Research papers

Hydrogeochemical characterization and CO₂ consumption in the Maqu catchment of the Qinghai-Tibetan Plateau by multiple hydrogeochemical methods

Mengna Li a,b,c,d, Hui Qian a,b,c, Maciek W. Lubiczynski d, Panpan Xu a,b,c, Zhongbo Su d,*, Yijian Zeng d,*, Jie Chen a,b,c, Kai Hou a,b,c, Qiying Zhang e

a School of Water and Environment, Chang’an University, Xi’an 710054, Shaanxi, China
b Key Laboratory of Subsurface Hydrology and Ecological Effect in Arid Region of Ministry of Education, Chang’an University, Xi’an 710054, Shaanxi, China
c Key Laboratory of Eco-hydrology and Water Security in Arid and Semi-arid Regions of Ministry of Water Resources, Chang’an University, Xi’an 710054, Shaanxi, China
d Faculty of Geo-Information Science and Earth Observation (ITC), University of Twente, Enschede 7500 AE, The Netherlands
e School of Architectural and Civil Engineering, Xi’an University of Science and Technology, Xi’an 710054, Shaanxi, China

ARTICLE INFO

This manuscript was handled by Huaming Guo, Editor-in-Chief

Keywords:
Hydrogeochemistry
Stable isotopes
Inverse modelling
CO₂ consumptions
Qinghai-Tibetan Plateau

ABSTRACT

The Qinghai-Tibetan Plateau (TP) is the source of many large Asian rivers and has significant social, ecological and economic importance. However, few hydrogeochemistry and stable isotope studies have been performed in the Maqu catchment of the eastern TP. In this study, the hydrogeochemical composition and stable isotopes (δD and δ¹⁸O) of surface water and groundwater samples collected in the Maqu catchment were analysed to characterise the surface water and groundwater, investigate the contributions of different sources, and determine CO₂ consumptions. Different techniques were used, including inverse modelling, end member mixing analysis (EMMA), and a forward mass balance model. The results indicated that all water samples are of the HCO₃⁻-Ca type. Both the surface water and groundwater are of meteoric origin and there is close contact between them (except wetlands). Water in the wetlands is substantially evaporated (0–45%). Calcite and illite generally precipitate, whereas chloride and CO₂ generally dissolve along groundwater flow paths in the east. The mean contributions of fresh surface waters, mountain-front groundwaters, and anthropogenic inputs to the surface water samples are 56%, 16%, and 28%, respectively. Carbonate and silicate weathering are the dominant sources of major cations. Moreover, high CO₂ consumption rates in both the surface runoff and groundwater make the Maqu catchment an important carbon sink in the Yellow River Basin. With many newly-found conclusions on the Maqu catchment, the present study not only provides insight into the catchment but also contributes to a comprehensive understanding of the water cycle and CO₂ consumptions on the TP.

1. Introduction

The Qinghai-Tibetan Plateau is the highest and largest plateau on the Earth (Zhang et al., 2020). It covers an area of approximately 2.6 × 10⁶ km², accounting for approximately two percent of the land surface area of the earth (Zhang et al., 2002). With a mean elevation exceeding 4000 m above sea level (asl), the TP is characterised by a peculiarly cold climate between the latitudes of 26°N and 40°N and has developed the largest number of glaciers outside of the polar regions (Deng et al., 2021; Xu et al., 2008; Yao et al., 2012). Due to the high elevation and a large amount of solid water storage, the TP is called the “Water Tower of Asia” and feeds many large rivers such as the Yellow and Yangtze Rivers (Huang et al., 2008; Zhou and Zhang, 2021). More than 1.4 billion people living in Southeast Asia depend on the waters that originate from the TP (Immerzeel et al., 2010). Therefore, the hydrogeochemistry of the TP is an important issue.

There are existing studies on the hydrogeochemistry and stable isotopes of the TP. Huang et al. (2011) studied the hydrogeochemical composition of the Yarlung Tsangpo and its major tributaries, the Tsangpo, Nyangchu, and Lhasa Rivers, on the TP and determined possible mechanisms controlling the hydrogeochemistry. Qu et al. (2019) provided an overview of the mechanisms governing the
hydrogeochemistry in 11 rivers of the TP. Yang et al. (2021b) used stable isotopes to trace the potential water sources of the Nagqu River on the TP. In addition to the ‘integrated results’ of studies on the large rivers on the TP, catchment-scale investigations are also important for understanding the local hydrology. Zhu et al. (2010) studied the hydrogeochemical characteristics and determined the source and dominant processes controlling the main ion composition in the Pumayum Co lake catchment, southern TP. Pan et al. (2022) published a comprehensive hydrogeochemical dataset of an alpine catchment in the northern TP including major and minor elements, dissolved organic carbon (DOC) and stable and radioactive isotopes. Zhou et al. (2021) investigated streamflow generation using isotopic and hydrogeochemical tracers in semiarid, glacier-covered, montane catchments in the upper Shule River, northeastern TP. However, in the Maqu catchment, the eastern TP, systematic hydrogeochemical and isotopic datasets are scarce.

Hydrogeochemistry and stable isotopes provide valuable information on the sources, age, water–rock interactions and mixing of different water bodies (Barberio et al., 2021; Chen et al., 2014; Gori et al., 2023; Guo et al., 2020; Kanduc et al., 2012; Kohfahl et al., 2008; Qian et al., 2020). The hydrogeochemical composition of natural waters reflects the history of water formations and transports to a certain extent (Chen et al., 2020; Gao et al., 2020; Gao et al., 2006; Guo et al., 2019; Li et al., 2022b). Stable isotopes have been used to identify water sources, the proportion of groundwater mixing and flow paths in recent studies (Bekele et al., 2019; Hassan and Ersoy, 2022; Li et al., 2019c; Ogrinc et al., 2018; Xu et al., 2019b). Cui and Li (2015) explored runoff processes and their relationship with climate change in the Qinghai Lake Basin river on the TP based on stable isotopes and hydrogeochemistry. Li et al. (2020a) clarified the main hydrological and hydrogeochemical effects of thermokarst lakes during frozen soil melting in summer in the Beiluhe Basin, TP, using stable isotopes and hydrogeochemistry. Thus, hydrogeochemistry and stable isotopes can provide valuable information on the TP. However, detailed analyses of the hydrogeochemistry and stable isotopes in the Maqu catchment are not common.

Inverse modelling is a powerful tool to quantify reactions along groundwater flow paths (Sharif et al., 2008; Slimani et al., 2017; Xie et al., 2013; Xu et al., 2021) that has been used in numerous studies (Chidambaram et al., 2012; Hashemi et al., 2013; Li et al., 2012; Sharif et al., 2008). Inverse hydrogeochemical modelling by PHREEQC calculates phase mole transfers to account for differences between the initial and final water composition along a groundwater flow path (Parkhurst and Appelo, 1999). Zheng et al. (2019) studied the evolution of shallow geothermal waters with a hydrogeochemical PHREEQC model in the Yangbajing geothermal field on the TP. Li et al. (2022a) found that the dissolution of silicate minerals and cation exchange controlled the groundwater composition in the Zhaxikang geothermal area, South TP, based on PHREEQC modelling. Wang et al. (2022b) studied the water–rock interactions in the Yangyi geothermal field on the TP and revealed that calcite and fluorite dissolve along the flow path, which leads to increased concentrations of Ca$^{2+}$, HCO$_3^-$, and F$^-$. In general, PHREEQC is more often used for geothermal waters than for nonthermal groundwaters on the TP (Chen et al., 2023; Li et al., 2021a; Liu et al., 2019c; Liu et al., 2022; Pan et al., 2021; Wang et al., 2018) and has never been used to quantify reactions along nonthermal groundwater flow paths in the Maqu catchment.

Mixing models have provided tremendous insights into water sources and watershed flow paths (Shanley et al., 2011; Wang et al., 2022a; Xu et al., 2019a). In the 1990s, Christophersen and Hooper (1992) introduced end member mixing analysis (EMMA). Since then, EMMA has often been used to quantify different water sources: groundwaters, surface waters, and anthropogenic inputs. (Doctor et al., 2006; Kim et al., 2017; Pelizardi et al., 2017; Roques et al., 2014; Zhang et al., 2018). In hydrology, it is particularly valuable to delineate surface water with various water sources. For example, Shi et al. (2021) applied EMMA to the middle reaches of the Yarlung Zangbo River on the TP and found that groundwaters play an important role in maintaining the winter–spring baseflow with a contribution rate of 45.1%, and that deep circulating groundwater accounts for a contribution of 19.6 ± 9.9%. Wang et al. (2022a) used EMMA in the Yarlung Zangbo River and proved that precipitation is a dominant component of river runoff (10.7% to 65.9%) and that glacier meltwater is also an important source of river runoff. Therefore, to gain more knowledge on the water sources on the TP, EMMA is a promising tool. However, in the Maqu catchment on the eastern TP, such an analysis has not yet been performed.

The forward mass balance model using ion concentrations can quantify the contribution of different sources, such as precipitation, anthropogenic inputs and rock weathering, which helps clarify
hydrogeochemical processes (Ollivier et al., 2010; Stallard and Edmond, 1987). Li et al. (2019b) used the forward mass balance model to calculate the contributions of atmospheric inputs, human activities and rock weathering to dissolved solutes in the Wei River of China and revealed the dominant role of rock weathering. Liu et al. (2016) quantified the contribution of the atmosphere, anthropogenic inputs and rock weathering to dissolved solutes in the Wei River of China and calculated the contributions of atmospheric inputs, human activities and rock weathering accounted for 76.3% of the total dissolved cations. Therefore, the forward mass balance model is useful in determining the role of rock weathering on ion concentrations. However, to the authors’ knowledge, such a model has never been applied in the Maqu catchment to quantify the contribution of different sources.

