

ANALYSIS ON WATER QUALITY OF THE TIBETAN PLATEAU BASED ON THE MAJOR IONS AND TRACE ELEMENTS IN THE NIYANG RIVER BASIN

WU, J.^{1,2,3} – ZHAO, Z. Q.^{4*} – MENG, J. L.^{1,3} – ZHOU, T.^{1,3}

¹*State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China*

²*School of Chemistry and Materials Science, Guizhou Education University, Guiyang 550018, China*

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

⁴*School of Earth Science and Resources, Chang'an Unveristy, Xi'an 710054, China*

**Corresponding author
e-mail: zhaozhiqi@chd.edu.cn*

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Abstract. Niyang River is the second largest tributary of the Yarlung Tsangpo River on the Tibetan Plateau. To establish the controlling factors of water quality in the river basin, this paper explores the hydro-chemical features of the major ions in the river water, and evaluates the water quality and health risk of trace elements. Multiple advanced technical instruments were adopted for our exploration including, the principal component analysis (PCA) and Water Quality Index (WQI). The hydro-chemical results show that the major ions in the river mainly originate from the weathering of rocks, with Ca-Mg-HCO₃ being the dominant type of hydro-chemical facies. Through PCA-based water quality assessment, we learned that the trace elements of Tl, Hg, Cd, Mo, Ti, U, As, Cr, Pb, Rb, Li, Sr, Ba, Fe and Al mostly come from rock weathering and groundwater leaching, while Cu, Zn and Mn are mainly attributable to natural and human sources. According to international and domestic standards, virtually no trace element surpassed the permissible limit, and the WQI values were basically low across the river basin, indicating that the river water is suitable for drinking directly.

Keywords: *Water Quality Index, trace elements, Niyang River, dissolved ion chemistry, principal component analysis*

Introduction

Water is one of the most important resources on the Earth. However, freshwater only makes up 2.5% of the total volume of the world's water. The Tibetan Plateau has an abundance of water resources, which greatly affect the local economy and ecology (Huang et al., 2008; Qu et al., 2019). Hailed as the water tower of Asia, the plateau is the source of the ten largest rivers on the continent, such as the Yangtze River, the Yellow River and the Nujiang River (Huang et al., 2010, 2008; Wu et al., 2005; Xu et al., 2019). Among the various rivers on the Tibetan Plateau, more than 20 rivers have a catchment greater than 10,000 km² (Guan and Chen, 1980). The largest catchment (>240,000 km²) belongs to the Yarlung Tsangpo River (Jiang et al., 2015; Zeng et al., 2018). On the Tibetan Plateau, the most important tributary of the Yarlung Tsangpo River is the Niyang River, the catchment of which catchment is larger than 10,000 km² (Liu et al., 2018). The existing studies on this river mainly focus on the potential effects of global warming on the chemical weathering of rocks in the catchment and on the eco-environmental changes

in the downstream (Liu et al., 2018; Yu et al., 2019). There is little report on the water quality in the Niyang River, from the perspectives of major ions and trace elements.

Water quality reflects the potential of river water to serve drinking and production purposes. It is generally agreed that the water quality of rivers is influenced by human factors (e.g. mining, wastewater discharge, and land use changes) and natural processes (e.g. rock weathering, grassland degradation, and glacier melting) (Huang et al., 2015; Wijesiri et al., 2018; Chen et al., 2019; Haldar et al., 2019; Jahin et al., 2020). For instance, rapid economic growth, which is accompanied by intense human activity, can push up the pollutant content in water systems, while rivers in pristine areas maintain good water quality (Wijesiri et al., 2018; Haldar et al., 2019). Under global warming, the pollutants accumulated in glaciers are released into the rivers, reducing the water quality (Huang et al., 2008). However, it is very difficult to assess the water quality of rivers in a comprehensive manner, because of the complex interplay between human factors and natural processes.

