

Research Article

Tracing the Origin of Groundwater Nitrate in an Area Affected by Acid Rain Using Dual Isotopic Composition of Nitrate

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Acid rain with a relatively high concentration of ammonium and nitrate can accelerate rock weathering. However, its impact on groundwater nitrate is uncertain. This study evaluated the dual isotopic composition of nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) from precipitation to groundwater in a rural mountainous area affected by acid rain. The average concentration for NH_4^+ is 1.25 mg/L and NO_3^- is 2.59 mg/L of acid rain. Groundwater NO_3^- concentrations ranged from <0.05 to 11.8 mg/L (baseline), and NH_4^+ concentrations ranged from 0.06 to 0.28 mg/L. The results show that groundwater $\delta^{18}\text{O}-\text{NO}_3^-$ values (-4.7‰ to +4.2‰) were lower than the values of rainfall $\delta^{18}\text{O}-\text{NO}_3^-$ (+24.9‰ to +67.3‰), suggesting that rainfall NO_3^- contributes little to groundwater NO_3^- . Groundwater $\delta^{15}\text{N}-\text{NO}_3^-$ values (+0.1‰ to +7.5‰) were higher than the values of $\delta^{15}\text{N}-\text{NO}_3^-$ derived from the nitrification of rainfall NH_4^+ (less than -4.7‰ in the study area), suggesting that nitrification of rainfall NH_4^+ also contributes little to groundwater NO_3^- . This implies that rainfall NO_3^- and NH_4^+ have been utilized. The dual isotopic composition of nitrate shows that baseline groundwater NO_3^- is derived mainly from nitrification of soil nitrogen. The denitrification process is limited in the groundwater system. This study shows that the rainfall NO_3^- and NH_4^+ contribute little to groundwater NO_3^- , improving the understanding of the nitrogen cycle in areas with a high concentration of NH_4^+ and NO_3^- in rainfall.

1. Introduction

Since the beginning of the twentieth century, the atmospheric concentration of acidic gases, such as SO_2 , NO_x , and NH_3 which are mainly a result of industrial activity and coal burning has increased steadily [1–4]. Consequently, there were large depositions of atmospheric acid in parts of Europe, North America, and SW China. Sulfur and nitrogen concentrations and deposition in North America and Europe have declined significantly due to emission reduction policies [5]. In the last 40 years, the southwest and southeast parts of

China have witnessed varying degrees of acid rain (rainfall with pH value lower than 5.6 is defined as acid rain) [6–9]. Based on the “China Environmental Status Bulletin in 2014”, released by the Ministry of Environmental Protection [8], 44% of 470 cities witnessed acid rainfall and rainfall in 30% of cities had an annual average pH lower than 5.6.

Acid rain has a high concentration of NH_4^+ and NO_3^- [8, 9]. During recharge to a river or groundwater system, NH_4^+ is nitrified into NO_3^- under oxidative conditions [10]. As two protons worth of acidity are produced for every NH_4^+ to form NO_3^- during nitrification, this process

tends to make the environment more acidic [11–13]. An acidic environment accelerates rock weathering, irrespective of the source of NH_4^+ either nitrogen fertilizers [14] or rainfall [15].

Increased inputs of anthropogenic nitrogen could lead to excess nitrogen in ecosystems [16]. The development of new agricultural practices to satisfy a growing global demand for food has led to extensive eutrophication of freshwaters and coastal zones [17]. In order to prevent methemoglobinemia, the maximum contaminant level for nitrate in drinking water has been set at 50 mg/L as NO_3^- by the World Health Organization [18] and 10 mg/L as NO_3^- -N by the United States Environmental Protection Agency and National Health Commission of the People's Republic of China (in this study, the concentration of nitrate is expressed as NO_3^-). As nitrogen is a reactive element in ecosystems [1], a series of reactions and processes control nitrogen dynamics in the soil and groundwater. These processes, which include assimilation, nitrification, denitrification, volatilization, sorption/desorption, and consumption by plants, significantly influence groundwater nitrate [19, 20].

Previous studies focused mainly on the sources of river/groundwater nitrate using multiple environmental tracers, such as the dual isotopic composition of nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) and the nitrogen isotope of ammonium ($\delta^{15}\text{N}-\text{NH}_4^+$). For example, the ranges of isotopic compositions of nitrate suggested that the major sources of nitrate in the large Changjiang (Yangtze) River come from modified fertilizer and urban sewage effluent [21]. Wastewater was found to be the main source of nitrate contamination in urban areas [22]. The nitrate input from rainfall to groundwater is often neglected, but nitrification is generally regarded as a prerequisite for nitrate leaching [23]. However, few studies on estimating groundwater nitrate concentrations accounted for atmospheric deposition of nitrogen [24–26]. Furthermore, the mixing model of the dual isotopic composition of nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) revealed that the nitrate from atmospheric deposition contributed 3% of the river nitrate in a river subbasin in Mecklenburg-Vorpommern (Germany) [27]. This proportion was found to be 30% for direct NO_3^- input to spring water from rainfall in northeast Bavaria (Germany) without any microbial interaction [23]; here, the $\delta^{18}\text{O}-\text{NO}_3^-$ values for spring water range from +11‰ to +33‰. Therefore, the impact of NH_4^+ and NO_3^- in rainfall on groundwater systems remains uncertain.

This study aims to assess the potential input of nitrate from acid rain using chemical and isotopic data of rainfall and groundwater in a rural mountainous area in SW China. The results would have important implications for the groundwater nitrogen cycle in areas with a high concentration of rain ammonium and assessment of the baseline level of nitrate related to nitrate contamination due to anthropogenic activities.

2. Study Area

The study area is located in the northern Xishui County (25°06'35"–28°50'15"N and 105°50'20"–106°44'30"E),

Zunyi, Guizhou Province, SW China. It has an average annual temperature of 13.1°C and average annual precipitation of 1138 mm. The study area is a mountainous area with elevation ranging from 750 m to 1700 m a.s.l. (Figure 1). The Xishui River flows into the Yangtze River. The land use/land cover (LULC) in Xishui County is mainly forest (62%) and farmland (31%) [28]. The study area has different lithologies from carbonates to silicates, and therefore, it is an ideal site to assess the impact of lithologies on nitrate concentration.

The study area tectonically belongs to the transitional zone between the northern part of the Central Guizhou Uplift and the southeastern part of the Sichuan Basin [29]. The sampling site is in the northwestern limb of the Sangmucang anticline (Figure 1). The oldest stratum exposed at the core of the anticline is the Proterozoic dolomite rock. The stratum layers from old to new (from the core to northwestern) are Cambrian, Ordovician, Silurian, Permian, Triassic, Jurassic, and Cretaceous [30]. Shallow groundwater aquifers in the study area can be divided into four types (Figure 1) based on lithology and water abundance [31]: (I) fracture-cave water occurring mainly in carbonate rock (limestone and dolomite), (II) cave-fracture water generally occurring in shale with little limestone (discharge of springs of 0.1–10 L/s), (III) pore-fracture water only occurring in the Triassic sandstone with a relatively rich yield of 25–125 m³ per day per meter for a well, and (IV) fracture water occurring in sandstone and mudstone with a groundwater runoff modulus of less than 2 L s⁻¹ km⁻². The varying lithology and strong anisotropy of shallow aquifers means that shallow groundwater in the study area generally emerges in the form of springs and shows heterogeneity due to the mixing of various geochemical components.

