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## 贵州清水江流域丰水期水化学特征及离子来源分析

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摘要:对清水江流域丰水期河水离子浓度及组成特征分析表明,流域水化学组成以  $Ca^{2+}$ 、 $HCO_3^-$  离子为主,其次为  $Mg^{2+}$ 、 $SO_4^{2-}$ ; TDS 均值 213.96  $mg \cdot L^{-1}$ ,高于世界流域均值.根据海盐校正分析得出,研究区大气降水中海盐输入对流域水化学的贡献率为 2.23%,低于世界河流均值 3%. Gibbs 图结合离子比值分析表明,流域水化学主要受碳酸盐岩风化影响,越往下游硅酸盐岩化学风化贡献越明显,碳酸和硫酸同时参与了流域岩石风化过程.离子来源分析表明, $Ca^{2+}$ 、 $Mg^{2+}$ 、 $HCO_3^-$  离子主要来自于白云石、方解石等碳酸盐岩风化溶解, $Na^+$ 、 $K^+$ 、 $Cl^-$ 主要来源于硅酸盐岩风化;  $SO_4^{2-}$  和  $NO_3^-$  主要来源于大气酸沉降和城镇废水输入.人为活动影响分析表明上游工矿企业活动对清水江流域水化学影响明显.

关键词:水化学: 化学风化: 离子来源: 影响因素: 清水江流域

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### Hydrochemical Characteristics and Sources of Qingshuijiang River Basin at Wet Season in Guizhou Province

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Abstract: According to the ion content and chemical characteristic analysis of Qingshuijiang River water during wet season, the result shows that the chemical composition of the river water is dominated by  $Ca^{2+}$ ,  $HCO_3^-$ ;  $Mg^{2+}$ , and  $SO_4^{2-}$ . The TDS concentration (213.96 mg·L<sup>-1</sup>) is significantly higher than the average value of rivers worldwide. Seawater correction approach ( $Cl^-$  normalized seawater ratios) was applied to estimate the contribution proportions of local precipitation to the solutes, and it is found that the contribution ratio of precipitation (2.23%) is lower than the average value (3%) of global catchments. Furthermore, Gibbs graph combining major ion element ratio analysis indicates that the catchment hydrochemistry is mainly originated from carbonate rock weathering, which becomes increasingly distinct as the river goes downstream. Both carbonic acid and sulfuric acid play crucial roles in the chemical weathering. Ion source analysis demonstrates that  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $HCO_3^-$  are mainly derived from chemical weathering of carbonate mineral (Dolomite and Calcite);  $Na^+$ ,  $K^+$  and  $Cl^-$  are primarily contributed by silicate mineral weathering;  $SO_4^{2-}$  and  $NO_3^-$  stemmed are mainly from acid atmospheric deposition and from urban sewage input. Anthropogenic analysis suggests that the chemical composition of Qingshuijiang River is greatly impacted by the upriver industrial and mining enterprises activities.

Key words: water chemistry; chemical weathering; ion sources; impact factors; Qingshuijiang River

流域水体的水化学对其所流经地区的环境具有指示意义,如反映流域岩石风化、土地利用变化、大气沉降输入、人为活动等的影响[1,2].从 20 世纪以来,学者开始对世界各大洲主要河流水化学进行研究,并探讨流域水化学的主要控制机制[3].我国河流水化学的研究始于 20 世纪 60 年代,如乐嘉祥等[4]利用 1957~1960 年间近 500 条河流 900 多个站点约4 000次的水化学资料,总结了我国各地区的河流水化学特征、空间变化规律.陈静生等[5]对1958~1990 年间的长江水系 191 个站点的水质资料进行分析,提出长江流域主要离子化学成分受碳酸盐矿物的风化控制;流域的水质酸化趋势主要受燃煤导致的酸沉降和农田化肥的流失影响[6].西南

喀斯特河流大量研究表明河水溶质主要受碳酸盐岩溶解控制<sup>[7,8]</sup>,硫循环中形成的硫酸广泛参与了流域碳酸盐矿物的溶解<sup>[9,10]</sup>.

清水江流域属于长江流域洞庭水系沅江上游河段,是长江流域上游重要支流之一,是贵州省第二大河流. 随着西部大开发的发展和城镇化建设的推进,清水江流域水质和水化学发生明显改变.

