing mineral dissolution that may lead to imbalances in groundwater chemical components, thus providing a scientific basis for the classified management of regional groundwater environments.

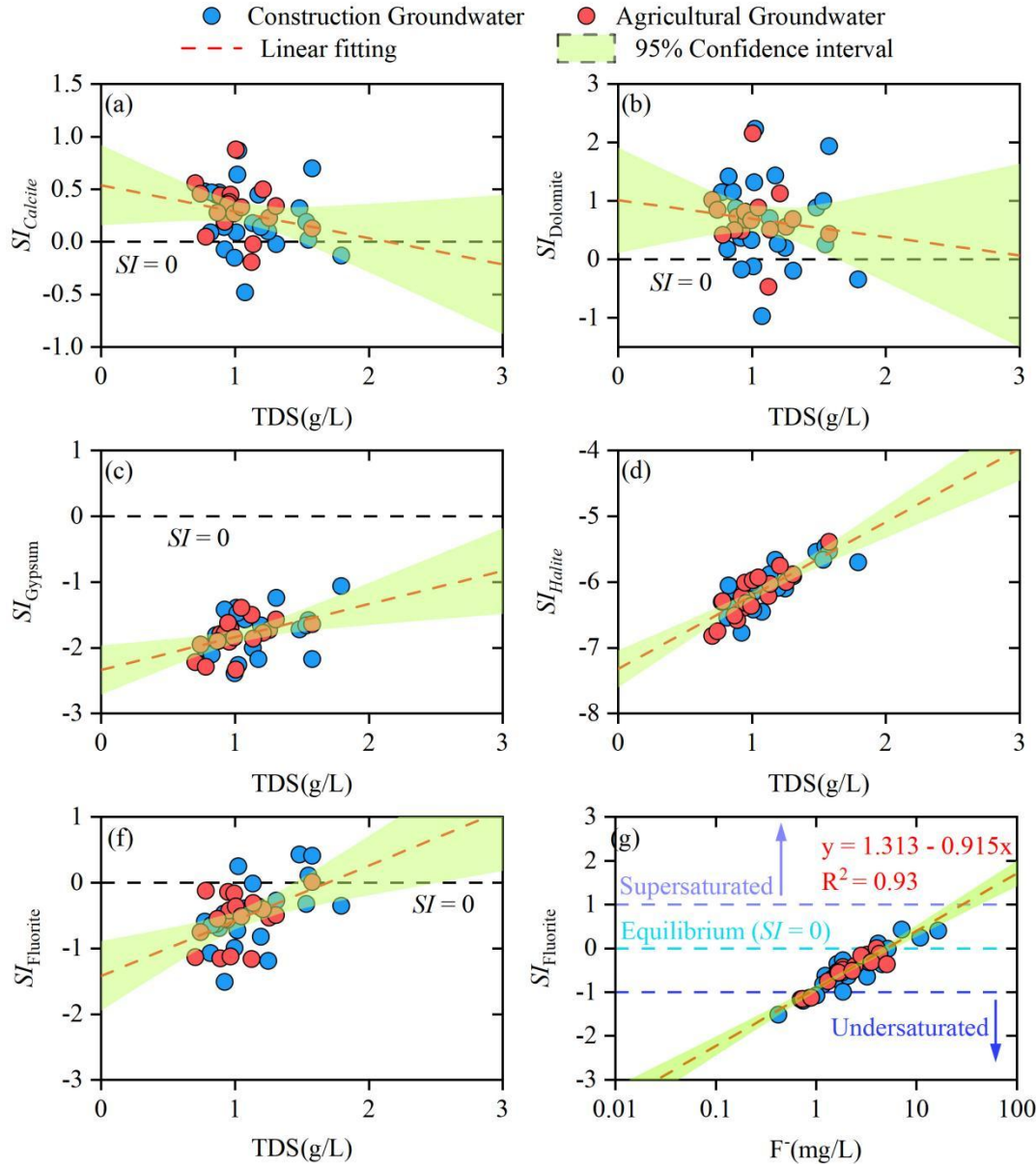


Figure 8: Mineral Saturation Indices

3.4.3 Cation Exchange

Cation exchange is an important chemical process between groundwater and aquifer minerals. By analyzing the direction and intensity of cation exchange, it is

possible to infer the chemical equilibrium state of groundwater, leading to a better understanding of the processes and mechanisms underlying groundwater chemical evolution (Huang Junchen et al., 2023).

Figure (a) shows a significant linear relationship between the total cations in groundwater ($\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$) and the total anions ($\text{HCO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-$) with an R^2 value of 0.946, indicating overall charge balance. However, agricultural land primarily clusters near the fitted line, while constructed land shows significant deviation. This reflects a more uniform ionic source in agricultural land, leading to a more stable charge balance; conversely, constructed land likely experiences additional ionic inputs that result in charge imbalance, complicating the hydrochemical processes.

Figure (b) presents an analysis of ion exchange characteristics, with agricultural land predominantly distributed near the line $y = -x$ (theoretical line for simple ion exchange), indicating that its hydrochemical processes are mainly dominated by the exchange of Na^+ with $\text{Ca}^{2+}/\text{Mg}^{2+}$ (Zhang Ziyang et al., 2024). In contrast, constructed land deviates significantly from this line, suggesting that, in addition to ion exchange, it is also influenced by complex processes such as evaporation concentration and anthropogenic inputs, weakening the dominance of ion exchange.

