

Hydrochemistry and Environmental Implications in the Western Alpine Region of China (Post-print)

Authors: ZHAO Yue

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Abstract

The western alpine region is an important freshwater supply and water conservation area for China and its surrounding areas. As ecological civilization construction progresses, the ecohydrology of the western alpine region in China, which is a crucial ecological barrier, has undergone significant changes. In this study, we collected 1077 sampling points and presented a comprehensive overview of research results pertaining to the hydrochemistry of river water, meltwater, groundwater, and precipitation in the western alpine region of China using piper diagram, end-member diagram, and hydrological process indication. Water resources in the western alpine region of China were found to be weakly alkaline and have low total dissolved solids (TDS). The mean pH values for river water, meltwater, groundwater, and precipitation are 7.92, 7.58, 7.72, and 7.32, respectively. The mean TDS values for river water, meltwater, groundwater, and precipitation are 280.99, 72.48, 544.41, and 67.68 mg/L. The hydrochemical characteristics of the water resources in this region exhibit significant spatial and temporal variability. These characteristics include higher ion concentrations during the freezing period and higher ion concentrations in inland river basins, such as the Shule River Basin and Tarim River Basin. The principal hydrochemical type of river water and meltwater is $\text{HCO}_3^- \cdot \text{SO}_4^{2-} \text{—Ca}^{2+}$, whereas the principal cations in groundwater are Mg^{2+} and Ca^{2+} , and the principal anions are HCO_3^- and SO_4^{2-} . In terms of precipitation, the principal hydrochemical type is $\text{SO}_4^{2-} \text{—Ca}^{2+}$. The chemical ions in river water and groundwater are primarily influenced by rock weathering and evaporation-crystallization, whereas the chemical ions in meltwater are mainly affected by rock weathering and atmospheric precipitation, and the chemical ions in precipitation are derived primarily from terrestrial sources. The main forms of water input in the western alpine region of China are precipitation and meltwater, and mutual recharge occurs between river water and groundwater. Hydrochemical characteristics can reflect the impact of human activities on water resources. By synthesizing the

regional hydrochemical studies, our findings provide insights for water resources management and ecological security construction in the western alpine region in China.

Full Text

Preamble

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Hydrochemistry and Environmental Implications in the Western Alpine Region of China

ZHAO Yue^{1, 2, 3}, LI Zongxing^{1, *}, LI Zhongping², AOBULI Gulihumaer, NIMA Zhaxi, WANG Dong

¹ Observation and Research Station of Eco-Hydrology and National Park by Stable Isotope Tracing in Qilian Mountains/Key Laboratory of Ecological Safety and Sustainable Development in Arid Lands, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China

² Oil and Gas Research Center, Northwest Institute of Eco-environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China

³ University of Chinese Academy of Sciences, Beijing 100049, China

College of Geography and Environmental Science, Northwest Normal University, Lanzhou 730070, China

Ali Branch of the Xizang Autonomous Region Hydrology Bureau, Ali 895000, China

Ali Branch of the Xizang Autonomous Region Hydrology Bureau, Ali 895000, China

Abstract: The western alpine region represents a critical freshwater supply and water conservation area for China and surrounding regions. As ecological civilization construction advances, the ecohydrology of this vital ecological barrier has undergone significant changes. This study synthesized data from 1,077 sampling points to provide a comprehensive overview of hydrochemical research on river water, meltwater, groundwater, and precipitation in the western alpine region of China, utilizing Piper diagrams, end-member diagrams, and hydrological process indicators. Water resources in this region are weakly alkaline with low total dissolved solids (TDS). Mean pH values for river water, meltwater, groundwater, and precipitation are 7.92, 7.58, 7.72, and 7.32, respectively, while mean TDS values are 280.99, 72.48, 544.41, and 67.68 mg/L. Hydrochemical characteristics exhibit significant spatial and temporal variability, including higher ion concentrations during freezing periods and elevated levels in inland river basins such as the Shule and Tarim River Basins. The principal hydrochemical type for river water and meltwater is HCO_3^{2-} - Ca^{2+} , whereas groundwater is dominated

by Mg^{2+} and Ca^{2+} cations and HCO_3^{2-} anions. Precipitation shows a hydrochemical type of SO_4^{2-} - Ca^{2+} . Chemical ions in river water and groundwater are primarily influenced by rock weathering and evaporation-crystallization, meltwater ions are mainly affected by rock weathering and atmospheric precipitation, and precipitation ions derive primarily from terrestrial sources. Precipitation and meltwater constitute the main water inputs, with mutual recharge occurring between river water and groundwater. Hydrochemical characteristics can reflect human impacts on water resources. By synthesizing regional hydrochemical studies, our findings provide insights for water resources management and ecological security construction in the western alpine region of China.

Keywords: hydrochemical type; ion source; Piper diagram; end-member diagram; hydrological process; western alpine region of China

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*Corresponding author: LI Zongxing (E-mail: lizxhhs@163.com)

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1 Introduction

Water is a vital natural resource whose storage, use, and quality are inextricably linked to human survival and social development. Water resources exist in various forms, including solids (glacier ice, ice sheets, sea ice, snow, hail, frozen soil), liquids (oceans, rivers, lakes, groundwater, snow meltwater), and gases (water vapor, clouds, fog). The chemical composition of natural water bodies is influenced by multiple factors, including rock lithology, climate, runoff, atmospheric deposition, vegetation, and human activities (Li et al., 2017a; Shen et al., 2021; Vorobyev et al., 2021). Hydrological processes in alpine regions are particularly complex and diverse (Dong et al., 2007; Tian et al., 2021; Liang et al., 2022; Zhang et al., 2022).