Concentrations of CO₂ in the atmosphere have recently risen (Navarro-Sticher and Thyne, 2007). Geochemical weathering plays an important role in regulating CO₂ in the atmosphere over geological time scales (Raymond, 2017; Yu et al., 2019). To understand how CO₂ in the atmosphere has evolved, we need to first quantify the weathering rates or CO₂ consumption rates (Berner, 1991; Berner and Kothavala, 2001). Liu et al. (2019b) found that the rock weathering of the Yarlung Tsangpo River Basin on the TP, which comprises only 0.16% of the global surface area, can consume 0.54% of the global CO₂ consumptions. Wang et al. (2016) proved that the TP as the source of the Yellow River that accounts for only 30% of the area of the Yellow River Basin, could contribute 61% of the atmospheric CO₂ consumptions of the entire basin. Therefore, the TP is a vital area for global CO₂ consumptions. Nevertheless, a detailed analysis of CO₂ consumption in the Maqu catchment has not been reported.

Hence, different techniques, including hydrogeochemistry, stable isotopes, inverse modelling and mass balance calculation, were employed in the present study to (1) identify the hydrogeochemical and stable isotopic characteristics in the surface water and groundwater samples, (2) investigate the contributions of different sources and (3) characterise CO₂ consumptions in the Maqu catchment. To the authors’ knowledge, this is the first study to use inverse modelling to quantify the reactions along groundwater flow paths, conduct mass balance calculations, and characterise CO₂ consumptions in the Maqu catchment. The present study contributes to the comprehensive understanding of the water cycle and CO₂ consumptions in the Maqu catchment.

2. Study area

The study area is a catchment located in Maqu County, China, extending between the latitudes of 33°43′–33°58′ N and the longitudes of 101°51′–102°16′ E (Fig. 1). It is located at the eastern edge and the lower section of the TP, with an area of 532.34 km². It is also part of the Zoige Wetland Nature Reserve, which is the largest wetland plateau in China and contains the world’s largest preserved highland peat swamp (Wu et al., 2018). With wetland water storage of up to 840 million m³, the Zoige wetland is a crucial ecological functional area for water conservation in the Yellow River source region and an important habitat for wetland biodiversity conservation.

Field measurements and water sampling were carried out during the summer of August 5–8, 2018. A total of 29 water samples were collected including 20 groundwater samples and nine surface water samples (Fig. 1). All groundwater samples were collected from the phreatic aquifer. Based on the groundwater piezometric map by Li et al. (2021c), with a hydraulic head of 3389.10 m asl as the threshold, 20 groundwater samples could be equally divided into two groups: samples from high-head areas (GW-H) with numbers of G3, G8, G9, G10, G11, G12, G14, G17, G23, G20, G23, G30 and low-head areas (GW-L) with numbers of G13, G15, G16, G20, G21, G22, G24, G25, G26, G27 (Fig. 1). Each group contained 10 samples. The surface water samples consisted of one sample from the spring (S4), one sample from the stream (S31), one sample from the Yellow River (S5), two samples from the reservoir (S7, S18), and four samples from the wetland (S6, S19, S28, S29) (Table 1). It is to note that this separation is based on the kriging pattern between the currently available sampling locations. If more samples were available, this separation may change.

Temperature (T), pH, total dissolved solids (TDS), total hardness (TH), sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), chloride (Cl⁻), sulfate (SO₄²⁻), ammonia nitrogen (NH₄⁺) and chemical oxygen demand (COD) were analysed for all water samples. In situ measurements of the water temperature and pH were conducted using a portable metre (AP-700, Aquaread Ltd.). Average values were calculated from three to five repeated measurements. For other parameters, samples were analysed at the Water and Soil Testing Centre of the Shaanxi Institute of Engineering Prospecting. TDS was determined by drying the samples at 105 °C and weighing them with an analytical balance. K⁺ and Na⁺ were analysed using flame atomic absorption spectrophotometry with detection limits of 0.05 mg/L and 0.01 mg/L, respectively; Ca²⁺, Mg²⁺, SO₄²⁻ and TH were measured by EDTA titration with a detection limit of 1.0 mg/L; Cl⁻ was measured by silver nitrate titration with a detection limit of 1.0 mg/L; NH₄⁺ and COD were measured using silver reagent spectrophotometry (detection limit of 0.03 mg/L). COD was measured using MnO₄⁻ as the oxidant. The calculated charge balance error (C. B. E.) of the analytical results range from −3.2 to 3.7% within the acceptable limit of ± 5% indicating the accuracy of the analyses.

Samples for stable isotope analysis were transferred to clean glass
bottles after being filtered through a 0.45 μm membrane. Hydrogen and oxygen stable isotopes ($\delta^D$ and $\delta^{18}O$) were determined by a liquid–water isotope analyser (IWA-35-EP) with analytical precisions of 0.6% and 0.2% for $\delta^D$ (VSMOW) and $\delta^{18}O$ (VSMOW), respectively, in the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences (CAS).

Sample collection, transportation, and analysis were all undertaken with strict adherence to the standards of the Ministry of Health of the People’s Republic of China (PRC).

3.2. Data processing

3.2.1. Stable isotope analysis

Hydrogen and oxygen stable isotopes have been recognised for decades as powerful natural tracers of the water cycle (Craig, 1961; Craig and Gordon, 1965; Dansgaard, 1964). They are conservative, thus they do not react with soil materials (Yang et al., 2011) and have been widely used in the hydrological field (Fritz et al., 2022; Gibson et al., 2005; Putman et al., 2019).

The global meteoric water line (GMWL) is expressed as follows:

$$\delta D = 8 \times \delta^{18}O + 10\text{‰}$$  \hspace{1cm} (1)

The slope of the GMWL reflects near-equilibrium isotopic fractionation during the condensation of water vapour to form precipitation. The slope and intercept are mainly determined by the extent of water evaporation (Hu et al., 2018). Dansgaard (1964) defined $d$-excess as $\delta D - 8 \times \delta^{18}O$ (2).

$$d\text{-excess} = \delta D - 8 \times \delta^{18}O$$  \hspace{1cm} (2)

The average $d$-excess for global precipitation is 10% according to Eq. (1) and Eq. (2).

Based on stable isotopes, an evaporation model can quantitatively assess evaporation. Evaporation increases the concentration of dissolved species in water. When evaporation processes significantly modify the hydrogeochemistry, an evaporation model can be used to quantify these processes (equations for the evaporation model are provided in Appendix A).

3.2.2. Inverse modelling

Inverse modelling, implemented by PHREEQC (Parkhurst and Appelo, 2013), is used to quantify the reactions controlling groundwater hydrogeochemistry along flow paths (Simani et al., 2017). PHREEQC calculates possible reactions that can produce the observed hydrogeochemical changes between initial and final water samples (Chen et al., 1999; Plummer and Back, 1980). Due to lack of detailed lithology or mineral information in the study area, the minerals used in inverse modelling were limited to those presented in the Zoige. Previous studies in the Zoige report the presence of calcite, K-feldspar, illite, kaolinite, and chlorite (Chen et al., 1999; Hejing et al., 2008; Wu et al., 1997; Zhang et al., 2022). Others, such as gypsum and halite, were chosen based on the hydrogeochemical compositions of water samples. Carbon dioxide was included in the list of potential reactive components. Cation exchange reactions of $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ were enabled in the inverse modelling. The flow paths were selected based on the ground-water flow direction in the eastern study area where piezometric heads were available from Li et al. (2021c).

3.2.3. Mass balance calculation

3.2.3.1. End Member Mixing Analysis (EMMA)

In general, three sources of mass in water can be identified in the study area: surface waters, groundwaters, and anthropogenic inputs. Using water solutions from distinct sources as end members, end member mixing analysis (EMMA) was developed to calculate the mixing proportions of different water sources in the surface water samples under the following assumptions: (1) the solutes used in the EMMA behave conservatively; (2) the mixing process is linear; and (3) the hydrogeochemical composition of the end members does not change over time (Hooper, 2001; Hooper, 2003). The collinear structure in the bivariate scatter plots confirm the first two assumptions, conservative behaviour and linear mixing. Therefore, in bivariate scatter plots, solutes with the best linear fits can be selected as tracers. In addition, tracers that could help differentiate between different water sources can be especially targeted (Inamdar et al., 2013).

Principal component analysis (PCA) was incorporated to determine the number of end members. Before implementing PCA, tracer concentrations of the surface water samples were first standardised by subtracting the mean and dividing by the standard deviation of each species. Standardising the dataset prevents data with large variations from having more influence on the PCA model than a dataset with small variations (Burns et al., 2001). The number of eigenvectors to be retained was based upon the “rule of 1” (i.e., all eigenvectors associated with eigenvalues of greater than or equal to 1 were retained). There should be one more end member than the rank of the standardised dataset (i.e., the number of eigenvectors) (Hooper, 2003).

