

Major element chemistry in the upper Yangtze River: A case study of the Longchuanjiang River

Siyue Li ^a, X.X. Lu ^{a,b,*}, Min He ^b, Yue Zhou ^b, Rongta Bei ^c, Li Li ^b, Alan D. Ziegler ^a

^a Department of Geography, National University of Singapore, 117570, Singapore

^b Global Change and Watershed Management Center, Yunnan University of Finance and Economics, Kunming 650221, China

^c Faculty of Environmental Science and Engineering, Southwest Forestry University, Yunnan Kunming 650024, China

ARTICLE INFO

Article history:

Received 19 May 2010

Received in revised form 14 January 2011

Accepted 14 January 2011

Available online 3 February 2011

Keywords:

Cations

Anions

Chemical weathering

CO₂ consumption

Anthropogenic activity

Yangtze (Changjiang) River basin

ABSTRACT

Water samples were collected twice per month over a two-year period from the Longchuanjiang River (Yunnan Province, China) to understand monthly variations in major elements and solute fluxes as related to rock weathering and associated CO₂ consumption rates. Solute concentrations were 5 times the median of 65 mg/l for global average. Total cationic exchange capacity (Tz⁺) ranged from 2.4 to 6.1 meq/l; and the mean (4.4 meq/l) was significantly higher than that of the global river waters. Calcium and bicarbonate dominated the annual ionic composition, accounting for more than 70% of the solute flux that exceeded 71×10^6 kg/yr. Lower concentrations of most measured elements during the monsoon high flow period could be explained by dilution effects from precipitation. Three major reservoirs contributed to the dissolved load: carbonates, silicates and anthropogenic inputs, i.e., some 83% of the riverine cations from carbonates and 17% from silicates. The chemical weathering rate of 26.1 t/km²/yr, with respective carbonate and silicate weathering rates of 20.3 t/km²/yr (8.46 mm/kyr) and 5.75 t/km²/yr (2.13 mm/kyr), was comparable to the average for global rivers, but higher than that for the Changjiang River in China. The CO₂ consumption rate was estimated to be 173.7×10^3 mol/km²/yr and 202.9×10^3 mol/km²/yr by silicate and carbonate weathering, respectively. The CO₂ consumed by rock chemical weathering in the upper Changjiang River reduced the atmospheric CO₂ level and constituted a significant part of the global carbon budget. Consequently the carbon sink potential of rock chemical weathering in the Qinghai-Plateau deserves extra attention. Population density and anthropogenic activities, particularly agricultural practices, contributed remarkably to dissolved solutes and associated CO₂ consumption worldwide, and anthropogenic inputs probably contributed some 10.4% to the dissolved solutes in the Longchuanjiang River.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The dissolved composition of rivers provides indications of the chemical weathering of rock/soil, weathering rates and associated CO₂ consumption within their associated drainage basins (Hu et al., 1982; Stallard and Edmond, 1983, 1987; Sarin et al., 1989; Gaillardet et al., 1997, 1999; Galy and France-Lanord, 1999; Chen et al., 2002; Li and Zhang, 2008; Li et al., 2009a). The conversion of atmospheric CO₂ to aqueous HCO₃⁻ and CO₃²⁻ during the chemical weathering of silicates and carbonates may also represent an important carbon sink at various scales (Berner and Kothavala, 2001). Recent investigations of the chemical weathering-atmospheric CO₂ consumption in several of the large world rivers have demonstrated that elemental signatures are not only related to physical basin characteristics (i.e., lithology and

precipitation), but also increasingly to anthropogenic processes (Chen et al., 2002; Meybeck, 2003a). Notable investigations included those conducted in the Amazon (Gibbs, 1972; Stallard and Edmond, 1981, 1983, 1987; Amiotte-Suchet and Probst, 1993; Gaillardet et al., 1997; Mortatti and Probst, 2003), Congo (e.g., Amiotte-Suchet and Probst, 1993; Probst et al., 1994); Ganges-Brahmaputra (Sarin et al., 1989; Galy and France-Lanord, 1999); Pearl River (Xu and Liu, 2007; Zhang et al., 2007; Gao et al., 2009), Yellow River (Li and Zhang, 2005; Wu et al., 2005; Chen et al., 2007) and Yangtze River (Hu et al., 1982; Chen et al., 2002; Han and Liu, 2004; Chetelat et al., 2008; Li and Zhang, 2008, 2009; Wu et al., 2008a, b). Two of the large continental Chinese rivers, the Pearl and the Changjiang (Yangtze) Rivers, have some of the highest elemental fluxes to the oceans in the world: TDS = 100×10^3 and 86×10^3 kg/km²/yr, respectively (Chen et al., 2002; Zhang et al., 2007), versus a world mean of about 40×10^3 kg/km²/yr (Galy and France-Lanord, 1999). These high fluxes are indicative of aggressive weathering in headwater tributaries, thus large-scale studies may underestimate some regional and small streams.

Recent investigations of the fluvial geochemistry of headwater tributaries of the Changjiang River reported wide ranges in the

* Corresponding author at: Department of Geography, National University of Singapore, 1 Arts Link, 117570, Singapore. Tel.: +65 65166135; fax: +65 67773091.
E-mail address: geoluxx@nus.edu.sg (X.X. Lu).

concentration of TDS, i.e. 190 to 1200 mg/l (Wu et al., 2008a, b). High seasonal variability largely reflected high heterogeneity of landscape features in the region (e.g., lithology and land use), with the highest values in the rivers draining basins with aggressive chemical weathering rates, such as those of the Qinghai–Tibet plateau (QHTP) (Galy and France-Lanord, 1999; Gaillardet et al., 1999; Wu et al., 2008a). Despite recent advances, more research is needed to ascertain the extent of natural versus anthropogenic phenomena associated with the elemental chemistry of rivers in the region. This paper reported the findings of a two-year investigation on this issue in the Longchuanjiang River, a previously unstudied tributary of the Changjiang River in southwest China.