In recent years, both anthropogenic factors and natural processes are posing a serious threat to the water quality of the Niyang River. About 94, 000 people now live along this water course, and economic activities (e.g. mining, agriculture and tourism) have been in full swing in the downstream. In addition, the water chemistry in the catchment is being changed by the growing volume of meltwater and rainwater. Through the above analysis, this paper aims to identify the chemical features of river water, assess the controlling factors of water quality, track the source of trace elements, and evaluate the water quality in the Niyang River basin. First, water samples were collected from the Niyang River and its major tributaries. Then, the major ions and trace elements were analyzed in the water samples. In addition, the suitability of the water samples as drinking water was evaluated based on multiple water quality indices. The research results shed new light on water management and health protection on the Tibetan Plateau.

Materials and Methods

General situation of research area

The Niyang River (92°10'-94°35'E; 29°28'-30°31'N) originates at 5,000 m above the sea level (m a.s.l.) from the Cuomuliangla, west of the Mila Mountain, China's Tibet Autonomous Region (TAR). With a catchment of 17, 679 km², the river flows 307.5 km from west to east, before entering the Yarlung Tsangpo River at 2,920 m a.s.l. The elevation difference between the source and confluence is up to 2,080 m (Zhang et al., 2009). Being the second largest tributary of the Yarlung Tsangpo River, Niyang River is of great importance to the regional water balance on the Tibetan Plateau. The annual runoff of river is estimated to be 17.23 billion m³. Meltwater and rainwater contribute to 47 and 40% of the annual runoff, respectively (Wang, 2011). The precipitation in the river basin is unevenly distributed, and largely controlled by the warm current in the Indian Ocean and the cold current from the north. The mean annual rainfall stands at 650 mm, 90% of which occurs in the summer months from June through September. The climate in the river basin changes significantly with the elevations. The annual mean temperature rises from 7.6°C in the upstream to 8.6°C in the downstream.

The river basin has a complex lithology. The bedrocks are mainly composed of granite, diorite and granodiorite. The dominant minerals include mica, feldspar and quartz. Quaternary deposits are widely developed on both banks of the river. Located in the downstream of the Niyang River, the Bayi District is home to more than 39,000 people,

serving as an important agricultural base on the Tibetan Plateau (Li, 2009). Every year, a large volume of agricultural and domestic wastewater is discharged into the river. What is more, fertilizers and pesticides are widely applied in this district to guarantee the agricultural output (Shi, 2015).

Experimental methods

In August, 2018, water samples were collected at 10 cm below the water surface from the Niyang River and its major tributaries (Fig. 1). The physical and chemical compositions of the samples are reported by Liu et al. (2018). The temperature (T), electrical conductivity (EC) and pH of the samples were measured in-situ by a Multi 3630 IDS multi-parameter portable meter (WTW, Germany). The alkalinity of the samples was obtained through Gran titration analysis in the field, using 0.02 mol/L HCl. The water samples were processed by 0.45 μm cellulose acetate (CA) membrane filters, and then stored in pre-cleaned polyethylene bottles. The filtrate was divided into two parts: one part was used directly for anion analysis (e.g. SO_4^{2-} , F^- , Cl^- , NO_3^-), and the other was acidified to $\text{pH} < 2$ with ultrapure 1:1 HNO_3 for cation analysis (e.g. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SiO_2). The cations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES) system (Vista MPX, US), while the anions were measured by ionic chromatography (IC), using an ICS-90 IC system (Dionex, US). The contents of trace elements were obtained through inductively coupled plasma mass spectrometry (ICP-MS) system (Agilent 7700X, US). The contents of anions, cations and trace elements were all measured in The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The measurement reproducibility was determined through repeated analysis, showing $\pm 5\%$ precision for the anions, cations and trace elements. For all the samples, the calculated total anion charge TZ^- was balanced by the total cation charge TZ^+ within the analytical uncertainties, and the normalized inorganic charge balance (NICB) fell within $\pm 5\%$ are reported in Liu et al. (2018).