By multiplying the standardised dataset (excluding surface water samples representing end members) by the matrix of the eigenvectors, tracer concentrations for all water samples (excluding end member samples) could be projected into the mixing space. Tracer concentrations for all end members were then normalised using the surface water (excluding surface water samples representing end members) mean and standard deviation, and projected into the mixing space as well. When a water sample fits into the space defined by end members, the contribution of each end member was calculated using the mass balance equation (Doctor et al., 2006) (equations are provided in Appendix B). The selection of tracers, end members, and EMMA results in the Maqu catchment are presented in the section 4.5.

3.2.3.2. A forward mass balance model

In addition to using the EMMA method, the contributions of precipitation, anthropogenic inputs, and rock weathering to major ions were also quantified using a forward mass balance model. The main formation minerals in the study area are carbonate rocks and silicate rocks (Li et al., 2021c; Ma, 2002). The mass budget equation that models the budget for any element “X” in water (Chetelat et al., 2008; Galy and France-Lanord, 1999; Li et al., 2019b; Liu et al., 2016; Shen et al., 2021) can be expressed as:

$$\text{[X]} = \text{[X]_{atm}} + \text{[X]_{anth}} + \text{[X]_{lith}} + \text{[X]_{act}}$$  \hspace{1cm} (3)

where atm represents atmospheric inputs, anth represents anthropogenic activities, lith represents silicate weathering, and act represents carbonate weathering. Four assumptions enable the use of this equation: First, $\text{Cl}^{-}$ in excess of the atmospheric origin is considered anthropogenic and balanced by $\text{Na}^+$ (Li et al., 2009); second, due to the
low proportion of K\(^+\) to the total cations (approximately 2.0%, calculated in meq/L), and considering that there is no industry in the study area, anthropogenic inputs of Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), and SO\(_4\)^{2-} are not significant (Flintrop et al., 1996; Kaushal et al., 2017; Li et al., 2019a; Roy et al., 1999); third, the dissolution of carbonate does not contribute to K\(^+\) and Na\(^+\) (Liu et al., 2013); fourth, all SO\(_4\)^{2-} after atmospheric correction is from sulfide oxidation (Liu et al., 2016; Xu and Liu, 2010).

For atmospheric inputs, the average concentrations of the major precipitation ions in Darlag, adjacent to Maqu County, were used (Li et al., 2018). The contributions of atmospheric inputs, anthropogenic inputs, carbonate weathering, and silicate weathering were calculated as the ratio of dissolved cations from atmospheric inputs, anthropogenic inputs, carbonate weathering, and silicate weathering, respectively, to the sum of dissolved cations in water (detailed equations are provided in Appendix C).

### 3.2.4. CO\(_2\) consumption

Silicate and carbonate weathering at the Earth’s surface are important to global CO\(_2\) balances (Berner et al., 1983). Silicate weathering could potentially control long-term (50–100 Ma episodicity) climate change (Berner et al., 1983; Liu et al., 2011), while carbonate weathering could play a role in short-term (less than 3 ka) climate change (Kump et al., 2000; Liu et al., 2018; Oki et al., 1999). CO\(_2\) consumed via the geochemical weathering of silicate and carbonate rocks can be calculated as follows (Jia et al., 2021):

\[
\delta CO_2|_{\text{sil}} = \left[\frac{[K]_{\text{sil}} + [Na]_{\text{sil}} + 2[Ca]_{\text{sil}} + 2[Mg]_{\text{sil}}]}{Q/A}\right]
\]

(4)

\[
\delta CO_2|_{\text{carb}} = \left[\frac{[Ca]_{\text{carb}} + [Mg]_{\text{carb}}}{Q/A}\right]
\]

(5)

where \(\delta\) (mol/km\(^2\)/yr) is the CO\(_2\) consumption rate; Q (m\(^3\)/yr) is surface runoff; and A (km\(^2\)) is the drainage area. Surface runoff can be obtained from the land dataset of the fifth-generation European Centre for Medium-Range Weather Forecasts (ECMWF) Reanalysis (ERA5), with a horizontal resolution of 9 km (https://cds.climate.copernicus.eu/). Frozen soil and snow, which play an important role in the study area due to the low temperature in winter, are taken into account during the calculation of surface runoff in the ERA5 land dataset. In general, when the water flux at the surface exceeds the maximum infiltration rate, the excess water is put into surface runoff. In case of frozen soil and snow, the infiltration rate is small and water transport is limited, due to small values of the effective conductivity and diffusivity for frozen water. Detailed explanations about how they are accounted for run off and their influences are given by (Balsamo et al., 2009; Balsamo et al., 2011; Dutra et al., 2010; ECMWF, 2021).

As a potential reactive component in groundwater inverse modeling, CO\(_2\) can also be consumed by hydrogeochemical reactions in groundwater. The total water volume of the groundwater within a depth of 150 m in the east can be estimated using the magnetic resonance sounding (MRS) data published by Li et al. (2021c). The lateral groundwater outflow from the aquifer to the Yellow River (LA) (m\(^3\)/d) can be estimated using the following equation:

\[
LA = K \times i \times A
\]

(6)

where \(K\) is the mean MRS-estimated aquifer hydraulic conductivity value of 2.24 m/d (Li et al., 2021c), \(i\) (dimensionless) is the hydraulic gradient calculated from the hydraulic heads (Li et al., 2021c), and \(A\) (m\(^2\)) is the cross-sectional area perpendicular to the flow based on Yan et al. (2020).

### 4. Results

#### 4.1. Hydrogeochemistry and stable isotopes

The statistical characteristics of the hydrogeochemistry and stable isotopes of the surface water and groundwater samples are shown in

---

**Table 2**

<table>
<thead>
<tr>
<th>Water type</th>
<th>T (°C)</th>
<th>pH</th>
<th>TDS (mg/L)</th>
<th>TH (mg/L)</th>
<th>K(^{+}) (mg/L)</th>
<th>Na(^{+}) (mg/L)</th>
<th>Ca(^{2+}) (mg/L)</th>
<th>Cl(^{-}) (mg/L)</th>
<th>HCO(_3)(^{-}) (mg/L)</th>
<th>SO(_4)(^{2-}) (mg/L)</th>
<th>C(_{\text{COD}}) (mg/L)</th>
<th>C(_{\text{NH}}) (mg/L)</th>
<th>C(_{\text{DO}}) (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water</td>
<td>16-50</td>
<td>6.97</td>
<td>7.92</td>
<td>38.10</td>
<td>38.20</td>
<td>8.51</td>
<td>5.91</td>
<td>1.91</td>
<td>0.32</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Groundwater</td>
<td>14.09</td>
<td>7.68</td>
<td>399.20</td>
<td>311.10</td>
<td>10.17</td>
<td>11.73</td>
<td>10.73</td>
<td>35.04</td>
<td>366.90</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>GW-L (n = 10)</td>
<td>14.09</td>
<td>7.68</td>
<td>399.20</td>
<td>311.10</td>
<td>10.17</td>
<td>11.73</td>
<td>10.73</td>
<td>35.04</td>
<td>366.90</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>GW-H (n = 10)</td>
<td>7.25</td>
<td>7.72</td>
<td>370.00</td>
<td>299.50</td>
<td>5.08</td>
<td>9.62</td>
<td>102.23</td>
<td>10.22</td>
<td>10.22</td>
<td>26.67</td>
<td>199.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Mean</td>
<td>20.50</td>
<td>7.90</td>
<td>213.00</td>
<td>163.00</td>
<td>2.85</td>
<td>9.41</td>
<td>51.67</td>
<td>8.37</td>
<td>5.91</td>
<td>26.67</td>
<td>199.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SD</td>
<td>3.31</td>
<td>0.18</td>
<td>57.00</td>
<td>40.00</td>
<td>3.28</td>
<td>8.31</td>
<td>13.51</td>
<td>2.82</td>
<td>1.91</td>
<td>18.60</td>
<td>14.13</td>
<td>2.12</td>
<td>1.17</td>
</tr>
</tbody>
</table>

