

Effect of atmospheric precipitation on the dissolved loads of the Dongjiang River, China

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Abstract: The atmospheric precipitation plays an important role in influencing the river chemistry of the Dongjiang River. The atmospheric contribution to river water is estimated by reference to Cl concentration called Cl_{ref} . The Cl_{ref} of 41.97 $\mu\text{mol/L}$ represents the highest chloride concentration of the rainwater inputs to river water, thus sea salts are responsible for total Cl concentration of the Dongjiang River. According to the principal compositions of precipitation and river water, two approaches—sea salt correction and precipitation correction were proposed in order to correct the contribution proportions of atmospheric precipitation on the solutes and to calculate chemical weathering rate. The results reflected that the atmospheric contribution ratios fluctuate from ~5% to ~20% of TDS (total dissolved solids) in the Dongjiang River. As compared with the other world watersheds, the lower dissolved ion contents and high runoff may result in the obvious influence of precipitation on river chemistry in the Dongjiang basin. The major elemental chemistry is mainly controlled by silicate weathering, with the anion HCO_3^- and cation Ca^{2+} and Na^+ dominating the major compositions in this basin. The estimated chemical weathering rate of 15.78—23.48 $\text{t}/(\text{km}^2 \cdot \text{a})$ is only 40%—60% of a global average in the Dongjiang basin. Certainly, the estimated results are still under correction gradually because the effect of human activities on the precipitation chemistry has never been quantified in detail.

Keywords: Dongjiang River; river solutes; precipitation chemistry; atmospheric inputs; chemical weathering rate

Introduction

The atmospheric precipitation has long been recognized as providing an input of substance to the surface water and a source of elements carried by rivers (Stallard, 1981; Meybeck, 1983). It is estimated that approximately 3.0% of solute loads of world rivers are derived from the rainwater on a global scale by Gaillardet *et al.* (Gaillardet, 1999). Though rainwater inputs appear to provide only a minor influence on the cationic and anionic charge composition of stream waters, subtracting rainwater contributions from stream waters is essential when using solute molar ratios to determine the stoichiometry of mineral weathering reactions or to identify dominant weathering sources within river systems. In addition, as a very important part of global geochemistry cycle, atmosphere circle plays a crucial role in affecting the surface water, for example, 75% of the acidification trend in the upper and middle reaches of the Changjiang (Yangtze) River is caused by serious acid deposition due to the increasing sulfur emission from coal combustion (Chen, 1998a; 2000). Thus, the special attention must be paid on the importance of atmospheric deposition on river chemistry as the monitored acidified precipitation covers as much as 40% of the total continental area in China.

More concern about the effect of atmospheric precipitation on the dissolved loads originates from correction for this input is required prior to calculating weathering rates in fluvial system (Chen, 1991; 1992; Roy, 1999; Grasby, 2000; Nakaganu, 2000). So far, scarce literatures can be used to understand the atmospheric input to the solute loads of surface water, especially in China. Knowledge of the chemical compositions of atmospheric deposition is critical in understanding local air pollution and its effects on the hydrological systems. Most studies on acid deposition in China have focused on the major cities, mainly serving for environmental protection. Consequently, it is difficult to quantify of atmospheric input to the large rivers usually due to insufficient precipitation chemistry database. So this paper chooses a small watershed—Dongjiang River (one of three tributaries in the Zhujiang system) as the studying object where precipitation chemistry database are relatively abundant because of severe acid rain.

The main objective of this study is to provide the atmospheric contribution percents of major ions of the Dongjiang River using Cl_{ref} as a tracer by ion correction where previous information is indeed limited. This paper is an attempt to fill in the gap in our knowledge of precipitation chemistry on river solutes and to estimate the average

chemical weathering rate (i.e., CDR). This study will be helpful roughly to retrospect solutes' resources and farther understand the long-term CO₂ consumption within the Dongjiang basin.

Water samples were collected and filtered in time through 0.45 μm acetate fibrous filters. The analytical procedures include conventional flame atomic absorption spectrophotometry for Ca, Na, Mg and K (analytical precision better than 10%), and hydrochloric acid titration for HCO₃⁻. The analysis of Cl⁻ and SO₄²⁻ are performed by AgNO₃ titration and BaSO₄ nephelometry. Dissolved silica is measured by spectrophotometric measurement of the Mo blue complex. Analytical errors in concentration measurements are estimated to be less than 2%. The mass balance is tested within 1 ± 10% between anion and cation equivalent concentrations.

1 Hydrology and geology of the Dongjiang basin

The Zhujiang water system has been known for its high runoff and complicated watersystem: three main tributaries, including the Xijiang River, Beijiang River and Dongjiang River, contribute an average 73.5%, 13.5% and 7.30% of Zhujiang water load, respectively. The Beijiang River and the Xijiang River drain the world famous karstic limestone areas in the South China. However, while the Dongjiang drainage basin is relatively simple and drains the South China granite area mainly consisting of granitoids terrains (Zhang, 2001), so its soil type is thus composed primarily of tropical crimson agrotype.