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目前,对清水江流域水体的研究仅限于部分河段的水质分析[11],而关于工业企业、农业发展和城镇化对流域整体水化学的影响却鲜见研究.本研究通过对清水江流域河水主量元素分析,辨识河水溶质的主要来源,探讨地质岩性、人为活动等对流域水化学的影响,以期为清水江流域保护提供

#### 1 材料与方法

科学参考.

#### 1.1 研究区概况

清水江位于贵州省东南部,地处东经 107°16′57″~109°35′24″,北纬 25°19′20″~27°31′40″之间,发源于黔南布依族苗族自治州,地跨扬子准地台与华南褶皱带两个大地一级构造单元.流域内出露地层从元古代的四堡群、下江群,震旦系至古生代的寒武系、奥陶、志留、泥盆、石炭、二叠系,到中生代的三叠、侏罗、白垩系及新生代的第三系、第四系均有出露.流域上游地区为岩溶地貌区,主要分布碳酸盐岩,中下游为贵州省岩溶地貌面积最少的非岩溶区,局部有石灰岩分布,大部分老地层多硅化,主要由碎屑岩组成.流域岩性见图 1.

清水江流域全长 452. 20 km,流域面积17 157 km², 占贵州省总面积的 9.74%, 天然落差 1 274. 70 m; 属亚热带季风湿润气候区,气候温暖湿润,年平均气温  $14 \sim 18 \, ^{\circ}$  ,多年平均降雨量为  $1\,050 \sim 1\,500$  mm. 其主要支流有重安江、巴拉河、

六洞河、南哨河、亮江、鉴江河.河源至重安江汇口为上游,重安江至锦屏六洞河汇口为中游,锦屏以下至贵州-湖南省界为下游.流域上游都匀、福泉、凯里地区矿产资源丰富、工业发达、尤其是重安江上游福泉地区已经建成中国大型的磷矿和磷化工基地;中游是主要的林业区,也是优质杉木的主要生产地;下游为主要的农业区,种植粮食作物以水稻、玉米为主.

#### 1.2 样品的采集与分析

本次采样时间为丰水期(2013 年 8 月),共采集样品 44 个(图 1),其中干流样品 23 个,支流样品 21 个. 采集的河水样品当天过滤(0.45 μm Millipore 滤膜),过滤后的样品装入洗干净的聚乙烯瓶中;水体 pH、电导(EC)、溶解氧(DO)、水温(t)采用便携式多参数测试仪(德国 WTW)现场测定,HCO $_3$ 用 0.025 mol·L $^{-1}$  HCl 现场滴定,误差在 ± 5% 以内.用于阳离子(Na $^+$ 、K $^+$ 、Ca $^{2+}$ 、Mg $^{2+}$ )分析的水样加入超纯盐酸酸化至 pH < 2,避光密封保存,用于阴离子(F $^-$ 、Cl $^-$ 、NO $_3$ 、SO $_4^{2-}$ )分析的样品直接密封避光保存. Na $^+$ 、K $^+$ 、Ca $^{2+}$ 、Mg $^{2+}$ 、Cl $^-$ 、NO $_3$ 、F $^-$ 、SO $_4^{2-}$  用离子色谱仪(DIONEX,ICS-1100,IonPac AG-19 阴离子柱,IonPac CS-12A 阳离子柱)分析测定,测试精度好于 ± 5%,SiO $_2$  采用钼酸黄分光光度法测定,总磷(TP)采用钼锑抗光度法测定.