The population is relatively sparse in the area, and people mainly live in towns and lowland areas. In the mountainous areas (main sampling area), the population is even more sparsely distributed. There are almost no wells in the study area; therefore, spring waters are sampled at different stratum. Some of these springs are used for distributed domestic water supply (one or more families use one spring).

3. Sampling and Analysis

A total of 23 samples were collected in 2018 from spring flowing from different types of aquifers. The locations of the sampling points are shown in Figure 1. Physical and chemical parameters such as electrical conductivity (EC), pH, oxidation-reduction potential (ORP), and temperature were measured in situ using a multiparameter device (Hach HQ40d). The titration of HCO_3^- and CO_3^{2-} was conducted on site using a 16900 Digital Titrator (Hach) with 0.8 mol/L sulfuric acid for titration and phenolphthalein and methyl orange as indicators. Samples used for cation (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Sr^{2+}) analysis were immediately acidified with distilled HNO_3 (1 mol/L) to a pH of less than 2. The anions, Cl^- , SO_4^{2-} , NO_3^- , and F^- , were analyzed by ion chromatography (ICS-1100), and the cations, Na^+ , K^+ , Ca^{2+} , and Mg^{2+} , were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) at the Beijing Research Institute of Uranium Geology (BRIUG). The trace

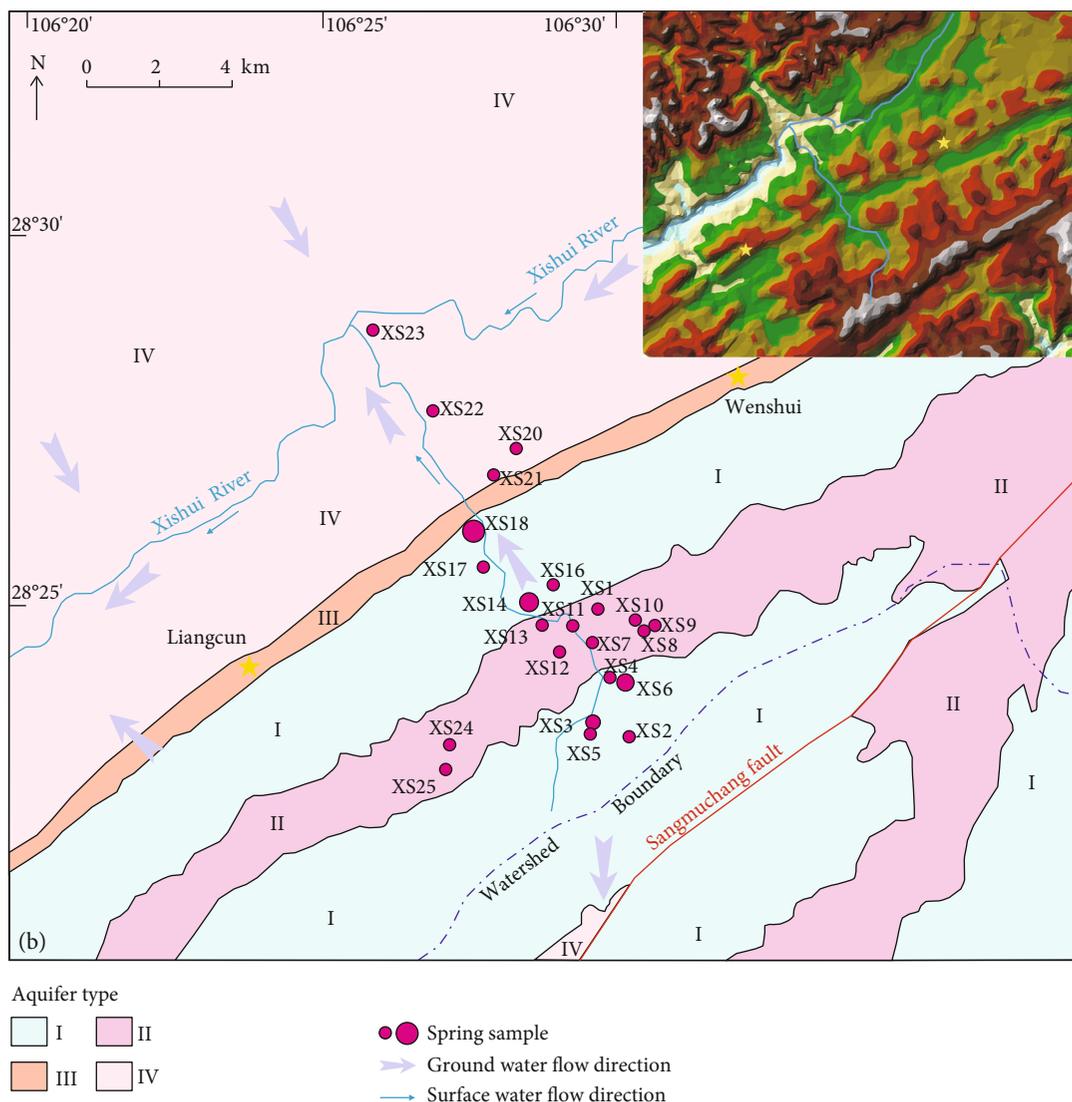


FIGURE 1: Study area. (a) Topography with the lowest elevation of 750 m a.s.l. and the highest elevation of 1700 m a.s.l.; (b) aquifer types (the introduction can be found in the text), groundwater and surface water flow direction, and spring sampling sites. The bigger dots indicate the spring samples with higher discharges.

element Sr^{2+} was analyzed using inductively coupled plasma mass spectrometry (ICP-MS). NH_4^+ and NO_2^- were measured using ultraviolet-visible spectroscopy, based on the methods of the GB/T 5750.6 standard, with a detection limit of 0.02 mg/L and 0.002 mg/L. The charge balance errors for all groundwater samples ranged from -1.1% to 4.8% and were within $\pm 5\%$.