The Dongjiang River (562 km length), one of tributaries of Zhujiang, originates from the Xunwu County in the Jiangxi Province and flows into the Zhujiang Estuary mainly through the Humen Channel and ultimately enters the South China Sea. With an annual river discharge of $2.97 \times 10^{10} \text{ m}^3$, the Dongjiang basin drains a surface of ca. $3.53 \times 10^4 \text{ km}^2$. The

draining cities such as Heyuan, Huizhou, Shaoguan, Guangzhou, Shenzhen and Dongguan are estimated that their monitoring areas account for 43.3%, 29.8%, 5.67%, 7.54%, 6.15% and 7.50% of the Dongjiang basin, respectively. The Dongjiang basin locates in the Zhijiang Delta where dense population and developed industry have turned into an important economy center in China.

The Dongjiang watershed drains a region of subtropic monsoon climate, which is characterized by high precipitation (1300—2400 mm, 1753 mm averagely) and high temperature (annual average temperature 20.4°C). The evapo-transpiration (680 mm) is more important and likely reaches about 40% of rainfall in the Dongjiang basin. Surface runoff is the major water supply for the Dongjiang basin, accounting for over 90% of its total water discharge. Historical records showed that average 80% of water discharge is concentrated in the flood seasons (April to September; Chen, 1998b).

2 Results

Data concerning major elemental concentrations are compiled in Table 1 for the river dissolved loads and Table 2 for the local rainwater of the Dongjiang River basin.

2.1 River water chemistry

Water samples were collected or analyzed from 1956 to 2000 (Zhang, 1985; 1999; Wu, 1989) at the draining area such as Huizhou, Longchuan, Boluo and Heyuan according to previous documents and this study. Streams examined in this study generally have a relatively uniform solute chemistry that is consistent well with previous investigations of the Dongjiang River (Zhang, 1999; Wu, 1989; Table 1). The results revealed that the equivalent concentrations of major ions collected in the different zones of the Dongjiang basin and on the different sampling dates agreed with each other as shown in Table 1.

Table 1 Major elemental concentrations and total dissolved solids of the Dongjiang River water

Sampling time	Location	TDS, mg/L	Mg ²⁺ , μmol/L	Ca ²⁺ , μmol/L	Na ⁺ , μmol/L	K ⁺ , μmol/L	HCO ₃ ⁻ , μmol/L	SO ₄ ²⁻ , μmol/L	Cl ⁻ , μmol/L	SiO ₂ , μmol/L
1983.8 ^a	Huizhou	42.28	109.2	220.0	70.00	30.00	362.0	53.95	23.10	186.0
1959—1967 ^b	Longchuan	77.36	107.1	144.5	446.1	53.85	790.0	77.00	30.14	—
1956—1984 ^b	Boluo	60.94	80.85	140.3	282.6	52.56	624.8	56.90	35.49	—
1985—1986 ^c	Heyuan	49.90	75.00	132.5	217.4	23.08	488.5	53.15	56.34	—
2002.2 ^d	Huizhou	82.87	75.00	310.3	290.4	58.72	787.7	97.30	64.79	213.5

Notes: a. Zhang, 1985; b. Zhang, 1999; c. Wu, 1989; d. this study

One measure of the data quality is the charge balance (eq/L) between total dissolved cations ($TZ^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$) and total dissolved anions ($TZ^- = Cl^- + HCO_3^- + 2SO_4^{2-}$). The average cationic vs. anionic charge balance for the waters analyzed [$(TZ^+ - TZ^-)/(TZ^+ + TZ^-)$] is on an average better than 5%, with exception of data from Zhang *et al.* (Zhang, 1985), which is generally within the combined analytical uncertainty for all measurements. This result indicates that the major ions

measured in this study by and large account for the charge balance.

The total cation charge (TZ^+) of the Dongjiang River ranges from ~ 650 to ~ 1120 μeq/L. On an average molar basis, Na⁺ is the most abundant major cation in stream water (43%), followed by Ca²⁺ (34%), Mg²⁺ (16%), and K⁺ (7%). Among the cations, Ca²⁺ is slightly dominant for the Na⁺, accounting for about 44% of the total cations (μeq/L). This corresponds to Na⁺, Mg²⁺, and K⁺ providing 30%,

21%, and 5% of the cationic charge, respectively.

On an average, HCO_3^- is the most abundant anion in the Dongjiang stream, followed by SO_4^{2-} and Cl^- . This corresponds to HCO_3^- , SO_4^{2-} , and Cl^- providing 77%, 18%, and 5% of the anionic charge, respectively. The concentrations of SO_4^{2-} and Cl^- ions are generally low, making up only 10% and 2% of the total dissolved solids (TDS), respectively. The chloride concentration measured in the dissolved loads of the Dongjiang River is $41.97 \mu\text{mol/L}$ averagely.

