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Analysis of Hydrochemical Characteristics of Rivers Polluted by Heavy Metal Cadmium

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Heavy metal cadmium pollution in water is a serious environmental pollution, its pollution degree depends on the content and chemical form of cadmium, and is affected by the original water chemical form. The water chemical ions of rivers have certain depletion effects on water pollutants. Based on this, by taking the Longjiang River in Guangxi as the research object, this paper analyses its water chemical characteristics and ion sources. This shall provide theoretical basis for the later management of Longjiang River. The results show that the water body of Longjiang River mainly includes Ca^{2+} and HCO_3^-, account for 65%-89% and 65%-98% of the total cations and anions, respectively. The river is weakly alkaline, the ions of the water are mainly derived from the dissolution of carbonate in the drainage basin, and are mainly affected by natural chemistry.

1. Introduction

Precipitation forms a river through the collection of surface runoff. The river is a flowing water body, and its characteristics of water chemical element are affected by many natural factors, such as climate, vegetation, soil, and human activities (Bartnik et al., 2011; Islam et al., 2017). Rivers in different regions exhibits different physical hydro-chemical characteristics, with the properties of comprehensiveness and complexity. Hechi City, Guangxi is a famous “Hometown of Non-ferrous metals” in China, among which the reserves of mineral resources such as lead, zinc, antimony and indium rank highest across the whole country. Long-term mineral development has led to the accumulation of heavy metal pollution in the basin and caused the serious heavy metal pollution incidents repeatedly (Huang et al., 2012). On January 15, 2012, a serious cadmium pollution accident occurred in Longjiang River, Guangxi. About 20 tons of cadmium was discharged into the Longjiang River, causing serious damage to the ecological environment of the Longjiang River and influencing the water supply to the downstream city of Liuzhou (Zhang, 2017).

After the accident, a large number of cadmium-containing ions entered the water body of Longjiang River, which must inevitably destroy the equilibrium state of the original water chemical composition, disturb the original water chemical balance system of the Longjiang River, and make the original stable water environment state in a new active period, thereby causing water quality variation problem. With the generated pollution, various anions and cations between the water bodies interact with each other to finally reach a neutral balance state. Therefore, by studying the interactions and changes of various ions in the original water body and the polluted water body, the law of heavy metal pollution and the pollution nature can be more deeply explored. This is of important guiding significance on how to carry out the treatment of polluted water bodies.

2. Composition of chemical components of Longjiang River

Water chemistry is mainly to study the chemical composition of river water and its distribution and evolution in space and time (Barbaro et al., 2016). Biogeochemical behaviors such as geological, climatic characteristics, and human activities in the drainage basin have a direct impact on the water chemistry characteristics of the river. For example, Chen et al. (2002, 2005) through analysis of the main ionic chemical characteristics and genesis of rivers such as the Yangtze River, the Yellow River and the Pearl River, believed that the main chemical components of rivers in the Yangtze River are affected by the weathering of carbonate minerals; the

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Yellow River is mainly affected by solute evaporation and crystallization; the upstream of the Pearl River basin is affected by the weathering of carbonate minerals, and the downstream is affected by the sedimentation of sea salt. Wen et al. (2016) studied the river water chemistry and heavy metal pollution in the karst area, and considered the main river section of the Pearl River basin is weakly alkaline, and the Ca^{2+}, Mg^{2+} and HCO_3^- ions are mainly derived from the dissolution of carbonate rocks. The formation and distribution of river water chemistry in karst areas is the result from the long-term effects of rivers and external conditions. It is a common product of natural factors and human activities. As the information carrier of various geophysical and chemical effects, it makes material exchanges with the external environment in the flow process under the influence of various external factors, and its water chemical composition has been also changing accordingly.

According to the water quality monitoring data of the Longjiang River from 1980 to 2016 in Guangxi Water Environment Monitoring Centre, the pH value of Longjiang River water body is between 7.59 and 8.32, with an average of 7.79, and the average annual water temperature is 21.2 °C. The long series water quality monitoring stations include Liujia Station (S1), Sanjiangkou Station (S2), 32nd Hospital Station (S3) and Sancha Station (S4), among which the historical water quality monitoring data series of Sancha Station is the longest. The drainage map and basic water chemical ion content of Longjiang River are shown in Figure 1 and Table 1.