The water stable isotopes were measured at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG-CAS) using a Picarro L1102-i isotopic water liquid analyzer. The results were reported in the form of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ($\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1,000$) using the Vienna standard mean ocean water (VSMOW) as the reference. The analytical precision was 0.5‰ for $\delta^2\text{H}$ and 0.1‰ for $\delta^{18}\text{O}$. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was measured at BRIUG using a Finnigan MAT 261 multiple collector thermal ionization mass spectrometer (MC-TIMS). Analysis of the NIST NBS

987 standard resulted in a ratio of 0.710235 ± 0.000026 . The groundwater N and O isotopes in NO_3^- were measured via the denitrifier method [32, 33] at the Isotope Bioscience Laboratory, Faculty of Bioscience Engineering, Ghent University, Belgium, where NO_3^- was converted to N_2O by denitrifying bacteria *Pseudomonas aureofaciens*. The results were reported in the form of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ using air (atmospheric nitrogen) and VSMOW as the standards. The analytical precisions for both $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ were both better than 0.5‰.

4. Results and Discussion

4.1. *Geochemical and Isotopic Composition of Rainfall.* No systematic observation data is available for rainfall in the study area. The Jinyunshan precipitation observation station managed by the Acid Deposition Monitoring Network in

TABLE 1: Chemical composition of rainfall for Jinyunshan (JYS) from 2002 to 2017 [9], Zunyi (ZY) from 2002 to 2006 [34, 35], Guilin (GL) in 2010 [38], and Guiyang (GY) from 2003 to 2009 [36, 37, 40]. The unit for precipitation (Preci) is mm/yr and the unit for concentration is mg/L.

Year	Location	Preci	pH	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	H ⁺
2002	JYS	1607	4.18	7.521	1.825	0.459	1.502	0.136	0.402	1.189	0.081	0.044
	ZY	1226	4.37	10.42	0.700		1.920			1.980		
2003	JYS	1233	4.36	7.986	2.136	0.364	1.541	0.115	0.336	1.228	0.069	0.050
	ZY	949	4.25	11.730	2.790		3.040			1.970		
	GY				2.259		1.041					
2004	JYS	1518	4.30	10.490	2.283	0.455	1.892	0.283	0.457	2.819	0.085	0.026
	ZY	1111	4.28	13.750	1.600		2.070			0.670		
2005	JYS	1461	4.59	9.784	2.131	0.549	1.895	0.352	0.443	2.308	0.076	0.024
	ZY		4.79									
	GY		4.74									
2006	JYS	1196	4.63	13.530	2.860	0.482	2.183	0.153	0.444	3.932	0.096	0.020
	ZY		4.30									
	GY		4.35									
2007	JYS	1645	4.69	8.676	1.951	0.309	1.353	0.143	0.264	2.205	0.067	0.030
	GY		4.44									
2008	JYS	1213	4.52	11.540	2.880	0.545	1.778	0.237	0.372	2.733	0.111	0.044
2009	JYS	1098	4.33	10.910	3.370	0.573	1.976	0.177	0.340	2.667	0.133	0.047
	GY	1107	4.23	25.500	0.453	0.736	2.030	0.320	0.375	7.316	0.252	0.059
2010	JYS	979	3.94	14.540	4.648	0.570	2.230	0.188	0.404	2.749	0.138	0.115
	GL	1950	4.83	16.760	3.728	0.815	1.653	0.359	0.364	4.374	0.287	0.015
2011	JYS	848	4.04	13.510	4.807	0.423	2.097	0.141	0.405	2.603	0.147	0.091
2012	JYS	1006	4.09	11.930	4.366	0.413	2.234	0.144	0.298	2.367	0.140	0.082
2013	JYS	1127	4.20	7.814	3.293	0.256	1.621	0.090	0.214	1.246	0.106	0.063
2014	JYS	1490	4.39	5.796	2.827	0.202	1.271	0.103	0.172	1.041	0.105	0.041
2015	JYS	1288	4.70	4.214	2.258	0.181	1.126	0.051	0.133	0.869	0.078	0.020
2016	JYS	1217	4.97	3.836	2.323	0.168	1.184	0.059	0.131	1.522	0.093	0.011
2017	JYS	1268	5.15	3.508	2.284	0.190	1.080	0.068	0.140	2.077	0.114	0.007

East Asia has long-term observation data. The station (106°22'E and 29°49'N) is located in Beibei District, Chongqing [9], about 40 km from the urban area of Chongqing. Jinyunshan forms one of the Natural Protection Region of Chongqing. The altitude of the Jinyunshan Mountain is about 700–900 m a.s.l., and the summit is at 952 m a.s.l. The physiognomy is typical low mountains. The climate in Jinyunshan is suitable for the growth of diversified plants due to high precipitation and high humidity of air and soil. The dominant plants consist of evergreen vegetation with a stable structure. As a Natural Protection Region, there are no industries, and only a few farming houses. Since this station, which is about 150 km far away from the study area, is situated in a rural site, it represents a rural district that is less impacted by anthropogenic activities than urban areas [9], similar to the study area. These areas experience acid rain with a similar pattern [8]. Therefore, the chemical composi-

tion of rainfall in Jinyunshan was used to represent the chemical characteristics of precipitation in the study area. The chemical compositions of rainfall over whole regions affected by acid rain in SW China are all similar, such as Zunyi [34, 35], Guiyang [36], and Guilin [37, 38] (Table 1). Unfortunately, there is no data on dry deposition. Therefore, only wet deposition was considered in this study.

As the water cycle is relatively short for spring water, rainfall data from 2013 to 2017 was used. Systematic observations of rainfall chemical composition show that the pH values ranged from 4.20 to 5.15 from 2013 to 2017 (Table 1) with a weighted average of 4.55, indicating the presence of acid rain. The main anions (in meq/L) are SO₄²⁻ (69%) and NO₃⁻ (27%), and the main cations are Ca²⁺ (39%), NH₄⁺ (37%), and H⁺ (16%) (Figure 2). The NO₃⁻ and NH₄⁺ concentrations showed limited variation, with averages of 2.59 mg/L and 1.25 mg/L, respectively. The total

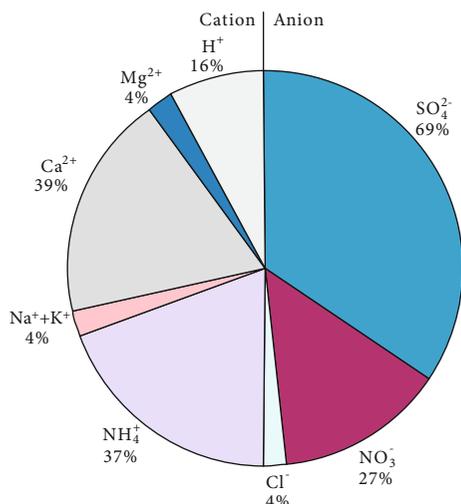


FIGURE 2: Precipitation ion compositions (% in meq/L). The ion compositions are the weighted average values from Jinyunshan, Beibei District, Chongqing, from 2013 to 2017. SO_4^{2-} , NO_3^- , Ca^{2+} , NH_4^+ , and H^+ are the main ions in precipitation (>15%). The data are from [9].

inorganic nitrogen from atmospheric wet deposition is expected to be $17.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, similar to the value of $18.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from southern Ontario, Canada, from 1980 to 1985 [24].