The TDS values, ranging from 42 mg/L to 83 mg/L, indicated that the Dongjiang River contains the lower total dissolved solids, which is generally far less than 100 mg/L compared to other unpolluted rivers of the world (Meybeck, 1996). On average, HCO_3^- accounts for 59% (mg/L) of the TDS, whereas both Ca^{2+} and Na^+ showed high abundance and account for about 13% and 9% of TDS. Among all ions, the order of components on an equivalent basis is: $\text{HCO}_3^- > \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{SO}_4^{2-} > \text{K}^+ > \text{Cl}^-$. In conclusion, the $\text{Ca} + \text{Na}^+$, HCO_3^- and SO_4^{2-} ions are the dominant ions and constitute over 91% of TDS in the Dongjiang stream.

The lithology within the Dongjiang basin is dominated by silicate rocks, dissolved silica concentration within the

Dongjiang River basin is about $200 \mu\text{mol/L}$ (interannual mean ranges from 186 to $213 \mu\text{mol/L}$) and is relatively abundant compared to other two Zhujiang tributaries-Beijiang and Xijiang. This difference may be explained by the quantity of silicate rocks that underlie the Dongjiang catchment. In addition, on a worldwide scale, Si concentrations found in the Dongjiang basin are far higher than $127 \mu\text{mol/L}$ of a world average (Gaillardet, 1999).

2.2 Atmospheric precipitation chemistry

The aim of the atmospheric input correction is to quantify and subtract the portion of the elements carried by rainwater in the chemical composition of the surface water. The quantification of atmospheric inputs due to rainwater requires knowledge of the chemical composition of the rainfall on the total watershed.

Within or around the Dongjiang basin, the multiyear chemistry data of local precipitation at different stations were collected and investigated previously by some scholars (Xu, 1991; Quan, 1992a; 1992b; Wang, 1992; Qi, 1995; Yang, 1996) given in Table 2, expressed in $\mu\text{mol/L}$ concentration. Recent chemical analysis of precipitation is based on a sampling network of six stations as Guangzhou, Heyuan, Huizhou, Shenzhen, Dongguan and Shaoguan distributed all over the basin, during the year 1980–1990.

Table 2 Major ion compositions of atmospheric precipitation in the Dongjiang basin

Year	Region	TDS, mg/L	Mg^{2+} , $\mu\text{mol/L}$	Ca^{2+} , $\mu\text{mol/L}$	Na^+ , $\mu\text{mol/L}$	K^+ , $\mu\text{mol/L}$	SO_4^{2-} , $\mu\text{mol/L}$	Cl^- , $\mu\text{mol/L}$	NO_3^- , $\mu\text{mol/L}$	NH_4^+ , $\mu\text{mol/L}$
- ^a	Guangzhou	21.99	6.875	103.1	24.97	25.05	114.8	29.07	22.98	148.6
1980–1985 ^b	Guangzhou	11.12	4.165	29.73	7.250	7.680	64.95	16.85	21.00	68.35
1986 ^c	Guangzhou	21.60	9.540	84.55	60.30	28.64	104.9	51.58	24.00	116.6
1987 ^d	Guangzhou	19.45	9.500	97.95	89.39	42.49	87.00	37.35	14.79	55.56
1988 ^d	Guangzhou	23.60	12.67	87.75	28.09	24.10	127.5	38.06	33.27	141.4
1988 ^e	Guangzhou	15.08	9.165	51.00	5.691	6.210	92.10	11.55	26.45	86.67
1989 ^d	Guangzhou	22.07	6.960	103.3	24.87	25.10	114.8	29.04	23.98	148.9
1990 ^d	Guangzhou	36.52	9.665	104.0	35.96	44.69	206.5	54.93	50.40	259.1
1980–1985 ^b	Shenzhen	8.811	2.455	19.95	24.82	60.78	22.75	27.77	15.10	50.39
1989 ^f	Shaoguan	15.85	13.96	35.78	15.30	9.440	87.80	15.89	48.90	74.28
- ^a	Shaoguan	10.92	1.735	49.52	5.200	3.850	66.60	17.29	18.10	27.43
1980–1985 ^b	Dongguan	19.35	6.745	60.20	26.85	105.9	78.95	35.60	46.50	17.00
1980–1985 ^b	Huizhou	13.46	14.87	40.78	27.34	19.85	63.15	43.51	34.30	18.58
- ^f	Lijiang	0.8983	0.90	2.30	0.90	1.60	4.50	0.13	2.30	6.80

Notes: a. Qi, 1995; b. Yang, 1996; c. Jin, 1992a; d. Jin, 1992b; e. Wang, 1992; f. Liu, 1992

The concentrations of major ions and TDS of Dongjiang precipitation showed the distinct spatial and temporal variations. For instance, TDS ranges from 8.8 mg/L to 36.5 mg/L with an average of 18.4 mg/L and varies several times throughout the drainage basin. The TDS of the Dongjiang precipitation is higher over one order of magnitude than the precipitation background value of 1 mg/L in the Lijiang of China (Liu, 1993).