Figure (c) reveals that the $\text{Ca}^{2+}/\text{Na}^+$ ratio in agricultural land primarily concentrates between 0.5 and 1.5 (with an average of approximately 1.0), while several points in constructed land exhibit ratios <0.5 (with a minimum around 0.2). This indicates relative enrichment of Ca^{2+} in agricultural land, whereas Na^+ is relatively enriched in constructed land (Ewusi et al., 2022; Qu et al., 2022). Coupled with Figure (d) (the relationship between CAI-2 and TDS), the CAI-2 values in constructed land significantly increase with rising TDS, indicating that as TDS increases, the ion exchange process of Na^+ displacing Ca^{2+} is enhanced, further exacerbating Na^+ enrichment. Conversely, the CAI-2 values in agricultural land show little variation with TDS, reflecting a lesser influence of TDS on its cation composition, leading to greater stability.

In summary, the chemical characteristics of groundwater in agricultural areas are predominantly driven by natural/agricultural processes, exhibiting stable charge balance and relative enrichment of Ca^{2+} . In contrast, constructed land is significantly affected by human interference, leading to potential charge imbalance and relative enrichment of Na^+ , with ion exchange processes intensifying as TDS increases. The fundamental difference between the two lies in the enhancement of natural hydrochemical processes by agricultural activities versus the disruption of these processes by anthropogenic activities.

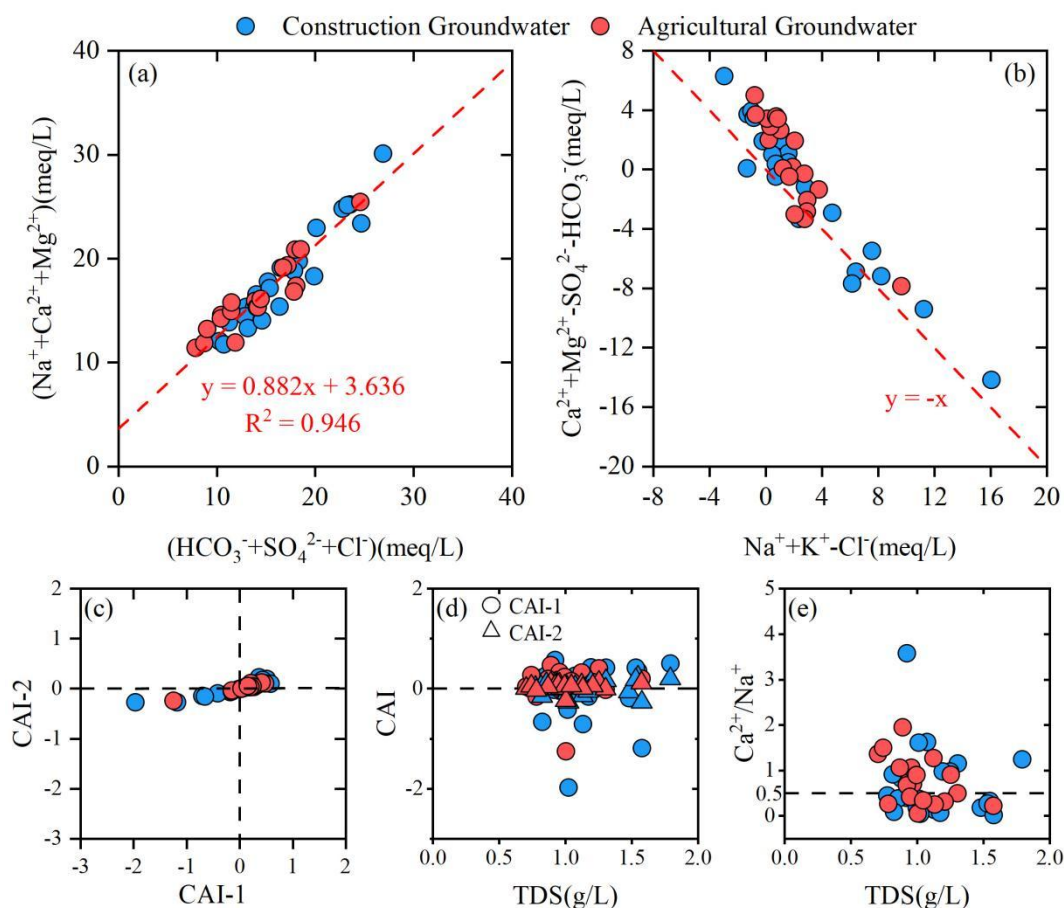


Figure 10: Cation Exchange Ratio and Chloride-Alkali Index Distribution Plots

3.4.4 Human Activity Impact

The study area, as a typical river-lake sedimentary region, possesses high-quality land resources that provide an important foundation for agricultural development. At the same time, agricultural activities and human disturbances have become the dominant factors influencing changes in groundwater chemical components. Through the analysis of the ratios $\gamma(\text{SO}_4^{2-})/\gamma(\text{Na}^+)$ and $\gamma(\text{NO}_3^-)/\gamma(\text{Na}^+)$, it is possible to accurately identify the impact characteristics of different human activities: industrial activities primarily contribute SO_4^{2-} , while NO_3^- and Cl^- mainly originate from agricultural activities (Li Zhenghong et al., 2018; Liu Haoyang et al., 2024).

Figure 11(a) shows that groundwater sampling points in the study area are concentrated in regions influenced by agricultural activities, with only one sampling point located in an industrial activity zone, indicating that the application of agricultural fertilizers is the main source of pollution. Furthermore, when combined with Figure 11(b), it can be observed that, aside from some points located in Zone D (domestic sewage area), the sampling points are primarily concentrated in Zone E (manure input area), confirming that the application of domestic wastewater and livestock manure is a key pathway for groundwater contamination in the study area. Overall, the chemical characteristics of groundwater in the study area are primarily controlled by domestic wastewater and agricultural non-point source pollution.

