

Article

Chemical Weathering and Riverine Carbonate System Driven by Human Activities in a Subtropical Karst Basin, South China

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Abstract: In the context of climate change, the input of acid substances into rivers, caused by human activities in the process of industrial and agricultural development, has significantly disrupted river systems and has had a profound impact on the carbon cycle. The hydrochemical composition and which main sources of the Lianjiang River (LR), a subtropical karst river in northern Guangdong Province, South China, were analyzed in January 2018. The objective was to explicate the influence on the deficit proportion of CO_2 consumption, resulting from carbonate chemical weathering (CCW), driven by nitric acid (HNO_3) and sulfuric acid (H_2SO_4), which is affected by exogenous acids from the industrial regions in north of the Nanling Mountains and the Pearl River Delta. The response of the riverine carbonate system to exogenous acid-related weathering was also discussed. HCO₃⁻ and Ca^{2+} , respectively, accounted for 84.97% of the total anions and 78.71% of the total cations in the surface runoff of the LR, which was characterized as typical karst water. CCW was the most important material source of river dissolved loads in the LR, followed by human activities and silicate chemical weathering (SCW). Dissolved inorganic carbon (DIC), derived from CCW induced by carbonic acid (H_2CO_3) , had the largest contribution to the total amount of DIC in the LR (76.79%), and those from CCW induced by anthropogenic acids (HNO₃ and H₂SO₄) and SCW contributed 13.56% and 9.64% to the total DIC, respectively. The deficit proportion of CO₂ consumption associated with CCW resulting from sulfuric acid and nitric acid (13.56%), was slightly lower than that of the Guizhou Plateau in rainy and pre-rainy seasons (15.67% and 14.17%, respectively). The deficit percentage of CO_2 uptake associated with CCW induced by sulfuric acid and nitric acid, accounted for 38.44% of the total CO₂ consumption related to natural CCW and 18.84% of the anthropogenic acids from external areas. DIC derived from CCW induced by human activities, had a significant positive correlation with the total alkalinity, SIc and pCO_2 in river water, indicating that the carbonate system of the LR was also driven by exogenous acids, with the exception of carbonic acid. More attention should be paid to the effects of human activities on the chemical weathering and riverine carbonate system in the karst drainage basin.

Keywords: karst basin; carbonate weathering; carbonate system; dissolved inorganic carbon; anthropogenic acids; the Lianjiang River



1. Introduction

A river system is one of the most important transport channels of material and energy to the ocean in a drainage basin, which records the environment evolution processes of the river basin. Chemical weathering processes in a drainage basin can be reflected by the river hydrochemical characteristics [1,2], which is the main part of the mass exchange between the ocean and the continent. It is generally recognized that silicate chemical weathering (SCW) induced by carbonic acid is a net depletion process of the atmospheric/soil CO₂. However, the CO₂ consumed by carbonate chemical weathering (CCW) associated with carbonic acid will return to the atmosphere with the precipitation of carbonate minerals on a geological time scale (>1 Ma). Thus, CCW only affects global climate change on a short time scale [3]. Recently, some scholars have discovered that organic carbon can be produced by natural aquatic ecosystems through photosynthesis or directly by using dissolved inorganic carbon (DIC), which is derived from CCW and is rich in karst river (the fertilizing effect of DIC), that enters the lithosphere through sedimentation and burial [4–6]. The CO₂ consumption associated with CCW have not only controlled climate change over a short time scale, but also dominated long-term climate change, since the emergence of aquatic photosynthetic organisms [7–9].

The karst basin ecosystem is subject to greater climate stress and intensifying human activities, which profoundly affect the river carbon cycle, and exhibits a higher sensitivity [10]. With the development of urbanization, human activities (e.g., acid deposition, industrial and domestic sewage discharge, nitrogen fertilizer application, etc.) have gradually become an important factor influencing the chemical composition of river water. More and more studies have paid attention to the CCW influenced by nitric acid or sulfuric acid, which is derived from industrial and agricultural activities [11–18]. Strong acid, such as sulfuric acid or nitric acid derived from anthropogenic sources, replaces carbonic acid agent and dissolves rocks in the process of rock chemical weathering. It also disturbs the rock weathering and the associated CO_2 consumption in natural conditions. Li et al. [19] analyzed the source of sulfate in the Jialingjiang River using stable isotopes (δ^{34} S and δ^{18} O) and found that domestic and industrial wastewater was an important source of sulfate. They also confirmed that sulfuric acid derived from the atmospheric input of high sulfur coal combustion was a weathering agent involved in rock weathering.

Chemical weathering in the drainage basin and fluvial chemical composition are more susceptible to human activities owing to the rapid dissolution kinetics of carbonate rocks and the special binary and three-dimensional geological structure in the karst area. A case study of two karst basins in Southern France showed that CCW induced by nitric acid, which was derived from nitrogen fertilizer, accounted for 30% [20] and 12–26% [21]. The study on the glacial runoff by Anderson et al. [22] showed that the amount of carbonate rocks dissolved by sulfuric acid constituted 22% of the total dissolved carbonates. Chemical weathering of surface rocks is a basic geological process, which converts atmospheric/soil CO₂ to DIC [23]. Generally, the DIC in the karst surface waters is mainly derived from carbonate rocks dissolved by carbonic acid. With the interference of human activities, the DIC produced by CCW induced by sulfuric acid and nitric acid may be an important part of the DIC flux in the karst surface water. Li et al. [24] reported that about 13% of DIC in the Yalongjiang River Basin in Southwest China was due to the involvement of sulfuric acid in CCW.

However, no atmospheric/soil CO₂ was consumed by CCW associated with strong acids. On the contrary, CCW with strong acids (especially sulfuric acid) has a net CO₂ release process on geological time scales [25], and Jiang [16] concluded that the atmospheric/soil CO₂ consumption of CCW should be strictly evaluated if sulfuric acid or nitric acid was involved by analyzing the main ions and $\delta^{13}C_{\text{DIC}}$ in the Nandong subterranean stream. Therefore, the carbon sink effect related to CCW needs to be reevaluated if sulfuric acid or nitric acid exists in a carbonate catchment. Perrin et al. [13] estimated that the CO₂ produced during CCW by nitric acid, which was derived from the nitrification of nitrogen fertilizers in the agricultural region of Southeastern France and around the world, were $2.2-5.3 \times 10^5 \text{ t} \cdot \text{a}^{-1}$ and $1.2-2.9 \times 10^7 \text{ t} \cdot \text{a}^{-1}$, respectively. Liu et al. [26] calculated the contribution of acid precipitation to the chemical composition of the Qiantangjiang River by the Galy Model and

concluded that the estimated CO₂ consumption rate was 23% lower than that before deducting sulfuric acid weathering, if sulfuric acid involvement was considered. As a result, CCW is disturbed to varying degrees under the influence of human activities. This is of great significance for the accurate identification of the role of exogenous acids during the chemical weathering process in drainage basins in evaluating the interference of human activities with CCW and gaining an insight into the current global climate change and carbon cycle. However, the CCW processes involving strong anthropogenic acids have not yet received sufficient attention in the current global carbon cycle model [15].

Due to the slower dissolution kinetics and lower solubility of silicate than those of carbonate, the CO_2 consumption related to SCW in the karst watershed and clastic interlayers of carbonate rocks has been ignored, and all of the HCO_3^- was attributed to the contribution of CCW in previous studies [14,27,28]. SCW consumes atmospheric/soil CO_2 to produce a net sink of atmospheric CO_2 over a geological time scale, and this cannot be neglected in the karst basins [29–31]. In addition, the effects of anthropogenically sourced sulfuric acid and nitric acid are not considered in the common method of using hydrochemical compositions and runoff for the estimation of the karst carbon sink [6], and general studies only considered the effects of a single strong acid (sulfuric acid or nitric acid), which would affect the assessment accuracy of the CO_2 consumption related to CCW.

To accurately determine the compound influence of sulfuric acid and nitric acid resulting from human activities on the chemical weathering of carbonate basins and the riverine carbonate system, hydrogeochemical parameters of the surface runoff were investigated in the Lianjiang River Basin (LRB), which is in north of the Pearl River Delta (PRD) of China and under the dual influence of acidic gases transported from the PRD and the industrial regions in north of the Nanling Mountains. The main objectives were as follows: (1) to identify the hydrochemical characteristics of the Lianjiang River (LR) and the main sources of river dissolved loads; (2) to quantify the contribution proportion of SCW and CCW with different dissolution media to riverine DIC; (3) to evaluate the deficit proportion of CO_2 consumption caused by nitric acid and sulfuric acid weathering; and (4) to explicate the response characteristics of the riverine carbonate system to human activities.