Hydrochemistry examines the chemical composition of natural water bodies and their spatial and temporal distribution and evolution. Integrating hydrology with chemical methods, it provides fundamental insights for understanding, identifying, and controlling water chemistry (Wang, 2010). Hydrochemical analysis reveals water body evolution, chemical weathering processes, ion sources,

and related information (Hindshaw et al., 2011; Zhou et al., 2014; Han et al., 2021). Research on natural water chemistry enables scientific analysis of water resource transformation relationships, source tracing, and objective water quality evaluation, providing a theoretical basis for rational development, utilization, and management (Liu et al., 2020c).

The western alpine region of China serves as a crucial water source for arid and semi-arid areas and functions as an essential ecological shield, playing an irreplaceable role in maintaining regional and national ecological balance. However, this region is highly sensitive to climate change, which significantly impacts water supply and accelerates water transformation (Chen et al., 2021; Zhang et al., 2023). Changes in water resources directly affect river runoff and the water conservation function of the “Asian Water Tower,” influencing water cycles and balance both regionally and globally (Shang et al., 2021; Wang et al., 2021d). To understand water resource stability and ecological security amid intensifying warming and humidification, this study expands previous research from single cold regions to the entire western alpine region, addressing data scarcity challenges in individual regional studies related to geographical and climatic constraints (Bai and Yang, 2007; Fan et al., 2014; Gao et al., 2019). By reviewing the current state of regional hydrochemistry, this study aims to elucidate the hydrochemical characteristics of river water, meltwater, groundwater, and precipitation. Specific objectives include: (1) identifying patterns of hydrochemical change influenced by environmental factors; (2) discerning variations in controlling factors across different river basins; (3) analyzing hydrochemical processes; and (4) determining human impacts on water resources in ecologically sensitive areas. These findings will provide a reference for future hydrochemical research and a practical basis for long-term environmental monitoring network establishment and policy development for environmental protection and water resources management.

2.1 Study Area

The western alpine region of China (73°40'12"–107°38'24" E, 21°00'36"–49°00'36" N; Fig. 1 [Figure 1: see original paper]) encompasses Gansu Province, Qinghai Province, Xinjiang Uygur Autonomous Region, Xizang Autonomous Region, Aba Tibetan and Qiang Autonomous Prefecture and Ganze Tibetan Autonomous Prefecture in western Sichuan Province, northern Yunnan Province, Yulong Snow Mountains, and northern Gaoligong Mountains (Ding et al., 2017). The region is bounded by the Pamir Plateau to the west, Hengduan Mountains to the east, Altay Mountains to the north, and Himalayas to the south. Characterized by high altitude and extensive snow and glacier cover, the region contains 48,571 glaciers covering a total area of 51,766.08 km², primarily distributed across the Kunlun, Tianshan, and Nyainqêntanglha mountain systems (Liu et al., 2015a). This region serves as the source of numerous major rivers and provides vital water resources to arid areas through

glacier and snow meltwater runoff (Feng et al., 2011). The climate features low average temperatures ($\sim 3^{\circ}\text{C}$), large diurnal temperature ranges, short frost-free periods, and intense ultraviolet radiation, with average annual precipitation of approximately 306 mm (Zhang et al., 2023). The region is highly sensitive to climate change, with warming trends intensifying in recent years. Sedimentary rocks (sandstone, shale, limestone), magmatic rocks (granite, pyroclastic, gabbro, basalt), and metamorphic rocks (gneiss, schist, marble) are widely distributed, reflecting a complex geological history that provides an important record for alpine hydrochemistry (Zhang, 1990; Qian et al., 2012; Ma et al., 2024).

Fig. 1 Overview of the study area and distribution of sampling points of different water bodies. Note that the figure is based on the standard map (GS(2020)4619) of the Map Service System (<https://bzdt.ch.mnr.gov.cn/>), and the standard map has not been modified.

2.2 Data Sources

To characterize hydrochemical features of the western alpine region, we conducted a literature search through January 2024 using keywords including “precipitation hydrochemistry,” “groundwater hydrochemistry,” “river hydrochemistry,” “meltwater hydrochemistry,” and “hydrological processes.” We selected papers with sampling point distributions within the study area that reported pH, total dissolved solids (TDS), electrical conductivity (EC), and concentrations of major ions (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , HCO_3^- , SO_4^{2-} , and NO_3^-). This yielded 198 relevant papers from Web of Science and China National Knowledge Network. Research data were primarily extracted from 89 articles published before January 2022, selected based on the presence of glaciers and frozen soil near sampling points, location in mountain runoff zones, and positioning in upper river basin reaches. These articles included 579 river sampling points, 142 glacial and snow meltwater points, 139 groundwater points, and 217 precipitation points, some without precise coordinates. Sampling covered the Ertix, Urumqi, Tarim, Heihe, Shiyang, Shule, Yarlung Zangbo, Yangtze, Nujiang, Jinsha, Minjiang, Yalong, Yellow, Lancang, Rongbuk, Kuytun, Ili, Baishui, and Nagqu River basins. Sampling point distributions are shown in Figure 1, with data sources detailed in Table 1.

Data quality was assessed using Pearson correlation coefficients and anion-to-cation concentration ratios (Liu et al., 2015b). The Pearson correlation coefficient between anion and cation concentrations was 0.67 ($P = 0.000$), with an anion-to-cation ratio of 0.96, close to 1.00. These results indicate good anion-cation charge balance and reliable data.