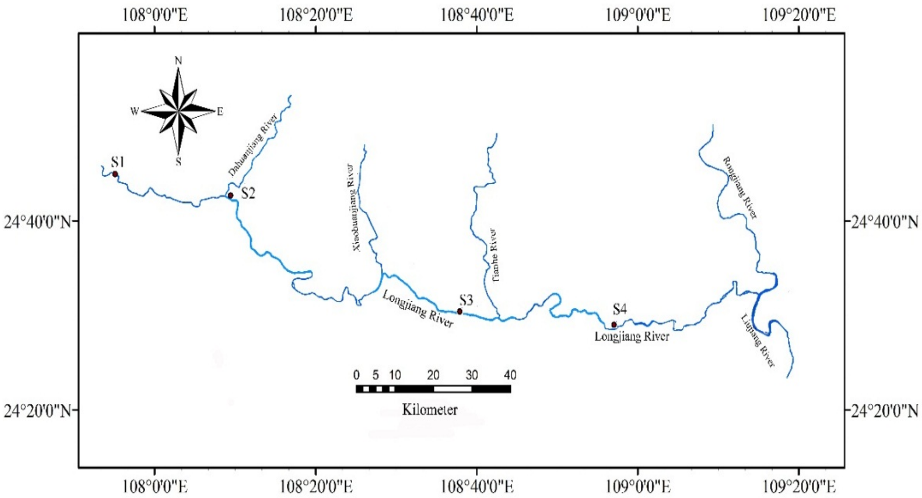

Figure 1: Distribution of station sites

Table 1: Chemical composition of Longjiang River

Station		pH	T	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	NO_3^-	SO_4^{2-}
			°C	mg·L^{-1}							
S1	max	8.32	30.3	1.603	4.046	7.06	58.12	6.736	181.22	11.286	22.574
	min	7.63	10.3	0.978	0.966	5.84	27.66	0.319	97.020	0.310	1.297
	AVG	8.11	20.5	1.095	2.575	6.32	48.90	3.616	157.43	5.271	11.047
S2	max	8.29	31.2	1.603	3.816	7.54	55.31	6.665	173.9	11.782	24.495
	min	7.64	11.0	1.056	1.104	5.84	31.26	0.319	97.02	0.310	1.297
	AVG	8.10	22.6	1.173	2.483	6.32	46.49	3.616	156.82	5.457	11.815
S3	max	8.31	29.8	1.486	4.138	7.54	59.72	7.090	172.68	13.022	23.054
	min	7.59	9.50	1.134	1.104	5.34	28.46	0.425	91.53	0.310	1.345
	AVG	8.10	21.6	1.212	2.529	6.56	49.70	3.651	153.77	6.015	11.527
S4	max	8.27	30.0	1.525	3.954	7.30	56.11	7.445	190.38	11.968	25.456
	min	7.65	10.0	1.095	1.081	6.08	31.26	0.355	95.80	0.310	1.441
	AVG	7.96	21.8	1.173	2.506	6.56	46.89	3.687	161.09	5.705	12.008

3. Analysis for chemical structure of Longjiang River

With different geographical locations of the rivers, the underlying rock layers are different, and the chemical composition of the river water is also different. The different combinations of ions in the river water and the amount of each ion also directly affect the chemical structure type of the water body. Based on related literature (Piper, 1984), the Piper ternary diagram was applied to analyze the chemical composition of the

Longjiang River, in order to illustrate the relative abundance and distribution characteristics of the main ions in Longjiang River, and the relative contribution of various rock weathering to the total solute composition of the Longjiang River. This tri-linear diagram consists of a diamond and two triangles, and each edge represents the equivalent percentage of water ions. Figure.2 shows the Piper diagram of the Longjiang River.