2. Materials and Methods

2.1. Study Area

The LRB (112°10′ E–113°18′ E, 24°09′ N–25°07′ N) is located in the north of Guangdong Province, South China and at the southern edge of the important geographic and climatic dividing line, in the Nanling Mountains, East Asia. The LR belongs to the Pearl River Basin from the perspective of hydrology, and is located near the watershed between the Pearl River Basin and the Yangtze River Basin (Figure 1), with a mesoscale drainage area of 10,061 km². The south end of the LRB is close to the Tropic of Cancer, and the climate type is a typical subtropical monsoon climate, with a humid climate, abundant rainfall between 1400 and 2200 mm (with an average of 1770 mm), and an average annual temperature of 19–20 °C. Most of the precipitation is observed from April to June, accounting for about 45–50% of rainfall throughout the whole year. After flowing from the headwater for 275 km, the LR flows into the Beijiang River at Jiangkouju, with an average gradient of 0.77%, and constitutes the largest tributary of the Beijiang River in the Pearl River System. The LR system belongs to the trellis drainage, extending from the northwest to the southeast of the drainage basin, and shows typical characteristics of a mountainous river. The main tributaries of the LR flow from the mountains at the edge of the drainage basin to the main stream (Table 1). The average annual runoff of the mainstream is 1.2×10^{10} m³ and mainly observed from March to August, accounting for about 70% of the total runoff.



Figure 1. Characteristics of location, sampling sites, river system, geological background, terrains and rainfall pH in the LRB. Nos. 1–84 stand for the serial number of 84 sampling sites distributed in the Lianjiang River System. A–N stand for the mainstream and main tributaries of the LR: mainstream of the LR (A), the Xingzihe River (B, XZHR), the Baoanhe River (C, BAHR), the Chaotianhe River (D, CTHR), the Dongbeihe River (E, DBHR), the Sanjiangshui River (F, SJSR), the Dongguanshui River (G, DGSR), the Guanbeihe River (H, GBHR), the Qigonghe River (I, QGHR), the Qinglianshui River (J, QLSR), the Shuibianhe River (K, SBHR), the Datanhe River (L, DTHR), the Jintanhe River (M, JTHR), and the Zhutianhe River (N, ZTHR). The Pearl River Delta and the industrial districts in north of the Nanling Mountains are represented as lowercase letters a and b, given in the upper left figure.

Catchment	Sample	T (°C)	рH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K+	HCO_3^-	Cl-	SO_4^{2-}	NO_3^-	DSi	TZ ⁺	TZ-	NICB	Location ^b
Catchinent	No.	1(0)	r	$(mg \cdot L^{-1})$	(µM) ^a	(μM)	(µM)	(µM)	(μ M)	(µM)	(µM)	(µM)	(µM)	(µEq) ^a	(µEq)	(%)	Location
LR	1	15.2	7.9	138	780	155	280	65	1660	107	153	53	86	2214	2126	3.97	ML
	2	16.4	8.18	150	960	190	184	62	2206	87	131	100	121	2547	2656	-4.26	ML
	3	15.6	7.75	142	840	167	285	78	1580	141	166	92	127	2377	2144	9.80	ML
XZHR	4	9.3	7.89	76	513	53	77	25	1020	39	52	47	130	1233	1210	1.83	ML
	5	13.5	7.97	128	853	162	129	50	1652	54	125	40	86	2207	1996	9.57	ML
	6	15	8.1	130	803	154	160	57	1696	90	113	42	67	2130	2053	3.64	ML
BAHR	7	11.6	7.77	75	433	111	98	26	1062	42	42	18	110	1211	1206	0.45	UT
	8	12.4	7.71	39	182	54	87	24	484	39	35	35	105	583	630	-8.04	MT
	9	11.2	7.36	45	184	57	104	27	474	45	38	31	125	611	625	-2.18	UT
CTHR	10	11.8	8	241	1540	483	94	43	3402	110	105	105	100	4184	3827	8.53	UT
	11	10.2	8.05	236	1505	438	160	71	3179	146	173	76	100	4115	3747	8.95	MT
	12	10.1	8.1	194	1285	306	413	123	2679	96	116	32	134	3718	3038	18.29	DT
	13	10.2	8.08	161	1250	115	170	45	2346	54	73	18	194	2944	2563	12.94	UT
DBHR	14	9.4	7.82	41	155	20	217	54	417	39	31	77	188	620	597	3.78	UT
	15	11.8	7.86	110	655	123	196	77	1391	101	82	68	112	1829	1725	5.68	MT
	16	15.1	8.42	122	765	134	197	69	1511	99	116	66	103	2064	1907	7.57	DT
	17	11.6	7.97	197	1303	307	183	117	2608	115	101	144	125	3519	3069	12.79	MT
	18	11.2	7.68	28	109	66	73	14	295	21	38	24	120	436	416	4.42	UT
	19	11.7	7.78	114	628	128	190	53	1100	68	213	69	146	1753	1662	5.21	MT
	20	13.3	7.45	38	106	135	77	13	374	45	77	19	121	572	593	-3.58	UT
	21	11.9	7.72	27	96	79	67	13	328	13	31	12	123	429	415	3.32	MT
SJSR	22	12.4	7.72	26	102	57	73	9	257	22	42	27	108	398	390	2.19	UT
	23	13.2	7.69	39	189	71	99	17	497	34	51	29	109	636	662	-4.09	MT
	24	15.8	7.83	155	895	219	321	78	1848	206	132	65	166	2627	2383	9.28	DT
	25	12.1	7.53	46	152	45	232	59	468	65	36	74	304	686	680	0.85	UT
	26	11.8	7.5	29	78	27	188	46	290	28	31	33	318	444	412	7.23	UT
	27	17.2	7.84	194	1363	265	87	42	2779	68	77	95	103	3383	3096	8.48	UT
	28	12.2	7.95	358	2185	479	362	216	2395	293	1123	419	125	5906	5353	9.36	UT
	29	13.3	7.76	32	145	68	71	12	371	20	42	19	94	510	494	3.11	MT
DGSR	30	11.8	7.78	38	213	29	107	33	430	34	38	53	195	623	592	4.96	UT
	31	13.4	7.88	132	780	169	238	55	1641	121	123	65	118	2190	2073	5.38	DT
	32	11.6	7.59	23	96	23	100	32	262	21	21	41	210	370	366	1.05	UT
	33	14	7.94	82	498	93	75	22	1102	51	42	71	103	1278	1307	-2.23	UT
	34	13	8.05	115	683	141	74	41	1359	42	100	60	166	1763	1660	5.81	UT
	35	11.9	8.15	119	708	227	98	48	1429	56	150	87	201	2014	1873	7.01	UT
	36	12.6	7.99	189	1213	343	150	86	2377	144	200	111	160	3345	3032	9.38	MT

Table 1. Main physical and chemical parameters of the LR water in January 2018.

Table 1. Cont.