2.3 Methods

2.3.1 Piper Diagram

The Piper diagram is an effective graphical method for classifying water sample chemical types and examining water-rock interactions around sampling points (Piper, 1944; Wang, 1983). The diagram consists of cation triangles (Ca^{2+} , Mg^{2+} , and $\text{Na}^+ + \text{K}^+$), anion triangles (Cl^- , SO_4^{2-} , and $\text{HCO}_3^- + \text{CO}_3^{2-}$), and a central diamond area.

2.3.2 Gibbs Diagram

Gibbs diagrams intuitively reflect hydrochemical characteristics of different water bodies. Based on relationships between TDS and molar concentration ratios of cations ($\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$) or anions ($\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$), influencing factors can be broadly categorized as atmospheric precipitation, rock weathering, or evaporative crystallization (Gibbs, 1970). When TDS is moderate (~70–300 mg/L) and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ or $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ ratios are less than 0.50 (sample points distributed in the middle or left side), rock weathering exerts obvious influence. When TDS is low (<70 mg/L) and these ratios approach 1.00 (lower right corner), atmospheric precipitation dominates. When TDS is high (>300 mg/L) and ratios approach 1.00 (upper right corner), evaporative crystallization prevails (Yang, 2017).

2.3.3 End-Member Model

Gaillardet et al. (1999) analyzed 60 global rivers and proposed end-member diagrams to identify weathering products affecting surface and groundwater chemistry, categorizing them as carbonate, silicate, and evaporite rocks. Rock weathering types are determined by calculating ionic molar concentration ratios of $\text{Ca}^{2+} / \text{Na}^+$, $\text{Mg}^{2+} / \text{Ca}^{2+}$, and $\text{HCO}_3^- / \text{Na}^+$. Generally, when $\text{Ca}^{2+} / \text{Na}^+ \approx 50.00$, $\text{Mg}^{2+} / \text{Ca}^{2+} \approx 10.00$, and $\text{HCO}_3^- / \text{Na}^+ \approx 120.00$, carbonate rock weathering dominates. When $\text{Ca}^{2+} / \text{Na}^+ \approx 0.35 (\pm 0.15)$, $\text{Mg}^{2+} / \text{Ca}^{2+} \approx 0.24 (\pm 0.12)$, and $\text{HCO}_3^- / \text{Na}^+ \approx 2.00 (\pm 1.00)$, silicate rock weathering controls water chemistry. When $\text{Ca}^{2+} / \text{Na}^+ < 0.20$, $\text{Mg}^{2+} / \text{Ca}^{2+} < 0.12$, and $\text{HCO}_3^- / \text{Na}^+ < 1.00$, evaporite rock weathering predominates (Anatolaki and Roxani, 2009).

2.3.4 Enrichment Factor and End-Member Contribution Method

Enrichment factors assess the relative enrichment of chemical ions in water bodies compared to ocean (EF_{sea}) and soil (EF_{soil}) references to determine element sources and contributions. Following Xiao et al. (1993), this study used Cl^- and Ca^{2+} as reference elements for ocean and soil, respectively (Wang et al., 2015; Lu et al., 2017). The formulas are:

$$EF_{sea} = \frac{[X/Cl^-]_{sample}}{[X/Cl^-]_{sea}}$$

$$EF_{soil} = \frac{[X/Ca^{2+}]_{sample}}{[X/Ca^{2+}]_{soil}}$$

where X is chemical ion concentration ($\mu\text{eq/L}$) in water samples; $[X/Cl^-]_{sample}$ is the equivalent ratio of ion concentration to Cl^- concentration; $[X/Ca^{2+}]_{sample}$ is the equivalent ratio to Ca^{2+} concentration; and $[X/Cl^-]_{sea}$ and $[X/Ca^{2+}]_{soil}$ are background values for sea and soil.

The end-member contribution method identifies and quantifies potential ion sources, calculating three fractions: sea salt fraction (SSF; %), soil/rock weathering fraction (CF; %), and anthropogenic fraction (AF; %). For precipitation:

$$SSF = \frac{[Cl^-]_{sample}}{[Cl^-]_{sea}} \times 100\%$$

$$CF = \frac{[Ca^{2+}]_{sample} - [Ca^{2+}]_{sea}}{[Ca^{2+}]_{soil}} \times 100\%$$

$$AF = 100\% - SSF - CF$$

3.1 Spatial Variations in pH, TDS, and EC of Different Water Bodies

Water resources in the western alpine region are generally weakly alkaline, with pH ranging from 5.50 to 9.87 (Fig. 2a [Figure 2: see original paper]). River water, meltwater, groundwater, and precipitation exhibit pH ranges of 6.50–9.87, 5.50–8.94, 6.31–9.32, and 5.90–8.20, respectively, with mean values of 7.92, 7.58, 7.72, and 7.32. Only meltwater from the Ertix River Basin source area (Wei et al., 2016), precipitation from the Yangtze River Basin source area (Li et al., 2020c), and river water from the Lancang River Basin (Zhou et al., 1996) show weak acidity. Previous studies indicate average pH \approx 6.60 in the Yangtze River Basin source area (Pu et al., 1988; Wang et al., 2019b).