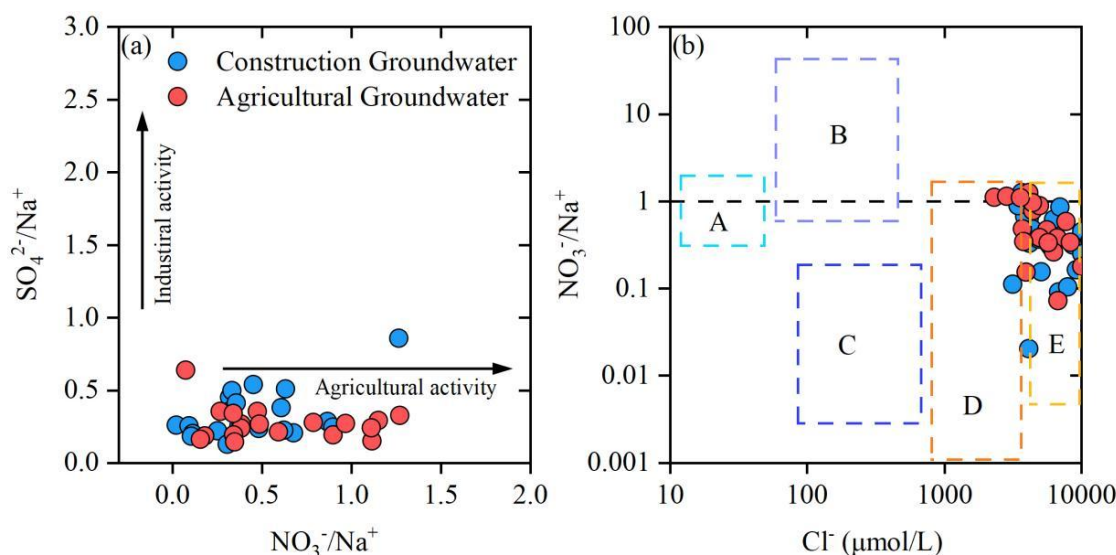


Figure 11: Ratio plots of $\gamma(\text{SO}_4^{2-})/\gamma(\text{Na}^+)$ and $\gamma(\text{NO}_3^-)/\gamma(\text{Na}^+)$, as well as $\gamma(\text{Cl}^-)/\gamma(\text{Na}^+)$ and $\gamma(\text{NO}_3^-)/\gamma(\text{Na}^+)$.

3.5 Analysis of Variance (ANOVA)

To ensure the validity of the results from the analysis of variance, this study examined the underlying assumptions. The results of the normality test (Shapiro-Wilk test) indicated that the data for Na^+ , Ca^{2+} , and NO_3^- (33.3% of the indicators) conformed to a normal distribution, while the data for K^+ , Mg^{2+} , HCO_3^- , F^- , Cl^- , and SO_4^{2-} (66.7% of the indicators) showed that at least one group did not meet the normality assumption. Although some indicators did not fully satisfy the normality assumption, considering the Central Limit Theorem, parametric tests can still be robust when the sample size is sufficiently large ($n > 30$). The results of the homogeneity of variance test (Levene's test) indicated that eight indicators (Na^+ , K^+ , Mg^{2+} , HCO_3^- , F^- , Cl^- , SO_4^{2-} , NO_3^- ; 88.9% of the indicators) satisfied the homogeneity of variance assumption, with only Ca^{2+} failing to meet this criterion ($p = 0.0431 < 0.05$). Overall, the vast majority of indicators satisfied the homogeneity of variance assumption, allowing for the conduct of ANOVA.

Building on prior spatial interpolation, correlation analysis, clustering analysis, and a series of hydrochemical causative diagrams, this study further conducted variance analysis (ANOVA) to quantitatively test the differences in groundwater chemical components under two land use types: construction land and cropland (Figure 12). The conclusions are as follows:

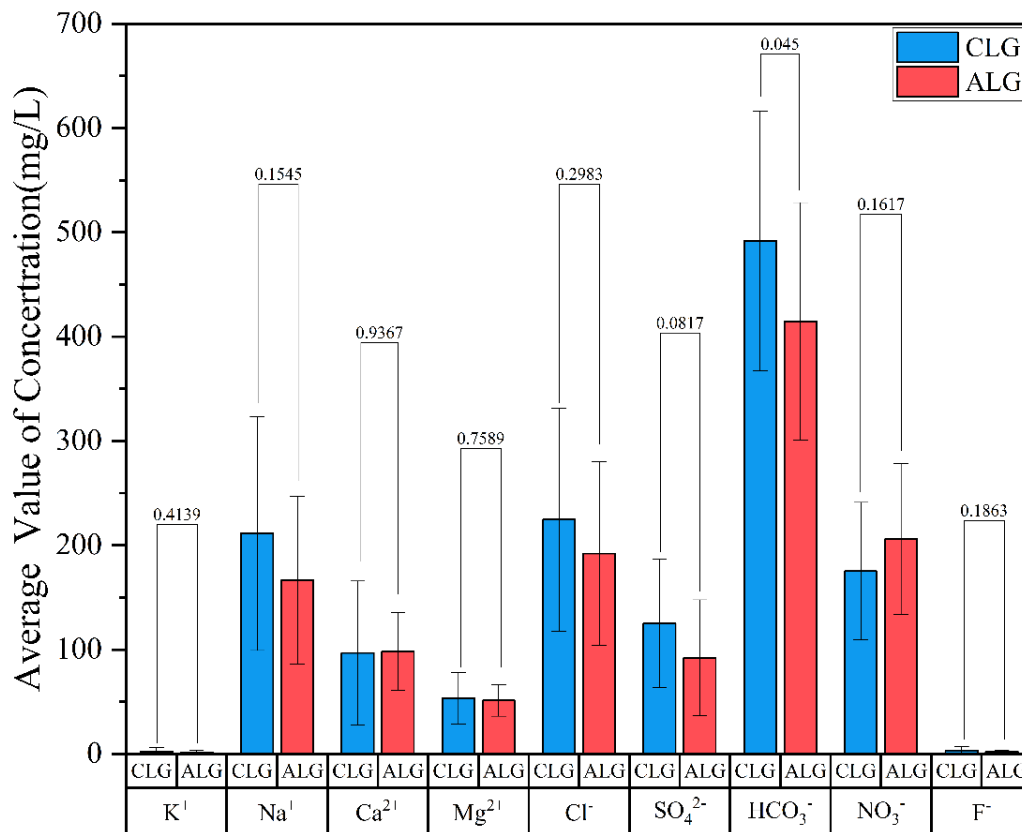


Figure 12: Variance Analysis of Groundwater Samples from Construction Land and Cropland in the Study Area

