

Article

Hydrochemical Characteristics and Controlling Factors of Groundwater in a Typical High-Water-Table Coal Mining Subsidence Area: A Case Study of the Luwa Mining Subsidence Area, Jining City, China

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Abstract

Understanding the hydrochemical characteristics of groundwater in coal mining subsidence areas is of critical scientific significance for water environment protection and ecological restoration in mining regions. A systematic hydrochemical campaign was undertaken in the Luwa collapse zone (Jining city, Shandong Province) to decipher the composition, evolutionary behavior, and governing factors of groundwater within a high-water-table subsidence context. The analytical protocol comprised three complementary components: conventional hydrochemical profiling, ion-ratio-based source identification, and multi-variate statistical modeling. The findings revealed that the groundwater in the study area was weakly alkaline ($\text{pH} = 7.33 \pm 0.217$), with total dissolved solids (TDS) ranging from 1180 to 2280 mg/L, and all sampled sites exceeded the Class III groundwater quality standard of China. Na^+ , SO_4^{2-} , and Cl^- were identified as the predominant pollutants, with exceedance rates of 91.3%, 95.7%, and 91.3%, respectively, which were primarily attributed to coal mine drainage and domestic sewage input. The groundwater chemical composition was governed by the combined effects of rock weathering, evaporation–concentration processes, and anthropogenic activities. Specifically, Na^+ and Cl^- originated mainly from the dissolution of silicate minerals and halite, as well as domestic sewage input; SO_4^{2-} was primarily controlled by evaporite dissolution and industrial wastewater discharge; carbonate and silicate mineral weathering was identified as the primary source of Ca^{2+} and Mg^{2+} ; and NO_3^- was predominantly influenced by agricultural activities. Principal component analysis (PCA) extracted three major controlling factors shaping the groundwater hydrochemistry in this area, namely: (1) evaporite dissolution and sewage input, (2) carbonate dissolution and pH buffering processes, and (3) agricultural input. This study reveals a dual-driven evolutionary model of groundwater in high-water-table coal mining subsidence areas, characterized by “natural enrichment superimposed by anthropogenic input,” whose work contributes to the knowledge base for sustainable groundwater stewardship and contamination risk reduction in mining-affected areas with analogous conditions.



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Keywords: coal mining subsidence area; groundwater; hydrochemical characteristics; controlling factors; principal component analysis

1. Introduction

Groundwater is a critical component of the global hydrological cycle, accounting for more than 30% of the total terrestrial freshwater storage [1]. It serves as a primary drinking water source for populations worldwide and plays an irreplaceable role in sustaining river runoff, lake wetlands, and ecosystem health [2]. The resource value and ecological functions of groundwater depend not only on its quantity but also, more critically, on its quality. In natural settings, the chemistry of groundwater is continuously modified by water–rock reactions with the surrounding aquifer framework during subsurface transit, during which solute components are progressively enriched and transformed, giving rise to specific hydrochemical facies and spatial gradients in total dissolved solids (TDS) [3]. However, over recent decades, driven by population growth and intensified industrial and agricultural activities, anthropogenic inputs have introduced substantial amounts of natural substances and artificial contaminants into groundwater systems through non-natural pathways, profoundly altering the intrinsic evolutionary trajectories of groundwater chemical composition [4,5]. Elucidating the spatiotemporal distribution, migration, and transformation patterns of groundwater chemical constituents, and unraveling the controlling mechanisms underlying hydrochemical evolution under the dual forcing of natural processes and anthropogenic activities, represent a frontier research topic in contemporary international hydrogeochemistry [6]. Such investigations bear significant scientific value and practical implications for groundwater pollution prevention and control, sustainable water resource utilization, and ecological security assurance.

Research on groundwater hydrochemical evolution has progressed from qualitative descriptions to quantitative simulations, and from single-process analyses to multi-process coupling. The gravity-driven groundwater flow system theory, represented by the Tóthian framework, has not only deepened our understanding of the driving forces and distribution patterns of groundwater but has also greatly advanced research on groundwater chemical evolution [7]. Contemporary studies on groundwater hydrochemical evolution are largely grounded in the Tóthian theory, and have systematically elucidated the hydrochemical evolution mechanisms—including leaching, precipitation, and cation exchange–adsorption processes—that occur during groundwater flow, by integrating advanced techniques such as isotopic tracing, elemental geochemical analyses, and numerical modeling [8–10]. With respect to the identification of controlling factors, it is generally accepted that regional groundwater hydrochemical evolution is governed by the synergistic effects of hydrogeological conditions, physicochemical properties of aquifer media, organic matter content, and microbial activity, and at broader spatiotemporal scales, is further modulated by climate change and anthropogenic disturbance [11,12].

In recent years, the hydrogeochemical effects of coal mining subsidence areas (CMSA) have progressively attracted research attention. Coal mining activities in high-water-table mining areas induce extensive land subsidence and surface water inundation, thereby altering the original surface water–groundwater transformation relationships and rendering the hydrochemical evolutionary processes in subsidence areas considerably more complex [13]. Existing hydrochemical studies in mining areas have demonstrated that subsidence ponding water and shallow groundwater are closely hydraulically connected, and both generally conform to evolutionary patterns of cognate natural water bodies [14]. For instance, research conducted in the Huainan CMSA, China, revealed that Na^+ is the dominant cation and HCO_3^- the dominant anion in subsidence ponding water, river water, and shallow groundwater, with the hydrochemical type being predominantly $\text{HCO}_3\text{--Na}$, and the chemical composition primarily controlled by silicate weathering and evaporite dissolution [15]. Nevertheless, existing studies on water environments in CMSA have largely focused on groundwater quality characteristics, pollution assessments, and water

recharge sources, whereas systematic investigations into the hydrochemical evolutionary characteristics and their governing factors in subsidence-area groundwater remain comparatively scarce. This knowledge gap constrains the effective implementation of groundwater protection and remediation efforts in CMSA.

The Luwa CMSA is a typical high-water-table subsidence zone within the Jining coalfield, Shandong Province, China. It is characterized by complex hydrogeological conditions, with multiple aquifer systems developed, including the Quaternary, Jurassic, and Carboniferous–Permian sequences. Long-term mining activities have resulted in the structural disturbance of underground aquifers, enhancing the hydraulic connectivity of structural conduits such as faults and collapse columns, which potentially facilitates hydraulic interconnection and hydrochemical mixing among previously relatively independent aquifer systems [16]. However, systematic studies specifically addressing the hydrochemical characteristics and controlling factors of groundwater in the Luwa CMSA have been rarely documented to date. In view of this, the present study takes the Luwa CMSA as the research site, and integrates hydrochemical analysis, ion ratio plots, and multivariate statistical techniques to systematically characterize the hydrochemical composition and characteristics of groundwater in the subsidence area. On this basis, multiple analytical tools—including multivariate statistical methods (correlation analysis and factor analysis), Gibbs diagrams, ion ratio coefficient analyses, and hydrogeochemical modeling—are employed to identify the predominant factors governing groundwater hydrochemical characteristics in the study area, and to elucidate the mechanisms by which mining activities influence groundwater chemical evolution processes. The findings of this research are expected to provide a scientific foundation for the rational utilization of groundwater resources, water environment protection, and ecological restoration in the Luwa CMSA, while also offering reference and insights for groundwater hydrochemical studies in analogous high-water-table CMSA.