Previous studies have shown that the $\delta^{15}\text{N}-\text{NO}_3^-$ of rainfall in Guiyang (about 190 km from the study area) ranges from -12.7‰ to $+15.8\text{‰}$ [39–42] with averages value of -1.9‰ [39], $+1.5\text{‰}$ [40], $+2.3\text{‰}$ [41], and $+3.1\text{‰}$ [42] during different sampling periods. The $\delta^{18}\text{O}-\text{NO}_3^-$ of rainfall ranges from $+25.2\text{‰}$ to $+40.1\text{‰}$ with an average of $+34.2\text{‰}$ [40]. In the Shapingba District, Chongqing (about 140 km from the study area, and close to the Jinyunshan station), $\delta^{15}\text{N}-\text{NO}_3^-$ values range from -1.0‰ to $+6.9\text{‰}$ with an average of $+1.5\text{‰}$ and those of $\delta^{18}\text{O}-\text{NO}_3^-$ ranged from $+24.9\text{‰}$ to $+67.3\text{‰}$ with an average of $+43.6\text{‰}$ (unpublished data from Dr. Pingheng Yang from Southwest University, China).

The $\delta^{15}\text{N}-\text{NH}_4^+$ of rainfall in Guiyang ranged from -28.7‰ to $+7.8\text{‰}$ [39, 40] with average values of -10.6‰ and -4.7‰ during different observation periods. In Chongqing, the value ranged from -8.6‰ to $+1.3\text{‰}$ [43] with an average of -6.7‰ .

The rainfall around the study area is similar to other global studies with respect to $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$, and $\delta^{15}\text{N}-\text{NH}_4^+$ [44, 45], and the average values are within the typical range, suggesting that they are important end-members with which to trace the origin of NO_3^- in springs in the study area.

4.2. Water Chemistry and Isotopic Composition of Springs.

The data for major ions, pH, and stable isotopic composition for spring water are shown in Tables 2 and 3. The pH values of spring water ranged from 6.39 to 8.29, with an average of 7.61, which is mostly neutral to slightly alkaline. The total dissolved solids (TDS) ranged from 53 mg/L to 368 mg/L (XS21 of 16 mg/L is not included), with an average

value of 210 mg/L. The Na^+ (0.1–6.8 mg/L) and Cl^- (0.4–7.6 mg/L) concentrations were extremely low, with median values of 1.4 and 1.3 mg/L, respectively. The Piper plot (Figure 3) shows that the main water types were $\text{HCO}_3^- \text{Ca}^{2+}$, $\text{HCO}_3^- \text{Ca}^{2+} \text{Mg}^{2+}$, and $\text{HCO}_3^- \text{SO}_4^{2-} \text{Ca}^{2+} \text{Mg}^{2+}$ (%meq/L > 10% is named). Some of the water types were $\text{HCO}_3^- \text{SO}_4^{2-} \text{Ca}^{2+} \text{Mg}^{2+} \text{Na}^+$ (XS21 and XS22), and the corresponding strata are the Triassic and Jurassic sandstone, siltstone, mudstone, and shale. The TDS were mainly composed of HCO_3^- (R^2 of 0.84 for TDS and HCO_3^-) and $\text{Ca}^{2+} \text{Mg}^{2+}$ (R^2 of 0.98 for TDS and $\text{Ca}^{2+} \text{Mg}^{2+}$).

The spring water in the study area corresponds to the local meteoric water line (LMWL) of $\delta^2\text{H} = 7.89 \delta^{18}\text{O} + 11.95$ for Zunyi, obtained from the GNIP database [46], compared with the global meteoric water line (GMWL) of $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ [47]. The difference in water stable isotopic composition for springs was mainly caused by recharge altitude. At higher altitudes, where the average temperatures are lower, precipitation will be isotopically depleted and for $\delta^{18}\text{O}$, the depletion varies between about -0.15‰ and -0.5‰ per 100 m rise in altitude [48]. The outcrops of springs with most depleted isotopic values ($\delta^{18}\text{O}$ less than -8‰ , XS2, 3, and 5) are located in the Cambrian carbonates with the highest altitudes within all samples, and the outcrop of spring with most enriched isotopic value ($\delta^{18}\text{O}$ of -6.1‰) was located in lower altitudes (Figures 1 and 4).

However, in the higher altitudes, the groundwater samples were found to deviate from the LMWL (Figure 4). The deuterium excess value ($d = \delta^2\text{H} - 8\delta^{18}\text{O}$) [49] was around 18‰, as compared to the value of 12‰–15‰ in the lower altitudes (Table 3). In general, evaporation decreases and moisture recycling increases the deuterium excess [50, 51]. In mountainous areas, moisture recycling could contribute to additional moisture with high deuterium excess value for precipitation [50, 52], resulting in high deuterium excess in spring water at higher altitudes.

In most cases, carbonate rocks have higher contents of strontium but lower $^{87}\text{Sr}/^{86}\text{Sr}$ as compared to strontium derived from silicate rocks with lower contents of strontium and higher $^{87}\text{Sr}/^{86}\text{Sr}$ [53]. Marine carbonate commonly has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of less than 0.710. Groundwater flowing through carbonate aquifers will more readily reach high concentration levels of Sr^{2+} , resulting in fluids with low $^{87}\text{Sr}/^{86}\text{Sr}$ [53]. This contrasts with silicate groundwaters that tend to have higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower concentrations of Sr^{2+} . In Guizhou, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for carbonate rocks (including calcite and dolomite) could range from 0.7075 to 0.7100 [54]. Meanwhile, the results of previous studies show that Sr^{2+} originating from weathering of silicate rocks commonly has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio higher than 0.7150 [55, 56]. The concentrations of Sr^{2+} in shallow groundwater ranged from 0.01 mg/L to 1.97 mg/L, with an average of 0.37 mg/L (Table 3). Figure 5 shows the relationship between $1/\text{Sr}^{2+}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 5(a)) and the relationship between $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 5(b)) for spring water. Generally, when Sr^{2+} concentration decreased (i.e., $1/\text{Sr}^{2+}$ increased), the $^{87}\text{Sr}/^{86}\text{Sr}$ value increased. When the end-members for limestone, dolomite, and silicate in Guizhou

TABLE 2: Geochemical composition of spring water (mg/L).