The ANOVA results indicate that, despite the preliminary spatial interpolation maps showing some spatial heterogeneity in the hydrochemical components of the study area, the groundwater framework components between construction land and cropland exhibit high homogeneity and similarity from a statistical perspective. Among the nine indicators tested, only HCO₃⁻ showed a significant statistical difference ($P = 0.045 < 0.05$), with the mean value for construction land (491.74 mg/L) significantly higher than that for cropland (414.13 mg/L). Combined with prior ion ratio maps and mineral saturation index analyses, this suggests that construction land (village and residential areas) is more significantly impacted by domestic sewage discharge or leaching of building materials, resulting in greater disturbance to the groundwater carbonate system. Additionally, SO₄²⁻ exhibited a "borderline significant" characteristic ($P = 0.082$), indicating that construction land may have more non-agricultural sulfur source inputs (e.g., domestic coal combustion or wastewater from washing).

It is noteworthy that although earlier clustering analyses and spatial distribution maps indicated fluctuations in ion levels between the two land uses, the ANOVA confirmed that major ions such as Na⁺, Ca²⁺, Mg²⁺, and Cl⁻ showed no significant differences between the two land uses ($P > 0.05$). This conclusion aligns closely with the analyses from Gibbs diagrams and ion end-member ratio plots, further confirming that the fundamental hydrochemical characteristics of groundwater in the study area are primarily controlled by natural evolutionary processes. Although changes in land use

have altered water quality responses on a local scale, they have not disrupted the overall patterns controlled by regional geological background.

Regarding the indicative agricultural activity parameter NO_3^- , although the mean value for cropland (205.92 mg/L) is higher than that for construction land (175.12 mg/L), the statistical test did not reach significance ($P = 0.162$). This suggests that under the complex habitat conditions of the area, the contributions of intensified agricultural fertilization to groundwater and the nitrogen sources generated by village domestic wastewater are intertwined, resulting in a "similar but different" fingerprint effect on the groundwater chemistry between the two typical land uses. In summary, the chemical evolution of groundwater in the study area displays a pattern dominated by geological background with localized anthropogenic disturbances. Future precise control measures should focus on abnormal fluctuations in carbonate balance around construction land and the cumulative effects of nitrogen in agricultural areas.

4 Conclusion

(1) The hydrochemical characteristics are significantly correlated with land use, exhibiting distinct differentiation patterns. The shallow groundwater in the study area is slightly alkaline, primarily characterized by HCO_3^- -Ca and Cl^- -Na types. Groundwater in construction areas is driven by domestic sewage and industrial point source pollution, resulting in high total dissolved solids (TDS) (mean 1140 mg/L), excessive Na^+ (40.9%), and high variability coefficients for K^+ and F^- . In contrast, groundwater in agricultural land is influenced by non-point source pollution from agricultural fertilization, with prominent NO_3^- contamination (mean 205.9 mg/L). The enrichment of Ca^{2+} and NO_3^- along transportation corridors reflects the cumulative impact of traffic emissions.

(2) The driving mechanisms of hydrochemical evolution present a binary differentiation of "direct transformation" and "indirect facilitation." The core of the evolution in construction land is the direct input of anthropogenic ions (such as Na^+ , SO_4^{2-} , Cl^-), primarily driven by industrial wastewater and domestic point sources. In contrast, agricultural land is mainly influenced by the dissolution of natural minerals (carbonates and silicates), supplemented by indirect weathering processes driven by irrigation return flow and fertilizer leaching. This differentiation essentially highlights the contrast between chemically driven industrial/domestic inputs from point source pollution and the agricultural ecological chemical cycles driven by non-point source pollution.

(3) Ion ratio characteristics clearly identify the contribution proportions of anthropogenic disturbance and natural mineral dissolution. High TDS sampling points are predominantly associated with Cl^- -Na types, indicating that anthropogenic salt inputs obscure the natural chemical background. Through ion ratio diagram analysis, samples from construction areas cluster towards regions of anthropogenic input, while samples from agricultural land are distributed near natural weathering and agricultural

leaching lines. This regional clustering pattern provides critical thermodynamic and statistical evidence for tracing groundwater pollution sources.

(4) The pattern is dominated by natural background influences, with localized anthropogenic disturbances leading to differentiation. Among the nine primary indicators, only HCO_3^- shows significant differences related to land use types ($P < 0.05$), with construction land significantly higher than agricultural land, reflecting the specific impacts of urban domestic discharge and building leachate. However, no significant differences were found for the remaining indicators such as Na^+ , Ca^{2+} , Cl^- , and NO_3^- ($P > 0.05$). This further confirms that the groundwater in the study area is primarily controlled by natural evolutionary processes such as mineral weathering and cation exchange. Although changes in land use have produced differentiated disturbances in local water quality, they have not fundamentally altered the overall hydrochemical evolutionary framework determined by geological background.

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Competing interests

The authors declare no competing interests.

Data availability statement

The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

Sampling authorization statement

Prior to sample collection, all necessary permissions and access rights were obtained. Informed consent was granted by local well owners and residents for collecting samples from domestic and agricultural irrigation wells. Access and sampling from hydrogeological exploration boreholes were authorized by the local water resources management department and relevant geological survey project authorities. No protected land was breached during the fieldwork.