Nevertheless, at first glance, concentrations of cations vary in the order: $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$ in the local rainwater ($\mu\text{eq/L}$). The major cations Ca^{2+} and NH_4^+ constitute ~ 15% and ~ 9% of TDS, respectively. The

molar concentrations of anions followed the order: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$, SO_4^{2-} is the most abundant anion in regional atmospheric precipitation; it accounts for 49% of TDS (mg/L), followed by NO_3^- and Cl^- , making up ~ 10% and ~ 6% of TDS, respectively. As usual, it is clear from Table 2 that the order of ion abundances of mean rainwater on an average molar basis is: $\text{SO}_4^{2-} > \text{NH}_4^+ > \text{Ca}^{2+} > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$, though the chemical compositions of local precipitation throughout the Dongjiang basin are highly variable.

Accordingly, SO_4^{2-} , NH_4^+ , NO_3^- and Ca^{2+} are dominate ions and constitute ~ 83% of TDS throughout the

Dongjiang basin. The NH_4^+ and NO_3^- will be considered nonsignificantly in this study because their contents of Dongjiang River water are very low probably due to participating in life activities, though NH_4^+ and NO_3^- concentrations are comparatively high in the rainwater of the Dongjiang basin.

3 Discussion

Correction for the atmospheric contributions to the dissolved materials of river water is important for the identification of weathering sources, because the atmospheric inputs may be significant in some rivers (Stallard, 1981). In order to determine the origins of the major element fluxes transported by the Dongjiang River and to calculate the chemical erosion rate in the basin, it is necessary to determine first the contribution of the atmospheric inputs (ions and CO_2) to the total river loads and to correct the river transport for these atmospheric inputs.

A simple mass balance model for the ionic budget can be written as follows (Meybeck, 1983):

Rock weathering + atmospheric inputs + human activities input = dissolved load. (1)

The mass balance approach requires the determination of an output-input budget with the determination of elemental origin. The chloride is usually used as an index for atmospheric input to rivers by the correction of sea salt or precipitation inputs.

3.1 Cl^- reference values

One usual approach for determining the amount of solutes derived from rainwater inputs is to multiply stream water Cl^- concentrations by the ion/ Cl^- ratios measured in precipitation/seawater (Stallard, 1981). This method assumes that all Cl^- of stream waters is derived from atmospheric inputs. The method also assumes that Cl^- is inert in natural environments and therefore behaves as a conservative tracer. Chloride ions behave conservatively through the hydrological cycle and the release of Cl due to rock weathering has not been showed clearly except in the weathering of salt rock (Meybeck, 1983). The absence of Cl-rich evaporites in the Dongjiang basin supports the validity of this assumption.

However, the atmospheric input contains three principal components: marine, terrestrial and anthropogenic. The terrestrial and anthropogenic sources are characterized by dominance of K, Ca, S and N (Stallard, 1981; Sarin, 1989). The marine components, which are transported through atmosphere to continents, have long been recognized as a significant source for some dissolved salts of surface water (Gibbs, 1970; Stallard, 1981; Sarin, 1989).

According to Meybeck (Meybeck, 1983), 72% of dissolved Cl^- is derived averagely from the atmospheric precipitation in the world watersheds despite that chloride can also result from a wide range of human activities. Chloride contents in the coal and/or fuel are less than 0.1% in

China, moreover, distribution regions of the high concentration SO_4^{2-} and NO_3^- (air pollution) are absolutely inconsistent with that of Cl^- in China (Duan, 2000). In summary, chloride ions of atmospheric deposition derived from human activities should be very low and thereby originate mainly from the sea salts. So they can be used as a reference of atmospheric inputs in the Dongjiang hydrological system.

For the mass balance equations, the highest concentration of Cl ions issued from the rainwater, termed Cl_{ref} , have to be determined. The Cl_{ref} is calculated with each mean weighted chloride content for the sampling station B and station C, multiplied by the concentration factor F of each region. This factor F represents the concentration effect of evapo-transpiration and is related to the total quantity of rainfall P (mm) and the evapo-transpiration process E (mm) by the Equation (2):

$$F = P / (P - E). \quad (2)$$

According to the climatic database, the factor F is approximately 1.6—1.7 on the investigated area. The equation to calculate the Cl_{ref} is as follows:

$$\text{Cl}_{\text{ref}} = [D_B \times (\text{Cl}^-)_B \times F + D_C \times (\text{Cl}^-)_C \times F] / (D_C + D_B). \quad (3)$$

Where D_B and D_C correspond to the monitored area proportions in the station B and C, respectively, $(\text{Cl}^-)_B$ and $(\text{Cl}^-)_C$ represent the Cl concentrations of atmospheric precipitation in the station B and C, respectively.