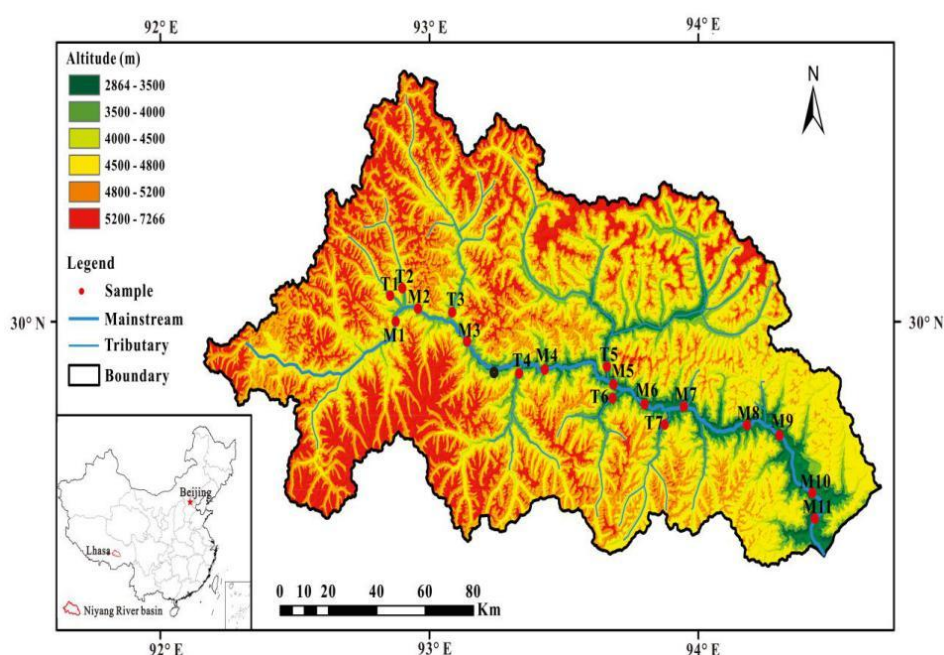


Figure 1. Sampling location map of Niyang River. Modified from Liu et al. (2018)

Statistical methods

Pearson correlation analysis was performed to disclose how different trace elements influence the water quality. If the Pearson correlation coefficient (r), is greater than or equal to 0.7, then the two variables have a strong correlation; if $0.4 < r < 0.7$, then the two variables have a moderately strong correlation; if $r \leq 0.4$, then the two variables have a weak correlation (Gidey and Amanuel, 2018).

The Water Quality Index (WQI) was introduced to evaluate the combined effects of several toxic elements considered detrimental to the aquatic ecosystem (Qu et al., 2019):

$$WQI = \frac{1}{n} \sum_{i=1}^n A_i = \frac{1}{n} \sum_{i=1}^n C_i/Q_i \quad (\text{Eq.1})$$

where C_i ($\mu\text{g/L}$) is the content of the i -th toxic element in the water sample; Q_i ($\mu\text{g/L}$) is the content limit of the i -th toxic element specified by the World Health Organization (WHO, 2011) and the Chinese national standard (GB) (MOH and SAC, 2006). According to the WQI value, the pollution level was divided into four classes: $WQI \leq 1$ (Class 1, unpolluted); $1 < WQI \leq 2$ (Class 2, slightly polluted); $2 < WQI \leq 3$ (Class 3, moderately polluted); and $WQI > 3$ (Class 4, heavily polluted) (Qu et al., 2019).

Results and Discussion

Characterization of the major ions of Niyang River systems

As mentioned before, the chemical compositions of the water in the Niyang River basin are reported in Liu et al. (2018). The pH of the water samples varied from 8.08 to 7.71, indicating the mild alkalinity of the water in the river basin. Due to the specific hydrology and geology, the major ion contents of the Niyang River were lower than those of other rivers in the world (Fig. 2). The total dissolved solids (TDS) of the samples ranged from 51.7 to 112 mg/L, averaging at 81.7 mg/L. This is far lower than the global mean level of 120 mg/L (Wetzel, 1975). In the mainstream of the Niyang River, the TDS decreased from 112 mg/L in the upstream to 72.3 mg/L in the downstream, owing to the dilution effect. The Ca^{2+} accounts for 60.5-80% of all cations (TZ^+) in the water samples, followed by Mg^{2+} (10.8-34.9%), Na^+ (3.58-8.74%) and K^+ (0.67-1.9%), while HCO_3^- accounts for 60.2% of all anions (TZ^-) in the samples, followed by SO_4^{2-} (36.4%).