2. Materials and Methods

2.1. Study Area Description

The Luwa CMSA is located in Yutai County, Jining City, in the southwestern part of Shandong Province, China, with geographic coordinates ranging from approximately 35°04′ to 35°07′ N latitude and 116°31′ to 116°35′ E longitude. Situated in the hinterland of the southwestern Shandong Plain, the area belongs to the Huang-Huai-Hai alluvial plain geomorphic unit. The terrain is generally flat, with ground elevations ranging from 34 to 36 m above sea level. The surface water system is well developed, with the Nansi Lake system (including Zhaoyang Lake and Weishan Lake) distributed in the vicinity, which constitutes an important water source conservation area for the Eastern Route of the South-to-North Water Transfer Project. The local climate is warm temperate and semi-humid monsoon, with a multi-year average temperature of 13.5 °C, mean precipitation of 700 mm year^{−1} (over 80% occurring in June–September), and evaporation of 1600 mm year^{−1}. The burial depth of shallow groundwater level in the study area ranges from 0.5–2.5 m, with an average burial depth of approximately 1.5 m.

The Luwa coal mine represents a significant component of the Jining coalfield, with a minefield area of approximately 28 km². The Shanxi Formation's No. 3 coal seam serves as the principal extraction target, and the site has witnessed more than two decades of continuous mining. Long-term underground extraction has induced extensive land subsidence, resulting in the formation of large areas of subsidence ponding water. By the end of 2023, the total area of coal mining-induced subsidence land in Jining City had reached 47,000 ha, accounting for more than 50% of the total subsidence area in Shan-

dong Province. The Luwa CMSA is one of the representative high-water-table CMSA in this region.

2.2. Regional Geology and Hydrogeology

The stratigraphic sequence in the study area, from bottom to top, comprises the Ordovician, Carboniferous, Permian, Jurassic, and Quaternary strata. The coal-bearing strata are primarily of Carboniferous–Permian age, within which the Shanxi Formation hosts the main mineable coal seam, with an average thickness of approximately 4–6 m. The minefield is characterized by relatively well-developed geological structures, including 35 normal faults and one reverse fault, as well as a certain number of karst collapse columns. These faults and collapse columns constitute potential groundwater flow conduits.

The Luwa mine is situated in a region with complicated hydrogeological characteristics. The entire minefield is overlain by a Quaternary unconsolidated sequence with a mean thickness of about 208 m. At the base of the Quaternary succession, clay and sandy clay layers with very low water-bearing capacity are developed, with individual layer thicknesses reaching 21.60 to 46.22 m, which collectively serve as an aquitard. According to previous studies, the primary water sources that may recharge the mine workings during coal extraction include: pore water in the lower subsection of the lower Quaternary sequence, Jurassic glutenite water, sandstone water in the roof and floor of the No. 3 coal seam, limestone water of the third limestone (No. 3 limestone) horizon, and Ordovician limestone water. Among these, the Jurassic red-bed water has historically posed a water-inrush hazard to mining operations. The predicted normal water inflow of the mine is $158.5 \text{ m}^3/\text{h}$, with a maximum inflow of approximately $328.85 \text{ m}^3/\text{h}$. The main recharge sources for the study area are atmospheric precipitation, supplemented by leakage recharge from surface water bodies, irrigation return flow, and lateral groundwater inflow. The general direction of groundwater flow is from the southwest toward the northeast, with an average hydraulic gradient of approximately 0.3‰. Groundwater discharge from the pore aquifers occurs primarily through artificial abstraction, lateral outflow, and evaporation.

2.3. Sample Collection and Analysis

June 2024 saw a sampling effort in the Luwa CMSA, during which 23 groundwater samples (all groundwater samples were collected from the Quaternary aquifer system) and 3 wastewater samples were retrieved for subsequent hydrochemical and source-apportionment analyses. The spatial distribution of sampling sites is illustrated in Figure 1. All samples were collected using 500 mL polyethylene bottles, which were pre-cleaned with ultrapure water and rinsed three times with the sample water prior to collection. For groundwater sampling, boreholes were purged thoroughly for approximately 20 min until stable readings of pH and electrical conductivity (EC) were achieved, after which samples were collected. Surface water samples were collected using a stainless-steel surface water sampler at a depth of 0.5 m below the water surface. Each collected sample was divided into two aliquots: one aliquot was acidified to $\text{pH} < 2$ with ultrapure-grade nitric acid for cation analysis (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}), while the other aliquot was left untreated for anion analysis (HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^-). All sample bottles were filled completely to eliminate headspace, sealed, and stored refrigerated in the dark until analysis, and all measurements were completed within one week after sample collection. Quality assurance and quality control (QA/QC) procedures included the analysis of field blanks, duplicate samples, and certified reference materials. Field blanks were prepared using ultrapure water and processed through the same sampling and analytical procedures; all blank measurements were below detection limits. Duplicate samples (approximately 10% of the total) were analyzed to assess precision, with relative standard deviations (RSD) $< 5\%$ for all

major ions. Detection limits were 0.01 mg/L for Na^+ , K^+ , Ca^{2+} , and Mg^{2+} , and 0.02 mg/L for SO_4^{2-} , Cl^- , and NO_3^- . Charge balance errors (CBE) for all groundwater samples were calculated using the formula: $\text{CBE} = (\sum \text{cations} - \sum \text{anions}) / (\sum \text{cations} + \sum \text{anions}) \times 100\%$, and were all within $\pm 5\%$, indicating the analytical data are of satisfactory quality for hydrochemical interpretation.

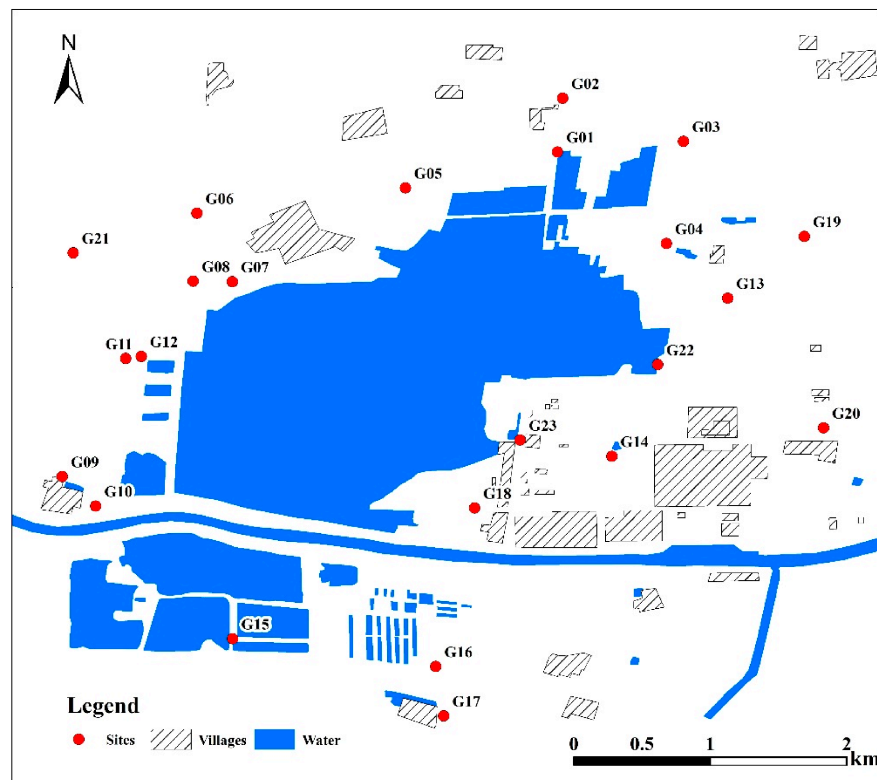


Figure 1. Spatial distribution of sampling sites in the study area.