References

- A., G., S., Reddy, Boraa, SaibabaGanji, & Sudarshan. (2012). Hydrogeochemical characterization of contaminated groundwater in Patancheru industrial area, southern India. *Environmental Monitoring & Assessment*.
- Aktar, S., Islam, A. R. M. T., Moniruzzaman, M., Siddique, M. A. B., Masud, M. A. A., Islam, A., Pal, S. C., Rao, N. S., & Maallick, J. (2025). Fluoride enrichment and hydrogeochemical characteristics in coastal multi-aquifers: Implications for public health and nutrition. *Physics and Chemistry of the Earth*, 139, 103924-103924. <https://doi.org/10.1016/j.Pce.2025.103924>

875 An, L., Zhao, Q., Ye, S., Liu, G., & Ding, X. (2012). Chemical characteristics and formation processes
876 of shallow groundwater in the Yellow River Delta. *Environmental Science*, 33(02), 370-378.
877 <https://doi.org/10.13227/j.hjxx.2012.02.005>

878 B., R., N., S. R., & N., D. R. E. (2022). Groundwater quality monitoring for assessment of pollution
879 levels and potability using WPI and WQI methods from a part of Guntur district, Andhra
880 Pradesh, India. *Environment, development and sustainability*, 25(12), 14785-14815.
881 <https://doi.org/10.1007/s10668-022-02689-6>

882 Bei, E., Wu, X., Qiu, Y., Chen, C., & Zhang, X. (2019). A Tale of Two Water Supplies in China: Finding
883 Practical Solutions to Urban and Rural Water Supply Problems. *Accounts of Chemical Research*.

884 Benadela, L., Bekkoussa, B., & Gaidi, L. (2022). Multivariate analysis and geochemical investigations
885 of groundwater in a semi-arid region, case of superficial aquifer in Ghriss Basin, Northwest
886 Algeria. *Journal of Groundwater Science and Engineering*, 10(3), 233-249.

887 Chen, H., Guo, L., Li, J., Lin, X., Zhang, T., & Zhang, Q. (2024). Hydrochemical characteristics of
888 shallow groundwater in the North Henan Plain based on principal component analysis. *Earth
889 and Environment*, 52(03), 386-396. <https://doi.org/10.14050/j.cnki.1672-9250.2023.51.019>

890 Cheng, Y. P., Zhang, F. W., Dong, H., & Wen, X. R. (2024). Groundwater and environmental challenges
891 in Asia. *Journal of Groundwater Science and Engineering*, 12(2), 223-236.

892 Choudhary, S., Rao, N. S., Chaudhary, M., & Das, R. (2024). Assessing sources of groundwater quality
893 and health risks using graphical, multivariate, and index techniques from a part of Rajasthan,
894 India. *Groundwater for Sustainable Development*, 27(000).

895 Das, R., Rao, N. S., Sahoo, H. K., & Sakram, G. (2023). Nitrate contamination in groundwater and its
896 health implications in a semi-urban region of Titrol block, Jagatsinghpur district, Odisha, India.
897 *Physics and Chemistry of the Earth*, 132(000), 15.

898 Davraz, A., & Aksever, F. (2025). Geochemical processes in groundwater chemistry: a case study.
899 *Carbonates & Evaporites*, 40(3).

900 Du, Q., Zhang, B., Dai, M., Sun, J., & Wang, Y. (2024). Hydrochemical characteristics and ion sources
901 of surface water and groundwater under different land use types. *Journal of Tianjin Normal
902 University (Natural Science Edition)*, 44(04), 53-61. <https://doi.org/10.19638/j.issn1671-1114.20240408>

904 Ekwere, A. S., Kudamnya, E. A., & Oyonga, O. A. O., Emmanuel E. (2023). Hydrogeochemistry, ionic
905 speciation, controlling processes and agricultural suitability of groundwaters in sections of the
906 semi-arid basement complex of north-central Nigeria. *solid earth sciences*, 8(3), 208-218.

907 Ewusi, A., Sunkari, E. D., Seidu, J., & Coffie-Anum, E. (2022). Hydrogeochemical characteristics,
908 sources and human health risk assessment of heavy metal dispersion in the mine pit water-
909 surface water-groundwater system in the largest manganese mine in Ghana. *Environmental
910 Technology & Innovation*.

911 Gaillardet, J., Dupré, B., Louvat, P., & Allègre, C. J. (1999). Global silicate weathering and CO₂
912 consumption rates deduced from the chemistry of large rivers. *Chemical Geology*, 159(1), 3-30.

913 Gan, Yiqun, Zhao, Ke, Deng, Yamin, Liang, Xing, Teng, & Wang. (2018). Groundwater flow and
914 hydrogeochemical evolution in the Jiangnan Plain, central China. *HYDROGEOLOGY
915 JOURNAL*.

916 Gibbs, R. J. Mechanisms Controlling World Water Chemistry. *Science*, 170.

917 Gong, S., Zhai, Z., Ding, W., Zhang, Z., Wang, T., & Li, H. (2025). Characteristics of manure pollution
918 from livestock in the water source area of the South-to-North Water Diversion Project and
919 potential for fertilizer substitution. *Journal of Chinese Eco-Agriculture*, 33(02), 324-337.
920 <https://link.cnki.net/urlid/13.1432.S.20241115.1447.001>

921 Gong, Y., Gong, X., Xu, S., Tang, X., Su, D., & Wu, X. (2022). Hydrochemical characteristics and
922 evolution analysis of groundwater in Southern Jiangsu. *Geological Review*, 68(6), 12.