Catchment	Sample	T (°C)	υH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ -	C1-	SO_4^{2-}	NO_3^-	DSi	TZ ⁺	TZ ⁻	NICB	Location ^b
Caterinient	No.	1 (C)	r	$(mg \cdot L^{-1})$	(µM) ^a	(μM)	(µM)	(µM)	(µM)	(µM)	(µM)	(μM)	(µM)	(µEq) ^a	(µEq)	(µEq) ^(%)	Locution
GBHR	37	11.1	7.85	35	208	48	83	28	499	25	25	39	174	622	613	1.48	UT
	38	17.1	8.61	150	915	327	75	30	2216	42	64	29	133	2589	2415	6.72	DT
QGHR	39	15	7.52	216	1573	142	70	79	2638	99	125	84	124	3578	3071	14.18	UT
	40	17	7.78	193	1288	261	172	82	2251	107	181	260	160	3352	2980	11.09	DT
	41	18.1	7.78	225	1683	234	39	16	3400	56	60	65	85	3888	3642	6.34	UT
	42	14.2	8.06	121	853	85	63	48	1525	51	122	47	166	1986	1866	6.01	UT
	43	14	8.11	146	978	180	87	51	2141	54	45	56	139	2452	2341	4.54	UT
	44	11.6	7.75	44	185	38	169	56	511	56	33	47	219	672	681	-1.43	UT
	45	13.6	7.94	74	283	49	88	37	590	48	45	74	161	788	801	-1.71	UT
	46	14.3	7.92	225	1280	283	142	212	2242	163	173	316	119	3479	3068	11.82	UT
	47	19.1	8.03	212	1695	135	48	14	3188	70	59	44	79	3723	3421	8.12	UT
QLSR	48	14.3	7.48	31	118	11	215	37	385	14	20	21	310	510	460	9.77	UT
	49	15.7	7.99	102	673	95	112	30	1445	34	55	37	132	1676	1626	2.96	MT
	50	16.8	8.13	161	950	137	120	59	1921	76	93	40	117	2354	2223	5.56	DT
	51	14.6	7.47	26	88	10	190	23	315	11	14	43	334	408	398	2.61	UT
	52	17.4	7.32	42	173	18	234	47	534	37	23	58	301	662	674	-1.88	UT
	53	14.5	8.07	121	758	143	122	55	1593	42	110	37	187	1978	1893	4.31	UT
	54	17.6	8.36	152	1213	140	94	19	2284	45	49	44	139	2817	2470	12.30	MT
	55	15.1	8.06	151	1138	117	114	42	2216	62	46	65	169	2665	2435	8.64	UT
	56	15.5	8.55	221	1740	309	85	53	3385	79	106	66	168	4236	3743	11.65	UT
	57	17.5	7.82	245	1798	192	102	64	3398	144	139	53	56	4144	3872	6.56	UT
SBHR	58	13.6	7.88	172	1180	131	97	123	2084	144	103	200	129	2842	2634	7.33	UT
	59	13.9	7.78	164	588	124	139	104	1157	118	95	95	118	1665	1560	6.33	MT
	60	13.6	7.64	89	475	100	230	75	1099	79	70	74	149	1454	1391	4.32	DT
	61	14.1	7.79	160	1055	122	122	139	1858	175	107	179	147	2615	2426	7.23	UT
	62	13.4	7.44	23	69	39	69	41	253	29	16	28	154	326	342	-4.78	UT
	63	11.6	7.36	31	103	29	85	81	234	45	38	72	188	430	426	0.85	UT
DTHR	64	15.2	7.74	124	720	250	128	44	1865	39	31	68	203	2113	2035	3.70	UT
	65	16.6	7.85	156	1220	147	122	45	2364	51	67	56	159	2902	2604	10.25	MT
	66	17	8.21	145	1053	169	125	51	2118	51	75	40	109	2619	2359	9.92	DT
	67	17.5	7.99	220	1723	275	75	52	3178	110	109	65	57	4122	3571	13.36	MT
JTHR	68	15.2	6.99	38	216	50	34	33	379	56	55	100	56	598	646	-7.98	UT
	69	18.1	7.2	82	515	75	44	37	759	76	141	98	86	1260	1215	3.62	MT
	70	18.5	7.65	198	1385	224	86	82	2526	158	146	121	99	3387	3096	8.57	DT
	71	17.1	7.79	192	1470	152	69	67	2559	85	140	71	80	3380	2994	11.44	UT

Table 1. Cont.

Catchment	Sample	mple T (°C)	T (°C)	ъH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO_3^-	C1-	SO_4^{2-}	NO_3^-	DSi	TZ^+	TZ^{-}	NICB	Location ^b
	No.	1(0)	r	$(mg \cdot L^{-1})$	(µM) ^a	(µM)	(µM)	(μM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µEq) ^a	(µEq) (%)	Location		
ZTHR	72	20.5	9.02	120	768	133	69	46	1488	121	76	63	90	1916	1824	4.77	UT	
	73	16.6	7.77	243	1675	194	230	143	3057	262	96	202	89	4111	3712	9.71	MT	
	74	16.4	7.26	60	353	62	42	29	643	48	61	69	63	899	883	1.83	DT	
	75	16.5	7.22	53	206	50	31	25	358	42	54	60	62	568	568	-0.09	UT	
Small	76	11.4	8.09	267	1978	207	70	64	3478	65	293	50	114	4502	4179	7.19	ST	
tributaries	77	11.2	8.24	293	2020	521	131	57	4199	113	142	92	87	5270	4687	11.06	ST	
	78	10.9	7.51	25	138	11	65	24	301	17	20	15	40	387	373	3.38	MT	
	79	16.3	7.62	315	2243	351	176	84	4530	141	120	100	171	5446	5010	8.01	ST	
	80	18	7.9	332	1890	925	77	48	4814	73	169	97	56	5755	5322	7.52	ST	
	81	17.9	7.54	303	2098	402	89	40	4337	87	144	102	141	5128	4813	6.13	ST	
	82	20.1	7.47	281	1705	504	92	58	1837	101	1115	48	119	4568	4216	7.71	ST	
	83	15.4	7.63	51	228	100	111	32	546	37	92	23	160	798	788	1.22	ST	
	84	15.9	6.79	32	110	67	106	43	388	35	27	8	207	502	485	3.51	ST	

^a μ mol·L⁻¹ and μ eq·L⁻¹ are expressed as μ M and μ Eq, respectively; ^b Abbreviations of ML, UT, MT, DT and ST stand for the mainstream, upstream of tributaries, mid-stream of tributaries, downstream of tributaries and small tributaries of the LR, respectively.

The LRB is located in the east border of the boundary between the Yangtze Block and the Cathaysian Block, from the geological perspective [32], and is distributed in the top and west limb parts of the frontal arc in the Northern Guangdong ε -type Tectonic System (a complete example of the ε-type Tectonic System in China) [33]. A large area of Carboniferous–Triassic limestone, dolomite and dolomitic limestone are outcropped in the central section of the LRB, which is characterized as a shallow marine carbonate formation and in which the limestone area accounts for more than 60% of the total basin area. There are Sinian metamorphic volcanic rocks, siliceous rocks and shales; Cambrian quartz sandstone and sandy shales; and Devonian purple and brown sandy shales distributed in the margin of upstream and mid-stream regions. In the former, the mineral composition is mainly potassium-sodium silicate, and there is a small amount of carbonate minerals, such as calcite and dolomite, in addition to silicate minerals in the latter. The Ordovician and Silurian strata in the LRB are missing, and the Jurassic and Cretaceous strata are scattered. A small fraction of Quaternary continental alluvial deposits and metamorphic rocks are observed in lower reaches (Figure 1). The terrains of the LRB are higher in the northwest and lower in the southeast with the main landform of karst plateau and basin. High mountains are distributed in the north and west, and karst basins and hilly areas are in the southeast. The karst plateau of the LRB is the eastern extension part of the karst area in Southwest China, which is one of the three largest concentrated karst areas in the world as well as the typical ecological vulnerable zone. The LRB is dominated by calcareous soil, which has developed as a consequence of the dissolution of carbonate rocks and was followed by red soil. There are numerous types of vegetation, including coniferous forests, evergreen broad-leaved forests, deciduous broad-leaved forests, mixed forests, bamboo forests and shrubs. Several cities, such as Lianzhou, Liannan, and Yangshan, are distributed in the upper and middle reaches of the mainstream (Figure 1). The upper reaches of the main tributaries are sparsely populated, yet the lower reaches are densely populated. Forest land accounts for the largest proportion of the drainage area (42%), and cultivated land accounts for about 10%.

The northern part of Guangdong Province has been seriously polluted by acid rain, and it has been a heavily acidic rain area ($4.5 \le pH < 5.0$ and acid rain frequency > 50%, Figure 1) in recent years [34]. In addition to local pollutant gas emissions, acid rain in the LRB is also relevant to the long-distance transmission of pollutants, such as SO₂ and NO_x from industrial activities of the economically developed PRD and the industrial districts in north of the Nanling Mountains [35]. Rainfall events in the LRB are generally affected by the Quasi-stationary Front of South China, which is the main weather system regulating the rainfall in South China in winter and frequently stagnates between 22° and 25° N [36]. It can easily form acid rain in rainfall events under the condition that acid substances are washed away by rainwater. The pH of acid rain in summer is higher than that in winter because of the large amount of rainfall from typhoons, which result in a high pH and low frequency of acid rain [37]. Except for acid precipitation, local human activities, such as industrial and agricultural activities, will also affect the biogeochemical cycle in the drainage basin. It also deserves to be mentioned that biogeochemical processes in winter in the LRB proceed as usual because there are no hydrological freezing phenomena in the LR in January, which is annually the coldest month.

2.2. Sampling and Measurements

To fully understand the impact of human activities on the chemical weathering processes and riverine carbonate system in the LRB, 84 sampling sites in the mainstream and tributaries (including tertiary tributaries in headwater areas) were selected and sampled from 2 January to 8 January 2018. All of the water samples were collected in or near the middle channel of each river/stream, obviously avoiding pollution. Polyethylene sample bottles were fully rinsed using river water near the sampling sites more than three times before sampling and filled with river water ensuring that no air bubbles remain in the bottles. Samples were brought back to the laboratory as soon as possible and refrigerated at 4 °C. Alkalinity titration, ion content analysis and other measurements were completed within 48 h after sampling. The water temperature (T), pH and total dissolved solids (TDS) were tested in situ

using an Ultrameter TM 6P portable conductivity meter (Myron L[®] Company, Carlsbad, CA, USA), with a test accuracy of ± 0.10 °C, ± 0.01 and $0.01 \text{ mg} \cdot \text{L}^{-1}$, respectively. The probe was calibrated before sampling and calibrated once during the sampling period according to the instructions.