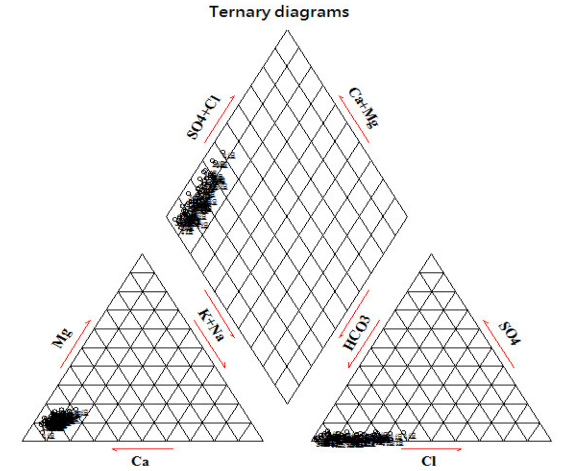

Figure 2: The ternary diagram of the Longjiang River

Then, it can be seen from Figure 2:

(1) In the piper diagram (diamond), the data of the Longjiang River water quality monitoring points are concentrated in the direction of HCO_3^- and Ca^{2+} (arrow direction), indicating that Ca^{2+} and HCO_3^- are the main ionic components of the Longjiang River water body. Then, the chemical type of Longjiang River is HCO_3^- - Ca^{2+}, which is consistent with the study of Wen (Wen et al., 2016) etc.

(2) In the cation piper diagram (bottom left), the cation is mainly concentrated at the end of calcium ion (Ca^{2+}), and the content accounts for 55% to 89% of the total ion number, which indicates that the cation of the Longjiang River is mainly Ca^{2+}.

(3) In the anion piper diagram (bottom right), most of the data in the four water quality monitoring stations of the Longjiang River are on the left side of the figure, which is biased/deflected toward the side of the bicarbonate ion (HCO_3^-), with the content occupying about 65% to 98% of the total anions.

Influenced by nature and human activities, the sources of different anions and cations also varies. If there exist certain good correlation between some water chemical ions, it indicates that these ions may have the same material source or physical-chemical reaction process. Generally speaking, rivers mainly composed of Ca^{2+} and HCO_3^- ions are mostly distributed in karst areas, and the ions in these river bodies are generally considered to be chemical dissolution of calcite and dolomite (Shen, 2011). The geographical lithology of the river basin and the underlying rock strata determine the chemical composition of the river. The chemical composition of the Longjiang River water is determined by carbonate dissolution, and the equivalent variation range of its total cation concentration ($TZ^+=K^++Na^++Ca^{2+}+Mg^{2+}$) is 1.59-1.72 meq/L, which is consistent with the world's 61 large rivers (Gaillardet et al., 1999) (TZ+=0.3~10 meq/L], and the average value is close to that of world rivers (TZ+=1.25 meq/L).

4. Analysis for water chemistry control factors in Longjiang River

The Gibbs diagram is often used to qualitatively determine the influence of the external environment in the area of the river on the chemical composition of water. Some scholars at home and abroad have studied many river water chemical control mechanisms, in which the relationship between TDS (total dissolved solids in water) and $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ ions to determine the main control types of key ions in water, and the factors affecting water chemistry are divided into four categories, namely seawater input, atmospheric precipitation, rock weathering and evaporative crystallization. Besides, the Gibbs diagram of the river is also drawn and used to study the influencing factors of the water chemistry.

4.1 Water chemical composition control

The anion and cation content of river water chemistry determines the water type in the river, and it is mainly determined by various external control solute units. Based on the water quality monitoring data of Longjiang River in Guangxi, the best-preserved water quality monitoring data in four monitoring stations of Longjiang

River were selected to calculate the TDS content in water (generally converted by water conductivity), and also the values of $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ respectively. Figure 3 shows the Gibbs diagram of the Longjiang River in Guangxi.