2. Study area

The 231-km Longchuanjiang River originates near Nanhua County and joins the lower Jinshajiang River, a tributary of the upper Changjiang River (Fig. 1). Situated in southwest China, the river drains an area of 5560 km² (24°45'N–26°15'N and 100°56'E–102°02'E). The 1788 km² upper catchment (the upper Xiaohékou station) has a sub-tropic monsoon climate, characterized by annual mean temperature of 15.6 °C, and annual rainfall of 825 mm with more than 80% of the annual total occurring in the rainy season from May to October (Lu, 2005; Zhu et al., 2007, 2008). Elevation varies from 700 to 3000 masl. The Jinshajiang including the Longchuanjiang drains the Tethyan Himalayan Tectonic Belt and the Sanjiang Fold Belt. The basement of rocks of the Longchuanjiang River is overlain with a sedimentary cover that is Permian to Quaternary in age and composed of Permian clastic rocks, continental basalts, Triassic carbonate rocks and Quaternary fluvial deposits. Also Precambrian granitoids and high-grade metamorphic rocks are sparsely exposed. Among which, carbonates are widely spread and abundant throughout the drainage basin (Wu et al., 2008a, b).

The area is dominated by purple soil (belonging to skeletal primitive soils in the Chinese classification of the China National Soil Survey,

1992), which is very susceptible to water erosion and weathering. The soils are mainly composed of weathered limestone, rich in phosphorous and potassium while lacking in organic matter. However, erosion has been accelerated by deforestation (in earlier times), intensified agriculture activity, reservoir building, stone excavation and road construction. For example, forest cover in the catchment declined from 36.9% in 1949 to 24.7% in 1985, followed by a gradual recovery in the late 1990s due to a series of water and soil conservation programs, and the vegetated land cover increased to 86% in 2005 (Fig. 2). In the meantime, as the central government changes its focus of economic development to western inland China, land-use changed greatly, e.g. the total road length in the catchment drastically increased from 451 km in 1949 to 14,801 km in 2002 (Lu, 2005; Zhu et al., 2007, 2008).

There are two main cities such as Nanhua county and Chuxiong city along the upper Longchuanjiang River. In the past 20 years, population increased to a density of 113 people/km² in 2005, and the proportion of urban area in the drainage basin increased from 0.4% in 1990 to 1.8% in 2005 (Fig. 2). With economic development of the western interior, Gross Domestic Product (GDP) ca. 7600 was enhanced by the primarily industrial activities of mining, metallurgy etc. (<http://www.cxz.gov.cn/>).

3. Methods

Monthly precipitation and daily discharge were recorded by station staff at the Xiaohékou discharge gauging locating in the Chuxiong County (Fig. 1). Water samples for chemical analysis were collected twice a month over a two-year period (September 2007 to August 2008) using the same mechanized pulley system employed by the station workers to determine the discharge rating curve. A total of 48 samples were collected in the center of the river at a depth of 10 cm in acid-washed 5-l high density polyethylene (HDPE) containers. Samples were filtered immediately through pre-washed 47-mm diameter Whatman Nucleopore filters (0.45-μm pore) into three 120-ml HDPE bottles and