Every water sample was divided into two parts. One part was filtered through a Whatman GF/F filter (GE Healthcare, Boston, MA, USA) (with a pore size of 0.45 µm), then used to determine the main cations and anions (K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, and SO₄²⁻) and dissolved silicon (expressed as DSi in this study). Samples for cations were acidified to pH < 2 with HNO₃. The cations and DSi were measured using an IRIS (HR) type Inductively Coupled Plasma-Atomic Emission Spectrometric (ICP-AES, manufactured by TJA, Boston, MA, USA), and anions (Cl⁻, NO³⁻, SO₄²⁻) were measured with ICS-900 Ion Chromatography, and the test accuracies were greater than 0.5%. The remaining unfiltered part of the sample was titrated to determine the total alkalinity (Alk.), according to Gran [38], with a Titralab-865 automatic titrator from the Hach Company (Loveland, CO, USA), the experimental error of which was less than 5%. Before titration, the pH meter was calibrated with the particular buffer solutions (with pH values of 4.005, 7.000 and 10.012). Using the titrant (HCl, 0.05 mol·L⁻¹), the filtrated sample (100 mL) was then taken and titrated to pH = 4.5, 4.2, 3.8 and 3.5, and the corresponding HCl volumes were recorded. The final titration point was controlled by a glass electrode in the titration process [38]. Each sample was titrated 3 times, and the sample alkalinity was calculated by the Graphics of Gran. The total alkalinity was approximately equal to the concentration of HCO_3^{-} , when the pH ranged from 6 to 10 in the water sample.

2.3. Data Processing

The DEM used in this study came from the digital elevation data of GDEMDEM 30 M resolution from the Geospatial Data Cloud website [39]. The geological map used was based on the "Geological Map of Guangdong Province, Hong Kong and Macao Special Administrative Region" (1:1,750,000), and the drainage system and rock distribution maps were extracted using ArcGIS 10.0 (Environmental Systems Research Institute, Inc., Redlands, CA, USA). IBM SPSS Statistics 19.0 (IBM, Armonk, NY, USA) was used for the data statistics and the Pearson correlation analysis. Graphs were drawn using Grapher 12.0 software (Golden Software, LLC., Golden, CO, USA) and Origin Pro 2018 (OriginLab Corporation, Northampton, MA, USA). The dissolved inorganic carbon (DIC) and partial pressure of carbon dioxide (*p*CO₂) were calculated through the CO2SYS based on the pH, water temperature and alkalinity of the water obtained from the sampling and measuring period [2]. The calcite saturation index (SIc) of the river water was calculated through the hydrogeochemical program of WATSPEC15 [28].

3. Results

3.1. Physical and Chemical Parameters

The hydrochemical compositions of the mainstream and main tributaries in the LR are listed in Table 1. The temperature of the river water samples varies from 9.3 to 20.5 °C, with an average of 14.3 °C in January 2018. The minimum value appears at the sample 4 in the upper reach of the mainstream, and the maximum value appears in the Zhutianhe River, a tributary in the lower reach of the LR, showing the coupled effects of the southern subtropical monsoon climate and elevation on the water temperature. The range of pH in the LR varies from 6.79 to 9.02, with an average of 7.82, and most of the water samples are characterized as weakly alkaline, which indicates the dominant effect of the karst water on the pH of the LR. The variation range of the total dissolved solids (TDS) are from 22.54 to 357.5 mg·L⁻¹, with an average of 131.8 mg·L⁻¹, which is higher than the average of 100 mg·L⁻¹ of most rivers worldwide [3], reflecting that the rock chemical weathering is relatively intense in the LRB.

Equivalent concentrations of total cations (TZ⁺ = 2 Ca²⁺ + 2 Mg²⁺ + K⁺ + Na⁺) of all samples from the LR are between 326 μ eq·L⁻¹ and 5906 μ eq·L⁻¹, with a mean of 2210 μ eq·L⁻¹, which is higher than the average value of 61 rivers in the world [40]. Equivalent concentrations of total anions

 $(TZ^{-} = HCO_3^{-} + 2SO_4^{2-} + NO_3^{-} + Cl^{-})$ are between 342 and 5353 $\mu eq \cdot L^{-1}$, with an average of 2041 $\mu eq \cdot L^{-1}$. The equilibrium state of river water can be reflected by the inorganic charge balance index [NICB = $(TZ^{+} - TZ^{-})/TZ^{+} \times 100$]. The NICB of 72 out of the 84 samples are in the range from -10% to 10%, which could be explained by the fact that the anions and cations in the LR are generally in equilibrium, and those of the remaining 12 samples (12, 13, 17, 39, 40, 46, 54, 56, 65, 67, 71, and 77) are not in equilibrium but vary from 10.25% to 18.29%, which is probably due to the presence of undetected anions, such as organic acids and phosphates, resulting from domestic sewage.

3.2. Cations and Anions

To conveniently clarify the hydrochemical type of the LR water and determine the main material sources of the dissolved loads, 84 water samples were categorized into five groups: the mainstream of the LR (ML), upstream of tributaries (UT), mid-stream of tributaries (MT), downstream of tributaries (DT) and small tributaries (ST) (Table 1). Ternary graphs of the main cations and anions in the LR were plotted according to the measured chemical compositions (Figure 2). Cations of the LR in January 2018 are dominated by calcium, accounting for 78.71% of the total cations, followed by magnesium, sodium and potassium, accounting for 9.35%, 6.92%, and 5.03%, respectively. The anions are dominated by bicarbonate, accounting for 84.97% of the total anions. Sulfate ion is the second largest anion, accounting for 8.98% of the total cations, followed by nitrate and chloride ions, accounting for 3.78% and 2.27%, respectively. Therefore, the hydrochemical type of the mainstream and tributaries in the LR belongs to the HCO₃–Ca type, indicating that the typical karst water characterized by "higher calcium and carbon" dominates the river hydrochemical composition, which is consistent with the geological background, dominated by carbonate rocks in the LRB (Figure 1).



Figure 2. Ternary graphs of cations and anions of the LR in January 2018.

It is worth mentioning that the SO_4^{2-} concentrations of Samples 28 and 82 are higher (1122 and 1114 µmol·L⁻¹), accounting for 37.13% and 47.41% of the total anions, respectively. In addition, some proportions of (K⁺ + Na⁺) in the upstream of tributaries to the total cations are greater than 40%, and the DSi concentrations vary from 55.71 to 333.57 µmol·L⁻¹, with an average of 159.22 µmol·L⁻¹ (Table 1), which is slightly higher than the average concentration of DSi in the global rivers (158 µmol·L⁻¹) [41]. The DSi concentrations of Samples 25, 26, 48, 51, and 52 (303.93, 317.86, 309.64, 333.57 and 301.43 µmol·L⁻¹, respectively) are close to that of the Changhuajiang River (376.39 µmol·L⁻¹), a silicate-dominated basin on Hainan Island, China [42], indicating that the chemical compositions in the upstream of tributaries were characterized by the chemical weathering of silicate rocks.

3.3. Spatial Patterns of pCO₂, SIc and DIC

The pCO_2 in the mainstream of the LR varies from 712 to 1624 µatm, with an average of 1025 ± 313 µatm, and those of the main tributaries are all supersaturated, relative to those of the atmosphere (407.54 µatm) [43], increasing from upstream to downstream by 1177, 1242 and 1394 µatm, respectively, which are lower than the average value of global rivers (2900 µatm) [44]. The SIc spatial distribution characteristics of tributaries are similar to those of pCO_2 , and the SIc values from upstream to downstream in tributaries are -0.74, -0.51 and -0.03, respectively, showing an increasing trend from upstream to downstream, which reflects that the calcite saturation state of the river water varies from an unsaturated to a saturated state from upstream to downstream in the main tributaries of the LR mainstream varies from -0.59 to 0.35, with an average of -0.11 ± 0.29 , which is generally considered as a calcite unsaturation state.

The calculated DIC in the mainstream and tributaries vary from 263 to 4982 μ mol·L⁻¹, with an average of 1740 μ mol·L⁻¹. HCO₃⁻ is the most abundant dissolved carbonate in river water, and its proportion to DIC varies from 70.24% to 98.06%, with an average of 94.6% (Table 2). The DIC contents in tributaries gradually increase from upstream to downstream (1461, 1645 and 1932 μ mol·L⁻¹, respectively).

Table 2. Variations and average values for pCO_2 , SIc, DIC and other parameters in the mainstream and tributaries of the LR.