#### 2 结果与分析

清水江流域水化学参数及主量元素浓度统计分

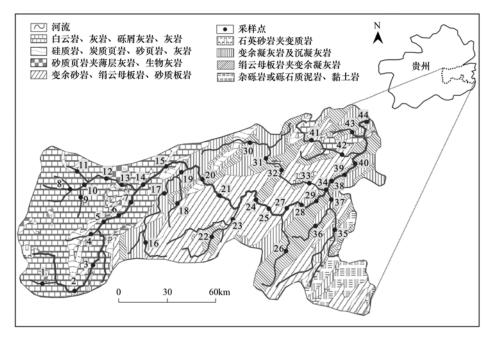


图 1 研究区采样点分布示意

Fig. 1 Sampling sites of the Qingshuijiang River basin

析结果(表 1)显示,流域丰水期河水温度均值 25.90℃,pH 值介于 5.96~9.90 之间,平均值为 8.00,中性偏弱碱性,部分地方偏弱酸性.流域水体 TDS 介于 44.30~432.88 mg·L<sup>-1</sup>之间,样品差异性较大,平均值 213.96 mg·L<sup>-1</sup>,上游流域 TDS 值较高,中下游流域相对较低.河水中阳离子浓度依次为  $Ca^{2+}>Mg^{2+}>Na^{+}>K^{+}$ ,阴离子浓度变化为  $HCO_{3}^{-}>SO_{4}^{2-}>Cl^{-}>NO_{3}^{-}>F^{-}$ ;  $Ca^{2+}$ 和  $Mg^{2+}$ 平均浓度为

0. 77 mmol·L<sup>-1</sup>和 0. 46 mmol·L<sup>-1</sup>,分别占阳离子总量的 58% 和 30%,HCO<sub>3</sub><sup>-</sup> 和 SO<sub>4</sub><sup>2</sup> 平 均 浓 度 1. 97 mmol·L<sup>-1</sup>和 0. 35 mmol·L<sup>-1</sup>,分别占阴离子总量的 70%和 22%.阳离子总浓度(TZ<sup>+</sup> =  $2Ca^{2+} + 2Mg^{2+} + Na^+ + K^+$ )与阴离子总浓度(TZ<sup>-</sup> =  $HCO_3^- + 2SO_4^{2-} + NO_3^- + Cl^- + F^-$ )平衡较好(r > 0.99).河流水体的无机电荷平衡 NICB[NICB =  $(TZ^+ - TZ^-)/TZ^+$ ]均值为 -4.48%,水体阴阳离子电荷基本平衡.

表 1 清水江流域丰水期水化学数据

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项目	单位	范围	均值	中值
t	${}^{\circ}\!C$	21. 7 ~ 30. 60	25. 90	25. 75
рН	_	5. 96 ~ 9. 90	8. 00	8.00
TDS	mg·L <sup>-1</sup>	44. 30 ~ 432. 88	213. 96	165. 74
${\rm SiO}_2$	mg·L <sup>-1</sup>	1. 86 ~ 14. 46	7. 73	7. 46
TP	$mmol \cdot L^{-1}$	0.00 ~ 0.33	0. 03	0.00
Ca <sup>2 +</sup>	$mmol \cdot L^{-1}$	0. 09 ~ 1. 62	0. 77	0.60
$Mg^{2+}$	$mmol \cdot L^{-1}$	0. 04 ~ 1. 12	0.46	0. 26
Na <sup>+</sup>	$mmol \cdot L^{-1}$	0. 04 ~ 0. 36	0. 18	0. 18
K <sup>+</sup>	$\operatorname{mmol} \cdot L^{-1}$	0. 02 ~ 0. 09	0.04	0.04
HCO <sub>3</sub>	$\operatorname{mmol} \cdot L^{-1}$	0. 37 ~ 4. 61	1. 97	1.50
SO <sub>4</sub> -	$mmol \cdot L^{-1}$	0. 04 ~ 1. 05	0. 35	0. 24
Cl -	mmol • L $^{-1}$	0. 03 ~ 0. 18	0. 10	0. 10
$NO_3^-$	mmol • L $^{-1}$	0.00 ~ 0.54	0. 09	0.03
F -	$\operatorname{mmol} \cdot L^{-1}$	0.00 ~ 0.08	0.01	0.01