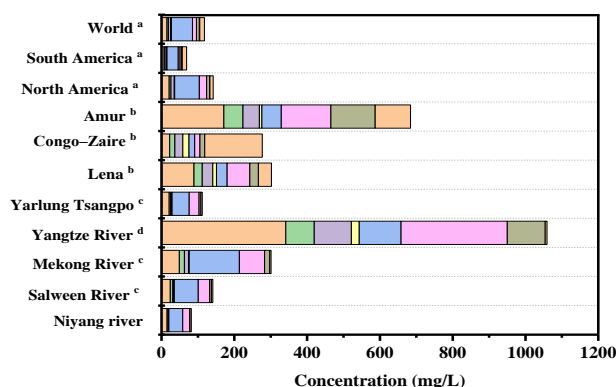


Figure 2. Average concentrations of major ions in Niyang River and other rivers of the world. Data source: a. Wetzel (1975); b. Gaillardet et al. (1999); c. Huang et al. (2011); d. Chetelat et al. (2008)

To evaluate the hydrogeochemical facies and types of the samples, the relative equivalent proportions of major ions were plotted as ternary diagrams. As shown in *Fig. 3*, the data clustered near the $[Ca^{2+} + Mg^{2+}]$ peak (*Fig. 3a*) and the HCO_3^- peak (*Fig. 3b*), suggesting the water in the Niyang River basin belongs to the type of $Ca-Mg-HCO_3$ river water. This is similar to that in the Yangtze River (Chetelat et al., 2008), but differs from that of the Wujiang River (Han and Liu, 2004) and the Yellow River (Fan et al., 2014).

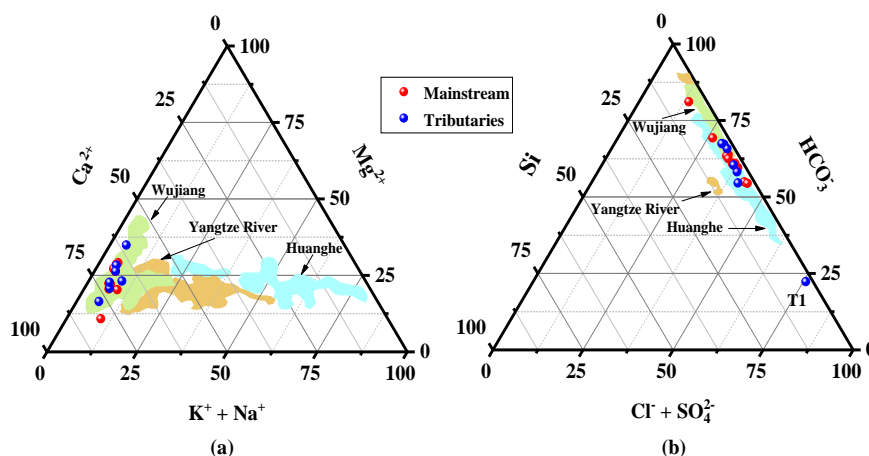


Figure 3. Ternary diagram of the relative equivalent proportions of major cations (a) and major anions (b) for the river waters, indicating that the Niyang River was dominated by Ca^{2+} and HCO_3^-

Major sources and controlling factors of the ions

The major elements dissolved in river water generally come from precipitation, groundwater leaching, human inputs (e.g. agriculture, industry and urbanization), and chemical weathering of rocks (e.g. silicate, evaporite, carbonate, and sulfide) in the catchment (Meybeck and Ragu, 1997; Gaillardet et al., 1999). On the Tibetan Plateau, the meltwater and rainwater are the two leading sources of the major elements in rivers (Hasnain and Thayyen, 1999). Zhang et al. (2003) calculated how much atmospheric inputs contribute to the total cations based on the measured ion/ Cl^- ratio in rainwater in Lhasa region, assuming that rainwater has the lowest Cl^- content measured in the catchment (Ding et al., 2017). In the Niyang River basin, the lowest Cl^- content was observed at the site T-2 ($3.30 \mu M$). According to Liu et al. (2018), the atmospheric inputs contribute to 5.5-12.9% of the total cations, with an average of only 8.0%. Thus, the contribution of atmospheric inputs to the major ions of our samples is very limited. Considering the major impact of human activities on water chemistry via wastewater input (Sun et al., 2017), it is necessary to evaluate the contribution of human inputs to the major ions in the water samples. In many large rivers, NO_3^- , among the dissolved ions, is generally associated with anthropogenic sources (Chetelat et al., 2008). In our water the NO_3^- content was below the global mean value of $21.7 \mu M$ (Meybeck, 1987). According to Liu et al. (2018), the human activities are responsible for 0-0.5% of all cations. Hence, the human inputs also have a limited contribution to the major ions in our samples. TDS contents and low weight ratios of $[Na^+]/[Na^+ + Ca^{2+}]$ and $[Cl^-]/[Cl^- + HCO_3^-]$. This means the dominant source of major ions in the Niyang River catchment is the chemical weathering of rocks. In general, the Mg^{2+} , Ca^{2+} and HCO_3^- in our samples are most likely