Parameter	I	ML		UT		MT	DT		
i ululitetei	Range	Average	Range	Average	Range	Average	Range	Average	
T (°C)	9.3–16.4	14.2 ± 2.3	9.4-20.5	13.9 ± 2.5	10.2-18.1	13.9 ± 2.5	10.1-18.5	15.5 ± 2.3	
$EC(\mu S \cdot cm^{-1})$	116-228	194 ± 36	35-517	169 ± 122	38-360	188 ± 109	94-299	220 ± 61	
pH	7.75-8.18	7.97 ± 0.14	6.99-9.02	7.79 ± 0.35	7.2-8.36	7.82 ± 0.24	7.26-8.61	7.95 ± 0.37	
pCO_2 (µatm)	712-1624	1025 ± 313	88-4609	1177 ± 930	349-3063	1242 ± 798	323-3416	1394 ± 87	
CO_3^{2-} (mg·L ⁻¹)	0.15 - 0.77	0.37 ± 0.21	0.01-3.9	0.38 ± 0.7	0.02 - 1.22	0.32 ± 0.32	0.03-2.08	0.57 ± 0.55	
SIc	-0.59 - 0.35	-0.11 ± 0.29	-2.4 - 1.09	-0.74 ± 1.09	-2-0.65	-0.51 ± 0.9	-1.46-0.75	-0.03 ± 0.59	
DIC (µM)	1062-2256	1690 ± 346	263-3549	1461 ± 1107	328–3275	1645 ± 1063	735–2753	1932 ± 587	

4. Discussions

4.1. Material Sources of River Dissolved Loads

4.1.1. Sea Salt Precipitation

Atmospheric precipitation is the dominant recharge source of the surface runoff in the LRB in the context of a humid subtropical monsoon climate. The distance between the southernmost border of the LRB ($113^{\circ}05'04''$ E, $23^{\circ}55'33''$ N) and the Pearl River Estuary ($113^{\circ}42'06''$ E, $22^{\circ}37'07''$ N) is only 158 km. Therefore, the LRB is obviously affected by the warm and humid air mass from the South China Sea and the Western Pacific Ocean, as well as that from the Indian Ocean. Cl⁻ is the main component of rainwater, with a conservative behavior during the water cycle process, and is gradually used as a reference element to estimate the contribution of sea salt precipitation to the river hydrochemical composition [45]. It is generally believed that the cyclic chloride in surface water is mainly derived from sea salt precipitation, evaporite dissolution and human activities (i.e., the common salt in domestic sewage) [46,47].

There are hardly any saline formations but distributes several cities and towns at the intersections of rivers in the LRB. Sample 51, which was collected in a small tributary of the Qinglianshui River flowing through a single lithology (granite) region that is not influenced by salt formation and human activities, has the lowest value of Cl⁻ concentrations (11.27 μ mol·L⁻¹) of all samples, and it can be assumed that the Cl⁻ of Sample 51 completely originates from sea salt precipitation. Therefore, the Cl⁻ concentration of Sample 51 is used to represent the Cl⁻ concentration in the rainfall of the LRB. Sea salt correction is performed with reference to the concentration ratios of other ions in standard seawater, where Cl⁻/Na⁺ = 1.15, Ca²⁺/Na⁺ = 0.02, Mg²⁺/Na⁺ = 0.11, and HCO₃⁻/Na⁺ = 0.004 [3].

The calculated proportions of sea salt precipitation and human activities to Cl⁻ concentrations are 23.23% and 76.77%, respectively.

Correlation analysis between ions shows that there is a significant positive correlation between K^+ , Na^+ , and Cl^- (Table 3), indicating that there is a consistent source for K^+ , Na^+ and Cl^- , which may result from sea salt precipitation or domestic sewage discharge. Furthermore, the correlation coefficient R between Na^+ and Cl^- is 0.472, and that of K^+ and Cl^- is 0.813 at a 0.01 test level, which indicates that the sources of K^+ and Cl^- are more consistent and largely due to the sea salt precipitation. However, the fluctuation ranges of Na^+/Cl^- molar ratios are relatively great, from 0.55 to 16.86, and the mean value of 2.42 is greater than that of standard seawater (0.86) [48]. The excessive Na^+ indicates that there are other sources with regard to Na^+ , such as the chemical weathering of silicate minerals (e.g., sodium feldspar) and common salt in domestic wastewater.

	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ³⁻	Cl-	SO_4^{2-}	NO ³⁻	DSi	TDS
Ca ²⁺	1	**		**	**	**	**	**	**	**
Mg ²⁺	0.764	1		**	**	**	**	**	**	**
Na ⁺	0.091	0.112	1	**		**	*	**	**	
K^+	0.454	0.34	0.539	1	**	**	**	**	**	**
HCO ³⁻	0.961	0.793	0.059	0.342	1	**	*	**		**
Cl-	0.632	0.483	0.472	0.813	0.53	1	**	**	*	**
SO_4^{2-}	0.462	0.497	0.249	0.46	0.252	0.509	1	**		**
NO^{3-}	0.456	0.386	0.298	0.823	0.333	0.744	0.493	1		**
DSi	-0.352	-0.309	0.33	-0.031	-0.338	-0.274	-0.145	-0.105	1	**
TDS	0.981	0.834	0.156	0.528	0.94	0.688	0.534	0.522	-0.348	1

Table 3. Correlations of the main ion concentrations in the LR in January 2018.

** Correlation is significant at the 0.01 level (two-tailed); * Correlation is significant at the 0.05 level (two-tailed).

4.1.2. Carbonate Chemical Weathering

 Ca^{2+} and HCO_3^- are dominant in the river water ions of the LR (Figure 2). It is found that there are significant positive correlations between Ca^{2+} and Mg^{2+} , HCO_3^- , TDS (Table 3), with correlation coefficients of 0.764, 0.961 and 0.981 (p < 0.01), which indicates that there is a consistent geological source of CCW for Ca^{2+} , Mg^{2+} and HCO_3^- . Therefore, it has an important controlling effect for CCW on the geochemistry of the LR, which is consistent with the geological background of carbonate rocks, which is the main type of the basin bedrock (the distribution area of carbonate terrains accounts for more than 60% of the total basin area). $(Ca^{2+} + Mg^{2+})$:HCO₃⁻ molar ratios, induced by calcite and dolomite dissolution, can be expressed as Equations (1) and (2) [49]:

Calcite dissolution :
$$CaCO_3 + H_2CO_3 \leftrightarrows Ca^{2+} + 2HCO_3^{-}$$
 (1)

Dolomite dissolution :
$$Ca_{(1-x)}Mg_xCO_3 + H_2CO_3 \rightleftharpoons (1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^-$$
 (2)

The relative contribution of calcite or dolomite dissolution to river solutes can be judged by the molar ratios of Mg/Ca and Mg/HCO₃ due to the fact that Mg^{2+} is mainly derived from the dissolution of dolomite minerals in drainage basins, and carbonates are predominant and hardly affected by the dissolution of gypsum. It can be observed that the molar ratio of Mg/Ca, produced by calcite dissolution, is less than 0.1, while that of dolomite dissolution is equal to 1 (Equations (1) and (2)). The equal dissolution of calcite and dolomite yields a Mg/Ca ratio of 0.33 and Mg/HCO₃ ratio of 0.125, and the resultant Mg/HCO₃ ratios are 0.08 and 0.16, which indicates that the amount of dolomite dissolution is half or twice that of calcite based on mass balance, respectively [50,51]. The calculated average values of Mg/Ca and Mg/HCO₃ in the LR are 0.18 (0.1–0.2) and 0.09 (0.05–0.11), respectively, indicating that the hydrochemical compositions of the LR, induced by CCW, should be attributed to the compound contributions of calcite and dolomite dissolution. Furthermore, calcite dissolution is

the dominant source, which is also consistent with the large-scale exposure of limestone in the basin, especially in the area where the mainstream of the LR drains.

4.1.3. Chemical Weathering of Silicates

It has shown that the contribution of silicate weathering to CO_2 consumption has often been ignored in previous studies of karst carbon sink [14,27,28,52,53], which may lead to an overestimation of the CCW rate and CO_2 consumption associated with CCW in karst watersheds. The contribution of SCW to riverine DIC in karst watersheds should not be ignored. The exogenous water from the non-carbonate terrains around the karst watershed plays an important role in the karst process. For instance, the exogenous water with a relatively low pH and SIc will result in the severe dissolution of carbonate rocks in karst areas, which will greatly strengthen the potential of karst carbon sink [54–56]. Ford and William [57] found that the amount of carbonates dissolved in the CCW processes will be enhanced by 50% when the recharge area of exogenous water accounts for 50%. On the other hand, clastic interlayers are often observed in carbonate formations and in which, the export of HCO₃⁻ induced by silicate weathering cannot simply be attributed to the contribution of CCW.

Although the rate of SCW is relatively slow, it consumes atmospheric/soil CO₂ on a geological time scale (>1 Ma), and which process constitutes the natural thermostat of the Earth [58]. The proportion of non-carbonate formations in the LRB is more than 30%, according to the computational geometry module in ArcMap (Environmental Systems Research Institute, Inc., Redlands, CA, USA). The silicate formations are mainly distributed at the edge of the river basin, in other words, in the upstream of the mainstream and main tributaries, as well as in the lower reaches of south bank of the LR, including igneous rocks, metamorphic rocks, clastic rocks and Quaternary alluvial sediments (Figure 1), and the former dominates the non-carbonate formations.