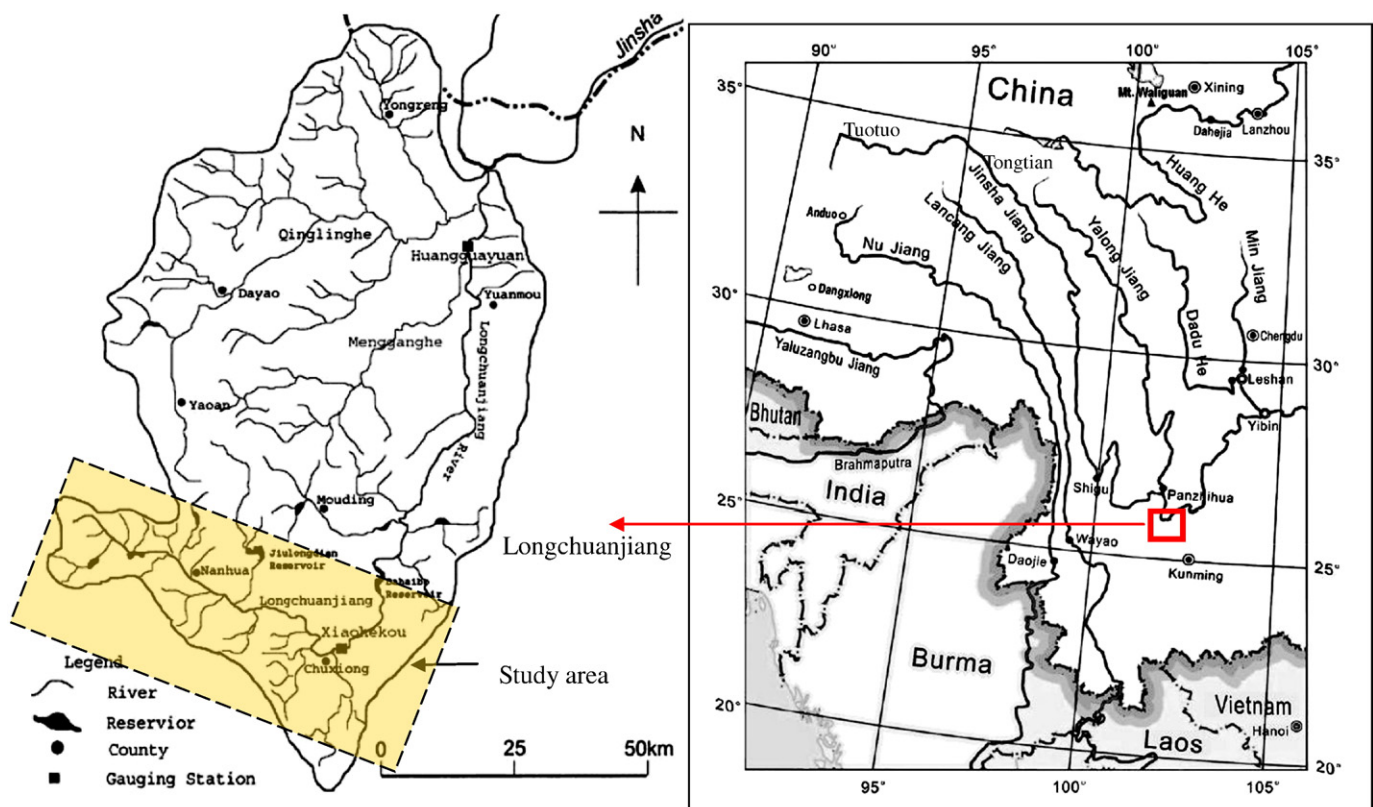


Fig. 1. Map of the Longchuanjiang River with sampling sites and gauge stations, and other Changjiang tributaries, China.

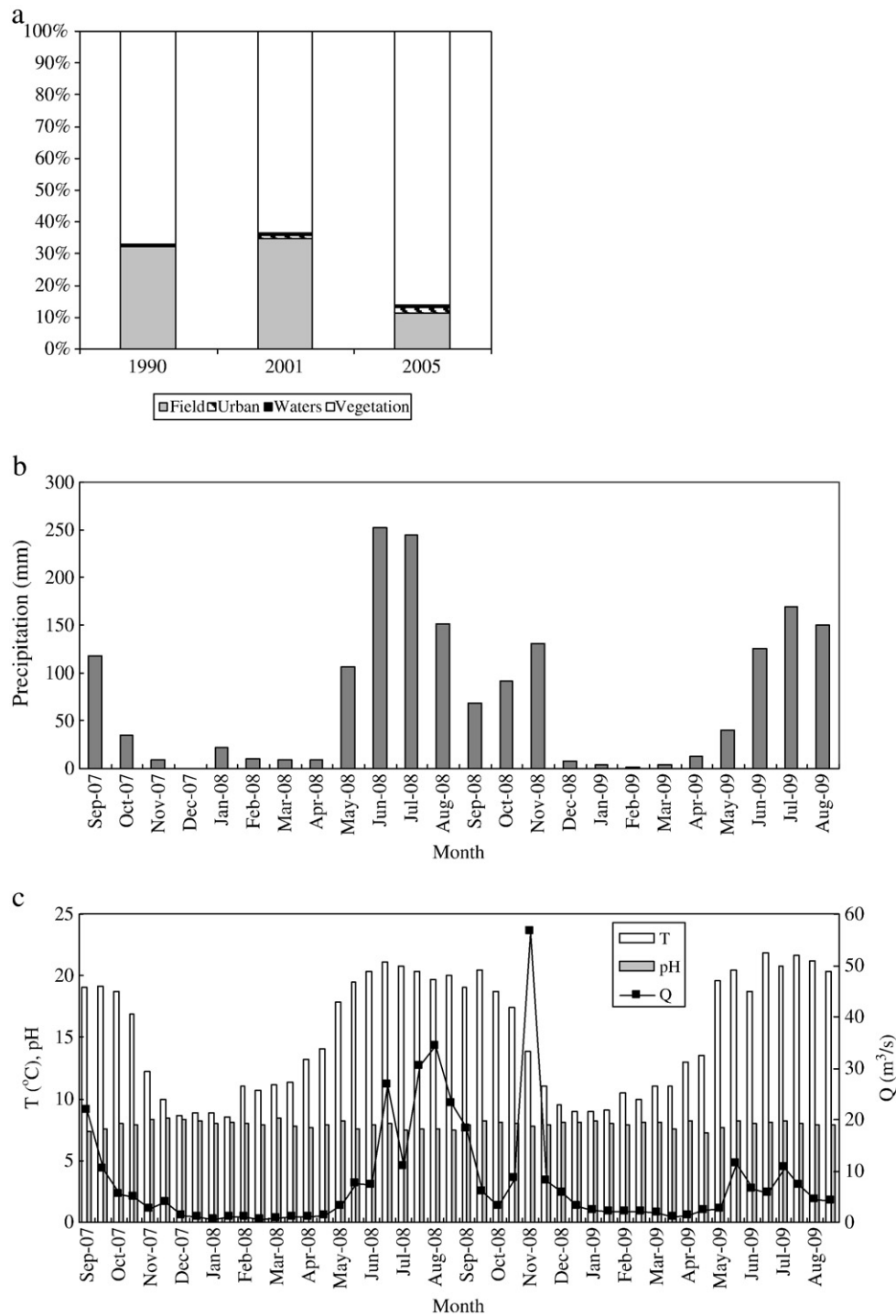


Fig. 2. Land use/land cover composition (a) and hydro-climatic characteristics including monthly precipitation (mm) (b), pH, water temperature (°C) and water discharge (m³/s) (c) of the upper Longchuanjiang River during the time period of 2007–2009 (observed at the Xiaohoukou hydrological station) (land use/land cover composition is sourced from Ding et al. (2009) and Li et al. (2009b); field includes paddy and dry fields, urban includes urban and residents, vegetation includes broad-leaved forest, coniferous forest and grassland).

stored at 4 °C until analysis. Filtrates were acidified (pH < 2) with ultra-purified 6 M HNO₃ prior to refrigeration.