---

**Table 3**

<table>
<thead>
<tr>
<th>Water type</th>
<th>T (°C)</th>
<th>pH</th>
<th>TDS (mg/L)</th>
<th>TH (mg/L)</th>
<th>K(^{+}) (mg/L)</th>
<th>Na(^{+}) (mg/L)</th>
<th>Ca(^{2+}) (mg/L)</th>
<th>Cl(^{-}) (mg/L)</th>
<th>HCO(_3)(^{-}) (mg/L)</th>
<th>SO(_4)(^{2-}) (mg/L)</th>
<th>C(_{\text{COD}}) (mg/L)</th>
<th>C(_{\text{NH}}) (mg/L)</th>
<th>C(_{\text{DO}}) (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water</td>
<td>16-50</td>
<td>6.97</td>
<td>7.92</td>
<td>38.10</td>
<td>38.20</td>
<td>8.51</td>
<td>5.91</td>
<td>1.91</td>
<td>0.32</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Groundwater</td>
<td>14.09</td>
<td>7.68</td>
<td>399.20</td>
<td>311.10</td>
<td>10.17</td>
<td>11.73</td>
<td>10.73</td>
<td>35.04</td>
<td>366.90</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>GW-L (n = 10)</td>
<td>14.09</td>
<td>7.68</td>
<td>399.20</td>
<td>311.10</td>
<td>10.17</td>
<td>11.73</td>
<td>10.73</td>
<td>35.04</td>
<td>366.90</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>GW-H (n = 10)</td>
<td>7.25</td>
<td>7.72</td>
<td>370.00</td>
<td>299.50</td>
<td>5.08</td>
<td>9.62</td>
<td>102.23</td>
<td>10.22</td>
<td>10.22</td>
<td>26.67</td>
<td>199.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Mean</td>
<td>20.50</td>
<td>7.90</td>
<td>213.00</td>
<td>163.00</td>
<td>2.85</td>
<td>9.41</td>
<td>51.67</td>
<td>8.37</td>
<td>5.91</td>
<td>26.67</td>
<td>199.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SD</td>
<td>3.31</td>
<td>0.18</td>
<td>57.00</td>
<td>40.00</td>
<td>3.28</td>
<td>8.31</td>
<td>13.51</td>
<td>2.82</td>
<td>1.91</td>
<td>18.60</td>
<td>14.13</td>
<td>2.12</td>
<td>1.17</td>
</tr>
</tbody>
</table>
The mean concentrations of all ions in the surface water samples are lower than those in the groundwater samples, also lower TDS and TH but higher pH and COD values (Table 2; Fig. 2; Fig. D.1). The higher COD and NH$_4^+$ values in the surface water samples than in the groundwater samples indicate that human activities can have more influence on the surface water samples than on the groundwater samples (Peng et al., 2018; Wang et al., 2007). The higher TDS value in the groundwater samples than in the surface water samples reveals that more solids are dissolved in the groundwater than in the surface water (Fig. 2a). Except for Cl$^-$, the mean values of the main ions and TDS in GW-H are higher than those in GW-L (Table 2; Fig. D.1a), which may indicate the dilution effect of precipitation (Li et al., 2019a). The Maqiu catchment is a pastoral area, so the most important anthropogenic impact on the hydrogeochemistry of water samples is livestock waste. High COD and NH$_4^+$ values occur in water contaminated with livestock waste (Cho et al., 2014; Ming et al., 2007; Peng et al., 2020; Wang et al., 2021a). The higher COD and NH$_4^+$ values in GW-H than those in GW-L reveal that there are more anthropogenic influences on GW-H than in GW-L (Table 2; Fig. D.1b).

The TDS values of the four water samples from the stream, the reservoir and the Yellow River range from 172 to 252 mg/L, with a mean of 198 mg/L. For all the water samples, the ranges of ion concentrations are narrow (Table 2), indicating that the waters within the study area have not undergone complicated hydrological and hydrogeochemical processes. Similar ranges of solute concentrations can be found in research by Wang et al. (2021b). The ranges of solute concentrations found in this study are generally within the range found in the Yellow River by Qu et al. (2019).

The average $\delta^{18}O$ and $\delta^D$ values of the wetland samples, other surface water samples, GW-H and GW-L are $-12.89\%$ and $-108.29\%$, $-12.56\%$ and $-97.58\%$, $-12.10\%$ and $-88.49\%$, and $-11.95\%$ and $-86.21\%$, respectively. The ranges of the $\delta^{18}O$ and $\delta^D$ values of wetland samples, other surface water samples, GW-H, and GW-L are $-9.36\%$ to $-9.36\%$ and $-120.45\%$ to $-96.29\%$, $-13.90\%$ to $-11.38\%$ and $-102.07\%$ to $-82.69\%$, $-13.65\%$ to $-9.99\%$ and $-100.88\%$ to $-72.69\%$, $-13.93\%$ to $-10.22\%$ and $-99.14\%$ to $-71.64\%$, respectively. The obtained $\delta^{18}O$ and $\delta^D$ values match those of previous studies on the TP (Kuang et al., 2019; Shi et al., 2014) and in nearby places (Shi et al., 2017). The large variation range of $\delta^{18}O$ values and the low average $\delta^{18}O$ and $\delta^D$ values of the wetland samples indicate the importance of evaporation processes due to long residency times (Ren et al., 2016). The spatial distributions of groundwater $\delta^{18}O$ and $\delta^D$ values (Fig. D.1c, d) are similar to that of groundwater TDS (Fig. D.1a). The low $\delta^{18}O$ and $\delta^D$ values in the north and south indicate that the groundwater samples do not experience strong evaporation. In the middle area of the eastern part of the study area, the groundwater $\delta^{18}O$ and $\delta^D$ values generally increase from upstream to the Yellow River, suggesting continuous evaporation.

To reveal the hydrogeochemical characteristics of the water samples,
a Piper ternary diagram was created (Piper, 1944). The Piper diagram (Fig. 3) shows that all samples are of the HCO$_3$-Ca type according to the Shukalev classification (Liu et al., 2020), with Ca$^{2+}$ and HCO$_3$-counting for 73.4% and 84.9% of the total cations and anions on average, respectively. Studies by Qu et al. (2017) and Huang et al. (2009) also confirmed the dominance of Ca$^{2+}$ and HCO$_3$ ions in water on the TP.

4.2. Water origin

Stable hydrogen and oxygen isotopes are employed to identify the water origin in the study area. The δD and δ$^{18}$O data of the precipitation from Lanzhou, Chengdu, and Maduo (Fig. 1) are used to construct an LMWL for the study area:

$$\delta D = 7.7 \times \delta^{18}O + 2.72$$  \hspace{1cm} (7)

When waters evaporate, they become enriched with stable isotopes, so the LMWL is located below the GMWL (Fig. 4a). The δD and δ$^{18}$O data of the precipitation from Lanzhou, Chengdu, and Maduro are distributed near the GMWL. Therefore, the difference between the LMWL and GMWL is not significant. Since there are no δD and δ$^{18}$O data for precipitation in the study area, we use this LMWL as a reference.

According to Fig. 4b, except for the water samples from the wetland, the linear regression curve equation of the δ$^{18}$O and δD values for all the other water samples can be defined as:

$$\delta D = 7.27 \times \delta^{18}O + 0.09$$  \hspace{1cm} (8)

The fitted line is located near the LMWL and GMWL, indicating that the waters in the present study area are recharged by meteoric waters. This is consistent with the findings of a previous study by Wang et al. (2021b).

The regression curve equation of δ$^{18}$O and δD for water samples from the wetland is:

$$\delta D = 3.94 \times \delta^{18}O - 57.55$$  \hspace{1cm} (9)

The low slope (wetland, Fig. 4b), indicating significant “oxygen drift”, is most likely due to the high exposure to evaporation (Yuan et al., 2011).

4.3. Evaporation

The d-excess values of the surface water samples, GW-H, and GW-L range from $-21.38\%$ to $10.34\%$, $4.58\%$ to $11.59\%$, and $7.19\%$ to $12.31\%$, with the means of $2.89\%$, $8.33\%$, and $9.40\%$, respectively. Since the surface water and groundwater samples are of the same water origin, different d-excess values are mainly caused by kinetic fractionation processes during evaporation (Masson-Delmotte et al., 2008). The kinetic fractionation for $^{18}$O is more than that for D (Gupta, 2011; Hui et al., 2007), which results in low d-excess values according to Eq. (2). The lower mean d-excess in the surface water samples than in
groundwater samples suggests that surface waters experience greater exposure to evaporation.

The obtained groundwater d-excess values match well with those of previous research conducted in the Yellow River source region on the TP by Kuang et al. (2019). The d-excess values in the two surface water samples are negative and much lower than the global average value of 10‰ (Fig. 5). Negative d-excess values also occur in other surface water bodies on the TP (Wu et al., 2015; Yuan et al., 2011) and in nearby places (Shi et al., 2017), indicating that surface water has undergone strong evaporation processes on the TP (Dansgaard, 1964; Gat and Matsui, 1991). This is because the TP is characterised by strong convective activity, high radiation levels, and high wind speed, which contribute to the strong evaporation in the TP (Kurita and Yamada, 2008; Xie and Zhu, 2013; Yao et al., 2022).

Except for the water samples from the wetland, the other water samples are distributed around the LMWL of the study area (Fig. 4b) and the global average precipitation d-excess of 10‰ (Fig. 5), which means that they do not experience considerable evaporation. Samples from the wetland deviate from the LMWL of the study area (Fig. 4b) and the global average precipitation d-excess of 10‰ (Fig. 5), indicating that the wetland waters are significantly modified by evaporation processes. Thus, the evaporation model is employed to quantitatively assess evaporation in the wetland. According to Su et al. (2020), the average air temperature (T) is 286.13 K, and the average relative humidity (h) is 0.75 during the sampling days. The minimum stable isotopic composition of the wetland water samples is used as the original stable isotopic composition of water in Eq. (A.1), the fraction of water evaporate in wetlands account for 0–45% of the total water volume (Fig. 6). Therefore, the evaporation process is important for wetlands.

From 31 July to 3 August 2018, in situ measured four-day precipitation was 41.1 mm, and there was 13.76 mm of precipitation on the night of 7 August 2018 (Su et al., 2020). The δ18O and δD values of the wetland samples follow the order of S6 < S28 < S19 < S29, with corresponding sampling dates of 5 August, 8 August, 7 August, and 8 August 2018, respectively. The evaporative loss fractions of the pool volume for S6, S28, S19, and S29 are 0%, 5%, 28%, and 45% respectively (Fig. 6). The low δ18O and δD values of S6, located 420 m north of the reservoir, may mainly be influenced by the precipitation from 31 July to 3 August. S28, located 420 m south of the reservoir, experiences two precipitation events and has 5% evaporative loss. S19, located 1300 m north of the reservoir, experiences precipitation from 31 July to 3 August and has 28% evaporative loss. S29, located 7150 m south of the reservoir, experiences two precipitation events and has the highest evaporative loss due to its long residency time (Ren et al., 2016). This phenomenon may indicate that the water circulation is faster for S6 and S28, which are located near the reservoir, than for S19 and S29, which are located relatively far from the reservoir, since it is easier for precipitation or overland flow to pool near the reservoir due to the local topography. Therefore, it is important to collect enough wetland water samples when investigating wetland-related problems, e.g., wetland hydrology, due to the spatial heterogeneity of soil properties and different water circulation conditions.