It is generally known that SCW is one of the important natural sources of K⁺ and Na⁺, for example, the chemical weathering of silicate rocks, such as granites and metamorphic rocks, can produce Na⁺, and that of K-feldspar and mica can produce K⁺. Being less polluted by human activities in the upper reaches of the LR's main tributaries, the average concentrations of Na⁺ and K⁺ are 113.86 and 53.12 μ mol·L⁻¹, respectively, and their proportions to the total cations, respectively, account for 19.6% and 7.07%. With the dilution effect of the karst water input (poor in Na⁺ and K⁺), this shows a decreasing tendency in the proportions of Na⁺ and K⁺ to the total cations in the midstream of tributaries to the downstream, which are 14.91% and 5.32% in the middle reaches, respectively, and 13.62% and 5.06% in the lower reaches.

The DSi in the runoff mainly originates from SCW. The average concentration of DSi in the tributaries of the LR is 138.15 μ mol·L⁻¹, which is slightly lower than the average value of DSi in the global rivers (158 μ mol·L⁻¹) [41] and the upper reaches of the Sorocaba River in Southeastern Brazil, where igneous and metamorphic rocks predominate (240.75 μ mol·L⁻¹) [59]. It is close to that of the Ganges (134 μ mol·L⁻¹) [60], but higher than that of the Yellow River (95.29 μ mol·L⁻¹) [61], the Sanchahe River (80–110 μ mol·L⁻¹, upstream of the Wujiang River) [62] and the Kochechum River (87.5 μ mol·L⁻¹) in the permafrost region of Central Siberia [63]. This indicates that the ratio of silicate formation to the drainage area dominates the output of DSi in the river basin, and it also shows that the SCW process in the LRB cannot be ignored from the perspective of the DSi concentration.

It was reported above that sea salt precipitation is the main source of K⁺ and Na⁺ in the LR. In addition, SCW in non-carbonate formations and carbonate interlayers also contribute significantly to K⁺ and Na⁺. The ratio of $(Na^+ + K^+)$ and $(Na^+ + K^+ + Cl^-)$ is used to determine the relative contributions of SCW to the riverine hydrochemical composition [64]. Calculations show that $(Na^+ + K^+)/(Na^+ + K^+ + Cl^-)$ varies from 0.47 to 0.95, with an average of 0.71. It can be assumed that the products of SCW relatively contribute 71% of K⁺ and Na⁺ in the LR, without considering other sources of K⁺ and Na⁺.

There is a positive correlation between DSi and $(Na^+ + K^+)/(Na^+ + K^+ + Cl^-)$ for the LR ($R^2 = 0.41$, p < 0.01) (Figure 3), which shows that the DSi content controlled by SCW increases simultaneously with the ratio of $(Na^+ + K^+)/(Na^+ + K^+ + Cl^-)$, indicating that the significant contribution of SCW in non-carbonate formations to K⁺ and Na⁺ is further confirmed in the karst basin of the LR. The lower correlation coefficient of DSi and $(Na^+ + K^+)/(Na^+ + K^+ + Cl^-)$ may be attributed to the DSi uptake from diatoms in the case of slower velocities, as in January [65]. It consumes atmospheric/soil CO₂ during the SCW process and produces HCO₃⁻ while releasing Na⁺ and K⁺. The contents of HCO₃⁻, Na⁺ and K⁺ should simultaneously increase. It can be seen in Table 3 that there is a significant positive correlation between HCO₃⁻ and K⁺ at 0.01 levels, with a correlation coefficient of 0.342. However, there is no correlation between HCO₃⁻ and Na⁺, and the correlation coefficient is only 0.059, which indicates that Na⁺ also has other sources, except for sea salt precipitation and SCW, which is probably related to the discharge of domestic sewage from the residents of cities and towns near the riverbank.



Figure 3. Relationship between DSi and $(Na^+ + K^+)/(Na^+ + K^+ + Cl^-)$ in the LR in January 2018.

4.1.4. Human Activities

Human activities, including atmospheric acid precipitation, urban and industrial wastewater, agricultural fertilization and other sources of pollution will affect river hydrochemical composition [66]. Acid precipitation and industrial wastewater mainly impact SO_4^{2-} and NO_3^{-} in surface runoff. Na⁺, Cl⁻ and NO_3^{-} will increase if the domestic sewage drains into the river system. The application of potassium and nitrogen fertilizer in agriculture activities results in non-point source pollution and increases the concentrations of K⁺ and NO_3^{-} in the river water, respectively [66,67].

The LRB is influenced by a large amount of SO_2 and NO_x from the industrial districts in north of the Nanling Mountains and the PRD, which is one of the most developed areas in East Asia. The middle and long distance transmission of acid substances has a profound impact on the northern part of Guangdong Province. The contribution rate of acid substances, transported from external lands to local acid rain, can reach 49%, according to previous research on rainfall by stable isotope techniques [68]. Therefore, the urbanization/industrialization of the PRD and industrial districts in north of the Nanling Mountains is a non-negligible factor that results in a low pH of rainfall in the LRB. Several cities, such as Lianzhou, Liannan, and Yangshan, are distributed in the upper and middle reaches of the LR, where the population density is relatively high. In addition, it is inevitable that agricultural activities, scattered near the main tributaries, will also influence the chemical composition of the LR.

The concentrations of SO_4^{2-} and NO_3^{-} in the mainstream of the LR (Sample 3) are 165.63 and 91.94 μ mol·L⁻¹, respectively, which is close to those of the Qiantangjiang River (223 and 146 μ mol·L⁻¹), which is affected by severe acid precipitation [26], but much less than those of the upper reaches in the Wujiang River (590 and 200 µmol·L⁻¹), which is drained in the Guizhou karst plateau and is significantly influenced by industrial activities and acid rain [53]. The ratio between SO_4^{2-}/Ca^{2+} and NO_3^-/Ca^{2+} is generally used to determine the anthropogenic sources of SO_4^{2-} and NO_3^- . NO_3^{-}/Ca^{2+} is not correlated with SO_4^{2-}/Ca^{2+} in the mainstream and major tributaries of the LR (Figure 4), indicating that there are different sources for SO_4^{2-} and NO_3^{-} . Several samples have a relatively high SO_4^{2-}/Ca^{2+} (>0.3) and low NO_3^{-}/Ca^{2+} (<0.5), indicating that these samples are more subject to wastewater, which is relevant to industry and mining in the upstream of some tributaries, while another small group of samples from the upstream and downstream of some tributaries have a lower SO_4^{2-}/Ca^{2+} (<0.3) and higher NO_3^{-}/Ca^{2+} (>1.5) and are connected with domestic sewage discharge, which can be demonstrated by the human activities of town residents in karst depressions and karst valleys within the LRB. As the sampling was conducted during a period with hardly any agricultural activities (January), the effect of nitrogen application on NO_3^- was neglected in this study. Most of the samples have a relatively low SO_4^{2-}/Ca^{2+} (average value is 0.16) and NO_3^{-}/Ca^{2+} (average value is 0.68) (Figure 4), therefore, SO_4^{2-} and NO_3^{-} in the river water are largely due to acid precipitation, and this phenomenon is consistent with the fact that the LRB is located in a severe acid rain area in East Asia (Figure 1).



Figure 4. Relationship between concentration values of SO_4^{2-}/Ca^{2+} and NO_3^{-}/Ca^{2+} in the LR in January 2018.

4.2. Evidence of Chemical Weathering Associated with Sulfuric and Nitric Acids

Equivalent data points of $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^-]$ in the LR deviate from the 1:1 line (Figure 5a), with most situated above the 1:1 line, indicating that extra anions are necessary to balance the excess Ca^{2+} and Mg^{2+} . Nevertheless, those of $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^- + SO_4^{2-} + NO_3^-]$ are close to the 1:1 line (Figure 5b), of which average ratio is 0.96. Therefore, the equilibrium between the anions and cations in the LR requires SO_4^{2-} and NO_3^- to compensate.



Figure 5. (a) Relationship between $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^-]$; and (b) relationship between $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^- + SO_4^{2-} + NO_3^-]$.

Furthermore, the equivalent ratio between $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^{-}]$ should be 1, and that of $[NO_3^{-} + SO_4^{2-}]$ and $[HCO_3^{-}]$ should be zero under the condition that the CCW only involves carbonic acid but without exogenous acid, such as sulfuric acid and nitric acid [69]. Equivalent ratios of $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^{-}]$ in the LR vary between 0.62 and 2.4, with an average of 1.17, and most of the ratios are greater than 1. $[NO_3^{-} + SO_4^{2-}]/[HCO_3^{-}]$ ratios vary from 0.05 to 1.24, with an average of 0.23, revealing that both anthropogenic sulfuric acid and nitric acid are involved in the chemical weathering process of the LRB as acid agents.