No.	Sample	T ($^{\circ}\text{C}$)	pH	EC ($\mu\text{s}/\text{cm}$)	ORP (mV)	TDS	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
1	XS2	15.5	8.07	350	-14.9	213	1.0	36.6	210	0.09	2.8	0.11	0.1	0.7	22.3	43.7
2	XS3	16.6	7.76	398	-26.3	235	0.8	48.5	215	0.13	2.4		0.1	0.5	24.7	49.6
3	XS5	15.8	7.74	370	-21.7	236	0.9	51.3	210	0.12	1.7		0.1	0.5	24.9	50.3
4	XS6	16.3	7.92	247	-31.5	155	0.9	15.6	168	0.08	2.9	0.21	0.1	0.6	18.0	32.2
5	XS25	18.0	7.25	152	+0.2	88	0.8	16.3	78	0.12	0.2	0.06	2.1	1.5	1.6	26.4
6	XS4	19.0	8.13	276	-45.1	162	1.0	15.2	178	0.10	4.6		0.1	0.7	18.5	32.3
7	XS7	17.8	7.35	328	-1.5	216	2.5	13.4	222	0.10	8.4	0.28	2.0	1.2	2.0	74.7
8	XS8	17.6	7.59	343	-14.1	228	1.3	26.3	234	0.07	1.8	0.08	1.1	0.4	3.3	75.8
9	XS9	22.5	8.01	366	-38.3	227	2.4	39.0	198	0.07	6.1		1.8	0.6	5.4	71.9
10	XS24	15.2	7.93	235	-36.7	148	1.4	18.6	129	0.07	10.5	0.08	1.6	2.3	1.5	47.6
11	XS10	17.8	7.44	429	-5.7	277	1.4	50.4	249	0.08	5.5		2.6	0.9	9.6	81.5
12	XS11	17.6	7.20	426	+5.5	279	1.1	21.7	305	0.07	<0.05	0.08	0.7	0.2	3.3	98.9
13	XS12	18.1	7.12	514	+10.0	356	1.4	35.7	382	0.11	3.2	0.13	3.2	0.7	11.5	108.1
14	XS1	23.1	8.10	277	-46.0	165	0.8	18.2	173	0.07	0.2	0.11	0.1	0.3	2.2	55.9
15	XS13	18.0	6.62	160	37.6	95	5.0	29.8	38	0.07	11.8	0.18	4.0	3.0	7.3	15.0
16	XS14	21.6	8.15	397	-50.4	228	2.9	37.5	207	0.30	4.5		0.6	0.1	5.3	72.0
17	XS16	20.4	8.29	338	-57.6	207	1.1	19.3	231	0.06	2.9		0.1	0.3	24.9	42.7
18	XS17	18.1	7.66	426	-22.2	287	7.6	53.6	146	0.16	63.9	0.08	5.0	0.8	6.9	76.0
19	XS18	17.8	7.67	415	-22.9	259	1.6	18.6	288	0.13	3.4	0.07	0.1	0.9	13.8	76.4
20	XS21	20.5	7.09	31	+11.6	16	0.4	6.3	8	0.00	<0.05	0.17	1.4	0.7	0.9	1.7
21	XS20	21.4	8.19	210	-50.4	130	0.9	30.2	108	0.21	<0.05	0.09	5.2	0.6	5.0	33.7
22	XS22	17.7	6.39	87	+49.9	53	2.7	15.0	30	0.08	3.3	0.08	6.8	0.1	2.9	6.7
23	XS23	18.7	7.39	549	-6.0	368	2.9	76.8	310	0.16	7.5	0.07	6.0	0.7	13.4	103.3

[54] were used, silicate weathering contributed partially to the input of Sr^{2+} . However, no relationship was found between NO_3^- concentration and Sr^{2+} concentration ($R^2 = 0.01$), $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio ($R^2 = 0.01$), and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ($R^2 = 0.00$) for spring waters, suggesting that the impact of lithology on NO_3^- concentration is limited.

Nitrate concentrations for spring samples ranged from undetected (<0.05 mg/L) to 63.9 mg/L with a median value of 3.2 mg/L. NH_4^+ concentrations for all spring water samples ranged from 0.06 mg/L to 0.28 mg/L with a median value of 0.08 mg/L. The NH_4^+ concentrations were significantly lower than those from rainfall (1.25 mg/L). Nitrite (NO_2^-) was not detected in any spring water sample. The $\delta^{15}\text{N}-\text{NO}_3^-$ for all spring water samples ranged from +0.1‰ to +7.5‰, while the $\delta^{18}\text{O}-\text{NO}_3^-$ ranged from -4.7‰ to +4.2‰ (Table 3).

4.3. Origin of Nitrate for Spring Water. According to the definition from Shand and Edmunds [57], the groundwater baseline quality is “The range of concentrations of a given element, isotope or chemical compound in solution, derived entirely from natural, geological, biological or atmospheric sources, under condition not perturbed by anthropogenic activity”. In terms of NO_3^- , the baseline value can be determined using spring water samples from the upper stream, which are not influenced at all by anthropogenic activity (no. 1 to no. 15, Table 2). The median (50%) and upper values for NO_3^- baseline level, calculated using SigmaPlot

(version 10.0), were found to be 2.9 mg/L and 11.0 mg/L. These values are consistent with the baseline value for NO_3^- (median value of 2–9 mg/L and upper value of 8.2–14.4 mg/L) in arid-semiarid northern China [58]. The natural baseline for nitrate is unlikely to be more than 9–13 mg/L in most temperate regions covered by forest or grassland [57, 59]. Based on the baseline level, NO_3^- concentrations in other springs were within the baseline level (from <0.05 to 7.5 mg/L), except for spring sample XS17, which had an NO_3^- concentration of 63.9 mg/L; it was affected by anthropogenic activity.

Potential origins of NO_3^- , with NO_3^- concentrations less than the upper baseline level in the study area, are (1) direct NO_3^- input from rainfall, because rainfall has an average concentration of 2.59 mg/L; (2) NH_4^+ from rainfall, because it has an average concentration of 1.25 mg/L NH_4^+ while concentrations of the latter in groundwater were less than 0.28 mg/L, suggesting that the nitrification of rainfall NH_4^+ could potentially contribute NO_3^- to groundwater; and (3) NH_4^+ from soil nitrogen, which is a common source of groundwater NO_3^- [19, 21]. Denitrification, however, is a multistep process involving various nitrogen oxides (e.g., N_2O , NO) as intermediate compounds resulting from a biologically mediated reduction of nitrate to N_2 [19]. This process would decrease NO_3^- concentration and increase $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in the residual NO_3^- by a factor of 2:1 [19, 48, 60].

When rainfall recharges springs, the enrichment factor (f) (evapotranspiration from rainfall to the spring) is

TABLE 3: Strontium and nitrate concentration and isotopic compositions for spring waters.