Determination of pH was performed *in situ* using an Orion 230A pH/Temp meter, which was calibrated at each sampling occasion using pH-7 and pH-10 buffer solutions. Major cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) and dissolved silica were determined for each of the three replicates by inductively coupled plasma-optical emission spectroscopy. Anions Cl[−] and SO₄^{2−} were determined by ion chromatography; HCO₃[−] was titrated using 0.025 mol/l hydrochloric acid on the sampling day. Analysis precision was better than ± 5%.

4. Results

4.1. Hydro-climatology

Mean water temperature during the study was 15.3 °C; minimum and maximum values were 8.6 (January) and 21.9 °C (June), respectively. Monthly precipitation varied from 7 mm (December) to 253 mm (June) in 2008; approximately 95% of the total fell between May and November (Fig. 2). A total 1045 mm of precipitation in 2008 was more than the annual mean 825 mm (Lu, 2005), in part

because of one large late season storm in November (Fig. 2). Consequently, river discharge was the highest in November 2008 (57 m³/s); the minimum low-flow value occurred in February 2008 (0.44 m³/s). Mean daily discharge for the entire two-year study period was about 8 m³/s (Fig. 2). River flow can be divided into two regimes that correspond to the monsoon climate: low-flow (December through April) and high-flow (May through November).

4.2. Major element chemistry

The Longchuanjiang River waters were mildly alkaline: pH ranged from 7.2 to 8.4 (Fig. 2). Total dissolved solids ranged from 220 to 433 mg/l; and the annual flow-weighted mean was 287 mg/l (Fig. 3, Table 1). Similar to most of the Changjiang's tributaries, water composition was dominated by Ca²⁺ and HCO₃⁻, which made up >75% of the total dissolved load (Tables 1 and 2, Fig. 3). Ca²⁺ concentration

varied from 34 to 90 mg/l; HCO₃⁻ from 145 to 257 mg/l. Annual flow-weighted means of major cations decreased in the following order: Ca²⁺ (49 mg/l) > Na⁺ (11 mg/l) > K⁺ (8 mg/l) > Mg²⁺ (6 mg/l). Annual flow-weighted means of major anions decreased as follows: HCO₃⁻ (172 mg/l) > SO₄²⁻ (28 mg/l) > Cl⁻ (8 mg/l) > Si (5 mg/l) (Table 1). Two-thirds of the annual cation load was made up of Ca²⁺; HCO₃⁻ made up 81% of the anions (Table 1).

The total cationic charge ($Tz^+ = Na^+ + K^+ + 2 Mg^{2+} + 2 Ca^{2+}$) ranged between 2.4 and 6.1 meq/l with an average of 4.4 meq/l, 3.5 times higher than the average of the Changjiang River (2.8 meq/l) while close to the Wujiang River (4.14 meq/l) (Han and Liu, 2004), a tributary of the Changjiang River draining the karst terrain controlled by carbonate dissolution. Mean Tz^- was 4.1 meq/l, with values ranging between 2.9 and 5.2 meq/l. The mean normalized inorganic charge balance (NICB = $(Tz^+ - Tz^-)/Tz^+$) was 5.8%, with the majority