All sample analyses were performed at the Testing Center of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. The pH and EC were determined in situ using a portable multiparameter water quality meter (HACH HQ40d, Loveland, CO, USA). Total dissolved solids (TDS) were determined by the gravimetric method after oven drying. Cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) were analyzed by inductively coupled plasma mass spectrometry (Agilent 7500ce, ICP-MS, Agilent Technologies Japan, Ltd., Tokyo, Japan), whereas anions (SO_4^{2-} , Cl^- , and NO_3^-) were determined by ion chromatography (Perkin-Elmer Lambda 35, Waltham, MA, USA). Bicarbonate (HCO_3^-) was quantified by hydrochloric acid titration.

2.4. Data Analysis

To visualize the sampling configuration, ArcGIS 10.5 (ESRI, Redlands, CA, USA) was employed for map generation. Descriptive statistics, including means and standard deviations of the hydrochemical parameters, were computed using Microsoft Excel for Microsoft 365 (Version 2405) (Microsoft Corp., Redmond, WA, USA). Ion ratio plots were constructed with OriginPro 2022 (64-bit) SR1 software (OriginLab Corp., Northampton, MA, USA). Correlation analysis and principal component analysis (PCA) of groundwater hydrochemical constituents were performed using R software (version 4.3.1, R Core Team, Vienna, Austria), with data standardization and visualization conducted within the same environment.

Among them, the calculation process of WQI is as follows:

$$WQI = \sum_{j=1}^n w_j q_j$$

$$q_j = \frac{\bar{c}_j}{s_j} \times 100$$

$$q_{pH} = \frac{c_{pH}}{8.5 - 7} \times 100$$

w is the weight factor or weight, ranging from 0 to 1, where $w_1 + w_2 + w_3 + \dots + w_n = 1$.

q_j denotes the quality grade of each parameter, and n is the number of parameters used for WQI evaluation.

C_j represents the concentration of each indicator in the water sample (mg/L).

S_j is the standard limit value of each indicator (mg/L).

3. Results and Discussion

3.1. Hydrochemical Characteristics of Groundwater in the CMSA

Table 1 provides a comprehensive statistical overview of the measured hydrochemical variables. The observed pH fell between 7.00 and 7.70, with an average of 7.33 ± 0.217 , pointing to a consistently weakly alkaline groundwater system. The total dissolved solids (TDS) varied between 1180 and 3090 mg/L, with an average value of 1791 ± 293 mg/L. Notably, all samples exceeded the Class III threshold limit of 1000 mg/L stipulated by the Chinese Groundwater Quality Standard (GB/T 14848-2017) [17], suggesting a considerably elevated degree of mineralization in the study area's groundwater.

Table 1. Statistical table of hydrochemical composition characteristics.

Parameters	Units	Standard	Range	Mean $\pm$ SD	EP (%)	CV (%)
pH	—	6~9	7.00–7.70	7.33 ± 0.217	0	2.90
K ⁺	mg/L	—	0.410–5.86	2.19 ± 1.92	—	85.7
Na ⁺	mg/L	200	155–414	295 ± 68.0	91.3	22.5
Ca ²⁺	mg/L	—	123–230	186 ± 33.9	—	17.9
Mg ²⁺	mg/L	—	64.2–159	105 ± 28.2	—	26.1
Cl [−]	mg/L	≤ 250	187–483	348 ± 74.8	91.3	21.0
SO ₄ ^{2−}	mg/L	≤ 250	208–642	464 ± 96.0	95.7	20.2
HCO ₃ [−]	mg/L	—	422–697	542 ± 91.0	—	16.3
NO ₃ [−]	mg/L	≤ 88.6	0.341–61.6	5.40 ± 13.0	0	235
TDS	mg/L	≤ 1000	1180–2280	1791 ± 293	100 =	16.0

Note: SD = Standard deviation; EP = Exceedance proportion; CV = Coefficient of variation. EP is calculated as $EP = (n/23) \times 100\%$, where n is the number of samples exceeding the Class III standard limit for a given parameter. The reference standard for groundwater quality is GB/T 14848-2017 (Class III). The Chinese national standard GB/T 14848-2017 is a general-purpose standard for groundwater survey, monitoring, and quality assessment. It classifies groundwater into five categories for various utilizations, including drinking water supply, agricultural irrigation, and industrial use. Class III groundwater serves as the threshold for centralized drinking water sources, whereas Class IV is suitable only for agricultural and certain industrial purposes.

The cation concentrations followed a decreasing order of Na⁺ (295 ± 68.0 mg/L) > Ca²⁺ (186 ± 33.9 mg/L) > Mg²⁺ (105 ± 28.2 mg/L) > K⁺ (2.19 ± 1.92 mg/L), whereas the anion concentrations exhibited the sequence of HCO₃[−] (542 ± 91.0 mg/L) > SO₄^{2−} (464 ± 96.0 mg/L) > Cl[−] (348 ± 74.8 mg/L) > NO₃[−] (5.4 ± 13.0 mg/L). Among the cations, Na⁺ showed the most prominent exceedance rate (91.3%), which is closely attributable to the infiltration of sodium-rich external waters, including surface ponding water and

surrounding sewage discharge in the subsidence area. The sustained recharge of such sodium-enriched waters not only directly elevates the Na^+ concentration in groundwater but also substantially alters the original water–rock equilibrium and the intrinsic chemical field characteristics of the groundwater system [18]. With respect to anions, SO_4^{2-} and Cl^- exhibited the most significant exceedance rates, at 95.7% and 91.3%, respectively. The widespread occurrence of SO_4^{2-} is primarily associated with the enhanced oxidative dissolution of sulfur-bearing minerals (e.g., pyrite) under conditions of mining-induced fracture development [19]; whereas the pervasive enrichment of Cl^- is indicative of the persistent influence of surface industrial wastewater discharge. Under the high-water-table and surface ponding conditions characteristic of the subsidence area, the oxidation products of sulfur-bearing minerals and Cl^- derived from wastewater are more readily transported into the groundwater system via infiltrating recharge water, thereby exacerbating the exceedance levels of anionic constituents [20]. Furthermore, the coefficient of variation (CV) for NO_3^- reached as high as 235%, reflecting strong spatial heterogeneity, which is likely closely linked to localized anthropogenic inputs such as agricultural fertilization and domestic sewage discharge [21]. Similarly, K^+ also exhibited a relatively high degree of variability, suggesting that its spatial distribution is jointly influenced by differential water–rock interactions and variations in external input intensity. Collectively, the groundwater system in the Luwa CMSA is subject to pronounced hydrochemical enrichment and substantial anthropogenic impacts, warranting further systematic investigation into the underlying controlling mechanisms.

3.2. Groundwater Quality Assessment in the CMSA

The groundwater quality in the study area was evaluated using the comprehensive water quality index (WQI) with reference to the Class III standard of GB/T 14848-2017 (applicable to centralized drinking water sources and industrial/agricultural water uses), and the results are presented in Table 2. The assessment revealed that 43.5% of the monitoring sites were classified as “poor” water quality, 52.2% as “very poor,” and the remaining 4.35% as “undrinkable,” with no site attaining the “excellent” or “good” grades. Collectively, these findings indicate that the groundwater quality in the Luwa CMSA is far from satisfactory, exhibiting a pervasive and severely polluted character.

Table 2. Water quality assessment results of groundwater in the CMSA.