Sample	Sr ²⁺ (mg/L)	⁸⁷ Sr/ ⁸⁶ Sr	NO ₃ ⁻ (mg/L)	δ ¹⁵ N-NO ₃ ⁻ (‰)	δ ¹⁸ O-NO ₃ ⁻ (‰)	δ ¹⁸ O-H ₂ O (‰)	δ ² H-H ₂ O (‰)	d (‰)
XS-2	0.76	0.709168	2.8	+3.2	-2.5	-8.1	-47.3	17.6
XS-3	0.91		2.4	+2.5	-0.3	-8.2	-47.3	18.3
XS-5	1.04		1.7	+2.7	-0.6	-8.2	-47.7	17.8
XS-6	0.10		2.9			-7.6	-44.3	16.5
XS-25	0.13	0.710342	0.2			-7.9	-45.5	17.6
XS-4	0.25		4.6			-7.7	-44.4	17.4
XS-7	0.12	0.712219	8.4	+6.6	+4.2	-7.1	-43.8	12.6
XS-8	0.18	0.712023	1.8			-7.0	-40.6	15.2
XS-9	0.24		6.1			-6.8	-38.9	15.9
XS-24	0.08	0.712827	10.5	+6.2	+0.2	-7.2	-39.4	17.9
XS-10	0.42	0.710713	5.5	+4.7	+1.3	-7.6	-45.0	16.1
XS-11	0.16	0.711593	<0.05			-6.4	-37.4	14.1
XS-12	0.64	0.710368	3.2			-7.1	-42.1	15.0
XS-1	0.09	0.710581	0.2			-6.8	-39.5	15.2
XS-13	0.11		11.8	+7.5	+2.3	-6.8	-40.0	14.5
XS-14	0.62		4.5			-6.5	-36.8	15.0
XS-16	0.02	0.711683	2.9			-7.6	-43.9	16.8
XS-17	0.26	0.707968	63.9	+2.2	+1.1	-6.8	-41.4	13.2
XS-18	0.12	0.709651	3.4	+5.7	-4.7	-6.9	-40.5	14.4
XS-21	0.01	0.715097	<0.05			-6.9	-40.0	14.8
XS-20	0.15	0.712698	<0.05			-7.3	-42.2	16.1
XS-22	0.06	0.711773	3.3			-6.1	-36.2	12.2
XS-23	1.97	0.711113	7.5	+0.1	+0.2	-7.2	-43.9	13.9

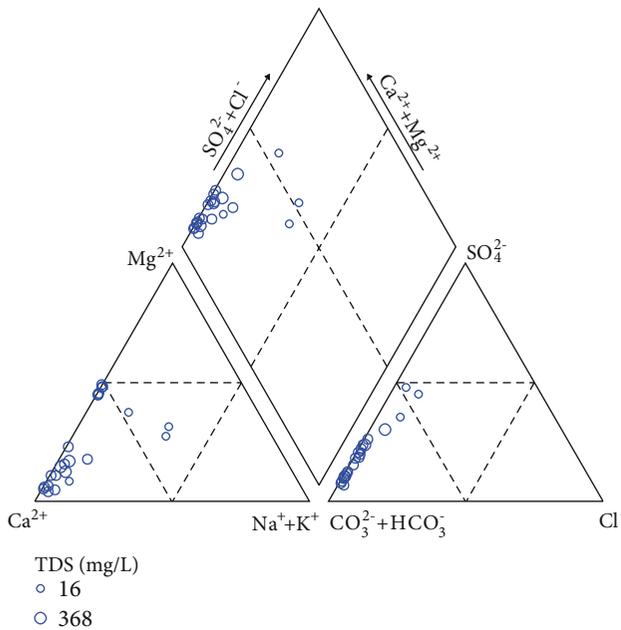


FIGURE 3: Piper diagram of spring water samples. The HCO₃⁻-Ca²⁺ and HCO₃⁻-Ca²⁺·Mg²⁺ types were found to be dominant.

difficult to determine in a complicated hydrogeological system. However, the range of 2–5 is used based on different sites with similar hydrogeological conditions in SW

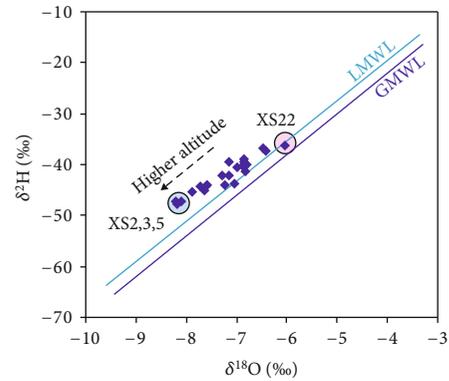


FIGURE 4: Stable isotopic composition of springs. All springs lie around the LMWL, suggesting limited evaporation during recharge. LMWL for Zunyi: δ²H = 7.89δ¹⁸O + 11.95 [46]; GMWL: δ²H = 8δ¹⁸O + 10 [47].

China [15, 61, 62]. As the NO₃⁻ concentration in rainfall was 2.59 mg/L, spring water should have NO₃⁻ concentrations of 5.2–13.0 mg/L if there is no loss during recharge. The value overlaps the spring NO₃⁻ value (from <0.05 to 11.8 mg/L). However, plot of δ¹⁵N-NO₃⁻ and δ¹⁸O-NO₃⁻ showed that the groundwater NO₃⁻ concentrations were similar to those of rainfall NO₃⁻ (Figure 6). The latter were less than +4.2‰ (Table 3) while the former were larger than +24.9‰ and up to +67.3‰ in Guiyang and Chongqing. Besides, groundwater NO₃⁻ concentrations were

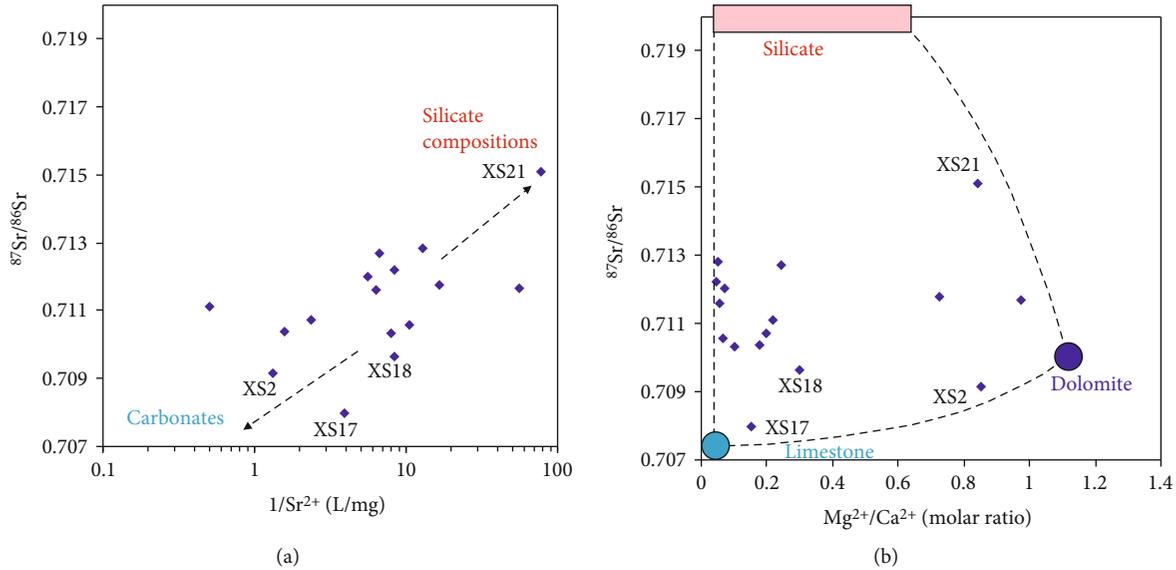


FIGURE 5: Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}^{2+}$ (a) and between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\text{Mg}^{2+}/\text{Ca}^{2+}$ (b). The three end-members of limestone, dolomite, and silicate are modified from [54].