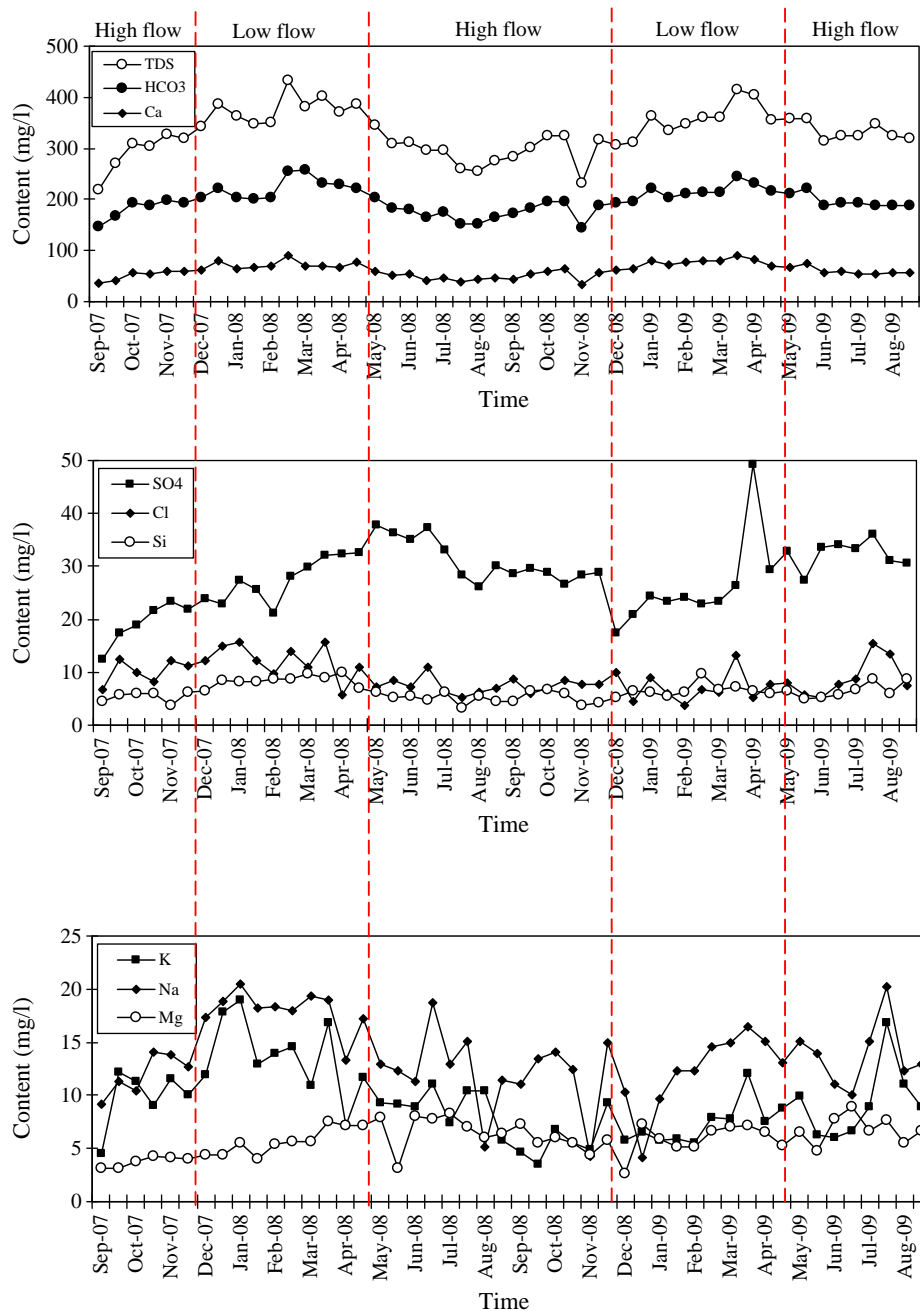


Fig. 3. Seasonal variations in major elements in the Longchuanjiang River, China.

Table 1Seasonal concentrations and flow-weighted means (derived from Figs. 2 and 3, unit in mg/l except Q in m³/s).

	Ca ²⁺	Na ⁺	K ⁺	Mg ²⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Si ⁻	TDS	Q
<i>Annual measurements</i>										
Mean	61.5	13.66	9.4	5.87	197.67	28.06	8.98	6.39	330.81	7.92
Stdev	13.56	3.79	3.63	1.54	25.76	6.44	3.2	1.65	44.88	10.79
Max	89.76	20.53	18.93	8.87	257.3	49.23	15.68	9.92	433.07	56.66
Min	34.45	4.2	3.52	2.69	144.74	12.45	3.81	3.26	219.92	0.44
Max/min	2.61	4.89	5.38	3.30	1.78	3.95	4.12	3.04	1.97	128.77
<i>Seasonal measurements</i>										
Mean low flow	73.5	15.16	10.53	5.78	218.69	26.85	9.71	7.49	366.19	1.71
Mean high flow	52.93	12.58	8.59	5.93	182.65	28.92	8.45	5.61	305.54	12.35
Dilution	-20.57	-2.58	-1.94	0.15	-36.04	2.07	-1.26	-1.88	-60.65	10.64
Dilution	-27.99%	-17.02%	-18.42%	2.60%	-16.48%	7.71%	-12.98%	-25.10%	-16.56%	622.22%
<i>Flow-weighted values</i>										
Annual	48.6	11.27	8.04	5.81	172.18	28.1	7.97	5.12	286.83	na
Low flow	71.82	13.26	8.75	5.46	212.31	25.01	8.65	6.9	351.46	na
High flow	46.31	11.07	7.97	5.85	168.21	28.4	7.9	4.94	280.44	na
Dilution	-25.52	-2.19	-0.78	0.39	-44.11	3.39	-0.75	-1.96	-71.02	na
Dilution	-35.53%	-16.54%	-8.92%	7.12%	-20.77%	13.56%	-8.62%	-28.43%	-20.21%	na
<i>Contribution to total cations or anions</i>										
Annual	65.93%	15.29%	10.91%	7.88%	80.70%	13.17%	3.74%	2.40%	na	na
Low flow	72.33%	13.35%	8.81%	5.50%	83.96%	9.89%	3.42%	2.73%	na	na
High flow	65.04%	15.55%	11.19%	8.22%	80.31%	13.56%	3.77%	2.36%	na	na

Values are flow-weighted for the low-flow periods (December through April, n = 20), high-flow periods (May through November, n = 28), and the entire data set. Percents are determined for respective cation or anion class.

of the samples being within $\pm 10\%$ of the mean (Fig. 3). The anionic charge (Tz^-) was strongly correlated with Tz^+ ($r = 0.89$, $p < 0.01$). Considering the absences of nitrate (varying from 44.6 to 140.7 $\mu\text{mol/l}$ with an

average of 70.4 $\mu\text{mol/l}$) and DOC (varying from 5.2 to 15.4 mg/l with an average of 8.5 mg/l; unpublished), the NICB was considered to be in balance.

Table 2

Comparison of chemical compositions in the Longchuanjiang River and other tributaries of the Changjiang River, China.