Water Quality Grade	Comprehensive Water Quality Score	Number of Sites (n)	Proportion (%)
Excellent	<50	0	0%
Good	50–100	0	0%
Poor	100.1–200	10	43.5%
Very poor	200.1–300	12	52.2%
Unsuitable for drinking	>300	1	4.35%

Spatial interpolation of the water quality assessment results was performed to obtain the spatial distribution of groundwater quality in the study area. As shown in Figure 2, the overall groundwater quality in the study area is poor, which is primarily attributable to the fact that the land use types are predominantly farmland and the coal-bearing strata are extensively developed, with agricultural activities and coal mining operations exerting significant influences on groundwater quality. Along the groundwater flow direction (from northwest to southeast), the WQI values exhibit an overall increasing trend. The highest value was recorded at Site 18, with a WQI of 337. Sites 23 and 22 also yielded WQI values of 238 and 217, respectively, both falling within the high-value zone of the study area.

Furthermore, sites closer to the subsidence wetland, such as Sites 7 and 10, had WQI values of 235 and 232, respectively, further demonstrating that groundwater quality in the study area is significantly affected by coal mining activities.

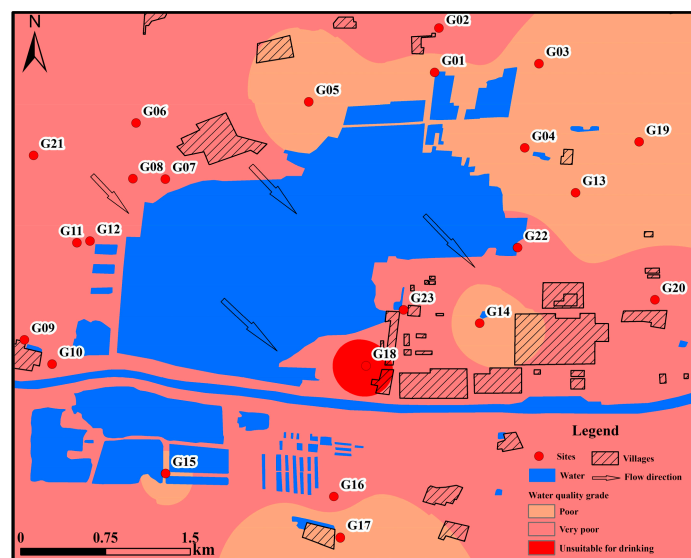


Figure 2. Map of the spatial distribution of groundwater quality in the CMSA.

This deterioration pattern is attributable to the combined effects of natural background conditions and anthropogenic activities. With respect to natural factors, the study area is located in a high-water-table mining district where intense evaporation favors the concentration and enrichment of dissolved constituents in groundwater. Concurrently, the oxidative dissolution of sulfide minerals, such as pyrite, within the coal-bearing strata continuously releases SO_4^{2-} into the groundwater system. Regarding anthropogenic influences, land subsidence and fracture development induced by mining activities have significantly enhanced the hydraulic connectivity between surface water and groundwater, thereby providing preferential pathways for vertical infiltration of contaminants. Furthermore, the land subsidence and fracture development induced by long-term coal mining activities have significantly enhanced the hydraulic connectivity between surface water and groundwater. Previous geological surveys in the Luwa coal mine have documented 35 normal faults and a number of karst collapse columns within the minefield [16]. These structural features, together with mining-induced fissures, serve as preferential seepage channels that facilitate vertical infiltration of surface ponding water and wastewater into the underlying aquifer systems [22]. In addition, the subsidence ponding area receives surface runoff, and the infiltration recharge from surrounding industrial wastewater and domestic sewage further exacerbates the enrichment of groundwater chemical constituents. The synergistic interplay between these geological predispositions and anthropogenic disturbances has collectively driven the systematic deterioration of groundwater quality in the study area.

3.3. Controlling Factors of Groundwater Hydrochemistry in the CMSA

We applied the Gibbs diagram (Figure 3) to decipher the dominant controls on water chemistry, which relies on the relationship between TDS and the ratios $[\text{Na}^+]/([\text{Na}^+] + [\text{Ca}^{2+}])$ and $[\text{Cl}^-]/([\text{Cl}^-] + [\text{HCO}_3^-])$. This diagram delineates three end-member controlling types: atmospheric precipitation dominance, rock weathering dominance, and evaporation–crystallization dominance. Specifically, the atmospheric precipitation end-member is situated in the lower right corner of the diagram, characterized by low TDS (typically <10 mg/L) and high ionic ratios (0.5–1.0); the rock weathering end-member occupies the mid-left re-

gion, with TDS ranging between 70 and 300 mg/L and ionic ratios generally below 0.5; and the evaporation–crystallization end-member is located in the upper right corner, exhibiting concurrently high TDS (>300 mg/L) and high ionic ratios (0.5–1.0) [23].

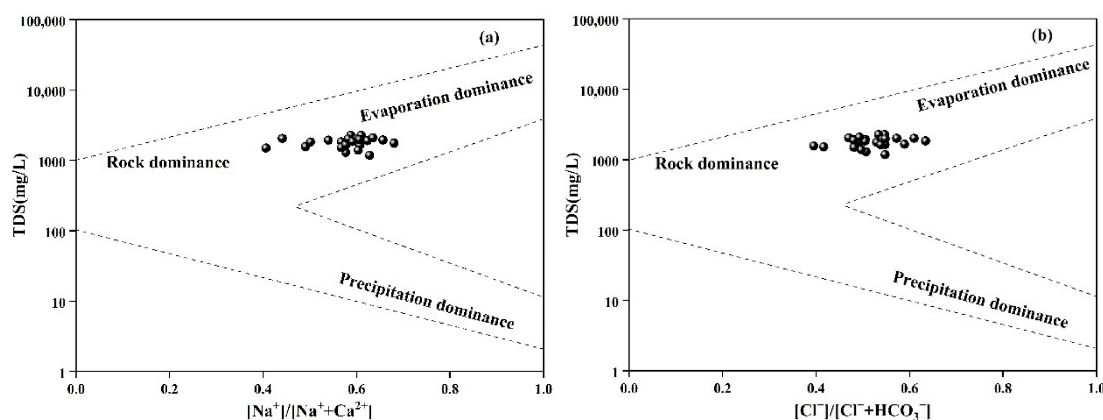


Figure 3. Gibbs diagram of groundwater in the CMSA ((a) $[Na^+]/[Na^+ + Ca^{2+}]$ vs. TDS; (b) $[Cl^-]/[Cl^- + HCO_3^-]$ vs. TDS).

As shown in Figure 3, most samples are distributed across the transitional zone separating the rock-weathering and evaporation–crystallization fields (Figure 2), which suggests that groundwater chemistry in the area is shaped by the interplay of these two processes. Notably, although the majority of samples tend toward the evaporation–crystallization domain on the Gibbs diagram, the hydrochemical analysis presented above reveals that the high TDS signature is more likely attributable to the infiltration recharge from external water sources (e.g., sewage and subsidence ponding water) than to in situ evaporation alone. This observation reflects the unique hydrogeochemical processes characteristic of CMSA. Specifically, the surface ponding water in the subsidence area is chronically exposed to evaporation, which progressively concentrates dissolved constituents (e.g., Na^+ , Cl^- , and SO_4^{2-}) and consequently elevates the ionic ratios of the ponded water [24]. Under conditions of well-developed subsidence-induced fractures, this highly concentrated ponding water preferentially infiltrates through the vadose zone with enhanced permeability and recharges the groundwater system, thereby transferring the chemical signature of evaporation concentration into the subsurface. In other words, the evaporation–crystallization signature manifested in the Gibbs diagram does not directly result from in situ evaporation of groundwater, but rather likely originates from infiltration and mixing of surface ponding water that had undergone evaporation concentration. In summary, the hydrochemical composition of groundwater in the study area is primarily governed by rock weathering, superimposed by the influence of infiltration recharge from evaporation-concentrated subsidence ponding water. The land subsidence and fracture development induced by mining activities have provided the hydraulic pathways for this “evaporation–infiltration–mixing” process, enabling the effective transmission of the evaporation concentration signal into the groundwater system.