TDS ranges from 2.10 to 2996.34 mg/L (Fig. 2b [Figure 2: see original paper]), showing considerable variation. Generally, TDS < 1000 mg/L indicates relatively low salinity. Most basins have river water, meltwater, precipitation, and groundwater TDS < 100 mg/L, classifying them as low-salinity waters (Zhu et al., 2010; Feng et al., 2011; Pu et al., 2011; Li et al., 2018c; Bao, 2019; Liu et al., 2020c). Groundwater shows the highest average TDS (544.41 mg/L), followed

by river water (280.99 mg/L), with meltwater (72.48 mg/L) and precipitation (67.68 mg/L) showing the lowest values. In the Ertix, Heihe, Shiyang, and Shule River Basins and the Yellow River Basin source area, groundwater and river water TDS increase with runoff (Zhu et al., 2010; Wang et al., 2014; LYU, 2017; Li et al., 2018b; Gao et al., 2019; Zhang and Song, 2020; Meng, 2021). Conversely, river water TDS in the Yalong and Nagqu River Basin main streams decreases with increasing runoff (Li et al., 2014a; Wang et al., 2019a).

Electrical conductivity (EC) indicates TDS levels, as dissolved solids concentration directly affects conductivity (Wei et al., 2010b; Gu et al., 2017). Figure 2d [Figure 2: see original paper] shows a significant positive correlation between EC and TDS ($R^2 = 0.83$, slope = 1.53).

3.2 Spatial and Temporal Variations in Hydrochemistry of Different Water Bodies

Hydrochemical characteristics show seasonal fluctuations (Wu et al., 2008). Typically, ion concentrations are lower during ablation periods for all water bodies (Xu, 2016; Labaciren, 2017; Li et al., 2018c; Yang et al., 2018; Zhu et al., 2018; Shi et al., 2021). Rising temperatures and increased precipitation during ablation initially decrease precipitation ion concentrations. Subsequent increases in glacial and snow meltwater reduce meltwater ion concentrations. Combined increases in precipitation and meltwater dilute river water ions, while surface water-groundwater interchange further diminishes groundwater concentrations (Li et al., 2016b; Webb et al., 2018). However, early melting releases large amounts of dust and chemicals into runoff, potentially increasing river water ion concentrations. Temporal variation depends on dilution intensity by precipitation/meltwater and chemical release intensity from meltwater (Yang et al., 2021). During freezing periods, decreasing temperatures, reduced ablation, and evapotranspiration increase ion concentrations in glacial and snow meltwater (Chang, 2019). In spring and winter, increasing precipitation ion concentrations correlate with meteorological events such as sand and dust storms (Dong et al., 2014; Li et al., 2016a). Different hydrological recharge modes during various periods create spatial differences in ion concentrations. For example, Binggou River hydrochemistry in the Shiyang River Basin is primarily affected by meltwater and groundwater before and after the rainy season, with precipitation exerting greater influence during the rainy season (Xiang, 2020).

Ion concentrations vary considerably among water bodies and show significant spatial differences (Meybeck, 2003). Figure 3 [Figure 3: see original paper] illustrates precipitation ion variations across river basins. Average total ion concentrations in precipitation are <20 mg/L in the Heihe (9.21 mg/L), Shiyang (15.24 mg/L), Yarlung Zangbo (9.14 mg/L), Yangtze (18.66 mg/L), Baishui (2.96 mg/L), and Urumqi (13.68 mg/L) River Basin source areas. The Shule River Basin source area shows the highest precipitation ion concentration due

to frequent dust events (Yu and Zhao, 2017). Ca^{2+} dominates cation concentrations (47.41–79.49% of total cations), while HCO_3^- dominates anions in most basins (45.97–84.90% of total anions), indicating strong crustal dust influence. In the Heihe River Basin, major anions are NO_3^- (2.93 mg/L), Cl^- (2.43 mg/L), and SO_4^{2-} (1.42 mg/L), with elevated NO_3^- potentially resulting from human activities and unestimated HCO_3^- (Li et al., 2015a).

Meltwater ion variations across basins (Fig. 4 [Figure 4: see original paper]) reflect different ion sources and dissolution processes (Li et al., 2015b). As another form of precipitation recharge, meltwater generally shows low ion concentrations (0.86–434.42 mg/L). The Shule River Basin exhibits the highest average cation (110.41 mg/L) and anion (324.01 mg/L) concentrations due to strong influence from Asian dust source region terrestrial minerals (Dong et al., 2013). The Kuytun River Basin shows the lowest concentrations (0.25 and 0.26 mg/L) due to high-altitude sampling points where westerly-driven marine water vapor is the main meltwater source (Dong et al., 2010). Ca^{2+} is the major meltwater cation (42.84–89.79% of total cations), indicating calcite and dolomite dissolution (Ma et al., 2023). HCO_3^- dominates anions in Tarim, Heihe, Shule, and Urumqi River Basin source areas, while SO_4^{2-} dominates in Shiyang, Rongbuk, and Kuytun River Basins, primarily from soil/dust sources like sulfate rocks (Wang et al., 2016). NH_4^+ and NO_3^- concentrations reflect human impacts, with the highest average NO_3^- concentrations in the Ertix, Yarlung Zangbo, Yangtze, Yellow, and Ili River Basin source areas, indicating anthropogenic interference. Anion concentrations in Urumqi, Tarim, Heihe, and Shule River Basin source areas follow $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$, showing similarities with inland river basin hydrochemistry.