### 4.4. Inverse modelling

Temperature, pH and major ions are the input data of PHREEQC which is good at performing various low-temperature aqueous geochemical transport and inverse calculations (Dai and Samper, 2004). The low ionic strength of the water samples (0.004 to 0.016 mol/L) obtained during PHREEQC simulation ensures the suitability of using
Precipitate based on the saturation indices values estimated during precipitation, whereas chlorite and CO$_3^-$. PHREEQC simulation. The modelling results show that calcite and illite generally dissolve along the flow paths (Fig. 2b) are listed in Table 3. And by dividing the inverse modelling results by water flow distances, mineral transfer rates per kilometre are obtained (Fig. 7). Positive values indicate the dissolution of minerals or gas, and negative values indicate precipitation or outgassing. The modelling results show that calcite and illite generally precipitate, whereas chlorite and CO$_2$ generally dissolve along the groundwater flow paths in the east (Table 3, Fig. 7). Cation exchange contributes to the relative abundance of Ca$^{2+}$ and K$^+$, while the relative abundance of Mg$^{2+}$ and Na$^+$ decreases. A stronger cation exchange can be observed in the GW-H than in GW-L along the groundwater flow paths.

Table 4 shows the PCA results based on the concentrations of five tracers (Ca$^{2+}$, HCO$_3^-$, COD, δ$^{18}$O and δD) in surface water samples (without S6 and S29). Accordingly, there are two eigenvectors associated with eigenvalues of greater than 1, so two eigenvectors should be retained following the “rule of 1” (i.e., all eigenvectors associated with eigenvalues of greater than or equal to 1 were retained). There should be one more end member than the rank of the standardised dataset (i.e., the number of eigenvectors) (Hooper, 2003).

4.5. Contributions of different water sources

High COD and NH$_4^+$ values occur in water contaminated with livestock waste (Cho et al., 2014; Ming et al., 2007; Peng et al., 2020; Wang et al., 2021a) which is the most likely anthropogenic impact in the Maqu catchment as a pastoral area. According to Table D.1, the NH$_4^+$ and COD values are within 0.15 mg/L and 12.4 mg/L, respectively, in most water samples and are comparable with the results of Sillanpää et al. (2004). However, the sample S29 from the wetland has the highest NH$_4^+$ and COD values of 7.59 mg/L and 51.90 mg/L, respectively. These two extremely high outliers are most likely to reflect anthropogenic influences. In addition, the surface water samples exhibit low δ$^{18}$O and δD values, and the groundwater samples show high concentrations of Ca$^{2+}$ and HCO$_3^-$ (Table 2). Bivariate scatter plots (Fig. D.2) reveal that Ca$^{2+}$ versus HCO$_3^-$, COD versus NH$_4^+$ and δ$^{18}$O versus δD in surface water samples have high correlation coefficients of 0.972, 0.936 and 0.758, respectively. High correlation coefficients ensure the suitability of using Ca$^{2+}$, HCO$_3^-$, NH$_4^+$, COD, δ$^{18}$O and δD as tracers in EMMA (Inamdar et al., 2013). However, NH$_4^+$ is below the detection limit in some surface water samples (Table D.1). Therefore, it is not used as a tracer in EMMA. Notably, this does not mean that anthropogenic impact should not be considered as a member, because most surface waters are clearly affected by the anthropogenic impact according to their COD and NH$_4^+$ values. Finally, Ca$^{2+}$, HCO$_3^-$, COD, δ$^{18}$O and δD are used as tracers.

The number of eigenvectors to be retained was based upon the “rule of 1” (i.e., all eigenvectors associated with eigenvalues of greater than or equal to 1 were retained). There should be one more end member than the rank of the standardised dataset (i.e., the number of eigenvectors) (Hooper, 2003).

Table 4 shows the PCA results based on the concentrations of five tracers (Ca$^{2+}$, HCO$_3^-$, COD, δ$^{18}$O and δD) in surface water samples (without S6 and S29). Accordingly, there are two eigenvectors associated with eigenvalues of greater than 1, so two eigenvectors should be retained following the “rule of 1”. Three end members should be considered, because there should be one more end member than the...
number of eigenvectors (Hooper, 2003). The following three samples are used as end members: G10, S6, and S29. Because G10, with the highest Ca\textsuperscript{2+} concentration, represents mountain-front groundwater; S6, with the lowest \(\delta^{18}O\) value, represents fresh surface water; and S29, with the highest NH\textsubscript{4} and COD concentration, indicates anthropogenic influence. All the samples are located within the triangle formed by these three end members, indicating that the end members are properly selected. In addition, most water samples are located near the line between S6 and S29 (Fig. 8) suggesting that fresh surface waters and anthropogenic inputs are the dominant sources, while mountain-front groundwaters have only limited contribution. On average, fresh surface waters, anthropogenic inputs, and mountain-front groundwaters contribute 56%, 28%, and 16%, respectively (Fig. 8). Among all the surface water samples, the highest contribution of mountain-front groundwaters occurs in the spring sample (45%), followed by the reservoir and stream samples (15–21%) and other samples (3–5%).

The performance of the EMMA model was tested using the relative root mean square error (RRMSE) and correlation coefficient (\(r_s\)). According to Table 5, RRMSE and \(r_s\) range from -0.15 to 1.36 and from 0.79 to 0.99, respectively, suggesting a generally good fit between observations and predictions and the good performance of the EMMA model.

This is the first time EMMA has been implemented in the Maqu catchment. Previous studies have used EMMA to analyse the source of surface water on the TP, but they all have been performed in very different environments: either glaciers or permafrost (Gui et al., 2023; Li et al., 2020b; Wünnemann et al., 2023; Yang et al., 2016; Zhou et al., 2021) or geothermal groundwater (Shi et al., 2021). Due to very different water sources, the results are incomparable.

### 4.6. Contributions of different sources to major ions

The ionic contributions from four sources were evaluated using the forward mass balance model, i.e., Eqs. (C.1)–(C.8) (Fig. 9). In general, the relative contributions to major ions are carbonate > silicate > anthropogenic > atmospheric inputs, from highest to lowest. For the

<table>
<thead>
<tr>
<th>Source</th>
<th>Ca\textsuperscript{2+}</th>
<th>HCO\textsubscript{3}</th>
<th>COD</th>
<th>(\delta^{18}O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre</td>
<td>49.39 38.10</td>
<td>171.97 153</td>
<td>11.28 0.76</td>
<td>-118.65 -118.27 -15.81</td>
</tr>
<tr>
<td>Max</td>
<td>119.06 80.20</td>
<td>334.73 329</td>
<td>33.49 21.30</td>
<td>-98.24 -82.69 -12.20</td>
</tr>
<tr>
<td>Mean</td>
<td>75.02 50.97</td>
<td>241.67 198</td>
<td>21.38 0.95</td>
<td>-107.08 -94.49 -13.36</td>
</tr>
<tr>
<td>RRMSE</td>
<td>0.34 0.26</td>
<td>0.26 0.36</td>
<td>0.94 0.99</td>
<td></td>
</tr>
<tr>
<td>(r_s)</td>
<td>0.97 0.86</td>
<td>0.79 0.79</td>
<td>0.99 0.99</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9. The contributions of atmospheric inputs, anthropogenic inputs, carbonate weathering, and silicate weathering to the total cations (in meq/L) in (a) surface water, (b) groundwater, and (c) all samples on average.
surface water samples, 2–4% of the total cations are from atmospheric inputs, 2–7% are from anthropogenic inputs, 0–31% are from silicate weathering, and 64–94% are from carbonate weathering. For the ground water samples, 1–2% of the total cations are from atmospheric inputs, 0–8% are from anthropogenic inputs, 0–36% are from silicate weathering, and 60–96% are from carbonate weathering. Atmospheric inputs have more influence on surface water samples than on ground water samples. GW-H have almost the same amount of anthropogenic and atmospheric inputs and higher carbonate weathering inputs in comparison to GW-L. Compared with urban areas, the incomplete sewage drainage and treatment systems in Maqu catchment lead to the infiltration of domestic wastewater and anthropogenic inputs of Cl− in surface water and groundwater (Chen et al., 2022). For all samples, cations are dominated by rock weathering, i.e., carbonate and silicate weathering, which together account for approximately 89–98% of the total cations. This result is consistent with the findings of other works on TP, such as those of Qu et al. (2017) and Qu et al. (2019).

4.7. CO2 consumption

CO2 consumption was calculated for the Yellow River and the surface runoff in the Maqu catchment. The location of the Yellow River water sample was at the Maqu Hydrological Station, with a drainage area of 8.60 × 10^4 km^2 (Jiu et al., 2011) and the annual average flow of the Yellow River at Maqu Hydrological Station was 1.30 × 10^10 m^3/yr during 1989–2018 (Zhang and Wang, 2018). The surface runoff in 2018 was obtained from the ERA5-land dataset. Using Eqs. (4)–(5), the calculated CO2 consumption is shown in Table 6.