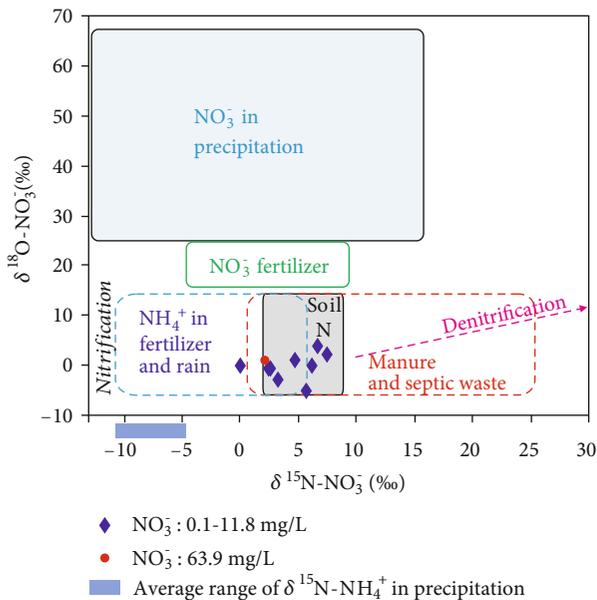
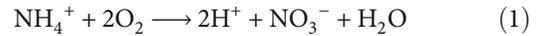


FIGURE 6: The relationship between $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ for spring water. The range for $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ and average range for $\delta^{15}\text{N}-\text{NH}_4^+$ for precipitation is from Guiyang and Chongqing. The schematic of typical ranges for other sources is from [44, 45].

lower compared with those in rain after during evapotranspiration (Figure 7(a)). Furthermore, groundwater NO_3^- enrichment was not caused by evapotranspiration (Figure 7(b)), because the $\text{NO}_3^-/\text{Cl}^-$ ratio would remain constant when NO_3^- increased. NO_3^- is the most usable form of nitrogen for plants [25]. Nitrate from atmospheric deposition is intensively cycled through the organic nitrogen pool in all watersheds [63] and can be taken up by plants [64]. The vegetation is dense in the study area.

Therefore, NO_3^- in spring water is not derived from rainfall NO_3^- .

The ammonium (NH_4^+) concentration in spring water (0.06–0.28 mg/L) is significantly lower than that in rainfall (1.25 mg/L), suggesting that most NH_4^+ in rainfall has been nitrified to NO_3^- during the recharge process [11, 13, 15, 65]:



where 1.00 mg/L NH_4^+ can produce 3.44 mg/L NO_3^- . When NH_4^+ concentration in rainfall is 1.25 mg/L and the enrichment factor is 2–5, NH_4^+ concentration for recharging spring would reach 2.50–6.25 mg/L, potentially resulting in 8.6–21.5 mg/L NO_3^- in spring water. This value is similar to or higher than the NO_3^- concentration in spring water (from <0.05 to 11.8 mg/L). Therefore, nitrification of NH_4^+ in rainfall may be a potential source for spring NO_3^- . The average values of $\delta^{15}\text{N}-\text{NH}_4^+$ for rainfall in adjacent areas (Guiyang and Chongqing) ranged from -10.6‰ to -4.7‰ [39, 41, 43]. There is isotopic fractionation for nitrogen, commonly a few per mill lighter [19] and up to -35‰ [66, 67] with respect to the ammonium source during nitrification of NH_4^+ . However, it is difficult to accurately predict $\delta^{15}\text{N}-\text{NO}_3^-$ from simple measurement of $\delta^{15}\text{N}-\text{NH}_4^+$ due to complicated transformation processes and transformation rate [10, 44, 68]. If spring NO_3^- is derived from nitrification of rainfall NH_4^+ , the $\delta^{15}\text{N}-\text{NO}_3^-$ of spring would have an average value of less than -4.7‰. When the average value of $\delta^{15}\text{N}-\text{NO}_3^-$ for spring water is +4.4‰, significantly larger than that from nitrification of rainfall NH_4^+ (less than -4.7‰), it can be concluded that spring NO_3^- is not derived from rainfall NH_4^+ through nitrification. Therefore, rainfall NH_4^+ can be said to have been consumed and contributes little to spring NH_4^+ and NO_3^- .

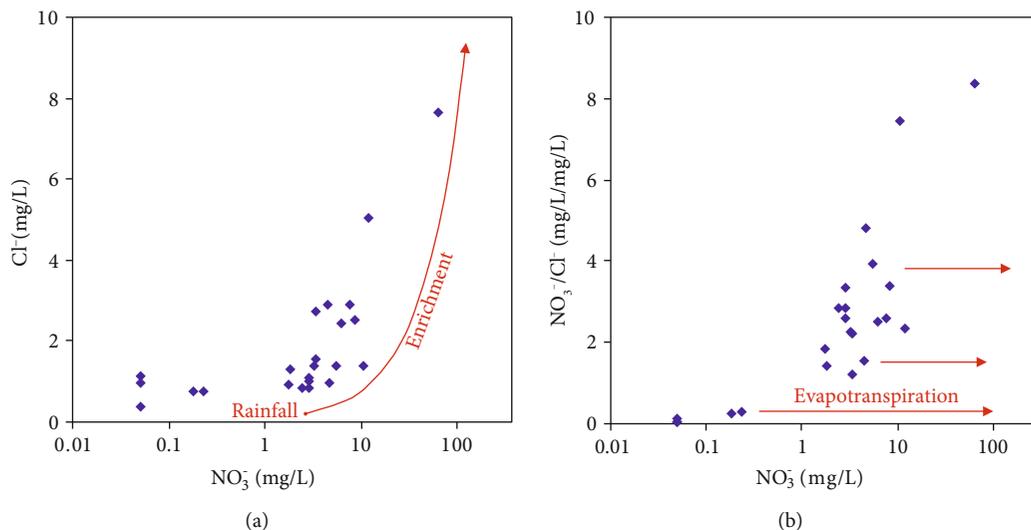


FIGURE 7: The relationship between NO_3^- and Cl^- for spring and evapotranspiration line for rainfall (a) and between NO_3^- and $\text{NO}_3^-/\text{Cl}^-$. During evapotranspiration, $\text{NO}_3^-/\text{Cl}^-$ would remain constant.