Basins	Area \times 10 ⁴ km ²	Discharge \times 10 ⁹ m ³ /yr	Na ⁺ $\mu\text{mol/l}$	K ⁺ $\mu\text{mol/l}$	Ca ²⁺ $\mu\text{mol/l}$	Mg ²⁺ $\mu\text{mol/l}$	Cl ⁻ $\mu\text{mol/l}$	SO ₄ ²⁻ $\mu\text{mol/l}$	HCO ₃ ⁻ $\mu\text{mol/l}$	Si $\mu\text{mol/l}$	TDS mg/l
<i>Annual values</i>											
Longchuanjiang	0.1788	0.25 \pm 0.34	593.9 \pm 264.9	240.9 \pm 93.2	1537.4 \pm 678.0	244.4 \pm 128.1	252.9 \pm 90.0	292.3 \pm 134.2	3240.4 \pm 422.2	228.4 \pm 59.0	330.8 \pm 44.9
Jinshajiang ^{a**}	39.4	145	412	36.4	940	475	213	110	2870		153
Jinshajiang ^b	39.4	145	783	42	805	404	557	221	2300	152	256
Tuotuo River ^a	1.6		10,609	278	1285	1275	12,857	1354	4614	143	1204
Tongtian River ^a	13.8		3483	103	1408	883	2286	470	4903	470	590
Han River ^c	9.52	41.1	102.1	18.1	884.2	393	157.4	302.6	2464.2	100.9	
Changjiang (mean) ^d	181	899	Na ⁺ + K ⁺ = 9.7 mg/l	807.5	345.8	156.2	177.1	2109.8	103.3	202.2	
Global averages (median) ^e			160.9	28.2	200	100	109.9	51	500	145*	65
<i>Low flow period values</i>											
Longchuanjiang	0.1788	0.25 \pm 0.34	651.8	270.5	1807.8	234.3	278.5	275.7	3550.7	259.2	362.3
Minjiang ^f	3.7	14.9	996	102.8	1605	571	480	476	4127	157	445
Lancang Jiang ^f	8.9	29	1013	36.2	1555	725	646	625	3925	157	434
Daduhe ^f	8.9	61.6	183	30.8	1030	493	35	213	2836	139	257
Nujiang ^f	11	53.1	343	30.5	998	546	44	341	2793	361	276
Yalong Jiang ^f	12.9	55.3	187	22.8	890	463	35	100	2712	136	233
Jinshajiang ^f	23.3	39.4	1026	35.4	1235	646	726	279	3835	164	385
<i>High flow period values</i>											
Longchuanjiang	0.1788	0.25 \pm 0.34	544.9	215.9	1308.7	253	231.3	306.3	2977.9	202.3	304.2
Minjiang ^f	3.7	14.9	417	53.1	1228	393	100	302	2901	135	190
Lancang Jiang ^f	8.9	29	306	25.1	1445	458	184	279	3466	126	327
Daduhe ^f	8.9	61.6	102	35.4	828	304	11	92	2198	107	190
Nujiang ^f	11	53.1	137	26.9	1088	409	21	220	2728	115	249
Yalong Jiang ^f	12.9	55.3	241	29.7	815	425	22	192	2318	111	211
Jinshajiang ^f	23.3	39.4	2391	58.5	1100	533	1269	388	3858	105	436

*Meybeck, 2003b.

^a Wu et al., 2008b (**1987 data, others using 2005 data; whole catchment for Jinshajiang).^b Chetelat et al., 2008 (2006 data; whole catchment for Jinshajiang).^c Li et al., 2009a (2005–2006 data).^d Chen et al., 2002 (1958–1990 data).^e Meybeck and Helmer, 1989.^f Wu et al., 2008a (2005 data; upper Shigu for Jinshajiang).

Cumulative flux of TDS and major ions in the considered two-year period decreased as flows: TDS (109,005 g/s) > HCO_3^- (65,432 g/s) > Ca^{2+} (18,470 g/s) > SO_4^{2-} (10,678 g/s) > Na^+ (4282 g/l) > K^+ (3056 g/s), Cl^- (3029 g/s) > Mg^{2+} (2209 g/s) > Si (1944 g/s) (Fig. 4). These fluxes increased greatly in the high flow period with good relationships with water discharge ($r > 0.90$, except 0.79 for Na, $p < 0.01$) (Fig. 4). The total dissolved flux transported by the upper Longchuanjiang River accounted for 0.47% of that by the Changjiang River. Considering its small drainage area, the TDS yield, reflecting chemical weathering rate, was adopted. Our results showed that TDS yield was much lower than that in the Changjiang and its tributaries, the Pearl River, Amazon and Ganges–Brahmaputra Rivers, but much higher with respect to Yellow, Congo and Lena Rivers, and comparable to the riverine yield in the world (Tables 2 and 3).

Total dissolved solids, Ca^{2+} , HCO_3^- and Si all demonstrated moderately strong correlations with water discharge, demonstrating the role of dilution from runoff water during high-flow periods (Fig. 5). Power functions provided the best fit for this negative relationship (Fig. 5), while the power index, significantly lower than 1, demonstrated that the seasonal variability in the concentrations of TDS and major ions was small compared to great variations (0.4–56.7 m^3/s) in water discharge (Figs. 2 and 3). The correlation between discharge and the other ions was non-existent or weak ($R^2 < 0.2$). Cation Ca^{2+} and anion HCO_3^- showed distinct dilution of 26–44 mg/l in flow-weighted concentration during the high-flow period (Table 1). Dilutions for Na^+ , K^+ , Cl^- and Si were all small (1–2 mg/l). In terms of percentage change in respective cation or anion class, Na^+ , K^+ , and Mg^{2+} increased in the high-flow period, as did the anions Cl^- and SO_4^{2-} (Table 1). These increases came at the expense of Ca^{2+} and HCO_3^- (Table 1). Surprisingly, Mg^{2+} and SO_4^{2-} increased by 1–3 mg/l.

5. Discussion

5.1. Sources of solutes

Mechanisms controlling riverine water chemistry include rock weathering, atmospheric precipitation, evaporation–crystallization processes, and anthropogenic activities. The fact of abundance in carbonate rocks in the drainage catchment and several indicators in the aqueous data suggested that the major ion chemistry in the Longchuanjiang River was likely to be dominated by the chemical weathering of carbonates: e.g., (a) the very low ratios of $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$ (<0.08) and $\text{Na}^+/(\text{Na}^+ + \text{Ca}^{2+})$ (<0.31) and moderate TDS

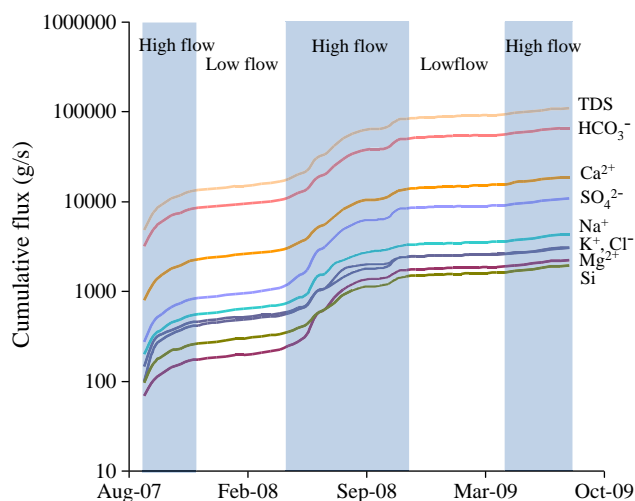


Fig. 4. Cumulative fluxes in the considered periods of the Longchuanjiang River, China.