3.4. Identification of Solute Sources for Groundwater Hydrochemical Constituents

Ion ratio end-member diagrams serve as effective tools for tracing solute sources in groundwater. The $[Ca^{2+}]/[Na^+]$ and $[Mg^{2+}]/[Na^+]$ ratios, which are insensitive to evaporation–concentration and hydrodynamic variations, can effectively discriminate the contributions of different rock weathering end-members [25]. Under conditions without pronounced anthropogenic disturbance, the major ion sources in natural waters have well-defined geological affinities: Ca^{2+} , Mg^{2+} , and HCO_3^- generally originate from the

weathering of carbonate and silicate minerals; Na^+ and Cl^- are primarily derived from the dissolution of silicate minerals and halite (NaCl); and SO_4^{2-} is mainly controlled by the dissolution of evaporite minerals (e.g., gypsum and mirabilite) and halite [26]. As shown in Figure 4a, the majority of groundwater samples fall close to the silicate end-member, while only 17.4% deviate toward the evaporite end-member. This indicates that the hydrochemical composition of groundwater in the study area is predominantly governed by silicate mineral weathering, superimposed by localized evaporite mineral dissolution signals, reflecting the complexity of multi-end-member mixing of solute sources.

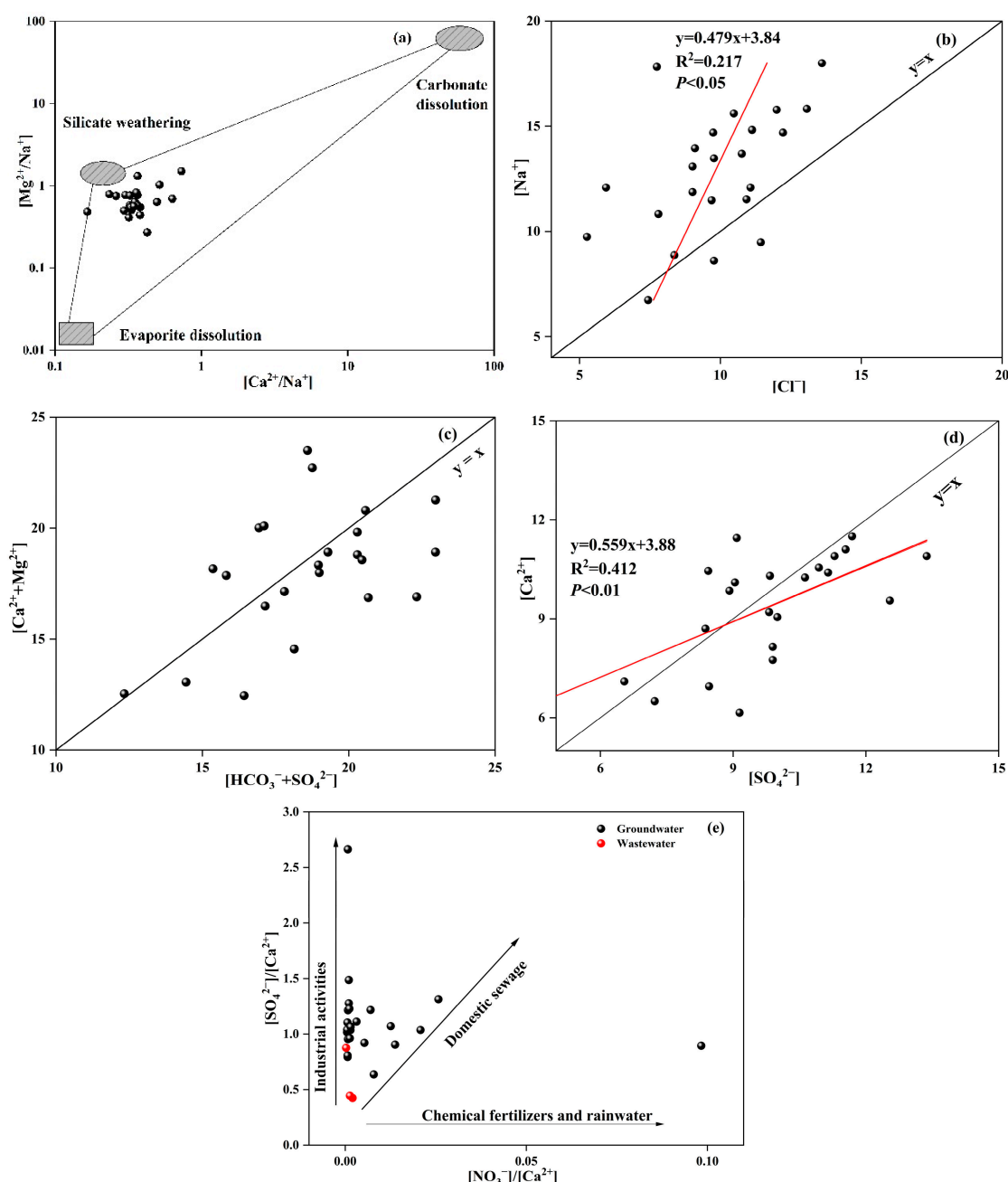


Figure 4. Diagram of Ion Ratio of groundwater in the CMSA ((a) $[\text{Ca}^{2+}]/[\text{Na}^+]$ vs. $[\text{Mg}^{2+}]/[\text{Na}^+]$; (b) $[\text{Na}^+]$ vs. $[\text{Cl}^-]$; (c) $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^- + \text{SO}_4^{2-}]$; (d) $[\text{Ca}^{2+}]$ vs. $[\text{SO}_4^{2-}]$; (e) $[\text{NO}_3^-]/[\text{Ca}^{2+}]$ vs. $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$).

3.4.1. Sources of Na^+ and Cl^-

To further elucidate the sources of Na^+ and Cl^- , the scatter plot of $[\text{Na}^+]$ versus $[\text{Cl}^-]$ is presented in Figure 4b. Theoretically, stoichiometric dissolution of halite (NaCl) yields equimolar concentrations of Na^+ and Cl^- , with a milliequivalent ratio of 1:1, corresponding to the $y = x$ line [27]. However, all groundwater samples in this study plot above this theoretical line, and a significant positive correlation ($p < 0.05$) is observed between Na^+ and Cl^- , indicating a same source for both ions. The systematic deviation of the samples suggests an excess of Na^+ relative to Cl^- , which may be attributed to the following mechanisms: (1) the weathering and dissolution of silicate minerals (e.g., plagioclase and albite) release additional Na^+ into the groundwater system; and (2) the infiltration of surface ponding water (subjected to evaporation–concentration) or external recharge water carrying high Na^+ concentrations mixes with the groundwater [28].