River water ion variations across basins (Fig. 5 [Figure 5: see original paper]) show average concentrations ranging from 8.01–76.63 mg/L for Ca^{2+} , 1.01–132.39 mg/L for Na^+ , 0.90–36.27 mg/L for Mg^{2+} , 0.72–4.83 mg/L for K^+ , 13.18–177.51 mg/L for HCO_3^- , 0.28–176.40 mg/L for SO_4^{2-} , 6.08–240.10 mg/L for Cl^- , and 0.03–7.15 mg/L for NO_3^- . The Shule River Basin shows the highest total cation (241.64 mg/L) and anion (584.01 mg/L) concentrations, while the Urumqi River Basin source area shows the lowest (16.85 and 49.43 mg/L). Ca^{2+} dominates river water cations in most basins (Hu, 2019; Liu et al., 2020a; Wang et al., 2021a; Zhang et al., 2021b; Xie et al., 2024), though Na^+ dominates in the Shule (54.79%), Yangtze source (58.73%), and Jinsha (55.17%) River Basins (Yang et al., 2021; Yuan et al., 2021; Li et al., 2023). Na^+ primarily derives from rock salt or groundwater mineral recharge (Qu et al., 2015), though dominant ions may change temporally. For example, Ca^{2+} dominated Jinsha River Basin source area samples collected in 2020, mainly from carbonate rock weathering (Kang and Li, 2023).

Groundwater ion variations are primarily influenced by flow-through area geology and depth, showing horizontal zonation with concentrations decreasing with depth (Ma et al., 2005; Bai and Yang, 2007; LYU, 2017; Miao et al.,

2020). Groundwater generally shows higher ion concentrations than other water bodies. Figure 6 [Figure 6: see original paper] shows groundwater ion variations across basins. The Tarim River Basin exhibits the highest total ion concentration (1095.80 mg/L) due to recharge by numerous rivers and sparse vegetation with low purification capacity (Wang et al., 2021e; Ma et al., 2021). The Yarlung Zangbo River Basin shows the lowest concentration (262.68 mg/L) due to its plateau climate, alpine meltwater-precipitation runoff sources, and abundant vegetation. Cation concentration orders vary by basin: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ in Heihe and Shiyang River Basins (Yang, 2017; Xie et al., 2024); $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ in Tarim, Yangtze source, and Yellow River source basins (Li et al., 2018c; Li et al., 2020b; Wang et al., 2021e); and similar concentrations of Na^+ , Mg^{2+} , and Ca^{2+} in the Shule River Basin (32.96%, 32.52%, and 32.22%, respectively) (Wang et al., 2015). Anion concentration orders also vary: $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ in Heihe, Shule, Yarlung Zangbo, and Yellow River source basins (Wang et al., 2015; Zhang et al., 2018a; Ma, 2019; Li et al., 2020b; Xie et al., 2024); $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$ in Shiyang River Basin (Ma et al., 2021); and $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$ in Yangtze River source basin (Li et al., 2018c). NO_3^- concentrations are low (<7.00%), indicating minimal human influence (Deng et al., 2007).

3.3 Hydrochemical Type of Different Water Bodies

Figure 7 [Figure 7: see original paper] illustrates hydrochemical types across water bodies. Precipitation, an important water source maintaining seasonal runoff (Lan et al., 2010), significantly impacts ion concentration variations. pH and concentrations of K^+ , Cl^- , Na^+ , SO_4^{2-} , and HCO_3^- show complex fluctuations with precipitation changes (Shi et al., 2015). Ca^{2+} dominates precipitation cations, while SO_4^{2-} dominates anions in the Tarim River Basin and HCO_3^- dominates in the Qinghai-Xizang Plateau permafrost area (Sun et al., 2002; Liu et al., 2004; Ma et al., 2012; Li et al., 2020c; Yu and Zhao, 2017). The hydrochemical type is HCO_3^- - Ca^{2+} .

Glacial and snow meltwater, the second-most important water source, is increasingly critical as accelerated glacier melting under global warming puts glaciers in negative equilibrium, making meltwater runoff a primary supply for major rivers (Pu, 2015; Li et al., 2020a). Glacier retreat intensifies the regional water cycle (Wang et al., 2011). Meltwater hydrochemistry is dominated by HCO_3^- - Ca^{2+} (Fig. 7b [Figure 7: see original paper]), particularly in Urumqi and Ili River Basin source areas (Li et al., 2011b; Zhao, 2012; Wei et al., 2016; Li, 2018; Ma et al., 2021). These types match those observed on the Qinghai-Xizang Plateau during 2008–2010 (Zhang et al., 2016).

Rivers, primary water cycle components and important surface water resources, reflect local water quality through their hydrochemistry (Li et al., 2022). River

water in the study area is characterized by alkaline earth metals and weak acidity, with Ca^{2+} as the dominant cation and HCO_3^- as the dominant anion, though SO_4^{2-} dominates in some basins. HCO_3^- - Ca^{2+} is the dominant hydrochemical type in the Ertix, Tarim, Yarlung Zangbo, Yangtze source, Yellow River source, Nujiang, Lancang, Yalong, and Minjiang River Basins (Huang et al., 2011; Li et al., 2014a; Tao et al., 2015; Wei et al., 2016; Li, 2018; Liu et al., 2019; Liu et al., 2020a; Wang et al., 2021a). This type also dominates alpine regions globally, such as the upper Indus River Basin and Koshi River Basin in China and Nepal (Bhat et al., 2023; Bishwakarma et al., 2024). SO_4^{2-} - Ca^{2+} dominates in the Urumqi River Basin source area and Rongbuk River Basin (Liu et al., 2000; Feng et al., 2011). Cl^- - Na^+ characterizes the Jinsha River Basin (Yuan et al., 2021). HCO_3^- - Ca^{2+} · Mg^{2+} dominates the Heihe River Basin (Zhu et al., 2008; Yang et al., 2011; Feng et al., 2017; Li et al., 2017a). The Shiyang River Basin shows strong acid dominance, with HCO_3^- - Ca^{2+} in upstream areas, changing with runoff increase (Yang, 2017). The Shule River Basin shows HCO_3^- - Ca^{2+} · Mg^{2+} and HCO_3^- - Ca^{2+} · Cl^- types (Zhou et al., 2004).