to originate from the weathering of carbonates and silicates, while the K^+ , Na^+ , SO_4^{2-} and Cl^- from the weathering of silicates and the dissolution of evaporites. To identify which type of rock weathering controls the ions in the water samples, the plotted the mixing diagrams of the Na-normalized of Ca^{2+} versus HCO_3^- and Ca^{2+} versus Mg^{2+} for identifying three endmembers of carbonates, silicates and evaporates. As shown in Fig. 4, our water samples were close to the carbonate endmember in the mixing diagrams, indicating that the weathering of carbonate is crucial to the major ion chemistry of the river water.

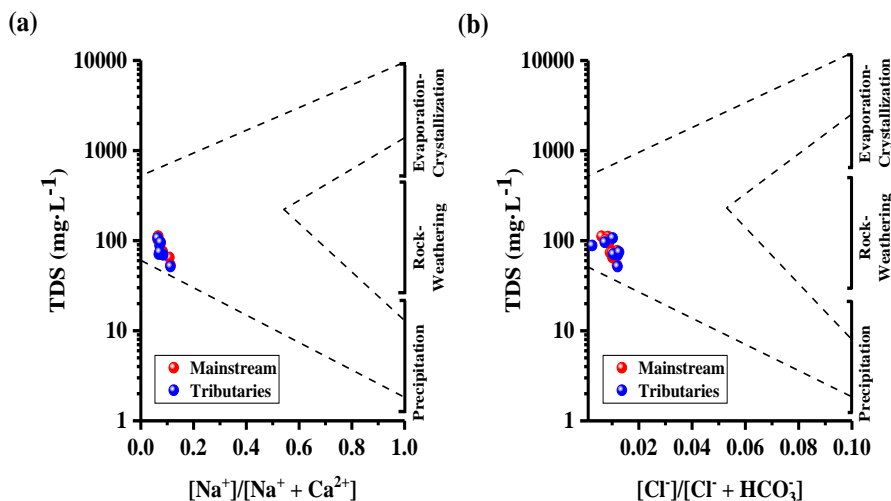


Figure 4. Gibbs diagram (weight ratios) of major ion compositions in Niyang River basin

This conclusion echoes with the previous results on the rivers in other parts of the High Himalaya region (Wu et al., 2008; Jiang et al., 2018; Zeng et al., 2018), and is supported by the relatively high mean $[Ca^{2+} + Mg^{2+}]/[Na^+ + K^+]$ molar ratios of 7.62 and mean $[HCO_3^-]/[Na^+ + K^+]$ molar ratios of 9.28. The molar ratios confirm that the river basin is dominated by the weathering of dolomite and calcite minerals in Fig. 5.