3.4.2. Sources of Ca^{2+} , Mg^{2+} , and SO_4^{2-}

The milliequivalent ratio of $[\text{Ca}^{2+} + \text{Mg}^{2+}]$ to $[\text{HCO}_3^- + \text{SO}_4^{2-}]$ was further employed to discriminate the relative contributions of carbonate and sulfate minerals to groundwater chemical composition. Previous studies have indicated that a ratio > 1 suggests dominance of carbonate mineral dissolution; a ratio < 1 indicates greater contributions from silicate weathering and sulfate dissolution; and a ratio approximately equal to 1 implies a near-equilibrium between carbonate dissolution and sulfate/silicate dissolution [29]. As illustrated in Figure 4c, 10 samples are distributed near the 1:1 line, 6 samples lie above this line, and 7 samples fall below it, suggesting a certain degree of divergence in the sources of SO_4^{2-} versus those of Ca^{2+} and Mg^{2+} . Beyond the dissolution of evaporite minerals such as gypsum, SO_4^{2-} may also originate from sulfuric acid-driven carbonate dissolution, in which SO_4^{2-} is introduced into the solution as an accompanying ion and does not maintain a fixed stoichiometric relationship with Ca^{2+} and Mg^{2+} . Meanwhile, Ca^{2+} and Mg^{2+} are derived from both the direct contribution of carbonate mineral dissolution and the indirect contribution of silicate mineral weathering release, which is consistent with the complex geological structure of multiple aquifer systems developed beneath the Quaternary overburden in the study area. Figure 4d further presents the ratio relationship between $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ to quantitatively evaluate the degree of control exerted by gypsum weathering dissolution on the hydrochemical composition. The analytical results reveal that approximately 63.2% of the samples fall within the theoretical domain indicative of gypsum and silicate weathering dissolution, and a highly significant positive linear correlation ($p < 0.01$) is observed between Ca^{2+} and SO_4^{2-} , further corroborating that gypsum dissolution serves as an important common source of both Ca^{2+} and SO_4^{2-} in the groundwater of the study area.

3.4.3. Impacts of Anthropogenic Activities on Groundwater

In areas where groundwater is substantially affected by anthropogenic activities, the levels of NO_3^- , Cl^- , SO_4^{2-} , and Na^+ tend to exhibit a concurrent increasing trend. Previous studies have demonstrated that mining activities are generally accompanied by elevated $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ ratios, whereas agricultural activities result in increased $[\text{NO}_3^-]/[\text{Ca}^{2+}]$ ratios [30]. Accordingly, a scatter plot of $[\text{NO}_3^-]/[\text{Ca}^{2+}]$ versus $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ was constructed to differentiate the impacts of industrial/mining activities and agricultural activities on groundwater quality (Figure 4e). The results show that the $[\text{SO}_4^{2-}]/[\text{Ca}^{2+}]$ ratios of all samples are significantly higher than their $[\text{NO}_3^-]/[\text{Ca}^{2+}]$ counterparts, and the distribution pattern of groundwater samples closely matches the wastewater end-member, indicating that industrial activities—particularly the infiltration recharge of coal mine wastewater—constitute the primary anthropogenic factor influencing the groundwater

chemical composition in the study area. In conjunction with the field investigation data and the hydrochemical analytical results presented above, sulfur-bearing wastewater discharged from the Luwa coal mine and surrounding industrial facilities infiltrates through subsidence-induced fractures and surface ponding water, thereby making a direct or indirect substantial contribution to the enrichment of SO_4^{2-} in the groundwater system. This further reinforces the dominant anthropogenic role of industrial wastewater in shaping the hydrochemical evolution of groundwater in the CMSA.

3.5. Correlation Analysis of Groundwater Hydrochemical Constituents

Correlation analysis can reveal the intrinsic associations among groundwater chemical constituents and the underlying hydrogeochemical processes [31]. In this study, Spearman correlation analysis was employed to examine the interrelationships among hydrochemical parameters of groundwater in the CMSA (Figure 5). The results show that TDS exhibits highly significant positive correlations with SO_4^{2-} ($r = 0.82, p < 0.01$), Na^+ ($r = 0.70, p < 0.01$), Ca^{2+} ($r = 0.66, p < 0.01$), and Cl^- ($r = 0.63, p < 0.01$), indicating that the groundwater salinity in this area is primarily governed by the combined enrichment of Na^+ , Ca^{2+} , SO_4^{2-} , and Cl^- . Significant or highly significant positive correlations are also observed between SO_4^{2-} and Na^+ ($r = 0.70, p < 0.01$), SO_4^{2-} and Ca^{2+} ($r = 0.62, p < 0.01$), as well as between Cl^- and Ca^{2+} ($r = 0.50, p < 0.05$) and Cl^- and Na^+ ($r = 0.50, p < 0.05$), suggesting that these constituents share common sources, such as the dissolution of evaporite minerals including gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and halite (NaCl) [32]. This interpretation is corroborated by the distribution pattern of samples plotting toward the evaporation–crystallization end-member on the Gibbs diagram (Figure 3), jointly suggesting that evaporite mineral dissolution exerts a discernible control on the groundwater hydrochemical composition in the study area. The strong correlation between Cl^- and Na^+ may imply the influence of halite dissolution and domestic sewage on groundwater hydrochemistry [33]. The significant correlation between Na^+ and Ca^{2+} ($r = 0.42, p < 0.05$) further suggests that silicate weathering dissolution may serve as a common geochemical source for both ions. Nevertheless, given that the study area is situated in the Huang-Huai-Hai alluvial plain, where the thick Quaternary unconsolidated overburden may host feldspar-bearing silicate minerals whose weathering dissolution could indeed contribute certain amounts of Na^+ and Ca^{2+} , whether this process is accelerated under mining-disturbed conditions requires further verification through mineralogical evidence and hydrogeochemical modeling.

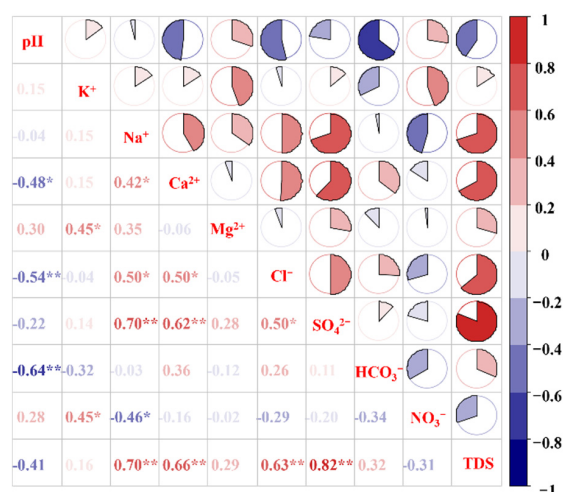


Figure 5. Correlation analysis diagram of hydrochemical components in groundwater from the CMSA. Note: “*” and “**” denote significant correlations between the two indicators at the $p < 0.05$ and $p < 0.01$ levels, respectively.