#### 3 讨论

#### 3.1 大气降水海洋输入对水化学组成的影响

清水江流域属山区雨源型河流,主要靠地表径 流补给,采样时期为流域雨水集中的夏季,因此有必 要估算流域大气降水远距离输送海盐物质对河水溶 质的贡献. 通过海盐校正的方法,根据流域大气降 水中Cl-浓度及流域蒸发量和降水量估算大气降水 对流域水化学的最大贡献[12],降水中其它离子用标 准海水离子的浓度比( $Na^+/Cl^- = 0.86, Mg^{2+}/Cl^-$ = 0. 21,  $K^+/Cl^-$  = 0. 004,  $Ca^{2+}/Cl^-$  = 0. 04,  $SO_4^{2-}/$ Cl-=0.11)进行计算[13]. 清水江流域黔南地区多 年平均降雨量为1220.50 mm, 多年平均蒸发量为 629.40 mm<sup>[14]</sup>. 由于缺乏研究区大气降水中 Cl<sup>-</sup>浓 度数据,选用大气环境条件与研究区接近的贵阳市 大气降水数据作为参考(Cl-浓度为 0.02 mmol·L-1[15]);估算结果表明,流域大气降水对流 域溶质的贡献约为 2.23%, 低于世界河流均值 (3%)[16]. 前人的研究显示,远离海洋的河流其化 学组成基本不受海洋输入的影响[17],研究区远离海 边,河水的 Cl<sup>-</sup>/Na<sup>+</sup> 比值平均值为 0.59,远低于世 界平均海水比值( $Cl^-/Na^+ = 1.15^{[18]}$ ). 可见,雨水海洋输入对研究区河水溶质的贡献很小.

#### 3.2 流域岩石风化及其对水化学的影响

Gibbs<sup>[3]</sup>对世界大多数河流水化学控制机制进行研究,将影响河流水化学组成的因素分为大气降水、岩石风化以及蒸发-结晶三类,利用 TDS 与Na<sup>+</sup>/(Na<sup>+</sup> + Ca<sup>2+</sup>)、Cl<sup>-</sup>/(Cl<sup>-</sup> + HCO<sub>3</sub><sup>-</sup>)的关系图可以判断河水主离子的主要控制类型. 如图 2 所示,在清水江流域河水 Gibbs 图中,流域所有样品基本都落在 Gibbs 图虚线框岩石风化控制区域,显示流域水化学组成主要受岩石风化作用控制.

阴阳离子三角图可以直观反映水体化学组成特征,辨别其控制端元<sup>[19]</sup>. 在清水江流域阴阳离子三角图中(图 3),阳离子主要分布在  $Ca^{2+}$ - $Mg^{2+}$ 线靠近  $Ca^{2+}$ 端元,与我国的长江<sup>[5]</sup>、乌江流域<sup>[8]</sup>相似;阴离子主要靠近  $HCO_3^-$ 端,与乌江流域<sup>[8]</sup>相似.与黄河流域<sup>[20]</sup>相比,流域明显富含  $Ca^{2+}$ 、 $HCO_3^-$ ,而  $Na^+$ 、 $K^+$ 、 $Cl^-$ 的浓度较低.

不同岩性端元间的对比可以判别流域不同岩石 风化对河水溶质的影响<sup>[12]</sup>,从图 4 清水江流域岩性 端元比值图可以看出,流域上游的样品点主要落在

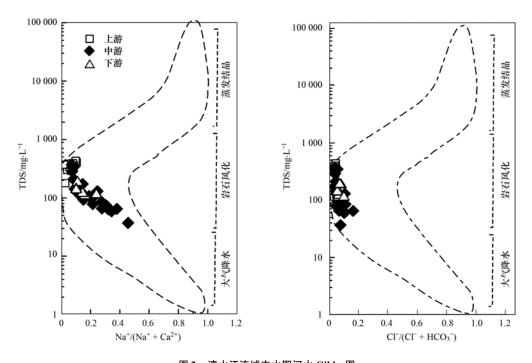


图 2 清水江流域丰水期河水 Gibbs 图

Fig. 2 Gibbs plots of waters from the Qingshuijiang River basin in wet season

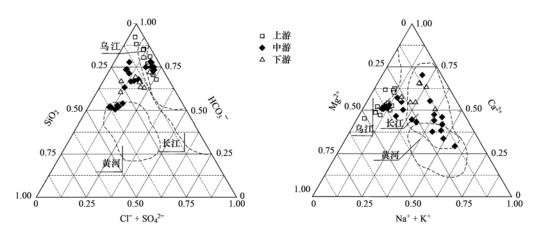


图 3 清水江流域丰水期河水阴阳离子三角图 [5,8,20]

Fig. 3 Triangle diagrams showing cation and anion compositions in waters from Qingshuijiang River basin in wet season

碳酸盐岩风化区域,中下游流域的样品相对更靠近硅酸盐类岩石风化区域,表明上游流域主要受碳酸盐岩风化影响,中下游流域硅酸盐类岩石风化影响比较大,这与清水江流域岩性分布特征基本吻合.