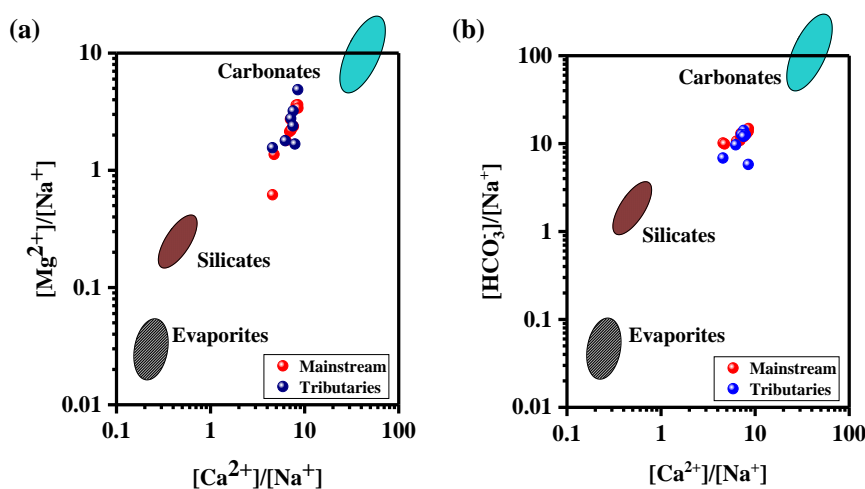


Figure 5. Mixing diagram of the Na-normalized molar ratios of (a) Ca^{2+} versus Mg^{2+} and (b) Ca^{2+} versus HCO_3^- in the Niyang River basin. The data for the three endmembers, i.e., carbonates, silicates and evaporites, are obtained from Gaillardet et al. (1999)

Dissolved trace elements and water quality assessment

Dissolved trace elements

Despite their excessively low content (<1 mg/L), the trace elements play an important role in human health (Xiao et al., 2019). This subsection discusses the features and possible sources of trace elements in our water samples, and assesses their risks to the residents in the river basin in *Table 1*.

Table 1. The trace elements and WQI in Niyang River basin

<i>Sample</i>	<i>Mn</i> μg/L	<i>Cu</i> μg/L	<i>Zn</i> μg/L	<i>Pb</i> μg/L	<i>Cr</i> μg/L	<i>As</i> μg/L	<i>Rb</i> μg/L	<i>Sr</i> μg/L	<i>Ba</i> μg/L	
M-1	98.3	6.24	24.6	5.02	0.54	2.55	1.88	76.2	45.6	
M-2	78.7	1.39	6.62	0.41	0.13	1.73	1.61	77.4	49.2	
M-3	48.2	1.78	6.45	0.57	0.14	1.17	1.62	59.7	46.5	
M-4	30.6	0.83	4.47	0.12	0.1	1.04	1.54	54.7	45.0	
M-5	9.6	0.48	4.71	0.13	0.08	0.52	1.93	41.8	38.3	
M-7	4.08	0.22	2.54	0.07	0.04	0.25	1.25	19.6	41.6	
M-10	11.5	0.59	2.55	0.36	0.12	0.75	1.81	43.9	9.89	
M-11	11.2	0.57	3.63	0.27	0.13	0.66	1.87	41.9	46.0	
T-1	451	1.59	76.9	0.40	0.08	0.24	2.26	52.6	46.6	
T-2	3.83	0.49	5.26	0.10	0.09	0.43	1.24	47.7	49.8	
T-3	2.22	0.19	3.00	0.03	0.05	0.31	1.69	58.1	50.7	
T-4	3.29	0.55	3.39	0.11	0.16	1.41	1.65	47.8	41.5	
T-5	4.55	0.31	3.13	0.11	0.07	0.32	2.05	37.3	43.3	
T-7	11.0	0.51	3.95	0.10	0.07	0.69	1.85	44.1	42.0	
<i>Sample</i>	<i>U</i> μg/L	<i>Li</i> μg/L	<i>Al</i> μg/L	<i>Ti</i> μg/L	<i>Fe</i> μg/L	<i>Mo</i> μg/L	<i>Cd</i> μg/L	<i>Hg</i> μg/L	<i>Tl</i> μg/L	<i>WQI</i>
M-1	0.76	2.84	113	0.51	69.6	0.89	0.09	0.03	0.01	0.41
M-2	0.51	2.48	9.99	0.08	5.96	1.49	0.01	0.06	0.01	0.14
M-3	0.66	3.4	136	1.64	53.1	0.73	0.07	na	0.01	0.27
M-4	0.49	3.09	85.4	0.64	41.7	0.84	0.07	na	0.01	0.23
M-5	0.68	3.18	17.3	0.06	4.52	1.03	0.02	0.02	0.01	0.08
M-7	0.21	1.34	18.7	0.11	9.6	0.4	0.01	0.01	na	0.05
M-10	0.59	1.86	41.3	0.6	32.4	0.47	0.02	0.01	0.01	0.10
M-11	0.56	2.74	40.8	0.57	21.34	0.79	0.02	0.01	0.01	0.10
T-1	0.17	3.43	19.9	0.1	5.92	0.41	0.76	0.03	0.05	1.74
T-2	0.4	0.85	20.6	0.1	8.34	0.38	0.03	0.03	na	0.10
T-3	0.5	4.73	11.7	0.13	8.1	0.75	0.02	0.01	na	0.07
T-4	0.42	1.71	19.2	0.4	16.5	1.36	0.01	0.03	na	0.07
T-5	0.75	3.15	7.47	0.14	6.55	0.89	na	0.02	na	0.03
T-7	0.54	2.88	11.6	0.07	4.66	1.06	0.01	0.01	0.01	0.06