It is noteworthy that NO_3^- exhibits a significant positive correlation with K^+ ($r = 0.45$, $p < 0.05$), indicating a common exogenous input pathway for both ions. In conjunction with the land use characteristics of the study area (i.e., the distribution of cultivated land and intensive agricultural activities in the surroundings), this correlation can be attributed to the application of potassium fertilizers and nitrogen-containing fertilizers in agricultural practices: potassium fertilizers (e.g., KCl or K_2SO_4) directly contribute K^+ , while nitrogen fertilizers (e.g., NH_4NO_3 and urea) are converted to NO_3^- through nitrification, both of which enter the groundwater system via infiltration of precipitation or irrigation water [34,35]. Furthermore, pH exhibits significant negative correlations with Cl^- ($r = -0.54$, $p < 0.01$) and HCO_3^- ($r = -0.64$, $p < 0.01$). In the CMSA, the generation of acid mine drainage (e.g., from pyrite oxidation) may introduce H^+ into groundwater, lowering pH and promoting carbonate mineral dissolution, thereby releasing HCO_3^- . As Cl^- serves as a conservative tracer, its negative correlation with pH may reflect hydrological processes associated with the mixing of different water sources—specifically, low pH groundwater may correspond to particular recharge sources, such as subsidence ponding water or shallow pore water affected by acidic water [36]. This explanation is consistent with the previously discussed mechanism of infiltration recharge from evaporation-concentrated surface ponding water into the groundwater system.

3.6. Controlling Factors of Groundwater Hydrochemical Constituents in the CMSA

Accurate identification of the primary controlling factors governing groundwater hydrochemical composition is a scientific prerequisite for the effective prevention and control of groundwater pollution. In this study, principal component analysis (PCA) was employed to decipher the dominant factors controlling groundwater hydrochemistry in the CMSA. The variables incorporated into the analysis comprised ten hydrochemical parameters, including pH, TDS, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , NO_3^- , and Cl^- . Prior to factor extraction, the KMO statistic and Bartlett's test were computed to examine the sampling adequacy and sphericity of the correlation matrix, respectively. The results yielded a KMO value of 0.625, exceeding the recommended threshold of 0.5, indicating substantial common variance among the variables. Bartlett's test of sphericity produced an approximate chi-square value of 130 ($p < 0.001$), reaching a highly significant level. Both tests collectively demonstrated that the groundwater hydrochemical dataset in the study area possesses adequate structural validity and statistical applicability for PCA. The eigenvalue > 1 rule led to the extraction of three PCs, whose cumulative variance contribution reached 77.9%—effectively covering the essential signal originally carried by the ten water quality variables. These three PCs respectively represent three major categories of controlling factors governing the groundwater chemical composition in the study area, and their factor loading matrix is presented in Table 3.

PC1 explains 38.4% of the total variance. It exhibits high positive loadings on TDS (0.894), SO_4^{2-} (0.844), Na^+ (0.829), Cl^- (0.614), and Ca^{2+} (0.608). This factor combination indicates mixed contributions from multiple end-members. On the one hand, the concurrent enrichment of SO_4^{2-} with Na^+ and Ca^{2+} reflects the dissolution of evaporite minerals, including gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and halite (NaCl), which is consistent with the geological occurrence of evaporite minerals within the coal-bearing strata [37]. On the other hand, the association of Cl^- and Na^+ serves as an effective tracer of domestic sewage input. Previous studies have demonstrated that domestic sewage is rich in anthropogenic NaCl , and the coupled enrichment of Cl^- and Na^+ may indicate the infiltration recharge of domestic sewage [33]. In the present study, wastewater samples collected from Yutai Town exhibited elevated concentrations of Cl^- (728 mg/L) and Na^+ (320 mg/L). Meanwhile, the high loading of SO_4^{2-} also points to the influence of industrial wastewater input, as

earlier investigations have identified sulfur-bearing industrial wastewater discharge as an important anthropogenic source of SO_4^{2-} exceedance in groundwater [38,39]. The mine drainage sample collected from the Luwa coal mine in this study exhibited a SO_4^{2-} concentration of up to 320 mg/L. Collectively, the composition of PC1 reflects a multi-source composite signature of “natural evaporite dissolution + domestic sewage input + industrial wastewater input” in the groundwater chemistry of the CMSA, which is consistent with the land use pattern of the study area characterized by the distribution of industrial and mining enterprises as well as residential agglomerations in the vicinity. Therefore, PC1 indicates that the groundwater hydrochemistry in the CMSA is controlled by both anthropogenic wastewater input and evaporite dissolution.

Table 3. PCA results of groundwater in the CMSA.

Parameters	PC1	PC2	PC3
TDS	0.894	0.351	−0.010
SO_4^{2-}	0.844	0.135	0.226
Na^+	0.829	−0.151	−0.240
Cl^-	0.614	0.346	−0.456
Ca^{2+}	0.608	0.512	0.378
pH	−0.151	−0.896	0.031
HCO_3^-	0.232	0.818	−0.229
Mg^{2+}	0.488	−0.544	0.320
NO_3^-	−0.165	−0.008	0.871
K^+	0.317	−0.378	0.756
Contribution rate%	38.4	25.5	14.1
Cumulative contribution rate%	38.4	63.9	78.0

PC2 accounts for 25.5% of the total variance, with strong positive loadings on HCO_3^- (0.818) and Ca^{2+} (0.512), and a strong negative loading on pH (−0.896), suggesting a link to carbonate dissolution and pH-buffering processes. The negative correlation between pH and HCO_3^- suggests that, under the specific hydrogeochemical conditions of the CMSA, the input of acidic substances (e.g., H^+ generated from pyrite oxidation) has promoted carbonate mineral dissolution, releasing HCO_3^- into the groundwater system [40]. This factor is orthogonally distributed with respect to PC1, indicating that the carbonate dissolution process is independent of the evaporite control mechanism, and its contribution is constrained by the abundance of carbonate minerals in the aquifer media and the modulation of the pH buffering system. This finding corroborates the results of the correlation analysis presented above, in which HCO_3^- showed no significant correlation with TDS. Thus, PC2 represents the influence of carbonate dissolution and pH-regulated buffering processes on the groundwater hydrochemistry in the CMSA.

PC3 explains 14.1% of the total variance. It exhibits high positive loadings on NO_3^- (0.871) and K^+ (0.756), representing a typical anthropogenic activity factor. The coupled enrichment of NO_3^- and K^+ can indicate the groundwater contamination effects of agricultural fertilization activities—potassium fertilizers (KCl and K_2SO_4) directly contribute K^+ , while nitrogen fertilizers are converted to NO_3^- through nitrification, with both ions entering the groundwater system via precipitation infiltration and irrigation return flow [41]. The orthogonality of this factor with respect to the preceding two controlling factors further corroborates the differential nature of the input pathways from various pollution sources, and also explains the negative correlation observed between NO_3^- and Na^+ in the correlation analysis. Therefore, PC3 indicates that the groundwater hydrochemistry in the CMSA is controlled by agricultural activities.

4. Management Implications

Based on the findings of this study, which indicate that groundwater chemistry in the high-water-table coal mining subsidence area is influenced by a combination of coal mine drainage, domestic sewage, agricultural fertilizers, coal-bearing strata, and evaporation concentration, the following management recommendations are proposed for groundwater pollution prevention and control in the study area:

(1) Control of industrial and domestic wastewater inputs

Given that Na^+ , SO_4^{2-} , and Cl^- are the predominant contaminants exceeding the standards, with exceedance rates of 91.3%, 95.7%, and 91.3%, respectively, and that principal component analysis (PCA) confirms evaporite dissolution and wastewater input as the primary controlling factor (PC1), stringent regulation of wastewater discharge is of critical importance. Specific recommendations are as follows: (1) Coal mine drainage and domestic sewage should be treated to meet the applicable discharge standards prior to release, and the discharge of untreated or inadequately treated wastewater into subsidence ponding areas should be strictly prohibited; (2) Regular monitoring of effluent quality from mining and domestic wastewater treatment facilities should be strengthened, and real-time surveillance systems should be installed at major discharge points; (3) Public environmental awareness campaigns should be conducted among local residents and mining personnel to emphasize the environmental risks associated with uncontrolled wastewater discharge, and community-based reporting of illegal dumping should be encouraged.