Groundwater, widely distributed and resistant to contamination, has become a significant potable water source (Zhang et al., 2021a), with security affecting human society's health and stability (Li, 2021; Li et al., 2021). Groundwater cations are mainly Mg^{2+} and Ca^{2+} , while anions are primarily HCO_3^- and SO_4^{2-} (Fig. 7d [Figure 7: see original paper]), consistent with findings in high-altitude Austrian alpine areas (Strauhal et al., 2016). HCO_3^- - Ca^{2+} · Mg^{2+} and HCO_3^- - Ca^{2+} · Cl^- - Na^+ dominate the upper Heihe River Basin (Ma, 2019). HCO_3^- - Ca^{2+} · Mg^{2+} characterizes recharge areas of the Shiyang, Shule, and Yarlung Zangbo River Basins (Wang et al., 2014; Liu et al., 2020c; Zhang and Song, 2020). Cl^- - Na^+ dominates frozen soil layers in the Yangtze River source area, affected by altitude (Li et al., 2018c). HCO_3^- - Ca^{2+} dominates the Yellow River source area (Wang et al., 2021f). HCO_3^- - Ca^{2+} · Mg^{2+} characterizes the northern Nagqu River in the Nujiang River source area (Zhao, 2020).

3.4.1 Factors Controlling the Hydrochemical Characteristics of Different Water Bodies

Precipitation ion sources include terrigenous material supply, sea salt aerosol transfer, anthropogenic influences, and climate change (Sun et al., 2002; Liu et al., 2004; Ma et al., 2012; Li et al., 2017a, 2020c; Yu and Zhao, 2017). The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model is commonly used to determine water vapor and ion sources (Li et al., 2015a; He et al., 2019). For example, most air masses reaching the Qilian Mountains originate from the west, traversing desert areas, while some monsoon air masses come from the Indian Ocean (Wang et al., 2016). Shiyang River Basin water vapor is influenced by monsoon precipitation, westerly precipitation, and local

water vapor cycles (He et al., 2019; Zhang et al., 2020). Shule River Basin ion sources show seasonal variation, with Na^+ typically from marine sources but terrestrial in winter (Zhao, 2017). Yangtze River source area water vapor sources exhibit seasonal variations and altitude effects (Li et al., 2020c). In the Urumqi River source area, local climate and human activities significantly influence precipitation ion concentrations, followed by ocean or surrounding salt lake effects (Hou, 2001). In the Tarim River Basin, 85.54% of precipitation ions come from crustal sources, only 4.87% from marine sources, with composition significantly influenced by westerly circulation (Wang et al., 2021a). Thus, precipitation chemistry is controlled by different atmospheric circulation backgrounds and air mass sources (Wang et al., 2019b).

River water ions primarily derive from combined rock weathering and evaporative crystallization (Fig. 8a [Figure 8: see original paper]). In the Ertix and Shule River Basin source areas, river water ions are more susceptible to combined rock weathering and atmospheric precipitation effects (Su and Tang, 1987; Deng, 1988; Wang et al., 2010; Li et al., 2014b; Wei et al., 2016; Wang et al., 2019a; Zhao et al., 2020; Wang et al., 2021f). Meltwater ion composition and concentration are mainly affected by rock weathering and atmospheric precipitation (Fig. 8b [Figure 8: see original paper]), with chemical formation processes involving adsorption, dissolution, and precipitation (Li et al., 2015b). In some regions like the Shule River Basin and Yuzhu Peak Glacier in the Kunlun Mountains, meltwater is also influenced by evaporative crystallization (Song et al., 2019; Yang et al., 2021). Glacier and snow melting rates also affect meltwater ion concentrations (Li et al., 2019b). During circulation, groundwater undergoes chemical reactions with aquifer media that determine component formation and evolution (Yu et al., 2021). Groundwater hydrochemistry is mainly affected by salt dissolution, weathering, and evaporation (Fig. 8c [Figure 8: see original paper]), with rock salt weathering affecting the Yarlung Zangbo River Basin. Groundwater hydrochemistry determination is complicated by natural factors such as aquifer lithology, geological formations, and human activities (Liu et al., 2020b). Chemical weathering of rock salts is an important ion source and a key link between the lithosphere, hydrosphere, atmosphere, and terrestrial-oceanic cycles (Balagizi et al., 2015), as observed in the Chena River, USA, and Gangotri Glacier, India (Douglas et al., 2013; Ahmad and Ansari, 2020).

3.4.2 Influence of Rock Types on Hydrochemistry of Different Water Bodies

Meltwater in the study area primarily interacts with carbonate and silicate rocks, with evaporite rocks (sulfuric acid rocks) present at some sites (Fig. 9a [Figure 9: see original paper]) (He et al., 2019; Song et al., 2019). River water primarily interacts with carbonate and evaporite rocks (Fig. 9b [Figure 9: see original paper]), mainly chlorinated sedimentary rocks and sulfate minerals. The Yellow River source area is also affected by silicate rocks, with rock weath-

ering contributions more evident during wet seasons (Xia et al., 2000; Zhou et al., 2004; Yang et al., 2011; Zhang et al., 2017; Bao, 2019; Liu et al., 2019; Li et al., 2020b; Ma et al., 2021; Renzeng et al., 2021; Wang et al., 2021c; Wang et al., 2021f). Groundwater hydrochemistry is affected by weathering and dissolution of surrounding salt rocks (dominated by carbonates) (Fig. 9c [Figure 9: see original paper]), such as calcite and dolomite dissolution. Human activities are more intensive in middle and lower river reaches under industrial and agricultural influences (Shi et al., 2001; Zhu et al., 2010; Guo et al., 2015; Liu et al., 2020c; Meng, 2021; Wang et al., 2021f).