Table 3
Fluxes and yields of dissolved elements in the Longchuanjiang and other rivers.

River	Area × 10 ⁶ km ²	Discharge × 10 ⁹ m ³ /yr	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	SiO ₂	TDS	Reference
Longchuanjiang	0.001788	0.25	2.81	2.01	12.13	1.45	1.99	7.02	42.99	2.74	71.62	This study
Changjiang	1.8	899	4500 ^a	1.57	6.79	0.81	1.11	3.92	24.04	1.52	40.06	Chen et al., 2002
Yellow River	0.75	32.9	1800 ^a	2.5	15	3.17	2.11	5.94	56.2	5.61	85.5	
Pear River	0.42	283.3	2360	2.40	1200	700	1500	2500	5500	27	13,100	Chen et al., 2007
Amazon	4.69	6930	10,800	5.62	6890	1150	770	2570	27,900	0.04	41,800	Zhang et al., 2007
Congo	3.7	1282	2600	2.30	5600	2200	3500	5200	9200	18.72	69.21	Stallard and Edmond, 1983
Ganges–Brahmaputra	1.48	1071	4200	0.70	18,500	4500	2100	12,700	72,300	12,400	42,300	
Lena	2.44	532	3300	2.84	7200	1700	4500	4800	25,800	2900	50,600	Probst et al., 1994
World total	101	37,400	195,000	1.35	500,000	126,000	217,000	202,000	1,946,000	609,000	3,843,000	Galy and France-Lanord, 1999
			1.93	0.48	4.95	1.25	2.15	2.00	19.27	6.03	38.05	Galy and France-Lanord, 1999

Units: Flux $\times 10^6 \text{ kg}/\text{yr}$; Yield $\times 10^3 \text{ kg}/\text{km}^2/\text{yr}$.

^a Sum of Na^+ and K^+ .

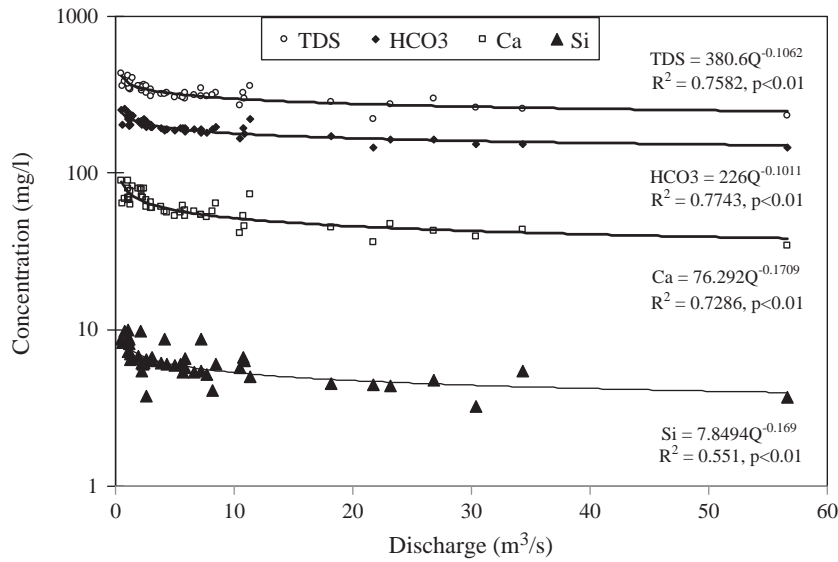


Fig. 5. Major elements vs. water flows at Xiaohokou Gauge station in the Longchuanjiang River, China.

(<450 mg/l) in Gibbs (1970) plots (Fig. 6); and (b) the position of Ca²⁺ and HCO₃⁻ at the apexes of the cation and anion ternary plots (Fig. 7).

Stoichiometry indicates the sources of several ions (Stallard and Edmond, 1983; Han and Liu, 2004). For example, equivalent mole ratios of Na⁺/Cl⁻ and (Na⁺ + K⁺)/Cl⁻ that were much higher than one (Fig. 8a) were indicative of Na⁺ and K⁺ sourcing from sodium and potassium aluminosilicate weathering and anthropogenic emissions, rather than the weathering of chloride evaporate such as halite. The equivalent mole ratios of (Ca²⁺ + Mg²⁺)/(SO₄²⁻ + HCO₃⁻) of approximately 1, along with a slight excess of SO₄²⁻ + HCO₃⁻ were indicative that extra HCO₃⁻ was contributed by silicate weathering (Fig. 8b). The high equivalent ratio of (Ca²⁺ + Mg²⁺)/Tz⁺ (0.7–0.9) (Fig. 8c) and low ratio of (Na⁺ + K⁺)/HCO₃⁻ (0.2–0.4) (Fig. 3) were indicative of a small contribution of silicates to dissolved solutes.