Silicate and carbonate weathering in surface runoff contributed 21.25% and 1.45% of the total CO2 consumption by silicate and carbonate weathering in the Yellow River, respectively. The CO2 consumed

### Table 6
Mean CO2 consumption rate.

<table>
<thead>
<tr>
<th>Water</th>
<th>Q</th>
<th>A</th>
<th>Silicates</th>
<th>Carbonates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m^3/yr</td>
<td>km^2</td>
<td>(mol/yr)</td>
<td>(mol/yr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0CO2/mol</td>
<td>0CO2/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>km^2/yr</td>
<td>km^2/yr</td>
</tr>
<tr>
<td>Yellow River</td>
<td>1.30 × 10^10</td>
<td>8.60 × 10^4</td>
<td>3.68 × 10^8</td>
<td>1.70 × 10^9</td>
</tr>
<tr>
<td>Surface runoff</td>
<td>1.58</td>
<td>532.34</td>
<td>7.82</td>
<td>4.28 × 10^3</td>
</tr>
</tbody>
</table>

Fig. 10. The groundwater TDS, δ18O, and δD along five inverse modelling paths.

Fig. 11. Yellow River drainage basin. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
by carbonate weathering was 46 times the CO$_2$ consumed by silicate weathering in the Yellow River (1.70 × 10$^5$ mol/yr versus 3.68 × 10$^4$ mol/yr) and three times that in surface runoff (2.47 × 10$^5$ mol/yr versus 7.82 × 10$^4$ mol/yr). Previous studies have also proven that the CO$_2$ consumed by carbonate weathering can be much more than the CO$_2$ consumed by silicate weathering in the Yellow River (1.70 × 10$^5$ mol/yr) and three times that in surface runoff (2.47 × 10$^5$ mol/yr versus 7.82 × 10$^4$ mol/yr). The rate in the Yellow River is likely to reflect the accumulation of fast surface runoff after precipitation, which does not experience much water–rock interaction. The low CO$_2$ consumption in the Maqu catchment is due to the smaller water volume compared to the Yellow River.

The CO$_2$ consumed by hydrogeochemical reactions in groundwater is 6.13 × 10$^{-3}$ mol/L on average according to Table 3. The MRS-estimated average groundwater volume above a 150 m depth is 8.82 m$^3$. With an area of 233.46 km$^2$ in the east, the total groundwater volume above a 150 m depth is 2.06 × 10$^9$ m$^3$. Thus, CO$_2$ consumed by hydrogeochemical reactions in groundwater within a 150 m depth in the eastern part of the study area is 1.26 × 10$^9$ mol or 5.56 × 10$^6$ tons. The lateral groundwater outflow from the aquifer to the Yellow River is estimated using Eq. (6). Detailed parameters and calculations are listed in Table E.1. The calculated lateral groundwater flow is 3.24 × 10$^3$ m$^3$/yr with a corresponding CO$_2$ consumption of 1.86 × 10$^5$ mol/yr and a CO$_2$ consumption rate of 7.95 × 10$^{-2}$ mol/km$^2$/yr. According to the study by Yu et al. (2021), the CO$_2$ consumption rate of shallow groundwaters in the eastern Hetao Basin of Inner Mongolia in the middle reaches of the Yellow River is 6.08 × 10$^{-2}$ mol/km$^2$/yr. Therefore, the groundwater CO$_2$ consumption rate in the study area in the Yellow River source region is larger than that in the middle reaches of the Yellow River.

Therefore, considering the high CO$_2$ consumption rates in both the surface runoff and groundwater, the Maqu catchment serves as an important carbon sink in the Yellow River Basin.

### 5. Discussion

#### 5.1. Stable isotopes

Previous studies have proven that the $\delta^{18}$O and $\delta$D values in the precipitation on the TP can be highly depleted. For example, according to Li et al. (2021b), the $\delta^{18}$O and $\delta$D in precipitation range from −30.5% to −0.8% and from −222.6% to −0.3% respectively, in 2018; according to Yu et al. (2016), the $\delta^{18}$O and $\delta$D in precipitation ranged from approximately −30% to 0% and from −210% to 10%, respectively, in 2012. This phenomenon can be explained by the progressive rainout of heavy stable isotopes when the precipitation moisture proceeds from the vapour origins to higher latitudes and inland areas (continental effect) (Liu et al., 2014). In addition to the continental effect and latitude effect, the altitude effect also enhances the depletion of $\delta^{18}$O and $\delta$D in precipitation on the TP, i.e., ascending orographic and cooling can result in gradual depletion of $\delta^{18}$O and $\delta$D in precipitation (Yao et al., 2009).

Similar to the low slope and low intercept of Eq. (9) for wetlands (Fig 4b), a low slope and low intercept are also reported in other parts of the TP: the slope and intercept of the local evaporation line (LEL) are 4.25 and −35.99, respectively, at Ximen Co Lake (Luo et al., 2018); the slopes of $\delta$D versus $\delta^{18}$O in soil water range from 2.91 to 5.42 in the Qilian Mountains (Qiu et al., 2019); and the slopes and intercepts of the linear regression curve equations of $\delta^{18}$O and $\delta$D at Drem-tso Lake are 4.39 and −45, respectively (Shi et al., 2014). A low slope and intercept suggest intense evaporation (Polissar et al., 2009; Yi et al., 2018; Zhang et al., 2019). Intense evaporation can be demonstrated in studies of Qinghai Lake, where the annual lake evaporation was 832.5 mm from May 2013 to May 2014, which was 2.5 times the corresponding precipitation (Li et al., 2016). The annual lake evaporation was approximately 832 mm in Nam Co Lake from 1980 to 2014, which was 1.8 times the annual precipitation of 457 mm (Lazhu et al., 2016). The annual lake evaporation was 1074.02 mm for Selin Co Lake from 2003 to 2012, which is 3.4 times the annual precipitation of 315 mm (Zhou et al., 2016).
Herbs can be found in the wetlands. The plant water uptake can leave an isotope signal in the remaining water, which has been observed in previous studies (Allison et al., 1984; Vargas et al., 2017; Walker and Richardson, 1991). According to Allison et al. (1984), transpiration leads to $\delta^{18}O$ enrichment and $\delta$ depletion in the remaining water. Since herbs mainly use water from the topsoil (0–30 cm) (Che et al., 2019; Priyadarshini et al., 2016), wetlands act as the main water supply for herbs. Therefore, the $\delta^{18}O$ value of sample S29, can be more enriched than those in other water bodies in the catchment (Fig. 4b). However, other studies indicate that transpiration leads to the enrichment of both $\delta^{18}O$ and $\delta$ in the remaining waters (Che et al., 2019; Vargas et al., 2017). In this case, the $\delta^{18}O$ and $\delta$ of the water samples in the wetland, for example, S29, may be mainly affected by evaporation due to the large decrease in $\delta$ compared to those of the water samples from other water bodies and partly affected by transpiration due to the small increase in $\delta^{18}O$.

5.2. Shallow water–rock interactions

When surface waters and groundwater are hydraulically connected, their hydrogeochemical features and stable isotopes should resemble each other, indicating a close interaction between them (Yang et al., 2021c). However, under disconnected conditions, the hydrogeochemistry and stable isotopes are likely to be different due to different water sources as well as changes occurring during the flow paths (Oyarzún et al., 2014). According to the Piper ternary diagram (Fig. 3) and the $\delta^{18}O$ and $\delta$ values of water samples (Fig. 4b), a large overlap of the surface water samples (except wetland) and groundwater samples can be observed, indicating a close contact between them. While for wetland samples and adjacent groundwater samples, for example S29 and G12, the isotope signatures and TDS values vary greatly (Table D.1), indicating weak hydraulic connection.

Waters in wetlands can be fed by groundwaters, surface waters and/or directly from precipitation (Verones et al., 2013). Large differences in $\delta^{18}O$ and $\delta$ values between wetland samples and other samples (Fig. 4b) suggest that there is not a clear contact between wetland waters and other waters. In addition, compared to groundwater samples, the samples from the wetlands show a lower d-excess but without obviously higher concentrations of TDS (Fig. 5), indicating that wetland waters undergo fewer water–rock interactions than groundwaters and that they are substantially modified by evaporation. Thus, it can be inferred that the main source of wetland waters can be attributed to the precipitation. Notably, the water samples were collected in the summer rainy season, during which wetlands can be recharged directly by precipitation. The main source of wetland water may change in the dry season.

According to the spatial distributions of TDS (Fig. D.1a), groundwater samples with TDS values of lower than 337 mg/L are located in the north and south. These samples are affected by local topography: Located near small hills (Fig. 1), they can be easily recharged by the groundwaters from hills with short flow distances and low TDS values. In the middle of the study area, groundwater TDS values decrease as groundwaters flow through the reservoir, and becomes high again near the Yellow River (Fig. D.1a). This can be explained by the mixing of groundwaters with surface waters and water–rock interactions, i.e., mineral dissolution. When groundwaters flow through the reservoir, they are recharged by the reservoir, resulting in a lower TDS value. When groundwater is near the Yellow River, the eastern boundary of the Maqo catchment, the groundwater depths become deeper (Li et al., 2021c) and water–rock interactions become more influential than surface water recharge from within the catchment, thus resulting in increasing TDS values.

The groundwater TDS, $\delta^{18}O$, and $\delta$ values along five inverse modelling paths (Fig. 2b) are shown in Fig. 10. According to Fig. 10, TDS, $\delta^{18}O$, and $\delta$ show a generally increasing trend along the G3–G22–G21 and G11–G13 paths, a generally decreasing trend along G10–G25–G26 and G12–G14–G16 and a complex trend along G30–G24–G27. The different trends can be attributed to the different recharge-discharge relationships between the surface water and groundwater.