 $2(Ca^{2+}+Mg^{2+})/(Na^++K^+)$ 浓度比值可用于判别流域不同岩石风化相对强度,比值越大,说明碳酸盐岩相对风化强度越高<sup>[21]</sup>. 清水江流域干流河水中  $2(Ca^{2+}+Mg^{2+})/(Na^++K^+)$ 浓度比值介于  $2.82\sim27.47$  之间,全流域平均值 14.04,与以碳酸盐岩风化为主的普莫雍错入湖河流比值相近( $2\sim25$ )<sup>[22]</sup>,远高于受蒸发岩影响的塔克拉玛干沙漠河流比值(0.89)<sup>[21]</sup>,也高于世界河流均值(2.2)<sup>[23]</sup>.

较高的 2(Ca<sup>2+</sup> + Mg<sup>2+</sup>)/(Na<sup>+</sup> + K<sup>+</sup>)比值表明该地区主要受碳酸盐岩风化影响。干流 2(Ca<sup>2+</sup> + Mg<sup>2+</sup>)/(Na<sup>+</sup> + K<sup>+</sup>)浓度比值从上游至下游逐渐降低(图 5),SiO<sub>2</sub>的质量浓度从上游至下游逐渐升高,显示从上游至下游,碳酸盐岩风化对干流水化学的影响逐渐减弱,而硅酸盐岩风化影响逐渐增强。

前人的研究显示,主要受方解石、白云石等碳酸盐岩风化控制的地区 2(Ca²++Mg²+)/HCO₃ 浓度比值应在 1:1左右[²⁴]. 如图 6 所示,清水江流域上游和部分中游地区 2(Ca²++Mg²+)/HCO₃ 浓度比值部分数据点分布在 1:1等值线的下方,部分中游和所有下游地区点基本分布在 1:1等值线左右,

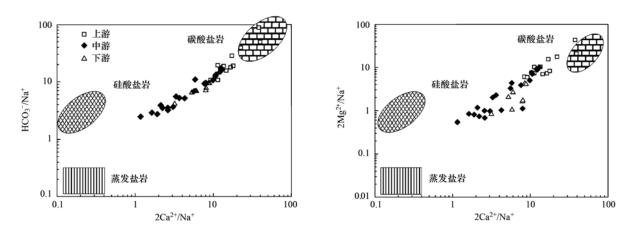


图 4 清水江流域河水 2Mg<sup>2+</sup>/Na<sup>+</sup> 和 HCO<sub>3</sub><sup>-</sup>/Na<sup>+</sup>与 2Ca<sup>2+</sup>/Na<sup>+</sup>浓度比值

Fig. 4 Plots of HCO<sub>3</sub>-/Na+ and 2Mg<sup>2+</sup>/Na+vs. 2Ca<sup>2+</sup>/Na+ of waters from Qingshuijiang River basin

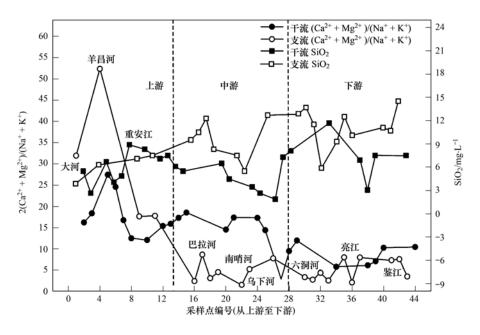


图 5 清水江流域河水 2(Ca<sup>2+</sup> + Mg<sup>2+</sup>)/(Na<sup>+</sup> + K<sup>+</sup>) 趋势

Fig. 5 Spatial distribution of  $2(Ca^{2+} + Mg^{2+})/(Na^{+} + K^{+})$  of waters from Qingshuijiang River basin

表明流域中上游地区部分点  $Ca^{2+}$ 、 $Mg^{2+}$  离子相对  $HCO_3^-$  有富余,碳酸盐岩风化还有其他酸的参与. 在  $2(Ca^{2+} + Mg^{2+})$  与 $(HCO_3^- + 2SO_4^{2-})$  比值图上 (图 6),样品点均均分布 1:1等值线附近(图 6),说明硫酸和碳酸共同参与的风化基本可以解释流域内所有岩石的风化过程.