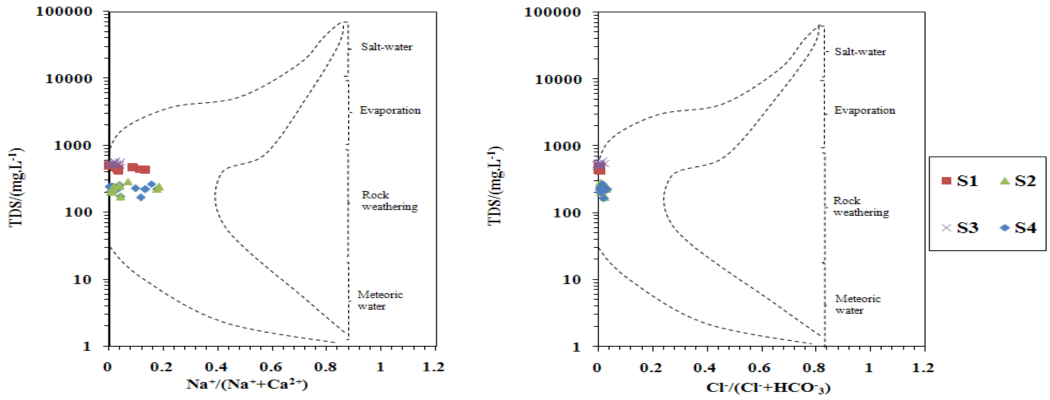

Figure 3: Gibbs diagram of chemical anion and cation in Longjiang River

It can be seen from Figure 3 that the values of the four water quality stations in Longjiang River all fall within the dotted line and the distribution is also concentrated. The corresponding area is the rock weathering control area, indicating that the source of the ion in the Longjiang River is mainly from the rock weathering. In order to further study the type of rock weathering, by calculating the values of Ca^{2+}/Na^+, HCO_3^- / Na^+, and Mg^{2+}/Na^+, the rock-ion relationship of Longjiang River is described in Figure 4.

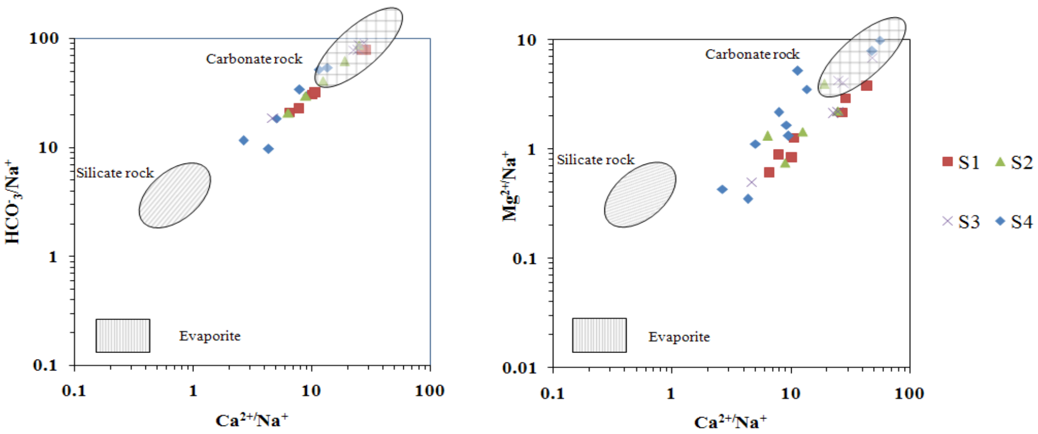

Figure 4: Main ion relationship diagram of Longjiang River

It can be seen from Figure 4 that in addition to the water quality monitoring data of the Sancha Station in certain period, the chemical samples of the Longjiang River are basically in or near the control area of the carbonate rock, indicating that the chemical composition of the Longjiang River is mainly derived from the weathering and dissolution of carbonate rock.

4.2 Correlation between conventional ions of Longjiang River

The mutual relation between two variables or multiple variables can be described by correlation coefficients. For multiple vectors, a correlation coefficient matrix between multiple vectors needs to be constructed. Pearson correlation coefficient matrix is often used to study the correlation and coexistence between variables in datasets, and to analyse the relationship between two vectors, e.g., if the corresponding correlation coefficient has a large absolute value, it indicates good positive correlation or negative correlation between the two vectors. In the water chemistry study of Longjiang River, a number of ions were involved, and the statistical software SPSS19.0 was applied to analyse the Pearson correlation coefficient matrix of the conventional components in Longjiang River, Guangxi.

Table 2: The Correlation between the water ions in Longjiang River

	K^+	Mg^{2+}	Na^+	Ca^{2+}	Cl^-	HCO_3^-	NO_3^-	SO_4^{2-}
K^+	1.000							
Mg^{2+}	-0.338	1.000						
Na^+	0.507*	0.190	1.000					
Ca^{2+}	-0.129	0.638**	0.005	1.000				
Cl^-	0.462*	0.209	0.533*	0.129	1.000			
HCO_3^-	0.232*	0.717**	-0.185	0.828**	0.044	1.000		
NO_3^-	0.221	0.160	0.082	0.276*	0.257*	0.106	1.000	
SO_4^{2-}	0.212*	-0.129*	0.039*	0.018	0.463*	0.133	0.309	1.000

Note: ** indicates significant correlation at the 0.01 level (both sides); * indicates significant correlation at the confidence level (double test) of 0.05