The Cl_{ref} is estimated to be 45.39—51.07 $\mu\text{mol/L}$ and represents the highest chloride concentration of the rainwater inputs to the Dongjiang River. The chloride concentration measured in the dissolved loads of the river is 41.97 $\mu\text{mol/L}$ averagely and hence is very similar to the Cl_{ref} . So the whole chloride content of the Dongjiang stream is assigned to the atmospheric precipitation origin, while the evaporite dissolution contribution is minimal. This is also in agreement with the granite lithology in the Dongjiang watershed. So the chloride is the most useful reference for rainwater input to river water and therefore used to quantify the precipitation input.

3.2 Atmospheric deposition correction model

To calculate the amount of rainwater-derived Ca^{2+} , Mg^{2+} , K^+ , Na^+ and SO_4^{2-} in streams, two methods are used to correct the precipitation contribution on the river water, that is, seawater correction and precipitation correction. One important concern of atmospheric correction to the dissolved load of rivers is how to know whether the dissolved load of rivers must be corrected for atmospheric inputs using local rainwater composition (i.e., precipitation correction, by the use of Cl-normalized rainwater ion ratios) or from its oceanic part (i.e., seawater correction, by the use of Cl-normalized seawater ion ratios, Table 3).

The major ion ratios of the seawater, rainwater and river

water throughout the Dongjiang basin are demonstrated as shown in Table 3. The stream water Cl^- concentrations are multiplied by the average rainwater/seawater ion/ Cl^- ratios. The correction formula for the ion M is as follows:

$$[M]'_r = [M]_r - ([M/\text{Cl}^-]_{s(p)} \times [\text{Cl}^-]_{\text{ref}}). \quad (4)$$

Where $[M]'_r$ refers to the ion concentration by the

atmospheric correction in the river, $[M]_r$ denotes the measured content in the Dongjiang River, $[M/\text{Cl}^-]_{s(p)}$ indicates the concentration ratio M/Cl^- in the seawater(s) or in the precipitation (p), $[\text{Cl}^-]_{\text{ref}}$ refers to the highest concentration of Cl ions issued from rainwater.

Table 3 Major ion equivalent concentration ratios in the seawater, rainwater and river water of the Dongjiang basin

Molar concentration ratios	Na^+/Cl^-	K^+/Cl^-	$\text{Ca}^{2+}/\text{Cl}^-$	$\text{Mg}^{2+}/\text{Cl}^-$	$\text{SO}_4^{2-}/\text{Cl}^-$
Seawater	0.86	0.02	0.04	0.21	0.11
Dongjiang precipitation	0.89	0.97	2.10	0.26	2.05
Dongjiang River water	6.22	1.04	4.52	2.13	1.61

Based on the above elemental ratios, combining with the concentration F factor, the contributions of natural wet fallout to the Dongjiang solute fluxes were calculated: Cl^- , 100%; K^+ , 1.92%; Ca^{2+} , 0.89%; Mg^{2+} , 9.86%; SO_4^{2-} , 6.82% and Na^+ , 13.8% on the basis of the

seawater ion molar ratios. As shown in Table 4, the estimated values of mean rainwater inputs for Dongjiang watershed were calculated. As a whole, the elemental contribution percent of precipitation on the dissolved substance was up to 4.90% of the Dongjiang River water.

Table 4 Estimated contribution percents of atmospheric precipitation to the dissolved loads in the Dongjiang basin(%)

Rivers	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
Dongjiang(seawater correction, this study)	13.8	1.92	0.89	9.86	100	6.82
Dongjiang(precipitation correction, this study)	14.3	93.3	45.4	12.2	100	70.7
Ganga(Sarin, 1989)	1.70	2.20	27.0	1.30	100	1.60
Amazon(Stallard, 1981)	0.10	1.30	6.90	0.40	17.6	3.60
World average(Meybeck, 1983)	6.00	19.0	53.0	27.0	72.0	42.0