The water sample S4 is from a spring in the west. It is located near the river, also it is general that the water table near the rivers are relatively shallow, justifying that spring is an intersection of water table to the topography (Saraf et al., 2000).
The above conclusions are obtained for the first time in Maqu catchment to the authors’ knowledge, it is difficult to compare and discuss it with previous studies since few related studies have been carried out in Maqu catchment and in Zoige and these conclusions can be very different in different areas.

5.3. CO\textsubscript{2} consumption

Different CO\textsubscript{2} consumption rates reflect differences in factors controlling geochemical weathering, such as climate, lithology, and vegetation (Gao et al., 2009; Goldsmith et al., 2010). Based on our results and previous studies, the CO\textsubscript{2} consumption rate is studied at eight locations from upstream to downstream of the Yellow River (Fig. 11). According to Table 7, the CO\textsubscript{2} consumption rate of carbonate weathering decreases from upstream to downstream of the Yellow River. This is consistent with previous studies (Gasper et al., 2014; Wang et al., 2016). The CO\textsubscript{2} consumption rate of silicate weathering increases at first and then decreases from upstream to downstream of the Yellow River. The trend can be cross-validated by the study of Wu et al. (2008). Changes in the CO\textsubscript{2} consumption rates from upstream to downstream are likely to reflect the change in local lithology along the Yellow River.

The CO\textsubscript{2} consumption rates of carbonate weathering in the Yellow River and the neighbouring rivers Changjiang, Xijiang, Mekong, Salween and Brahmaputra are much higher than the corresponding CO\textsubscript{2} consumption rates of silicate weathering (Table 7). In addition, the CO\textsubscript{2} consumption rates of carbonate and silicate weathering in Yellow River are low compared with the neighbouring rivers and world average rates. Compared to the Yellow River, other rivers experience a more humid climate and warmer temperatures (Ran et al., 2015). Since low precipitation and temperature can constrain weathering reactions, they are responsible for the low CO\textsubscript{2} consumption rates in the Yellow River; moreover, the low vegetation cover in the Yellow River Basin can lead to low soil CO\textsubscript{2} levels, which is also likely to reduce the CO\textsubscript{2} consumption rates (Decker et al., 2013; Goudie and Viles, 2012).

5.4. Limitations and future work

Only one water sample was collected in streams and the Yellow River, respectively. They were not representative along the flow paths. To further understand the changes in streams and the Yellow River, more samples should be collected along the flow paths.

Since there was no detailed lithology or mineral information in the study area, this inverse model was developed based on minerals that appeared in the Zoige. The uncertainties related to inverse modelling can be minimised by further collecting lithology or mineral samples in the study area.

In the evaporation model, because S6 had the extremely depleted values of stable isotopes, it was also the intersection of the evaporation line and the meteoric water line (LMWL) (Fig. 6), thus, it was used as the original stable isotopic composition of water \(\delta_p\), as suggested by Ladouche and Weng (2005) and Marimuthu et al. (2005). This led to an evaporative loss fraction of 0% for S6. The water sample S6 was sampled on 5 August 2018 and influenced by the precipitation from 31 July to 3 August. So an evaporative loss fraction of 0% suggests that \(\delta_p\) used in the evaporation model is likely to be larger than the actual value, and \(\delta_p\) needs further sampling.
According to the results of EMMA, anthropogenic inputs accounted for an average contribution of 28% to the surface water samples. However, the results of the forward mass balance model reveal that anthropogenic inputs accounted for 2\textendash}7% of the major ions in the surface water. The inconsistency can result from (1) the inherent differences between the two methods, which were applied based on different assumptions, each with its own limitation; (2) the limitation in selecting end members in EMMA; more representative water samples may exist for the study area but they were not collected during fieldwork. Therefore, to improve the application of EMMA in the study area, more representative water samples need to be collected in the future.

For the forward mass balance model, because of the lack of in situ precipitation water samples, atmospheric inputs were estimated using data from the adjacent Darlag site (Li et al., 2018). In addition, average values of silicate weathering from global rivers were used (Galy and France-Lanord, 1999). The lack of in situ measurements may have influenced the model results. Therefore, collecting in situ precipitation water samples and analysing silicate weathering conditions in the study area will help to improve the forward mass balance model.

In \( \text{CO}_2 \) consumption calculation, the surface runoff was obtained from the ERA5-land dataset due to data limitations. Studies focusing on the validation of the runoff data from the ERA5-land dataset on the TP are scarce. For the simplification of runoff estimates, it is important to have in situ runoff measurements or a good numerical model in the Maqu catchment to validate the runoff data from the ERA5-land dataset and further improve the accuracy of the \( \text{CO}_2 \) consumption calculation.

In general, the main study limitation is the lack of in situ data, including lithology samples, precipitation water samples, and runoff measurements. Data scarcity is always a problem limiting further understanding of the TP. Despite these inevitable limitations, the present study provides the first detailed insight on the Maqu catchment from different aspects based on the hydrogeochemical and stable isotope data of surface water and groundwater.

![Fig. D.2. Bivariate scatter plots with linear fits, 0.95 confidence intervals and correlation coefficient for surface water samples. ***, **, * and . represent the significance level is less than 0.001, 0.01, 0.05, and 0.1 respectively.](image)

Table E.1

<table>
<thead>
<tr>
<th>Section</th>
<th>Start point</th>
<th>End point</th>
<th>( K (\text{m/d}) )</th>
<th>( i )</th>
<th>( A (\text{m}^3) )</th>
<th>( LA (\text{m}^3/\text{yr}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>102(^{15}5.5) (^{33}47^\circ10.4^\prime)</td>
<td>102(^{14}48.8) (^{33}48^\circ36.0^\prime)</td>
<td>2.24</td>
<td>1.18E-03</td>
<td>2.94E+05</td>
<td>2.84E+05</td>
</tr>
<tr>
<td>1</td>
<td>102(^{14}48.8) (^{33}48^\circ36.0^\prime)</td>
<td>102(^{14}46.8) (^{33}52^\circ19.4^\prime)</td>
<td>2.24</td>
<td>1.03E-03</td>
<td>6.26E+05</td>
<td>5.27E+05</td>
</tr>
<tr>
<td>2</td>
<td>102(^{14}46.8) (^{33}52^\circ19.4^\prime)</td>
<td>102(^{13}33.7) (^{33}52^\circ26.9^\prime)</td>
<td>2.24</td>
<td>7.78E-04</td>
<td>6.81E+05</td>
<td>4.33E+05</td>
</tr>
<tr>
<td>3</td>
<td>102(^{13}33.7) (^{33}55^\circ26.9^\prime)</td>
<td>102(^{13}42.8) (^{33}57^\circ23.8^\prime)</td>
<td>2.24</td>
<td>1.42E-03</td>
<td>4.13E+05</td>
<td>4.79E+05</td>
</tr>
<tr>
<td>4</td>
<td>102(^{13}42.8) (^{33}57^\circ23.8^\prime)</td>
<td>102(^{13}11.3) (^{33}57^\circ31.4^\prime)</td>
<td>2.24</td>
<td>3.23E-03</td>
<td>5.74E+05</td>
<td>1.51E+06</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td>3.24E+06</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to the results of EMMA, anthropogenic inputs accounted for an average contribution of 28% to the surface water samples. However, the results of the forward mass balance model reveal that anthropogenic inputs accounted for 2\textendash}7% of the major ions in the surface water. The inconsistency can result from (1) the inherent differences between the two methods, which were applied based on different assumptions, each with its own limitation; (2) the limitation in selecting end members in EMMA; more representative water samples may exist for the study area but they were not collected during fieldwork. Therefore, to improve the application of EMMA in the study area, more representative water samples need to be collected in the future.

For the forward mass balance model, because of the lack of in situ precipitation water samples, atmospheric inputs were estimated using data from the adjacent Darlag site (Li et al., 2018). In addition, average values of silicate weathering from global rivers were used (Galy and France-Lanord, 1999). The lack of in situ measurements may have influenced the model results. Therefore, collecting in situ precipitation water samples and analysing silicate weathering conditions in the study area will help to improve the forward mass balance model.

In \( \text{CO}_2 \) consumption calculation, the surface runoff was obtained from the ERA5-land dataset due to data limitations. Studies focusing on the validation of the runoff data from the ERA5-land dataset on the TP are scarce. For the simplification of runoff estimates, it is important to have in situ runoff measurements or a good numerical model in the Maqu catchment to validate the runoff data from the ERA5-land dataset and further improve the accuracy of the \( \text{CO}_2 \) consumption calculation.

In general, the main study limitation is the lack of in situ data, including lithology samples, precipitation water samples, and runoff measurements. Data scarcity is always a problem limiting further understanding of the TP. Despite these inevitable limitations, the present study provides the first detailed insight on the Maqu catchment from different aspects based on the hydrogeochemical and stable isotope data of surface water and groundwater.
6. Conclusions

Water resources on the Qinghai-Tibetan Plateau are important for people, ecosystems and economic development in Asia and the world. Hydrogeochemistry is a significant indicator of water supply and demand. In the present study, hydrogeochemical and stable isotope data of water samples collected from the Maqu catchment were analysed by different techniques to characterise surface water and groundwater, investigate the contributions of different sources, and determine CO₂ consumption. The following conclusions are obtained:

(1). All the water samples are of the HCO₃-Ca type, with Ca²⁺ and HCO₃⁻ accounting for 73.4% and 84.9% of the total cations and anions on average, respectively. Surface waters and groundwater are both of meteoric origin, and there is close contact between the surface water (except wetlands) and groundwater. Water in the wetlands is likely directly recharged by precipitation and substantially evaporated (0–45%). Calcite and illite generally precipitate, whereas chlorite and CO₂ generally dissolve along the groundwater flow paths in the eastern study area, with mineral transfer rates generally between −9.05 × 10⁻³ and 6.45 × 10⁻³ mol/L/km.