3.4.3 Correlations Between Chemical Ions in Different Water Bodies

Pearson correlation coefficients between ions reflect material origins and chemical reaction characteristics (Başak and Alagha, 2004). Figure 10 [Figure 10: see original paper] shows significant positive correlations ($P < 0.01$) between TDS, EC, and ion concentrations across all water bodies (Zhang et al., 2018b). High positive correlations indicate consistent ion sources and forms (Wang et al., 2019b).

For precipitation, correlation coefficients between Cl^- and Na^+ , Cl^- and Ca^{2+} , and Cl^- and SO_4^{2-} all exceed 0.80 (Fig. 10a [Figure 10: see original paper]), consistent with enrichment factor analyses. This correlation analysis broadly encapsulates ion relationships across basins. In the Shiyang River Basin, significant correlations between Ca^{2+} with Na^+ and K^+ with Mg^{2+} reflect crustal source contributions, while Cl^- and Na^+ may derive from marine sources, soil dust aerosols, and human activities (Ma et al., 2012). In the Yangtze River source area, significant positive correlations among Na^+ , Ca^{2+} , and Mg^{2+} , and between Cl^- with Ca^{2+} , Mg^{2+} , and K^+ , indicate multiple source control (Li et al., 2020c).

Meltwater ion correlations (Fig. 10b [Figure 10: see original paper]) show the highest coefficient between Cl^- and Na^+ (0.75). SO_4^{2-} correlations with Mg^{2+} , K^+ , and HCO_3^- exceed 0.70, while K^+ correlations with Ca^{2+} , HCO_3^- , and SO_4^{2-} are 0.74, 0.78, and 0.72, respectively. Sources include dolomite, silicates, carbonates, and evaporites. Na^+ shows significant correlation with HCO_3^- ($r = 0.74$). This analysis reflects regional characteristics and demonstrates universal applicability. Significant correlations exist between cations in meltwater from Huohugou No.12 Glacier in the Qilian Mountains and Hasilegen No.51 Glacier in the Tianshan Mountains (Dong et al., 2010, 2013), and between EC/TDS and other ions (Song et al., 2019). In the Urumqi River source area, significant Ca^{2+} - SO_4^{2-} correlation likely reflects Central Asian dust source crustal minerals, with good EC-pH correlation (Li et al., 2011b). Significant SO_4^{2-} - Mg^{2+} correlation occurs in Glacier No.72 of Qingbingtan, Tomur Peak (Zhao et al., 2012). In the

Qilian Mountains, Cl^- derives mainly from sea salt, soil dust, and saline lake materials, while Na^+ is primarily marine-sourced (Dong et al., 2013; Wang et al., 2016).

River water ion correlations (Fig. 10c [Figure 10: see original paper]) show significant positive correlations between Cl^- and Na^+ ($r = 0.83$) and Cl^- and K^+ ($r = 0.77$). SO_4^{2-} and Ca^{2+} show significant positive correlation ($r = 0.86$). HCO_3^- is positively correlated with Ca^{2+} , Na^+ , and K^+ ($P < 0.001$), indicating carbonate rock weathering. K^+ - Na^+ correlation is 0.67. Mg^{2+} is positively correlated with K^+ , SO_4^{2-} , Cl^- , Na^+ , and Ca^{2+} ($P < 0.001$). This analysis is consistent with individual basin studies. In the Yarlung Zangbo River, TDS is positively correlated with Ca^{2+} , Mg^{2+} , K^+ , Na^+ , HCO_3^- , Cl^- , and SO_4^{2-} , indicating these constituents are TDS sources. SO_4^{2-} is significantly correlated with Ca^{2+} and Mg^{2+} due to carbonate and sulfate mineral weathering, while Na^+ , K^+ , and Cl^- may derive from evaporite dissolution (Liu et al., 2018). In the Ertix River Basin, Na^+ , K^+ , and Cl^- generally derive from atmospheric precipitation, evaporite weathering, and anthropogenic input (Liu et al., 2020a). In the Nujiang River source area, significant correlations exist between Ca^{2+} and HCO_3^- and among Mg^{2+} , Na^+ , and K^+ (Zhao et al., 2020). Significant positive correlations exist among ions in the Yellow River Basin (He et al., 2017).

Groundwater ions show significant positive correlations ($P < 0.001$), with Cl^- - Na^+ , Ca^{2+} - SO_4^{2-} , and Mg^{2+} - HCO_3^- coefficients all exceeding 0.80 (Fig. 10d [Figure 10: see original paper]). Shule River Basin TDS changes are mainly related to Na^+ and SO_4^{2-} , reflecting ion correlations (Guo et al., 2015). HCO_3^- and Mg^{2+} significantly contribute to TDS in the Lhasa River Basin of the Yarlung Zangbo River, indicating rock weathering dominance in hydrochemical evolution (Zhang et al., 2018a). In the Yangtze River source area suprapermafrost water, Ca^{2+} is significantly positively correlated with Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , and Cl^- , suggesting common sources, with SO_4^{2-} and Cl^- mainly from evaporite dissolution (Li et al., 2018c). Yellow River source area groundwater TDS is positively correlated with HCO_3^- , Ca^{2+} , and Mg^{2+} , indicating carbonate karst hydrolysis as the main chemical component source (Wang et al., 2021f). In the Heihe River Basin, HCO_3^- and Mg^{2+} may derive from dolomite weathering, while Ca^{2+} and SO_4^{2-} come from gypsum, dolomite, and surface water leaching (Zhu et al., 2010).