Applying a marine correction to the dissolved loads means that surplus of Ca, Mg, K and other ions of rainwater are part of the continental weathering flux. However, above discuss approves that only chloride ions of the Dongjiang precipitation come wholly from sea salts, for other ions, terrestrial and anthropogenic sources may be important because of the following observations: (1) the pH values of local precipitation are far less than 5.60, showing an acid rain peculiarity; (2) moreover, it is confirmed that SO_4^{2-} abundances of local precipitation show a strong positive correlation with SO_2 emission produced by human activities (e. g., automobile, industrial emission, plastic burning; Qi, 1995) in the Zhujiang Delta. So the very high SO_4^{2-} concentrations of rainwater are mainly derived from high atmospheric SO_2 emission from anthropogenic origin in the Dongjiang basin; (3) the high Cl/ions ratios of Dongjiang precipitation vs. seawater (Table 3, e. g., K^+/Cl^- , $\text{Ca}^{2+}/\text{Cl}^-$) suggest that a majority of other ions (with the exception of Cl^-) may be originate from terrestrial and anthropogenic origins. For example, rainwater has a much higher $\text{SO}_4^{2-}/\text{Cl}^-$ ratio than seawater, most likely from anthropogenic emissions; (4) the TDS of local rainwater are far higher than a precipitation background value. These characteristics reflect that human activities have a significant influence on precipitation and river water chemistry in the Dongjiang basin. Rapid economic growth and increasing energy demand have resulted in serious air pollution problems throughout the Zhujiang Delta. The contribution of the anthropogenic source

to this river is probably significant, e. g., it is roughly estimated that over 90% of Mg^{2+} content is probably derived from anthropogenic activities because the highest concentration of marine inputs only accounts for ~10% of the river water in the Dongjiang River.

For comparison, in the same way, precipitation correction method is utilized to estimate the contributions of natural wet deposition to the Dongjiang dissolved substance as follows: Cl^- , 100%; K^+ , 93.3%; Ca^{2+} , 45.4%; Mg^{2+} , 12.2%; SO_4^{2-} , 70.7% and Na^+ , 14.3% (Table 4). The estimated percent of mean rain input to the Dongjiang River is ~19.5% of TDS and thus far higher than the estimated proportion based on seawater correction.

The Na and Mg charges of the Dongjiang stream water showed a similar influence from rainwater or marine aerosols. Ca^{2+} as well as the sum of SO_4^{2-} and K^+ represent a greater proportion of the cationic charge in rainwater compared to seawater. The higher proportion of Ca^{2+} may reflect the input of terrestrially derived solutes as throughout the Dongjiang basin.

On one hand, seawater correction is widely used in the inshore watershed (e. g., Dongjiang River). In such an approach, it supports the assumption of no atmospheric compositions from the human activities. Nevertheless, the Dongjiang basin is situated in the South China Coast where developed economy and dense population have resulted in the high-concentration acid precipitations. So the estimated results by seawater correction may be lower than the reality. On the other hand, the precipitation correction method is very

limited because of the following reasons: (1) the precipitation chemistry is highly variable with time and space; (2) it is difficult to attribute which part of ion concentrations is derived from human activity or terrestrial weathering, therefore the contribution proportion of continental weathering flux also has been included as anthropogenic origins. Hence the estimated results should be far higher than the actual proportions. The Cl-normalized seawater and rainwater have been used to correct the atmospheric contribution to dissolved loads of the Dongjiang River in this paper, respectively. It can be seen that the proportions of each element depending on two approaches are dissimilar to each other with the exception of Mg^{2+} and Na^+ . The actual contribution percentage should be within the estimated values by two correction approaches. In summary, it means that approximately 5%—20% of TDS of Dongjiang River is constituted of atmospheric precipitation. We clearly favor the above Cl-normalized seawater ratios for correcting atmospheric inputs in this study.

Compared with a world average value of 3.0% (Gaillardet, 1999), the Dongjiang River water is obviously affected by the local precipitation chemistry and several times higher than a world medial level. Among the major cations, rainwater inputs are the highest for K^+ , followed by Na^+ , Mg^{2+} , and Ca^{2+} . Rainwater also accounts for 6.8%—70% of stream water SO_4^{2-} . Accordingly, atmospheric precipitation inputs are significant since the proportions of local precipitation inputs contribute at least more than 5.0% of the total dissolved solutes in the Dongjiang River water. The higher contribution proportion of rainwater may be caused primarily by the local abundant precipitation and diluted TDS in the Dongjiang River.

3.3 Chemical weathering rate

No significant correlations between HCO_3^- and Ca^{2+}/Mg^{2+} may imply that they should be derived from different origins and hence HCO_3^- comes mostly from atmospheric CO_2 , rather than from the carbonates, consistent with the granite bedrock in the Dongjiang basin. Accordingly, the HCO_3^- flux would not be taken into account in estimating the atmospheric input proportion to the river and calculating the weathering rate because total alkalinities come wholly from the atmospheric CO_2 in the Dongjiang basin.