 $H_2CO_3$  风化碳酸盐岩, $2(Ca^{2+} + Mg^{2+})/HCO_3^-$ 的浓度比值为 1, $H_2SO_4$  风化碳酸盐岩  $2(Ca^{2+} + Mg^{2+})/HCO_3^-$  的浓度比值为 2, $2SO_4^{2-}/HCO_3^-$  浓度比值为  $1^{[25,26]}$ . 如图 7 所示,清水江流域样品点大部分都落在硫酸与碳酸共同风化碳酸盐岩之间.清水江流域内都匀市、凯里市是贵州省主要的"酸雨

控制区"之一, $SO_2$  是首要大气污染物<sup>[27]</sup>. 赵晓韵等<sup>[27]</sup>对 2012 年 3 月至 2013 年 2 月间都匀地区大气降水的研究表明,都匀大气降水中  $SO_4^{2-}$  浓度为 0. 30  $mmol \cdot L^{-1}$ . 可见,大气沉降的硫酸对清水江流域风化的贡献不可忽略.

#### 3.3 流域主要离子来源

#### **3.3.1** Ca<sup>2+</sup>、Mg<sup>2+</sup>、HCO<sub>3</sub><sup>-</sup>、SO<sub>4</sub><sup>2-</sup>、NO<sub>3</sub><sup>-</sup>来源

相关性较好的离子通常具有相同的来源或经过了相同的化学反应过程<sup>[28]</sup>,清水江流域丰水期各离子相关性见表 2.  $Ca^{2+}$ 与  $HCO_3^-$ 、 $Ca^{2+}$ 及  $Mg^{2+}$ 、 $Mg^{2+}$ 与  $HCO_3^-$ 分别在 0.01 检测水平下显著相关,反映了流域内碳酸盐岩的溶解;流域河水中( $Ca^{2+}$ 

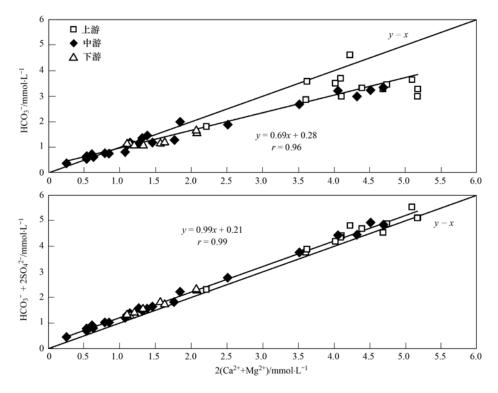


图 6 清水江流域河水中  $HCO_3^-$  和  $(HCO_3^- + 2SO_4^{2-})$  与 2  $(Ca^{2+} + Mg^{2+})$  的浓度关系

Fig. 6 Plots of  $HCO_3^-$  and  $(HCO_3^- + 2SO_4^{2-})$  vs. 2  $(Ca^{2+} + Mg^{2+})$  of waters from Qingshuijiang River basin

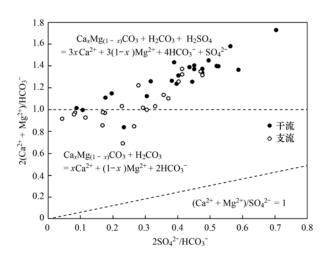


图 7 清水江流域河水中 2(Ca<sup>2+</sup> + Mg<sup>2+</sup>)/HCO<sub>3</sub><sup>-</sup> 与 2SO<sub>4</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> 浓度比值关系

Fig. 7 Plots of  $2(Ca^{2+} + Mg^{2+})/HCO_3^-$  vs.  $2SO_4^{2-}/HCO_3^-$  of waters from Qingshuijiang River basin