na, not determine

The Niyang River has fewer dissolved elements than most rivers around the world. The contents of trace elements were extracted to identify the correlations and covariances between varying sample parameters through the principal component analysis (PCA). Three main parameter clusters were observed in the PCA loading-plot (PC1, PC2 vs PC3) in *Fig. 6*, which represent 74.0% of the total variances in the data of river waters. The Sr, Cu, Cr, Al, Fe, Ti, and Pb in PC1 had the highest loadings among the PCs, which explains

33.1% of the variance. This is supported by the positive correlation among these elements (Table 2): the correlation coefficients of Cu and Pb, Al and Fe, and Cr and Pb were 0.975, 0.952, 0.944 and 0.971, respectively. Meanwhile, the Cd, Mn, Zn, Rb and Tl in PC2 could explain 26.6% of the variance; the Mo and Hg in PC3 was responsible for 14.2% of the variance.

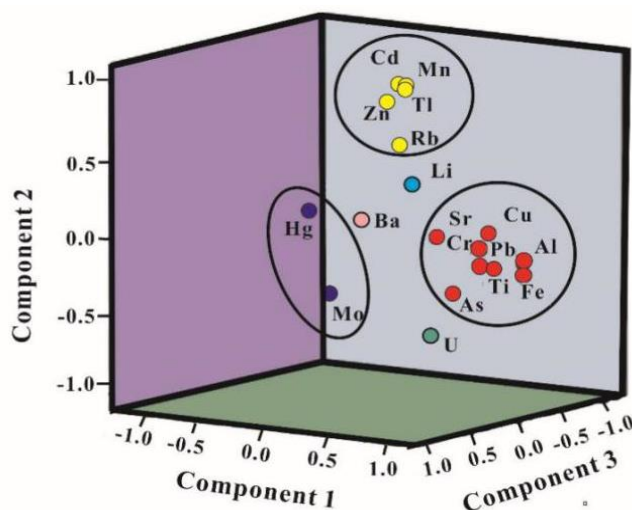


Figure 6. Principal component analysis (PCA) for dissolved trace elements in the Niyang River basin

Table 2. Correlation coefficient matrix of trace elements in Niyang River basin

	Mn	Li	U	Cu	Zn	Pb	Cr	As	Rb	Sr	Ba	Al	Ti	Fe	Mo	Cd	Hg	Tl
Mn	1																	
Li	0.241	1																
U	-0.461	0.305	1															
Cu	0.301	0.103	0.345	1														
Zn	.986**	0.225	-0.434	0.361	1													
Pb	0.161	0.056	0.402	.975**	0.244	1												
Cr	0.086	-0.021	0.443	.952**	0.161	.971**	1											
As	-0.04	-0.059	0.425	.793**	-0.037	.759**	.855**	1										
Rb	.544	.563	0.275	0.213	.562	0.182	0.146	-0.026	1									
Sr	0.255	0.344	0.318	.650	0.222	.549	.592	.747**	0.138	1								
Ba	0.166	0.285	-0.155	0.14	0.166	0.068	0.041	0.075	-0.143	0.308	1							
Al	0.019	0.156	0.387	.635	0.03	.564	.594	.564	-0.072	0.426	0.028	1						
Ti	-0.098	0.131	0.335	0.256	-0.129	0.172	0.254	0.332	-0.089	0.231	-0.109	.861**	1					
Fe	-0.035	0.074	0.444	.741**	-0.002	.719**	.759**	.688**	-0.036	0.457	-0.118	.944**	.749**	1				
Mo	-0.249	0.155	0.38	0.081	-0.301	0.055	0.18	.541	0.125	0.43	0.204	-0.111	-0.084	-0.07	1			
Cd	.980**	0.239	-0.52	0.188	.978**	0.059	-0.019	-0.186	0.528	0.121	0.137	-0.008	-0.092	-0.078	-0.363	1		
Hg	0.298	-0.248	-0.107	0.257	0.268	0.21	0.246	0.387	0.071	0.476	0.239	-0.367	-0.478	-0.281	0.453	0.16	1	
Tl	.946**	0.283	-0.371	0.223	.920**	0.081	0.019	-0.082	.624	0.202	0.013	0.06	-0.016	-0.014	-0.233	.938**	0.15	1