923 Guo, Q., Xiong, X., & Jiang, J. (2016). Hydrochemical characteristics of surface water and groundwater
924 in the Kuye River Basin. *Environmental Chemistry*, 35(7), 1372-1380.

925 He, J., Zhang, F., Han, S., Li, X., Yao, X., & Zhang, H. (2010). Distribution characteristics and genesis
926 of high-fluoride groundwater in Northern China. *Geological Journal of China*, 37(03), 621-626.

927 He, J., Zhang, Y., Zhao, Y., Han, S., Liu, Y., & Zhang, T. (2019). Hydrochemical characteristics and
928 controlling factors of groundwater in the Xia Latou Basin along the Xianshui River fault zone.
929 *Environmental Science*, 9.

930 Hu, S., Wu, G., Wu, B., & Gao, F. (2023). Hydrochemical evolution and causes of groundwater in the
931 plain area of Fuhai City over the past 20 years. *Acta Scientiae Circumstantiae*, 43(05), 79-88.
932 <https://doi.org/10.13671/j.hjkxxb.2022.0430>

933 Huang, J., Yan, B., & Liu, P. (2023). Hydrochemical characteristics of the Bangong Lake Basin and
934 analysis of main controlling factors. *Geological and Resource Studies*, 32(4), 453-461.

935 Jiang, F., Zhou, J., Zhou, Y., Sun, Y., Han, S., & Lu, H. (2023). Hydrochemical characteristics and
936 pollution source identification of groundwater in the Baiyi Basin plain area. *Environmental*
937 *Science*, 44(11), 6050-6061. <https://doi.org/10.13227/j.hjlx.202211078>

938 Kammoun, Siwar, Trabelsi, Rim, Re, Viviana, Zouari, Kamel, Henchiri, & Jihed. (2018). Groundwater
939 quality assessment in semi-arid regions using integrated approaches: the case of Grombalia
940 aquifer (NE Tunisia). *Environmental Monitoring & Assessment An International Journal*.

941 Kou, X., Zhao, Z., Duan, L., & Sun, Y. (2024). Hydrogeochemical Behavior of Shallow Groundwater
942 around Hancheng Mining Area, Guanzhong Basin, China. *Water* (20734441), 16(5).

943 Kou, Y., Xu, Z., Zhang, H., He, G., Yin, D., Ren, H., & Wu, T. (2023). Hydrochemical characteristics
944 and genesis analysis of shallow groundwater in the Daiwenkou chemical cluster area, Taian,
945 Shandong. *Land and Resources of Shandong*, 39(06), 15-25.

946 Lall, U., Josset, L., & Russo, T. (2020). A Snapshot of the World's Groundwater Challenges. *Annual*
947 *Review of Energy and the Environment*, 45, 171-194.

948 Li, M., Wu, P., Ma, Z., Lv, M., Yang, Q., & Duan, Y. (2022). The decline in the groundwater table depth
949 over the past four decades in China simulated by the Noah-MP land model. *Journal of*
950 *Hydrology*, 607(000), 127551.

951 Li, X., & Li, J. Hydrochemical characteristics and influencing factors of shallow groundwater in the mid-
952 lower reaches of the Dawen River Basin. *Research on Environmental Science*, 37(5), 1015-
953 1026.

954 Li, Z., Cao, W., Wang, Z., Li, J., & Ren, Y. (2022). Hydrochemical characteristics and irrigation
955 suitability analysis of shallow groundwater in the Hetao Irrigation District, Inner Mongolia.
956 *Modern Geology*, 002, 036.

957 Li, Z., Zhang, Y., Hu, B., Wang, L., Zhu, Y., & Li, J. (2018). Impact of human activities on nitrate-
 958 nitrogen pollution in shallow groundwater in Tokto County, Inner Mongolia. *Journal of Earth*
 959 *Sciences*, 039(003), 358-364.

960 Liu, B., Wang, H., Jiang, Y., Jia, Y., Yang, Y., Gu, H., & Xun, H. (2021). Study on the transformation
 961 relationships of different water bodies in the Donggong River Basin based on hydrochemistry
 962 and hydrogen-oxygen isotopes. 1979-1982.

963 Liu, H., Liu, W., Yang, G., Wang, J., Zhang, H., Zhang, H., Liu, D., Li, J., & Ma, L. (2024). Distribution
 964 characteristics and mechanism of major hydrochemical ions in the Qingshui River.
 965 *Environmental Science*, 45(12), 7134-7145. <https://doi.org/10.13227/j.hjxx.202312275>

966 Liu, W., Su, Y., Yang, R., & Lü, X. (2009). Temporal and spatial changes of hydrochemical characteristics
 967 and salinity of groundwater in Minqin. *Environmental Science*, 30(10), 7.

968 Liu, Y., Zhou, L., Lü, L., Li, W., Wang, X., Deng, Q., Zheng, Y., & Li, C. (2023). Hydrochemical
 969 characteristics and controlling factors of pore water in the upper and middle reaches of the
 970 Muwen River. *Environmental Science*.

971 Ma, T., Sun, S., Fu, G., Hall, J. W., Ni, Y., He, L., Yi, J., Zhao, N., Du, Y., & Pei, T. Pollution exacerbates
 972 China's water scarcity and its regional inequality. *Nature Communications*.

973 Mandal, U., Dhar, A., Panda, S. N., & Sena, D. R. (2022). Correction to: Spatiotemporal evaluation and
 974 assessment of shallow groundwater quality for irrigation of a tropical coastal groundwater basin.
 975 *Environmental Science and Pollution Research*, 1-1.

976 Mei, S. (2023). Hydrochemical characteristics and health risk assessment of shallow groundwater in the
 977 Weigang River Basin [Master's thesis].
 978 <https://link.cnki.net/doi/10.27431/d.cnki.gxnyu.2023.000071>

979 Meng, C., Zheng, X., & Wang, C. (2019). Distribution characteristics and formation mechanisms of high-
 980 fluoride groundwater in Pingdu City. *Journal of Ocean University of China: Natural Science*
 981 *Edition*, 49(11), 9.