Nitrification of soil nitrogen could be an important source for the natural groundwater system [69]. The $\delta^{15}\text{N}$ values of total soil N vary from -10‰ to $+15\text{‰}$, but typically range from $+2\text{‰}$ to $+9\text{‰}$ [19, 45, 70]. During mineralization of soil N to NH_4^+ (sometimes it is called ammonification), there is very little isotopic fractionation for $\delta^{15}\text{N}$ [19]. However, the further nitrification process will result in a slightly lighter (few per mill) $\delta^{15}\text{N}$ for nitrate in N-limited systems [19]. The $\delta^{15}\text{N}\text{-NO}_3^-$ for spring water was within the range of NO_3^- derived from soil N nitrification (Figure 6). In addition, nitrate derived from nitrification should have $\delta^{18}\text{O}\text{-NO}_3^-$ between -9‰ and $+11\text{‰}$ as the O in NO_3^- is derived from H_2O (2/3) with $\delta^{18}\text{O}$ values in the normal range of -25‰ to $+4\text{‰}$ and from O_2 (1/3) with $\delta^{18}\text{O}$ of $+23.5\text{‰}$ [71, 72]. However, these values can vary due to changes in ammonium abundance and nitrification rates [10]. The $\delta^{15}\text{N}\text{-NO}_3^-$ for spring water ranged from $+0.1\text{‰}$ to $+7.5\text{‰}$, while the $\delta^{18}\text{O}\text{-NO}_3^-$ ranged from -4.7‰ to $+4.2\text{‰}$, all within the acceptable range for nitrification of soil nitrogen (Figure 6). Therefore, nitrate from nitrification of soil nitrogen is a potential source for spring nitrate.

A weakly positive relationship was found between NO_3^- concentration and $\delta^{15}\text{N}\text{-NO}_3^-$ ($\delta^{15}\text{N} = 0.356 \text{NO}_3^- + 2.22$, $R^2 = 0.31$), suggesting that the increase in $\delta^{15}\text{N}\text{-NO}_3^-$ is not related to denitrification, which would result in a decrease in NO_3^- concentration. In addition, the ORP values ranged from -57.6 to $+49.9$ mV (Table 1) with an average value of -16 mV. The absence of correlation for ORP and NO_3^- suggests that denitrification process is limited in the study area.

Based on the aforementioned results, NO_3^- with concentration less than 12 mg/L in spring waters in the study area mainly originated from the nitrification of soil N, rather than direct input of rainfall NO_3^- or nitrification of rain NH_4^+ (Figure 8). Although the latter two processes can potentially contribute up to $13.8\text{--}34.5$ mg/L NO_3^- in a spring, NO_3^- and NH_4^+ transformation could affect the fate of nitrate in

this mountainous area affected by regional acid rain. In similar study areas in Guizhou Province, Li et al. [69] attributed the origin of NO_3^- with similar concentration and similar isotopic composition ($^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$) to nitrification of soil N. This study has provided isotopic evidence that rainfall input has contributed little to NO_3^- in spring waters.

For spring water XS17, which has been affected by anthropogenic activities, the NO_3^- concentration was 63.9 mg/L with $\delta^{15}\text{N}\text{-NO}_3^-$ value of $+2.2\text{‰}$ and $\delta^{18}\text{O}\text{-NO}_3^-$ value of $+1.1\text{‰}$ (Figure 6). There are two potential sources: (1) nitrification of ammonium from fertilizer and (2) manure and septic wastewater. Based on field surveys, this spring water was found to be affected by distributed croplands. The infiltrating water or/and overflow may flow into the recharge area of the spring XS17. The high NO_3^- concentration is related to the use of ammonium fertilizers. NO_3^- from manure and septic waste would have higher $\delta^{15}\text{N}\text{-NO}_3^-$ (typically $+7\text{‰}\text{--}+25\text{‰}$) value [27, 44, 45, 73]. The $\delta^{15}\text{N}\text{-NO}_3^-$ value of $+2.2\text{‰}$ is significantly lower than that from manure and septic wastewater, suggesting that the spring XS17 with NO_3^- concentration of 63.9 mg/L was derived from nitrification of ammonium fertilizers (Figure 6).

5. Conclusions

While some studies have considered the atmospheric input of nitrate to groundwater systems, this study shows that the direct input of rainfall nitrate and input through nitrification of rainfall ammonium contributes little to groundwater nitrate, even when nitrate and ammonium concentrations in rainfall are high. The inorganic nitrogen from rainfall is consumed, and groundwater nitrate is mainly derived from nitrification of soil nitrogen at the natural groundwater system. In the study area, the moisture recycling in higher altitudes could contribute to additional moisture, resulting in high deuterium excess in spring samples at higher altitudes.

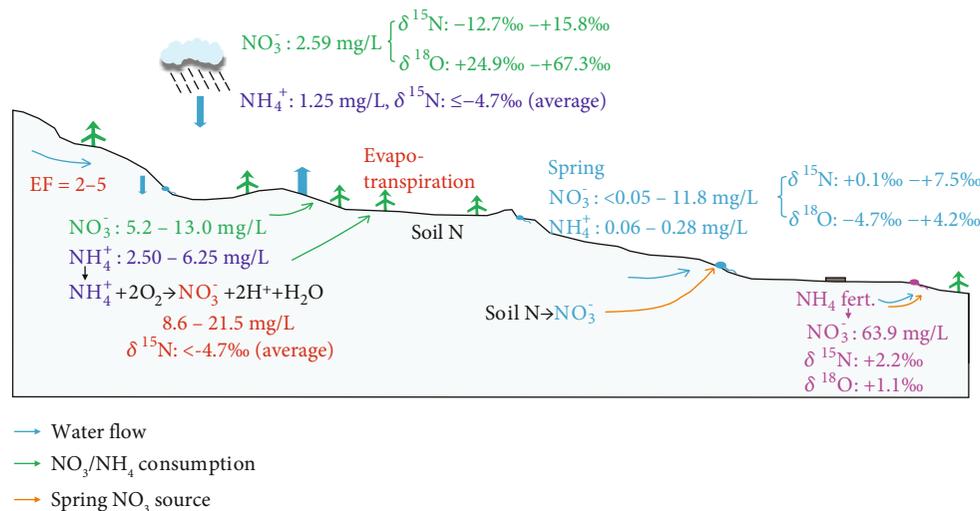


FIGURE 8: Conceptual model of the nitrogen cycle in the study area. Note: FE = enrichment factor.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show the chemical types of spring water are controlled by lithology. However, the impact of lithology and evapotranspiration on NO_3^- concentration is limited in the study area. This study helps understand the nitrogen cycle and trace groundwater nitrate sources.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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