** Correlation is significant at $p < 0.05$ level (2-tailed). The bold number indicates the strong correlation ($r \geq 0.7$)

Overall, the contents of trace elements in samples varied with the differences in the weathering of rocks, groundwater supply, rainwater and human inputs (Tatsi et al., 2015; Qu et al., 2017). In the Niyang River systems, Fe and Al mainly come from the weathering of chlorite and calcite (Yokoo et al., 2004), Cu, Zn and Mn mostly originate from mineral exploration, due to the abundance of mineral deposits (e.g., manganese ore, copper ore and lead zinc ore) in the river basin (Lü et al., 2019). As shown in *Table 2*, Tl and Cd had a positive correlation coefficient of 0.93, suggesting that the two trace elements are both attributable to mining and meltwater (Tatsi et al., 2015). Note that the heavy metals Mn and Zn at site T-I were 13 times and 128 times more concentrated than those in other rivers (Gaillardet et al., 1999), respectively, reflecting the major contribution of the human activity of metal mining.

Water quality assessment

The water quality indices of our samples were compared against the drinking water standards of the World Health Organization (WHO) (WHO, 2011) and the GB (MOH and SAC, 2006). The comparison shows that most of the Al, As, Ba, Hg, Pb, Tl, Cr, Cu, Fe, Mo, Sr and Zn in our samples were below the lower limits of toxic elements for drinking water. As shown in *Table 1*, the trace element contents and the Water Quality Index (WQI) were relatively high in the upstream of the Niyang River, owing to high evaporation and limited precipitation. Across the river basin, the WQI values ranged from 0.03 to 0.4, except for the relative high WQI at site T-1. The latter is attributable to the mineral exploration at the site. Therefore, almost all samples from the river basin belong to the unpolluted class.

The Niyang River supplies agricultural water to the entire Bayi District. More than half of the population in that district live along the water course. The tourism and agriculture are booming along the river. This research reveals that water in the Niyang River is still undisturbed, because the impacts from agriculture and industrial activities (mining) are mitigated by the strong dilution and buffering capacity of the river. However, the boom in tourism, coupled with the mining activities, will put heavy burdens on the water quality in the region. The degradation of water quality is foreseeable, due to the intensified weathering of rocks and growing human activities in the river basin. Therefore, the local government should implement strict environmental regulations on solid waste and waste water treatment.

Conclusions

In the context of sustainable development, water quality is an important environmental issue across the globe, especially in the Tibetan Plateau, the water tower of Asia. This paper mainly explores the geochemistry features of major ions in the Niyang River, and assesses the water quality in the river basin. It is learned that the water chemistry in the river is greatly affected by the natural process of rock weathering, with Ca-Mg-HCO₃ being the dominant type of hydro-chemical facies. Under the alkaline aquatic environment, the river basin has low contents of trace elements, which originate from bedrock weathering. Through water quality assessment, the rivers water in the basin was found safe for direct drinking, for no trace element surpasses the lower limit in international and domestic water quality standards, except for Mn and Zn at site T-I. However, the elemental abundances in the air, soil, and water of the river basin may be perturbed by the growth in economy, human activities (e.g. mining and wastewater

discharge) and natural processes (e.g. rock weathering). Considering the potential damages of this possibility to human health and the essential role that rivers on the Tibetan Plateau play in terms of water resources of Asia, the region should consistently monitor the pollutant loads and implement pollutant control in the rivers, e.g. increasing of the sampling and adding the analysis of water quality parameters.

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