The chemical reaction equation of CCW induced by nitric acid and sulfuric acid can be expressed as Equation (3) [19,53]. It can be observed that the equivalent ratio of $[Ca^{2+} + Mg^{2+}]/[HCO_3^{-}]$, produced by CCW associated with sulfuric acid and nitric acid, is 2, and that of $[NO_3^{-} + SO_4^{2-}]/[HCO_3^{-}]$ is 1.

$$3Ca_{(1-x)}Mg_{x}CO_{3} + H_{2}SO_{4} + HNO_{3} \leftrightarrows 3(1-x)Ca^{2+} + 3xMg^{2+} + SO_{4}^{2-} + NO_{3}^{-} + 3HCO_{3}^{-}$$
(3)

It shows that the data points of $[Ca^{2+} + Mg^{2+}]/[HCO_3^-]$ and $[NO_3^- + SO_4^{2-}]/[HCO_3^-]$ are distributed between the endmember of carbonic acid-involved CCW and nitric acid and sulfuric acid-involved weathering in Figure 6, which demonstrates that nitric acid and sulfuric acid play important roles in CCW, and once again proves that carbonic acid is not the only weathering medium in the LRB from this distribution pattern.



Figure 6. Relationship between equivalent ratios of $[Ca^{2+} + Mg^{2+}]/[HCO_3^{-}]$ and $[NO_3^{-} + SO_4^{2-}]/[HCO_3^{-}]$ in the LR in January 2018.

4.3. Chemical Weathering and the Related CO₂ Consumption Driven by Anthropogenic Acids

4.3.1. Influence from Sea Salt Precipitation and SCW

The riverine DIC is composed of bicarbonate (HCO_3^{-}), carbonate ions (CO_3^{2-}), true carbonic acid (H_2CO_3) and aqueous carbon dioxide (CO_{2aq}) [70]. HCO_3^{-} is the most abundant dissolved carbonate species in the LR, accounting for 94.6% of DIC. Additionally, almost all of the alkalinity in the LR is contributed by HCO_3^{-} . HCO_3^{-} can be regarded as DIC because the pH in the LR is lower than 10 [71].

Based on the above analysis, the contribution of sea salt precipitation and SCW to DIC must be subtracted from the total riverine DIC to calculate the effect of acid precipitation on DIC. Sea salt correction (see Section 4.1.1) was used to evaluate the contribution of a sea salt precipitation endmember to riverine DIC in this work. The calculated contribution proportion of sea salt precipitation to DIC concentration is very small, only accounting for 0.01%, which is because the pH of rainwater in the LRB is below 5.6 (Figure 1), and the pCO_2 in the river water is generally higher than that in the atmosphere.

The hydrochemical characteristics of the LR are mainly controlled by the geological background of the watershed. The chemical weathering of carbonate has a dominant role in riverine DIC. Additionally, SCW cannot be ignored. The reactions of SCW followed Mortatti and Probst [72], which are shown as follows:

$$Ca_{x}Mg_{(1-x)}Al_{2}Si_{2}O_{8} + 2H_{2}CO_{3} + 2H_{2}O \rightarrow xCa^{2+} + (1-x)Mg^{2+} + 2HCO_{3}^{-} + 2SiO_{2} + 2Al(OH)_{3}$$
(4)

$$Na_{x}K_{(1-x)}Al_{2}Si_{2}O_{8} + H_{2}CO_{3} + H_{2}O \rightarrow xNa^{+} + (1-x)K^{+} + HCO_{3}^{-} + 3SiO_{2} + Al(OH)_{3}$$
(5)

Since SCW associated with sulfuric acid and nitric acid cannot produce HCO_3^- , the carbonic acid-involved SCW was only considered to estimate the CO_2 consumption of SCW in this paper. According to Equations (4) and (5), the HCO_3^- generated from SCW can be calculated as half of the DSi concentration, and the ions of Ca^{2+} and Mg^{2+} , derived from SCW, can be calculated as 1/5 of the DSi concentration [73]. The calculated contribution proportions of SCW to riverine DIC range from 0.59% to 54.89%, with a mean value of 9.64%. The average DIC produced by SCW is 49.97 μ mol·L⁻¹, indicating that the SCW plays a relatively important role in the DIC concentration of the LR.

4.3.2. CO₂ Consumption Deficit Related with Anthropogenic Acid-Involved CCW

Carbonic acid, nitric acid and sulfuric acid were involved in CCW in the LRB. To estimate the relative contribution to riverine DIC of CCW induced by nitric and sulfuric acid, we assumed that k_1 (mol) carbonic acid, k_2 (mol) nitric acid and k_3 (mol) sulfuric acid were involved in the CCW process, rewriting Equation (3) as [53,74]:

$$(k_1+k_2+2k_3)Ca_{(1-x)}Mg_xCO_3+k_1CO_2+k_1H_2O+k_2HNO_3+k_3H_2SO_4 \rightarrow (k_1+k_2+2k_3)(1-x)Ca^{2+}+(k_1+k_2+2k_3)xMg^{2+}+k_2NO_3^{-}+k_3SO_4^{2-}+(2k_1+k_2+2k_3)HCO_3^{-}$$
(6)

Afterwards, the molar concentrations of $(Ca^{2+} + Mg^{2+})$ and HCO_3^- produced by CCW in the LRB are:

$$[Ca^{2+} + Mg^{2+}]_{carb} = k_1 + k_2 + 2k_3$$
(7)

$$[HCO_{3}^{-}]_{carb} = 2k_{1} + k_{2} + 2k_{3}$$
(8)

$$[Ca^{2+}+Mg^{2+}]_{carb} = [Ca^{2+}+Mg^{2+}]_{riv} - [Ca^{2+}+Mg^{2+}]_{sil} - [Ca^{2+}+Mg^{2+}]_{cyc}$$
(9)

$$[HCO_{3}^{-}]_{carb} = [HCO_{3}^{-}]_{riv} - [HCO_{3}^{-}]_{sil} - [HCO_{3}^{-}]_{cyc}$$
(10)

Thus:

$$k_1 = [HCO_3^{-}]_{carb} - [Ca^{2+} + Mg^{2+}]_{carb}$$
(11)

In the above equations, the subscripts of "riv", "carb", "sil" and "cyc" represent the river water, carbonate weathering, silicate weathering and cyclic salt, respectively.

According to the above equations, the concentration of carbonic acid (k_1) involved in CCW can be calculated by subtracting the corresponding values of cyclic salt (sea salt precipitation) and SCW from the measured HCO₃⁻, Ca²⁺, and Mg²⁺ concentration data at each sampling point (Equations (7)–(11)). The difference between the residual amount of HCO₃⁻ after deducting those from the sea salt precipitation and SCW in river water and $2k_1$ (the molar concentration of HCO₃⁻ derived from CCW by carbonic acid is double that of carbonic acid) is the sum of k_2 and $2k_3$ (the values of k_2 and k_3 cannot be calculated separately). Therefore, the k_1 value can be used to calculate the molar concentrations of carbonic acid that participates in the CCW and the DIC concentrations from each endmember, respectively, and then the deficit proportion of CO₂ consumption induced by nitric acid and sulfuric acid can also be calculated according to the above results.

As mentioned in Section 3.2, SO_4^{2-} is abnormally high for Samples 28 and 82. To prevent the calculated results from significantly deviating from the actual ones, these two samples were not considered here. The calculation results show that the relative proportions of carbonic acid and anthropogenic acids (nitric acid and sulfuric acid) in CCW are 76.97% and 23.03%, respectively. DIC from carbonic acid weathering accounts for 76.79% of the total DIC in rivers and streams, of which 38.4% is derived from atmospheric/soil CO₂, and the deficit proportion of CO₂ consumption, associated with CCW resulting from anthropogenic acids, is approximately 13.56%. Thus, the proportion attributed to acid substances from other areas outside the LRB is 6.64% (see Section 4.1.4), and the above results show that the exogenous acid sourced from human activities has a non-negligible interference with the water-rock interaction and the geochemical cycle of carbon across the basin. The calculation of the deficit proportion is slightly lower than the loss of CO_2 consumption caused by nitric acid and sulfuric acid, in both the rainy and pre-rainy seasons in the Guizhou Plateau (15.67% and 14.17%, respectively) [53], which is mainly attributed to the severe acid rain pollution, frequent industrial activity, and high percentage of carbonate rock distribution. The output of DIC, caused by anthropogenic acids in the LR, represents 38.44% of the CO₂ consumption associated with natural carbonate weathering, and the proportion will reach 18.84% for the external acids, both of which are higher than that of SCW associated with nitric acid in France (6–15%) [13]. Thus, chemical weathering influenced by human activities in the carbonate basin, especially in which affected by the heavy acid rain, need to be paid more attention.