982 Moussa, A. B., Zouari, K., & Marc, V. (2011). Hydrochemical and isotope evidence of groundwater
 983 salinization processes on the coastal plain of Hammamet–Nabeul, north-eastern Tunisia.
 984 *Physics & Chemistry of the Earth Parts A/b/c*, 36(5-6), 167-178.

985 Mukherjee, A., & Fryar, A. E. (2008). Deeper groundwater chemistry and geochemical modeling of the
 986 arsenic affected western Bengal basin, West Bengal, India. *Applied Geochemistry*, 23(4), 863-
 987 894.

988 N., S. R., A., D., & L., S. (2022). Estimation of groundwater pollution levels and specific ionic sources
 989 in the groundwater, using a comprehensive approach of geochemical ratios, pollution index of
 990 groundwater, unmix model and land use/land cover – A case study. *Journal of Contaminant*
 991 *Hydrology*, 248, 103990-103990. <https://doi.org/10.1016/j.Jconhyd.2022.103990>

992 Piper, A. M. (1984). A graphic procedure in the geochemical interpretation of water - analyses.
 993 *Neurochemistry International*, 6(1), 27-39.

994 Promilton, A. A. A., Ravindran, A. A., Pitchaimani, V. S., Kingston, J. V., & Karuppannan, S. (2025).
 995 Comprehensive hydrogeochemical characterization and seasonal water quality index analysis
 996 for sustainable groundwater management in Valliyur region, Southern Tamil Nadu, India.
 997 *Scientific Reports*, 15(1).

998 Qingling, Z., Qingcai, L. I., Hua, B. U., & Miao, W. Hydrochemical Characteristics and Cause Analysis
999 of Karst Water in Middle and South Shandong Province: Case of Shuangcui Karst Water System.
1000 Journal of China Hydrology.

1001 Qu, S., Duan, L., Shi, Z., Liang, X., Lv, S., Wang, G., Liu, T., & Yu, R. (2022). Hydrochemical
1002 assessments and driving forces of groundwater quality and potential health risks of sulfate in a
1003 coalfield, northern Ordos Basin, China. *The Science of the total environment*, 835, 155519.

1004 Ren, T. (2019). Early Cretaceous sedimentary sequences and lithofacies paleogeography of the Laiyang
1005 Group in the eastern margin of the Jiaolai Basin. *Land and Resources of Shandong*, 35(07), 38-
1006 45.

1007 Rezaei, A., & Saatsaz, M. (2021). Large-scale climate indices teleconnections with hydrochemical and
1008 isotopic characteristics of a karst spring using wavelet analysis. *Environmental Earth Sciences*,
1009 80(8), 1-15.

1010 Sacks, L. A., & Tihansky, A. B. (1996). Geochemical and isotopic composition of ground water, with
1011 emphasis on sources of sulfate, in the upper Floridan Aquifer and intermediate aquifer system
1012 in southwest Florida.

1013 Su, H. M., Zhang, F. W., Hu, J. Y., Lei, J. F., Zuo, W., Yang, B., & Liu, Y. H. (2024). Identified the
1014 hydrochemical and the sulfur cycle process in subsidence area of Pingyu mining area using
1015 multi-isotopes combined with hydrochemistry methods. *Journal of Groundwater Science and*
1016 *Engineering*, 12(1), 62-77.

1017 Sun, Y., Gao, B., Ma, L., Yang, H., & Wang, D. (2024). Comprehensive study of multiple water quality
1018 evaluation methods based on principal component analysis—A case study of shallow
1019 groundwater in the middle reaches of the Yitong River. *Geological and Resource Studies*, 33(06),
1020 813-821. <https://doi.org/10.13686/j.cnki.dzyzy.2024.06.009>

1021 Wagh, V., Raut, V., Tadse, K., & Sahu, U. (2025). Hydrogeochemical evaluation of groundwater in
1022 Deccan Volcanic Province, Maharashtra, India through GIS and statistical techniques. *Scientific*
1023 *Reports*, 15(1), 32329-32329. <https://doi.org/10.1038/s41598-025-17782-9>

1024 Wang, C., Zhao, H., Zhu, C., Yu, Y., Mao, J., & Wu, J. (2025). Study on the distribution characteristics
1025 of salt ions in different land use types of the Hetao Irrigation District. *China Rural Water and*
1026 *Hydropower*, 12, 108-113. <https://link.cnki.net/urlid/42.1419.tv.20241220.1125.014>

1027 Wang, G., Zhang, Y., Gou, Q., Zhang, Z., & Sun, J. (2022). Analysis of hydrochemical characteristics of
1028 surface water and groundwater at the oasis edge in the middle reaches of the Heihe River Basin.
1029 *Geographic Science*, 42(10), 11.

1030 Wang, J., Yu, F., Tian, P., Pan, D., Li, T., & Sun, M. (2023). Analysis of hydrochemical characteristics
1031 and controlling factors of phreatic water in the alluvial plain of the South Taihang Mountains.
1032 *Resources and Environment in Arid Areas*, 37(05), 130-138.
1033 <https://doi.org/10.13448/j.cnki.jalre.2023.121>

1034 Wang, L., Ren, T., Huang, Y., Zhu, X., Zhang, G., & Zhang, X. (2024). Geochemical characteristics and
1035 significance of dinosaur eggs in the Qingdao area of the Jiaolai Basin. *Land and Resources of*
1036 *Shandong*, 40(10), 18-25.