 $+ Mg^{2+}$ )与  $HCO_3^-$  的相关性(r = 0.96, P < 0.01)和  $Mg^{2+}$ 与  $HCO_3^-$  的相关性大于  $Ca^{2+}$ 与  $HCO_3^-$  的相关性(表 2),表明流域河水中  $Ca^{2+}$ 、 $Mg^{2+}$ 、 $HCO_3^-$  离子主要来自于白云石的溶解,其次是方解石<sup>[29]</sup>,即流域河水中的  $Ca^{2+}$ 、 $Mg^{2+}$ 、 $HCO_3^-$  主要来自于白云石和方解石等碳酸盐岩的风化溶解.  $SO_4^{2-}$ 与  $NO_3^-$ 相关性良好,往往反映了二者共同为人为来源,如化

石燃料导致的酸沉降、城镇污水排放等 $^{[19,30]}$ . 前面讨论已经表明,研究区酸沉降对清水江流域  $SO_4^2$ 的影响不可忽视. 因此,大气酸沉降和上游密集的城镇可能是流域内  $SO_4^2$  与  $NO_3$  的重要来源.

#### **3.3.2** Na<sup>+</sup>、K<sup>+</sup>、Cl<sup>-</sup>、Si 主要来源

清水江流域丰水期  $SiO_2$  质量浓度介于  $1.86 \sim 14.46 \text{ mg·L}^{-1}$ 之间,平均值  $7.73 \text{ mg·L}^{-1}$ ;流域  $SiO_2$  浓度也可能受到生物作用的影响,如东西伯利亚沼泽地中的一些小流域, $Si/(Na^+ - Cl^- + K^+)$  比值约  $0.2 \sim 0.5^{[31,32]}$ . 清水江流域  $Si/(Na^+ - Cl^- + K^+)$  比值介于  $0.56 \sim 11.79$  之间,平均值为 2.70,可以看出,流域  $SiO_2$  受生物作用影响很小,主要来源于硅酸盐岩风化.

清水江流域河水中  $Na^+$ 、 $K^+$ 浓度较低,仅占阴阳离子总量的 5.01% 及 1.01%. 河水中  $SiO_2$  仅与阳离子( $Na^+ + K^+$ )、 $Na^+$ 存在相关性,与  $Na^+$ 、( $Na^+ + K^+$ ) 在 0.05 检测水平下显著相关(r=0.38,P<0.05; r=0.34,P<0.05),与  $K^+$ 相关性很小. 清水江流域中下游地区为流域碎屑岩地区,大部分地层多硅化,可知河水中的  $Na^+$ 、 $K^+$ 有可能来自于石盐的溶解和硅酸盐风化, $K^+$ 离子来源于钾长石和云母的风化[ $^{18}$ ]. 清水江流域  $Na^+$ 、 $K^+$ 与  $Cl^-$ 在

1.00

	F -	Cl -	$NO_3^-$	$SO_4^{2-}$	$HCO_3^-$	Na +	K +	$\mathrm{Mg}^{2}$ +	Ca <sup>2 +</sup>	${\rm SiO_2}$
F -	1.00									
Cl -	0. 86 * *	1.00								
$NO_3^-$	0. 45 * *	0. 55 * *	1.00							
$SO_4^{2-}$	0. 72 * *	0.66 * *	0.76 * *	1.00						
$HCO_3^-$	0. 51 * *	0. 59 * *	0. 67 * *	0. 70 * *	1.00					
Na +	0. 51 * *	0. 63 * *	0.49 * *	0. 46 * *	0.09	1.00				
K +	0. 60 * *	0. 84 * *	0. 55 * *	0. 68 * *	0. 54 * *	0. 63 * *	1.00			
$Mg^{2}$ +	0. 59 * *	0. 54 * *	0. 75 * *	0. 78 * *	0. 96 * *	0. 16	0.49 * *	1.00		
Ca <sup>2 +</sup>	0. 67 * *	0.71 * *	0. 74 * *	0. 90 * *	0. 91 * *	0. 29	0.71 * *	0. 89 * *	1.00	

-0.40 \* \*

-0.31\*

表 2 清水江流域河水主要离子相关性1)

1)\* 为 P < 0.05, \* \* 为 P < 0.01

0.01 检测水平下显著相关(r = 0.63, P < 0.01、r = 0.84, P < 0.01), 但流域无明显的蒸发岩(KCI、NaCl)出露,河水中的Na<sup>+</sup>、K<sup>+</sup>除了岩石风化来源外,还有一定人为活动来源,如工业、生活废水排放(含 NaCl),农业活动钾肥(KCI)的施用等.