3.4.4 Quantification of Hydrochemical Ion Sources

Table 2 shows that Ca^{2+} , Mg^{2+} , K^+ , and HCO_3^- in all water bodies are typical crustal source ions. For Ca^{2+} and HCO_3^- , non-marine source contributions exceed 99.00%, while K^+ shows 96.75–98.65% non-marine contributions. Mg^{2+} anthropogenic contributions can be clearly quantified, though crustal sources re-

main dominant: 78.98% crustal and 17.96% anthropogenic in meltwater; 76.31% and 23.14% in river water; and 48.56% and 50.15% in groundwater. Sources and contributions for Ca^{2+} , Mg^{2+} , K^+ , and HCO_3^- are consistent with findings in terrestrial ecosystem and karst valley areas in China (Huang et al., 2019).

As an ocean indicator, Cl^- sources are mainly sea salt and water vapor under atmospheric circulation, with minimal crustal contribution. Despite significant Na^+ - Cl^- correlation (Fig. 10), Na^+/Cl^- ratios are high: 1.97 in precipitation, 2.12 in meltwater, 12.48 in river water, and 4.45 in groundwater, indicating additional Na^+ sources beyond marine inputs, such as rock weathering (Li et al., 2024). SO_4^{2-} EF_{sea} and EF_{soil} values >1.00 indicate enrichment relative to ocean and soil. Anthropogenic contributions for SO_4^{2-} can exceed 88.05%, though remote and local contributions through atmospheric circulation and crustal dust cannot be ignored. For example, increased NO_3^- concentration in the Chena River, USA, is also associated with precipitation events (Douglas et al., 2013).

3.5 Hydrological Processes Indicated by Hydrochemistry

The study area is dominated by the Qinghai-Xizang Plateau, where frequent precipitation and widespread glaciers and frozen soils create diversified runoff recharge forms (Yao and Yao, 2010), subjecting river runoff ion concentrations to change. Precipitation in glacier areas recharges glacial and snow meltwater (Wu et al., 2008), consistent with Cl^- source analysis (Table 2) (Dong et al., 2013). Isotope analysis typically demonstrates hydrological transformation processes (Liu et al., 2019; Shi et al., 2021). Mutual recharge between surface water and groundwater is observable through ion concentration changes and TDS differences (Wu et al., 2008; Ma, 2019; Yang et al., 2021). Acid ion concentrations can indicate precipitation and meltwater recharge effects on groundwater (Zhu et al., 2018). Li et al. (2022) confirmed hydrological recharge processes by combining hydrochemical evolution with hydrochemical type characteristics. Figure 11 [Figure 11: see original paper] illustrates these processes.

Precipitation hydrochemistry is affected by meteorological factors, atmospheric circulation, human influences, and aerosols, forming through aerosol scouring and wrapping rather than direct surface interactions. Consequently, precipitation shows the lowest ion concentrations, followed by meltwater. Meltwater forms in a pure alpine environment with weak rock weathering and low temperatures that reduce weathering intensity, resulting in relatively low ion concentrations (Li et al., 2020a). Groundwater and river water experience the most intense water-rock interactions, with significant silicate and carbonate weathering, groundwater infiltration by surface water, and mutual conversion, producing the highest ion concentrations. The difference in mean ion concentrations between groundwater and river water is relatively small, with similar proportions (Fig. 11a and b [Figure 11: see original paper]). However, data collection biases

create observable anion-cation imbalances. In summary, western alpine region hydrological processes are influenced by temperature, precipitation, water-rock interactions, rock weathering (mainly silicates and carbonates), atmospheric circulation, and human activities, with precipitation and meltwater as main inputs and mutual river water-groundwater recharge.

4 Conclusions

This study synthesized hydrochemical research findings across the western alpine region of China at regional and basin scales. Water resources are generally weakly alkaline with low TDS. Hydrochemical characteristics show significant seasonal fluctuations, with relatively high ion concentrations in inland river basins (e.g., Shule and Tarim River Basins). River water and meltwater hydrochemistry is dominated by HCO_3^{2-} - Ca^{2+} types. Groundwater cations are dominated by Mg^{2+} and Ca^{2+} , with HCO_3^{2-} as the dominant anion. Precipitation is dominated by Ca^{2+} cations and SO_4^{2-} anions, followed by Mg^{2+} and HCO_3^- . River water chemistry is primarily influenced by combined rock weathering and evaporation-crystallization. Meltwater composition is mainly affected by rock weathering and atmospheric precipitation. Groundwater chemistry is affected by surrounding salt rock weathering, dissolution, and evaporation-crystallization. Precipitation ion inputs derive from sea salt, crustal, and anthropogenic sources, with non-marine contributions exceeding 96.00% for Ca^{2+} , K^+ , and HCO_3^- , and anthropogenic contributions exceeding 88.00% for SO_4^{2-} and NO_3^- . Marine source contributions for Na^+ in precipitation and meltwater are relatively high (43.73% and 40.57%, respectively). Precipitation and meltwater are the main water inputs, with mutual recharge between river water and groundwater. This systematic review and analysis of hydrochemical characteristics provides a thorough understanding of spatiotemporal patterns and influencing factors, laying a strong foundation for long-term monitoring networks and enhancing understanding of hydrochemical changes in cold regions. Future work will integrate remote sensing technology for comprehensive hydrochemical dynamics analysis and combine this with meteorological data to explore underlying change mechanisms.

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