(2) Mitigation of agricultural non-point source pollution

Given that NO_3^- is predominantly derived from agricultural activities, and that PCA identifies agricultural input as an independent controlling factor (PC3), targeted agricultural management measures should be implemented, particularly during the rainy season when surface runoff and infiltration are most pronounced. Recommended measures include: (1) promoting the adoption of controlled-release fertilizers and optimizing fertilization schedules to match crop uptake patterns, thereby minimizing nitrate leaching; (2) establishing vegetated buffer strips along field margins and drainage ditches to intercept and retain pollutants from agricultural runoff; (3) implementing cover cropping and reduced tillage practices during fallow periods to reduce soil erosion and nutrient loss.

(3) Engineering and ecological interventions for subsidence wetlands

Given that subsidence ponding water serves as a preferential pathway for contaminant infiltration into the underlying aquifer (as supported by the observation that high TDS and elevated ionic ratios are concentrated in areas adjacent to ponding water), a combination of engineering and ecological measures is recommended: (1) installation of impermeable liners at the bottom and side slopes of subsidence wetlands located near high-risk industrial zones or residential areas to reduce vertical seepage of contaminated water; (2) construction of ecological buffer walls and ecological ditches around the periphery of subsidence wetlands to intercept and treat surface runoff, thereby preventing contaminants from entering the ponding areas; (3) planting of macrophyte species with high nitrogen and phosphorus uptake capacity (e.g., emergent plants such as *Phragmites australis* and *Typha* spp., as well as submerged plants) within the wetlands to enhance nutrient removal and improve water quality prior to infiltration; (4) development of integrated constructed wetland systems that combine physical filtration, biological uptake, and chemical precipitation for in situ treatment of ponding water, thereby reducing contaminant loads before they enter the groundwater system.

5. Limitations and Prospects

Although this study has systematically elucidated the hydrochemical characteristics, and controlling factors of groundwater in the Luwa CMSA, several limitations remain that warrant further investigation.

(1) Limitations in temporal-scale investigation. This study was based on a single sampling campaign conducted in June 2024 (wet season), which failed to capture the seasonal and inter-annual variations in groundwater hydrochemistry. The groundwater system in CMSA is subject to periodic influences from multiple factors, including precipitation recharge, surface water infiltration, and anthropogenic abstraction, which may induce pronounced seasonal fluctuations and inter-annual evolutionary trends in hydrochemical constituents. Static data derived from a single sampling event are inadequate for comprehensively characterizing the temporal dynamics of groundwater chemical composition, nor can they effectively identify the chronological effects of climatic wet–dry alternations and variations in mining intensity on hydrochemical evolution. Future research should design systematic monitoring schemes covering multiple time points and frequencies across different hydrological seasons (wet, normal, and dry seasons) and multiple hydrological years, establishing a long-term dynamic monitoring network to reveal the temporal evolution patterns of groundwater hydrochemical constituents and their response mechanisms to natural variability and anthropogenic disturbances.

(2) Limitations in pollution source apportionment techniques. In this study, pollution sources were indirectly inferred through conventional hydrochemical ion ratio analyses and multivariate statistical techniques, without employing high-precision isotope tracing methods (e.g., $\delta^{15}\text{N}\text{--NO}_3^-$, $\delta^{18}\text{O}\text{--NO}_3^-$, $\delta^{34}\text{S}\text{--SO}_4^{2-}$, and $\delta^{11}\text{B}$) for quasi-quantitative identification of contributions from different pollution sources [42]. As NO_3^- and SO_4^{2-} constitute the predominant contaminant parameters in the groundwater of the study area, their sources likely involve a mixture of multiple end-members, including agricultural fertilizers, domestic sewage, industrial wastewater, and atmospheric deposition. Conventional hydrochemical methods exhibit notable limitations in discriminating among multiple pollution sources with similar chemical compositions. A quantitative partitioning of the contributions from candidate pollution sources to CMSA groundwater chemistry remains a priority for follow-up research. The combination of multi-isotope tracers with Bayesian mixing models (e.g., MixSIAR) represents a promising pathway toward achieving this goal and informing targeted remediation efforts.

(3) Absence of modeling and simulation approaches. This study primarily focused on static characterization of groundwater hydrochemical features and qualitative identification of controlling factors, without incorporating numerical simulations or machine learning approaches for quantitative simulation and prediction of contaminant transport dynamics. The groundwater flow and chemical fields in CMSA are subject to continuous evolution under the interplay of multiple factors, including mining-induced fracture development, changes in subsidence ponding area, and artificial water recharge. The absence of model-based projections impedes the prediction of future water quality trends and potential environmental risks. Future studies could construct hydrogeochemical numerical models (e.g., PHREEQC, MODFLOW/MT3DMS) to simulate the migration and transformation processes of key ions in groundwater. Concurrently, machine learning algorithms (e.g., Random Forest, Support Vector Machine, and XGBoost) [43] could be introduced to establish water quality prediction models based on existing monitoring data, enabling the identification of non-linear controlling factors in hydrochemical evolution and achieving intelligent early warning and trend prediction of groundwater quality, thereby providing scientific support for sustainable water resource management in mining regions.

6. Conclusions

Groundwater quality in the CMSA is generally poor, being subject to the combined influences of coal mine drainage, coal-bearing strata, agricultural fertilizers, and domestic sewage. Sulfate (SO_4^{2-}), sodium (Na^+), and chloride (Cl^-) are the predominant contaminants, with exceedance rates of 95.7%, 91.3%, and 91.3%, respectively. Hydrochemical source identification reveals that Na^+ and Cl^- originate primarily from silicate mineral dissolution, halite dissolution, and domestic sewage input; SO_4^{2-} is mainly controlled by evaporite mineral dissolution and industrial wastewater discharge; Ca^{2+} and Mg^{2+} are derived from carbonate and silicate mineral weathering; and NO_3^- is predominantly influenced by agricultural activities. Principal component analysis (PCA) further distinguishes three major controlling factors: (1) evaporite dissolution and wastewater input, (2) carbonate dissolution and pH buffering, and (3) agricultural input.

What distinguishes the high-water-table coal mining subsidence area from conventional mining areas is not merely the presence of these contamination sources, but rather the unique “evaporation–infiltration–mixing” pathway driven by the region’s high-water-table and mining-induced subsidence fractures. Specifically, prolonged evaporation of surface ponding water progressively concentrates dissolved constituents, and the well-developed fractures serve as preferential seepage channels that efficiently transmit this evaporation-concentrated signature downward into the shallow aquifer. This mechanism, combined with continuous wastewater infiltration, results in a distinctive hydrochemical pattern whereby high TDS and elevated ionic ratios are spatially concentrated in areas with dense fractures and proximity to ponding water—a feature rarely observed in non-subsidence mining districts. Collectively, groundwater chemistry in the CMSA is governed by a triple-mechanism framework of “natural enrichment—evaporation–concentration—anthropogenic superimposition,” with the evaporation–infiltration pathway being the most characteristic and distinguishing process.

Future research should incorporate multi-seasonal and multi-year systematic monitoring, combined with multi-isotope tracing techniques (e.g., $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{34}\text{S}$, $\delta^{15}\text{N}$) and numerical modeling, to quantitatively apportion the relative contributions of different pollution sources and predict water quality evolution trends, thereby providing a scientific basis for groundwater pollution prevention and water resource protection in analogous high-water-table mining regions worldwide.

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