After correction for precipitation inputs, the dissolved load of a river represents the result of mixing of water derived from chemical weathering of main lithologies, here silicate rocks. In addition to major ions, the dissolved silica of the river should be calculated because it is wholly derived from silicate weathering. The rate of silicate (e.g., granite) weathering rate (CDR) is thus calculated using the soluble SiO_2 , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} and Na^+ dissolved concentrations from silicate weathering:

$$CDR = ([M]' + [Si]) \times Q/A, \quad (5)$$

$$([M]' = [Na^+]' + [K^+]' + [Ca^{2+}]' + [Mg^{2+}]' + [SO_4^{2-}]').$$

Where $[M]'$ refers to ion M concentration corrected by deducting the precipitation contribution part ($10^{-6} t/m^3$), Si represents the measured concentration of dissolved silica in the river ($10^{-6} t/m^3$), Q denotes average water discharge annually (m^3/a), A indicates the drainage area (km^2). For subsequent discussions, precipitation inputs are subtracted from the measured stream water concentrations listed in Table 1.

The so-calculated weathering rates amount to 27.94 mg/L (including the measured dissolved silica concentration of 5.59 mg/L) by using the elemental ratios of seawater, while 18.78 mg/L deduced by atmospheric precipitation correction. The corresponding silicate weathering fluxes are about 23.48 $t/(km^2 \cdot a)$ or 15.78 t/km^2 yearly, respectively. Consequently, the weathering rate in the Dongjiang watershed accounts for only 40%—60% of a world average value of 36 $t/(km^2 \cdot a)$.

The contribution of the atmospheric inputs to the dissolved loads transported by the Dongjiang River to the ocean is estimated for each chemical species as Table 4. The atmospheric inputs of Na^+ and Cl^- are closely related to the cyclic salts and those of K^+ , SO_4^{2-} , Ca^{2+} , and Mg^{2+} to terrestrial and anthropogenic emissions derived inside the basin. After corrections for atmospheric input (including CO_2), the mean riverine transport of dissolved material by the Dongjiang River is calculated as 5.58—8.30 $\times 10^5 t/a$, i.e., 15.78—23.48 $t/(km^2 \cdot a)$. The terrestrial weathering flux excluding atmospheric CO_2 represents only 21.5%—36% of the total dissolved river loads carried out to the ocean. The lower chemical weathering rate and lesser terrestrial weathering fluxes are closely associated with granite rocks with the strong capability of avoiding erosion. Silicate weathering rates calculated for the Dongjiang basin are higher on a global scale though the total weathering rate is lower than a world average. All evidences suggested that the Dongjiang basin is dominated by silicate weathering, which is entirely different with the Xijiang and Beijiang River. The lithology and climate (high temperature, high runoff) could be responsible for above features in the Dongjiang basin.

4 Conclusions

To critically evaluate the atmospheric wet deposition input to river poorly documented formerly, we have chosen the granite basin—Dongjiang and proved that the chloride ion of Dongjiang River is wholly from the sea salt. The atmospheric correction is complied with Cl_{ref} as the rainwater input. Subsequently, two approaches, that is, seawater correction (Cl-normalized seawater ratios) and precipitation correction (Cl-normalized precipitation ratios), are used to estimate the contribution proportions of local precipitation on

the solutes of the Dongjiang River. The Cl/ions ratios demonstrated that the precipitation chemistry of the Dongjiang basin is seriously influenced by the human activities. The estimated results revealed that local precipitation contributes 5%—20% of dissolved loads to the Dongjiang River, though the estimated values may be on the high or low side and under correction in future. The results showed the greater importance of local precipitation on the river solute compared to a world average in the Dongjiang basin. The chemical weathering rate was estimated to be 15.78—23.48 t/(km² · a) and only 40%—60% of the world average value in response to granite lithology in the Dongjiang basin. However, high runoff and high temperature can explain such feature that the silicate weathering rates calculated for the Dongjiang basin are higher on a global scale.

References:

- Berner E, Berner R, 1987. The global water cycle: geochemistry and environment. prentice-hall[M]. USA: Englewood Cliffs. 397.
- Berner E K, Berner R A, 1996. Global environment: water, air and geochemical cycles[M]. New Jersey: Prentice Hall.
- Chen J S, Xie G B, Li Y H, 1991. Denudation rate of Hainan Island and its comparison with Taiwan Island and Hawaiian Islands [J]. Quaternary Sciences, (4): 289—299.
- Chen J S, Chan M, 1992. Chemical characteristics and genesis of major ions of the rivers in Hainan Island[J]. Tropical Geography, 12(3): 272—281.
- Chen J S, Xia X H, Cai X Y, 1998a. Evolution trend and analysis of major ion contents in the mainstream and some tributaries of Yangtze River in Sichuan and Guizhou provinces[J]. China Environmental Science, 18(2): 131—135.
- Chen Z S, 1998b. Record of Chinese bay (Volume 14) [M]. Chinese Ocean Press. 246—332.
- Chen J S, Xia X H, Hong S, 2000. A study of water-quality acidification trend of Changjiang and condensation trend of Huanghe and their controlling factors [J]. China Engineering Science, 2(3): 54—58.
- Datta D K, Subramanian V, 1997. Nature of solute loads in the rivers of the Bengal drainage basin, Bangladesh[J]. Journal of Hydrology, 198: 196—208.
- Duan L, Hao J M, Xie S D *et al.*, 2000. Critical loads of acidity for surface waters in China[J]. The Science of the Total Environment, 246: 1—10.
- Gaillardet J, Dupre B, Louvat P *et al.*, 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers [J]. Chemical Geology, 159: 3—30.
- Galy A, Lanord C F, 1999. Weathering processes in the Granges-Brahmaputra basin and the riverine alkalinity budget [J]. Chemical Geology, 159: 31—60.
- Gibbs R J, 1970. Mechanisms controlling world water chemistry [J]. Science, 170: 1088—1090.
- Grasby S E, Hutcheon I, 2000. Chemical dynamics and weathering rates of a carbonate basin Bow River, southern Alberta [J]. Applied Geochemistry, 15: 67—77.
- Grosbois C, Negrel P, Fouillac C *et al.*, 2000. Dissolved load of the Loire River: chemical and isotopic characterization [J]. Chemical Geology, 170: 179—201.
- Liu J Q, William C K, Wu G P, 1993. Study of precipitation background values in Lijiang, China [J]. China Environmental Science, 13(4): 246—251.
- Meybeck M, 1983. Atmospheric inputs and river transport of dissolved substances [C]. Dissolved loads of rivers and surface water quantity. Proceedings of the Hamburg Symposium, 173—191.
- Meybeck M, Ragu A, 1996. River discharges to the oceans. An assessment of suspended solids, major ions and nutrients. Environmental Information and Assessment [M]. UNEP/WHO, UNEP, Nairobi. 245.
- Nakaganu Y, Iwatsubo G, 2000. Water chemistry in a number of mountainous streams of East Asia [J]. Journal of Hydrology, 240: 118—130.
- Qi L W, Wang W X, 1995. Precipitation chemistry and trends of rainwater acidification at the low latitude and subtropics of China [J]. Research of Environmental Sciences, 8(1): 12—20.
- Quan W Z, 1992a. Regional distribution and developing trend of acid rainwater in the Guangzhou [J]. Guangzhou Environmental Sciences, 11(1): 11—18.
- Quan W Z, 1992b. A study on the actuality and trend of acid deposition in Guangzhou City [J]. Shanghai Environmental Sciences, 11(1): 20—23.
- Roy S, Gaillardet J, Allegre C J, 1999. Geochemistry of dissolved and suspended loads of the Seine River, France: anthropogenic impact, carbonate and silicate weathering [J]. Geochimica et Cosmochimica Acta, 63(9): 1277—1292.
- Sarin M M, Krishnaswami S, Dilli K *et al.*, 1989. Major ion chemistry of the Ganga-Brahmaputra river system: weathering processes and fluxes to the Bay of Bengal [J]. Geochimica et Cosmochimica Acta, 53: 997—1009.
- Stallard R F, Edmond J M, 1981. Geochemistry of the Amazon. 1. Precipitation chemistry and marine contribution to the dissolved load at the time of peak discharge [J]. Journal of Geophysical Research, 86: 9844—9858.
- Wang M R, 1992. Chemistry of acid deposition on the mountains in south China during spring [J]. Acta Scientiae Circumstantiae, 12(1): 37—47.
- Wu J Z, Huang A Z, 1989. Natural ion characteristics in the Zhujiang water system [J]. Demotic Zhujiang, (2): 14—18.
- Xu B X, 1991. Rainfall monitoring and its physicochemical characteristics in the east suburb of Guangzhou [J]. Research of Environmental Sciences, 4(5): 50—54.
- Yang Y T, Su W G, Mao W F, 1996. Regional characteristics of the chemical composition of precipitation in the Pearl River Delta [J]. Chongqing Environmental Sciences, 18(2): 5—9.
- Yao X H, Cui P, Gao H W *et al.*, 1998. The mechanism of reaction between sea salt with atmospheric pollutants to acidify rainwater in coastal area [J]. Environmental Science, 17(4): 320—325.
- Zhang C S, Wang L J, 2001. Multi-element geochemistry of sediments from the Pearl River system, China [J]. Applied Geochemistry, 16(9—10): 1251—1259.
- Zhang J, Huang W W, Letolle R, 1995. Major element chemistry of the Huanghe, China—Weathering processes and chemical fluxes [J]. Journal of Hydrology, 168: 173—203.
- Zhang L T, 1999. Regional distribution of total ion contents in Zhujiang River system and the relationship between total ion contents and natural factors [J]. Acta Scientiarum Naturalium Universitatis Sunyatseni, 38(5): 104—108.
- Zhang Q Y, Lin F, Li X *et al.*, 1985. Major chemical compositions and dissolved fluxes of coastal rivers in the southeast China [J]. Acta Oceanologica Sinica, 7(5): 561—566.

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