4.4. Response of Riverine Carbonate System to Human Activities

It consumes CO₂ from the atmosphere/soil in the chemical weathering process and directly releases the carbon sequestered in carbonate rocks during CCW and then, the yielded HCO₃⁻ are transported to the river system through surface runoff. Therefore, the chemical weathering of rocks will directly influence the riverine carbonate system [75]. A correlation analysis between DIC_{riv} and the parameters related with the riverine carbonate system in the LR shows that riverine TDS, pCO_2 , alkalinity and SIc all increase with the DIC_{riv} concentration, and there are extremely significant positive correlations among those parameters, with correlation coefficients of 0.975, 0.633, 0.999 and 0.8, respectively, p < 0.01 (Table 4). Carbon dioxide, as an important driving force of the occurrence of the karst process, will promote the dissolution of carbonate rocks after entering the karst dynamic system, which represents an increase of Ca²⁺, Mg²⁺ and HCO₃⁻, and an enhancement of pCO_2 . On the contrary, the escape of CO₂ from the karst system may result in the carbonate precipitation, and the HCO₃⁻ promotes the combination of Ca²⁺ and Mg²⁺ with HCO₃⁻ in the river water, which will lead the saturated state of calcite to be over-saturated and provide favorable conditions for calcite precipitation, thus causing a rise in pCO_2 .

	Т	TDS	pН	pCO ₂	Alk.	SIc	DIC _{N-S}	DIC _C	DIC _{riv}
Т	1			**				*	
TDS	0.213	1		**	**	**	**	**	**
pН	0.001	0.239	1	**	*	**		*	*
pCO_2	0.381	0.624	-0.446	1	**		**	**	**
Alk.	0.234	0.974	0.284	0.606	1	**	**	**	**
SIc	0.231	0.796	0.706	0.197	0.813	1	**	**	**
DIC _{N-S}	0.141	0.853	0.112	0.517	0.785	0.615	1	**	**
DICC	0.249	0.936	0.306	0.587	0.985	0.804	0.668	1	**
DIC _{riv}	0.244	0.975	0.259	0.633	0.999	0.8	0.787	0.984	1

Table 4. Correlation analysis of parameters related with carbonate system in the LR.

** Correlation is significant at the 0.01 level (two-tailed); * Correlation is significant at the 0.05 level (two-tailed); DIC_{riv}, DIC_C and DIC_{N-S} represent the total amount of DIC in water samples, DIC derived from carbonic acid-involved CCW and DIC derived from nitric acid and sulfuric acid-involved CCW, respectively.

The correlation between the DIC_{riv} and pH in the LR water is relatively weak, with a correlation coefficient of 0.259 (p < 0.05), and there is no correlation between the water temperature and DIC_{riv}. However, there is a weak positive correlation between the water temperature and DIC_c, with a correlation coefficient of 0.249 (p < 0.05, Table 4), showing that temperature constrains the chemical weathering of carbonate rocks and have an impact on the output of DIC. Within a certain range of temperature conditions, higher temperatures give rise to faster dissolution and yields more HCO₃⁻ [77]. In addition, it can also reflect that there are different sources of DIC in the LR by the weak correlation between the water temperature and DIC_C and the uncorrelated relationship between water temperature and DIC_{N-S}, and the CCW associated with sulfuric acid and nitric acid derived from human activities, which is discussed in this paper, is one of the important sources of riverine DIC.

The participation of nitric acid and sulfuric acid in the CCW results in a weakening of carbon sequestration capacity induced by chemical weathering. In addition, it promotes the activation of carbon sequestered in carbonate rocks [78,79]. HCO₃⁻, which derived from the product of chemical weathering, contributes significantly to the riverine DIC, which constitutes a non-ignorable part of the river carbon flux that transports to the ocean. There is a significant positive correlation between the DIC produced in CCW induced by carbonic acid in the LR and the total riverine DIC, with a correlation coefficient of 0.984, and the DIC produced by anthropogenic acid-involved CCW is also positively correlated with the total DIC in river waters (R = 0.787, *p* < 0.01) (Table 4 and Figure 7a,b), which shows that the riverine DIC is mainly constrained by the mechanism of the CCW process induced by carbonic acid. The DIC derived from the latter is also important for the riverine DIC in the LR. The scattered data points of DIC_{N-S}/DIC_{riv} show that carbonate systems in different regions of the LRB are driven by varying degrees of weathering processes associated with nitric acid and sulfuric acid (Figure 7b).



Figure 7. Relationship between DIC from different sources and the relationship among DIC_{N-S} , SIc and pCO_2 .

 DIC_{N-S} is also significantly positively correlated with the major parameters related with the riverine carbonate system, such as TDS, pCO_2 , alkalinity and SIc, with the correlation coefficients of 0.853, 0.517, 0.785 and 0.615 (p < 0.01) (Table 4). The logarithmically increasing relationship between DIC_{N-S} and SIc (R = 0.615, p < 0.01) also indicates that the carbonate system of the LR responds positively to CCW induced by anthropogenic nitric acid and sulfuric acid (Figure 7c,d). As CCW influenced by anthropogenic acids continues to occur, carbon sequestered in carbonate rocks will continuously release into the river system, and DIC derived from CCW will also increase. The saturation state of calcite will also be gradually transformed from being unsaturated to saturated, or even oversaturated accompanied with the increase of DIC_{N-S} . The increase in the saturation of calcite in river water will drive CO_2 release to the atmosphere through the water–air interface, prompting the transition of the river to a carbon source [80], and, in turn, affecting the source and sink effects of drainage basins. The associated event should be considered in the estimation of the CO₂ consumption induced by chemical weathering. Therefore, a systematic view of the river carbon transport process is crucial for the accurate estimation of the CO₂ consumption in the drainage basin.

There is a weak exponentially increasing relationship between DIC_{N-S} and $p\text{CO}_2$ (R = 0.517, p < 0.01), which reflects that $p\text{CO}_2$ may be affected by other factors, except for the effects of the CCW, for instance, the terrestrial CO₂ produced by root respiration will enter the river system through surface runoff, subsurface flow and groundwater [81,82]; in addition, $p\text{CO}_2$ can also increase due to the precipitation of calcite in supersaturated water and the decomposition of organic carbon in river sediments and river waters [83,84]. In brief, chemical weathering caused by anthropogenic sulfuric acid and nitric acid is also the critical factor driving the increase of SIc and $p\text{CO}_2$ in the LR and constrains the carbonate system of the karst river, together with the chemical weathering involved with carbonic acid.

5. Conclusions

Anions and cations in the mainstream and main tributaries of the LR were dominated by $HCO_3^$ and Ca^{2+} in January 2018, accounting for 84.97% of the total anions and 78.71% of the total cations, respectively. The average concentration of DSi in the drainage basin (159.22 µmol·L⁻¹) was slightly higher than that of global rivers (158 µmol·L⁻¹). Therefore, SCW in karst basins should not be ignored. HCO_3^- was the most abundant dissolved carbonate species in the LR, accounting for an average of 94.6% of DIC. Most of the dissolved loads originated from mineral weathering, dominated by calcite dissolution. SO_4^{2-} and NO_3^- were mainly derived from acid precipitation, induced by acid substances from external transmission (from the PRD and industrial districts in north of the Nanling Mountains) and local supply, but the contribution from local industrial wastewater and domestic sewage was less.

The SCW contributed an average of 9.64% to riverine DIC. Sulfuric acid and nitric acid from human activities were the weathering agents that participated in the CCW. The relative proportions of carbonic acid and anthropogenic acids, participating in CCW, were 76.97% and 23.03%, respectively. The deficit proportion of CO_2 consumption, associated with CCW resulting from sulfuric acid and nitric acid in winter, was approximately 13.56%, which was slightly lower than those of the Guizhou Plateau in the rainy and pre-rainy seasons (15.67% and 14.17%, respectively). The deficit percentage of CO_2 consumption by nitric acid and sulfuric acid to the CO_2 consumption associated with natural CCW was found to be 38.44% and 18.84% for anthropogenic acids from external areas, and these values may be lower than the actual values because the utilization of DIC by aquatic photosynthetic organisms was not considered in this study. In addition, the relative proportion of sulfuric acid and nitric acid, which is involved in CCW, needs to be further identified.

The DIC produced by CCW associated with nitric acid and sulfuric acid showed a significant positive correlation with riverine DIC, and there was a logarithmically increasing relationship with SIc and an exponentially increasing relationship with pCO_2 , indicating that the carbonate system of the LR was driven by human activities. The exogenous acids derived from human activities had a non-negligible interference with the water–rock interaction and the geochemical cycle of carbon across the basin. Therefore, the chemical weathering and riverine carbonate system, influenced by anthropogenic acids in the carbonate basin, should be paid more attention.

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