(2). On average, fresh surface waters, mountain-front groundwaters, and anthropogenic inputs contribute 56%, 16%, and 28%, respectively, to surface water samples. Predictions from EMMA agree well with the observations, with a low RRMSE (-0.15–1.36) and a high correlation coefficient (r₂) (0.79–0.99). The relative contributions to major ions are carbonate > silicate > anthropogenic > atmosphere inputs. Carbonate and silicate weathering are the dominant sources of cations.

(3). For surface runoff, the CO₂ consumed by silicate and carbonate weathering is 3.25 × 10⁸ mol/yr. For groundwater lateral flow, the CO₂ consumed by hydrogeochemical reactions is 1.86 × 10⁷ mol/yr. The Maqu catchment is an important carbon sink in the Yellow River Basin. CO₂ consumption rates of carbonate and silicate weathering in Yellow River are low compared to the neighbouring rivers.

Conclusion (1) and (2) reveal the water origin, hydraulic connections between different water types, and contributions of different water sources, which help to delimitate the water cycle in the study area. Many conclusions are drawn for the first time in the Maqu catchment on the eastern TP. The methods used in the present study should be applied in more places on the TP to provide a fuller understanding of the TP. To further improve this study in the future, more samples, including precipitation samples and rock samples, need to be collected, and in situ runoff measurements and/or a good numerical model for the Maqu catchment are also important.

CRediT authorship contribution statement

Mengna Li: Conceptualization, Methodology, Software, Visualization, Writing – original draft. Hui Qian: Conceptualization, Project administration, Supervision, Resources, Writing – review & editing. Maciek W. Lubczynski: Supervision, Project administration, Resources, Writing – review & editing. Panpan Xu: Formal analysis, Writing – review & editing. Zhongbo Su: Supervision, Project administration, Resources. Yijian Zeng: Supervision, Project administration, Resources. Jie Chen: Investigation, Writing – review & editing. Kai Hou: Investigation, Writing – review & editing. Qiying Zhang: Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

the data are provided in appendix

Acknowledgments

This study was financially supported by the Second Tibetan Plateau Scientific Expedition and Research (STEP) program (grant no. 2019QZKK0103), the National Natural Science Foundation of China (Grant No. 42102288, 41931285, 41790441, 41572236, 41971033, 42007184, and 41931285), the ESA MOST Dragon V program (Monitoring and Modelling Climate Change in Water, Energy and Carbon Cycles in the Pan-Third Pole Environment), the Fundamental Research Funds for the Central Universities, CHD (No. 300102291726 and 30010229009) and the Programme of Introducing Talents of Discipline to Universities (B08039), the Natural Science Foundation of Shaanxi Province (2022JQ-243). And the completion of this article was inseparable from the contributions of all authors. Their support is gratefully acknowledged.

Appendix A. Evaporation model and parameters

Craig and Gordon (1965) proposed a model describing the stable isotopic enrichment of an evaporating surface water body. Gonfiantini (1986) further improved the model, according to which the evaporative loss fraction of the pool volume (f) can be estimated as follows:

\[ f = 1 - \frac{\delta_l - \delta^*}{\delta^* - \delta} \]  \hspace{1cm} (A.1)

\[ \delta^* = \frac{h + \delta_k + \varepsilon}{h + \frac{\delta_k}{1000}} \] \hspace{1cm} (A.2)

\[ m = \frac{h - \frac{\delta_k}{1000}}{1 - h + \frac{\delta_k}{1000}} \] \hspace{1cm} (A.3)

where \( \delta_l \) (%) is the original stable isotopic composition of water; \( \delta_f \) (%) is the final stable isotopic composition of water; \( \delta^* \) (%) is the limiting isotope enrichment; \( m \) (dimensionless) is the enrichment slope; \( h \) is air humidity expressed as a fraction; \( \delta_k \) (%) is theotope composition of moisture in ambient air; \( \varepsilon \) (%) is the total enrichment factor; \( \varepsilon_k \) (%) is the kinetic fractionation factor (Allison and Leaney, 1982; Gat, 1981; Gat and Gat, 1978; Welhan and Fritz, 1977).

The isotope composition of moisture in ambient air \( \delta_k \) can be defined as (Gat, 1995; Gibson and Reid, 2014; Skrzypek et al., 2015):
\[ \delta A = \frac{\delta_{\text{rain}}}{\alpha^+} \]  

(A.4)

Where \( \delta_{\text{rain}} \) (‰) is the stable hydrogen and oxygen isotope composition of precipitation; \( \epsilon^+ \) (‰) is the equilibrium isotope fractionation factor defined as \( \epsilon^+ = (\alpha^+ - 1) \times 1000 \); \( \alpha^+ \) (‰) is the equilibrium fractionation factor which is dependent on the water temperature at the evaporating surface. Empirical equations can be used to determine \( \alpha^+ \) (Horita and Wesolowski, 1994):

for \( ^{18}O \):

\[
\ln \alpha^+ \times 10^3 = -7.685 + 6.7123 \left( \frac{T}{10^3} \right) - 1.6664 \left( \frac{T^2}{10^3} \right) + 0.35041 \left( \frac{T^3}{10^3} \right)
\]

(A.5)

for D:

\[
\ln \alpha^+ \times 10^3 = 1158.8 \left( \frac{T^3}{10^3} \right) - 1620.1 \left( \frac{T^2}{10^3} \right) + 794.84 \left( \frac{T}{10^3} \right) - 161.04 + 2.9992 \left( \frac{T^3}{10^3} \right)
\]

(A.6)

where temperature \( T \), expressed in Kelvin units, is available from Su et al. (2020).

The kinetic fractionation factor \( \epsilon_k \) can be evaluated using the following equations:

for \( ^{18}O \):

\[ \epsilon_k = 14.2(1 - h) \]  

(A.7)

for D:

\[ \epsilon_k = 12.5(1 - h) \]  

(A.8)

where air relative humidity \( h \) is available from Su et al. (2020). The total enrichment factor \( \epsilon \) can be estimated using:

\[ \epsilon = \frac{\epsilon^+}{\alpha^+} + \epsilon_k \]  

(A.9)

The original stable isotopic composition of water \( \delta_p \) can be either the intersection of the evaporation line and the local meteoric water line (LMWL) (Ladouche and Weng, 2005), or the minimum stable isotopic composition of the water samples (Marimuthu et al., 2005).

Appendix B. EMMA

When a water sample fits into the space defined by end members, the contribution of each end member was calculated using the mass balance equation (Doctor et al., 2006):

\[ 1 = \sum_{i=1}^{n} p_i \]  

(B.1)

\[ U_{1j} = \sum_{i=1}^{n} p_i \times U_{1i} \]  

(B.2)

\[ U_{2j} = \sum_{i=1}^{n} p_i \times U_{2i} \]  

(B.3)

where \( p_i \) is the proportion of ith end member; \( U_{1j} \) and \( U_{2j} \) are the values of the first and second principal components for the jth water sample; \( U_{1i} \) and \( U_{2i} \) are the end member compositions projected into a two-dimensional mixing space.

Using the above equations, tracer concentrations in water samples can be predicted. The predictive capability of the EMMA model was determined through the relative root mean square error (RRMSE) and correlation coefficients \( r_j \), which further tested the assumption of time-invariance and proper selection of end members (Doctor et al., 2006; Hooper, 2003). The RRMSE was expressed as:

\[ r_j = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{\bar{x}_{ij} - \bar{x}_j}{\bar{x}_j} \right)^2} \]  

(B.4)

where \( r_j \) is the RRMSE for solute \( j \), \( x_{ij} \) are the observations, \( \bar{x}_{ij} \) are model predictions, \( \bar{x}_j \) are the mean observations for solute \( j \), and \( n \) is the number of observations.

Appendix C. Forward mass balance model

Based on four assumptions, Eq. (3) can be expressed as:

\[ [\text{Cl}] = [\text{Cl}]_{\text{int}} + [\text{Cl}]_{\text{anh}} \]  

(C.1)
For silicate weathering, average values in the world’s rivers from silicate weathering are used (Galy and France-Lanord, 1999): \[(\text{Ca}/\text{Na})_{\text{sol}} = 0.4, \text{and} (\text{Mg}/\text{K})_{\text{sol}} = 0.5.\] Therefore, \([\text{Ca}]_{\text{sol}}\) and \([\text{Mg}]_{\text{sol}}\) can be written as:
\[
[\text{Ca}]_{\text{sol}} = 0.4 \times [\text{Na}]_{\text{sol}}
\]
\[
[\text{Mg}]_{\text{sol}} = 0.5 \times [\text{K}]_{\text{sol}}
\]

By applying the above equations, the contribution of carbonate weathering can be finally derived.

Appendix C Hydrogeochemistry and stable isotopes

Appendix D Lateral groundwater flow calculation

References


Geosci. Model Dev. 7 (5), 2531–2543.