Pearson correlation analysis was carried out on the main ions of Longjiang River. It can be seen from Table 2 that Ca^{2+} and Mg^{2+} ions are significantly correlated at a confidence level (both sides) of 0.01; HCO_3^- ions, Ca^{2+} and Mg^{2+} ions are significantly correlated at the 0.01 confidence level (both side), indicating that the source of water ions in the Longjiang River Basin is mainly the dissolution of carbonate in the basin. According to the Pearson correlation coefficient, Cl^- and SO_4^{2-} ions are significantly correlated when the two-sided confidence interval is 0.05, indicating that the two ions have the same input source or the same effect. Studies have shown that SO_4^{2-} ions are mainly derived from the sedimentation of acid rain. Hechi City, located in Heilongjiang River Basin, mainly adopts the industrial model of non-ferrous metal processing, with many coal-fired enterprises, so Cl^- and SO_4^{2-} ions are mainly from emissions of human activities (Wang and Yang, 2018).
Factor analysis is a multivariate statistical method that attributes some information-overlapping variables to a few uncorrelated comprehensive factors, that is, using several main information points to express the whole, and then achieve the purpose of dimensionality reduction. For the water chemical composition and water pollution, factor analysis is often used to study the main impact factors. According to the water quality monitoring data of Longjiang River, the SPSS software was used to perform the factor analysis for the water quality monitoring data, and four main components were extracted. The cumulative contribution rate of these four main components to the original data reached 81.229%, exceeding the principal component analysis and inspection requirements of 80%. The results are shown in Table 3.

Table 3: Conventional ions of Longjiang River

	Factor 1	Factor 2	Factor 3	Factor 4
Ca^{2+}	0.822	-0.257	-0.299	0.058
Mg^{2+}	-0.600	-0.059	0.530	0.575
$K^+ + Na^+$	0.501	0.704	0.324	-0.087
Cl^-	0.200	0.204	-0.629	0.718
SO_4^{2-}	0.412	-0.411	0.164	0.182
HCO_3^-	0.780	0.533	0.388	0.334
NO_3^-	-0.051	0.773	-0.433	-0.170
Variance contribution rates(%)	28.819	20.177	17.644	14.589
Accumulative contribution rate(%)	28.819	48.966	66.640	81.229

It can be seen from Table 3, the first principal component mainly includes Ca^{2+} and HCO_3^- ions, which are mainly derived from the dissolution of carbonate as mentioned above, so the first principal component can be defined as the natural chemical action. The second principal component mainly includes K^++Na^+ ions and NO_3^- ions; K^++Na^+ is derived from the dissolution of granite and potassium-containing and sodium- containing mineral rocks, but in the Longjiang River Basin, few rocks contains potassium and sodium mineral, mainly the carbonate rocks, so the source of K^++Na^+ ion can only be derived from the use of chemical fertilizer in agricultural production; NO_3^- ions are mainly derived from the influence of industrial production, thus, from the perspective of the second principal component, there also exists certain agricultural non-point source pollution in the Longjiang River Basin, and then the second principal component can be defined as the impact of human activities. The third principal component mainly includes Mg^{2+} ions; under geochemical action, Mg^{2+} is mainly derived from the dissolution of dolomite. The fourth principal component is mainly Cl^- ions, which are mainly derived from pollution sources such as atmospheric input. The results of factor analysis showed that the water chemical variables of the Longjiang River were mainly determined by the dissolution of carbonate rocks, and there also existed some human activity pollution.

5. Conclusions

(1) Diatom, Based on the water quality monitoring data of Longjiang River for many years, the chemical composition of Longjiang River water was analysed. The results show that the water body of Longjiang River is mainly $Ca^{2+}$and HCO_3^-, and the water body is weakly alkaline.
(2) The Longjiang River is a typical river in the karst region. Its water chemical composition is mainly derived from the weathering and dissolution of carbonate rocks, and is affected by the rock mass of the riverbed.
(3) Through correlation analysis, HCO_3^- ions and Ca^{2+}/Mg^{2+} ions are significantly correlated at a confidence level (both sides) of 0.01, indicating that the source of water ions in the Longjiang River Basin is mainly the dissolution of carbonate in the basin. Through principal component analysis, the chemical ion content of Longjiang River water is mainly affected by natural chemistry, and is also affected by human activities to a certain extent.

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