-0.20

#### 3.4 人为活动输入对河流水化学的影响

人为活动排放污染物的特征是富含  $K^+$ 、 $Ca^{2+}$ 、 $SO_4^{2-}$ 、 $Cl^-$ 和  $NO_3^-$ ,其中  $K^+$ 、 $Ca^{2+}$ 、 $SO_4^{2-}$ 、 $Cl^-$ 同时又是岩石风化的产物, $NO_3^-$ 则常作为反映人类活动的特征离子[33]. 通常认为,河水中的  $SO_4^{2-}$  主要源于硫化物的氧化、工业活动燃煤产生的  $SO_2$  排放和大气沉降等[34]. 清水江流域上游流域为我国重要的磷化工基地,磷化工企业排放的废水造成大量的磷、氟进入水体[35],因此,本研究用  $NO_3^-$ 、 $SO_4^{2-}$ 、 $F^-$ 及 TP 表征人为活动对流域水化学的影响.

如图 8 所示,清水江流域干流河水中的  $SO_4^{2-}$ 、 $NO_3^{-}$  与  $F^{-}$ 、TP 变化趋势基本相同,流域上游都匀、

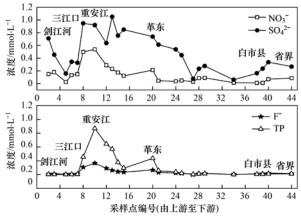


图 8 清水江流域干流河水  $SO_4^2$ 、 $NO_3$ 、 $F^2$  及 TP 浓度变化趋势

Fig. 8 Spatial distribution of  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $F^-$  and TP of the Qingshuijiang River mainstream

福泉、三江口地区至重安江段最高,中下游地区较低. 从上游至下游流域河水中的 SO<sub>4</sub><sup>2-</sup>、NO<sub>3</sub><sup>-</sup>、F<sup>-</sup>及 TP 浓度逐渐降低,说明随着水体自净及中下游森林 区域支流的汇入,工业活动对流域水化学的影响逐 渐降低,水质逐渐改善,可见上游工业发达地区对清水江流域水化学的影响是非常显著的.

-0.46\*

-0.32\*

0.07

0.38 \*

#### 4 结论

- (1)清水江流域丰水期 pH 平均为 8.00, 呈中性偏弱碱性, TDS 均值 213.96 mg·L<sup>-1</sup>, 阳离子浓度依次为  $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ , 阴离子浓度变化为  $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$ .  $Ca^{2+} \setminus Mg^{2+}$  是主要阳离子, 分别占阳离子总量 58% 和 30%,  $HCO_3^- \setminus SO_4^{2-}$  是主要阴离子, 分别占阴离子总量 70% 和 22%.
- (2) Gibbs 图、主量元素三角图和离子比值分析 表明,清水江流域丰水期的水化学组成主要受岩石 风化控制;其中以碳酸盐岩风化贡献为主,到中下 游碎屑地区,硅酸盐类岩石风化的贡献逐渐增加; 碳酸和硫酸同时参与了流域岩石的风化.
- (3)离子来源解析表明,清水江流域丰水期河水 Ca<sup>2+</sup>、Mg<sup>2+</sup>、HCO<sub>3</sub><sup>-</sup> 主要来自于碳酸盐岩的风化溶解,SO<sub>4</sub><sup>2-</sup>、NO<sub>3</sub><sup>-</sup> 受区域酸沉降和城镇污水排放影响,Na<sup>+</sup>、K<sup>+</sup>、SiO<sub>2</sub> 主要来自于硅酸盐岩风化溶解,有部分 Na<sup>+</sup>、K<sup>+</sup>和 Cl<sup>-</sup>来自于人为活动输入. 对整个流域人为活动影响分析表明,清水江流域上游受工矿企业和城镇影响明显,从中游至下游,人为活动影响逐渐减弱.

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## **HUANJING KEXUE**

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