1037 Wang, X., Zhang, M., Yin, D., Ma, T., Han, S., Wu, X., Wang, W., & An, Y. (2024). Distribution
1038 characteristics and genesis analysis of fluoride in groundwater in the middle reaches of the

1039 Heihe River mainstream. Environmental Science, 1-13.
 1040 <https://doi.org/10.13227/j.hjxx.202405061>
 1041 Wen, X., Diao, M., Wang, D., & Gao, M. (2012). Hydrochemical characteristics and salinization
 1042 processes of groundwater in the shallow aquifer of Eastern Laizhou Bay, China. *Hydrological*
 1043 *Processes*, 26(15), 2322-2332.
 1044 Wen, Y., Qiu, J., Cheng, S., Xu, C., & Gao, X. (2020). Hydrochemical Evolution Mechanisms of Shallow
 1045 Groundwater and Its Quality Assessment in the Estuarine Coastal Zone: A Case Study of Qidong,
 1046 China. *International Journal of Environmental Research and Public Health*, 17(10), 3382.
 1047 Xu, P., Qian, H., Zhang, Q., Zang, Y., Liu, Y., & Dong, J. (2024). Hydrological geochemical mechanisms
 1048 and secondary environmental challenges of groundwater in southern Jingyang, Shaanxi.
 1049 *Geological Bulletin*, 1-17. <https://link.cnki.net/urlid/11.4648.P.20250320.1417.020>
 1050 Yang, D., Yang, Y., & Hua, Y. (2023). Source Analysis Based on the Positive Matrix Factorization Models
 1051 and Risk Assessment of Heavy Metals in Agricultural Soil. *Sustainability* (2071-1050), 15(17).
 1052 Yong-Hong, S. U., Qi, F., Gao-Feng, Z., Jian-Hua, S. I., & Yan-Wu, Z. (2007). Identification and
 1053 Evolution of Groundwater Chemistry in the Ejin Sub-Basin of the Heihe River, Northwest China.
 1054 *Pedosphere*, 17(3), 331-342.
 1055 Zeng, J., Li, H., Xu, H., Chu, H., Zhao, Z., Pang, G., Wang, L., & Kong, L. (2024). Genesis analysis and
 1056 water quality assessment of hydrochemical characteristics in the Laiwu-Pingdu area of
 1057 Shandong Province. *Marine Geology Frontiers*, 40(11), 15-24.
 1058 Zhang, J., Shi, H., Yu, S., Wang, D., & Zhu, G. (2024). Evaluation of shallow groundwater quality in the
 1059 Haimen area of Nantong based on principal component analysis and water quality identification
 1060 index method. *Groundwater*, 46(05), 16-20. <https://doi.org/10.19807/j.cnki.DXS.2024-05-005>
 1061 Zhang, L., Dong, D., Lv, S., Zhang, J., Yan, M., Han, G., & Li, H. (2023). Hydrochemical
 1062 Characterization and Quality Assessment of Groundwater in the Southern Plain of Hebei
 1063 Province, China. *Water* (20734441), 15(21).
 1064 Zhang, M. H., Zhou, S. Y., Liu, D. D., Zhang, Y., Zhang, Y. X., Chen, X., Wang, H. W., Li, B., Kang, W.,
 1065 & Yi, B. (2024). Characteristics and genesis of groundwater salinization in coastal areas of the
 1066 Lower Reaches of Oujiang Basin. *Journal of Groundwater Science and Engineering*, 12(2), 190-
 1067 204.
 1068 Zhang, Y., Xiao, Y., Yang, H., Wang, L., Wang, J., Hu, W., Wang, N., Xu, Z., Liu, G., Chen, F., & Guo,
 1069 X. (2024). Hydrogeochemical features, genesis, and quality appraisal of confined groundwater
 1070 in a typical large sedimentary plain. *Water environment research : a research publication of the*
 1071 *Water Environment Federation*, 96(8), e11088. <https://doi.org/10.1002/wer.11088>
 1072 Zhang, Y., Zeng, J., Zhang, Z., Peng, B., Wang, J., Qiao, X., Lin, S., & Yu, J. (2025). Hydrochemical
 1073 characteristics and genesis analysis of groundwater in the coastal area of Sandu Bay, Ningde.
 1074 *East China Geology*, 46(04), 552-565. <https://doi.org/10.16788/j.hddz.32-1865/P.2024.07.003>
 1075 Zhang, Z., Fu, Y., Wang, N., Tan, J., & Liu, Y. (2024). Hydrochemical characteristics and influencing
 1076 factors of surface water and groundwater in the mountainous area of the Danjiang Basin.
 1077 *Environmental Science*, 45(4), 2107-2117.
 1078 Zhao, G., Su, C., Huang, Q., Zhu, Y., Yang, Y., Luo, F., & Li, X. (2024). Characteristics of mineral
 1079 saturation index, Sr²⁺, and SO₄²⁻ sources of strontium-rich karst water in Xintian County, Hunan

1080 Province, and its development potential. Geological Journal of China, 51(03), 1046-1058.
1081 <https://link.cnki.net/urlid/11.1167.P.20220516.1817.004>
1082 Zheng, T., Jiao, T., Hu, B., Gong, J., Hou, X., & Wang, H. (2021). Hydrochemical characteristics and
1083 genesis analysis of groundwater in the central region of the Guo River Basin. Environmental
1084 Science.
1085 Zhou, Z., Zhang, J., Pan, Y., Yin, C., Wang, Y., & Tian, Z. (2018). Major ion chemical characteristics and
1086 source analysis of surface water and groundwater in the Shuanghe Cave system. Science and
1087 Technology and Engineering, 18(6), 9.
1088 Zou, J., Liu, F., & Zhang, J. (2022). Hydrochemical characteristics and genesis of shallow groundwater
1089 in typical receiving areas of the South-to-North Water Diversion Project. China Environmental
1090 Science, 005, 042.