Carbonate dissolution mainly by carbonic acid was suggested by (a) equivalent ratios of (Ca²⁺ + Mg²⁺)/HCO₃⁻ around unity; (b) low SO₄²⁻/HCO₃⁻ ratios; and (c) the location of these signatures well away from the trend line characterizing carbonate mineral dissolution by both carbonic and sulfuric acids (Fig. 8d). Further, Fig. 8e illustrated approximately 94% (73%–114%) of HCO₃⁻ balanced by Ca²⁺ and the low equivalent ratio of Mg²⁺/Ca²⁺ (<0.3, varying from 0.07 to 0.31 with an average of 0.17), indicated a minor contribution to solutes by dolomite compared with limestone. Mg²⁺ showed positive correlations with SO₄²⁻

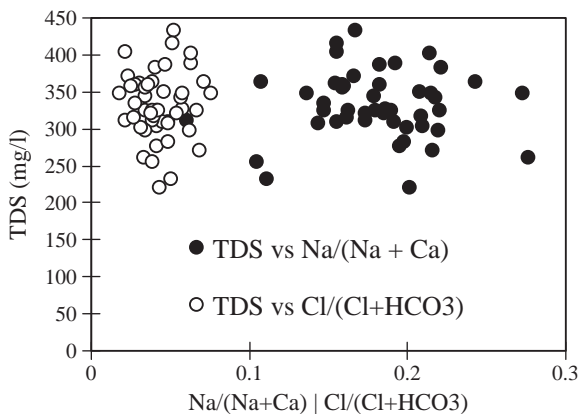


Fig. 6. The Gibbs graph of major ion compositions (TDS was the sum of major ions) in the Longchuanjiang River, China (x axis represents the ratio of weight concentrations).

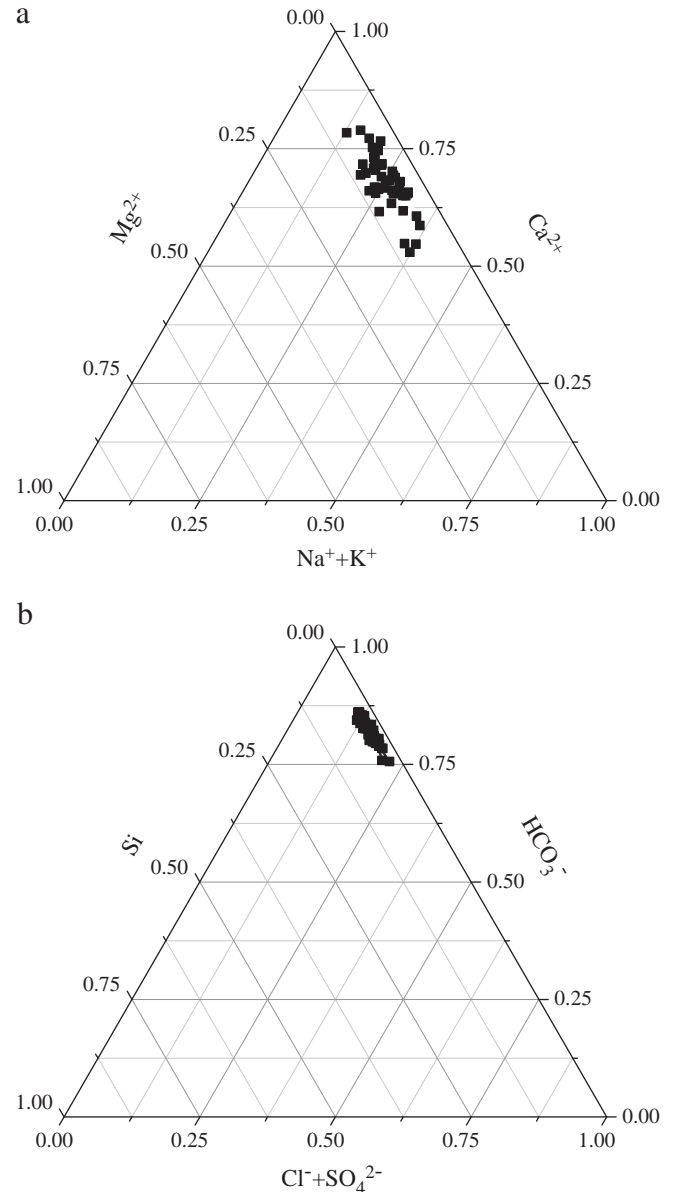


Fig. 7. Ternary diagrams showing cation (diagram a) and anion (diagram b) compositions in the Longchuanjiang River, China.

with low coefficient ($R^2 = 0.38$, $p < 0.01$; Fig. 8f). Mg^{2+} thus seemed to originate from $MgSO_4 \cdot 7H_2O$. However, considering the lithology of the catchment where carbonate rocks including dolomites and calcites are widespread throughout the drainage basin, the contribution of $MgSO_4$ to Mg^{2+} did not necessarily form in proportion. In fact, in the Changjiang basin, sulfate in river water generally sources from dissolution of gypsum, oxidation of sulfides (i.e., pyrites) and anthropogenic inputs rather than $MgSO_4$, this is due to geological stratum that are sparse in $MgSO_4 \cdot 7H_2O$ in the river systems (Berner and Berner, 1996; Chen et al., 2002; Chetelat et al., 2008). Thus, we primarily attributed the positive associations between Mg^{2+} and SO_4^{2-} to anthropogenic inputs such as mineral processing and chemical inputs, and in particular metallurgical industry outputs, which supported local economic development in the Longchuanjiang basin (i.e., Chuxiong). It is reported that sulfate concentrations in the Changjiang basin have been increasing in the past 50 years due to the drastic increase of industrial and agricultural activities (Chen et al., 2002). In the mountainous regions, wastes discharge directly into the rivers, and the industries and domestic housing are fuelled predominantly by sulfur-rich coals, resulting in acid rain and persistent increases in

riverine SO_4^{2-} concentration. Meanwhile, the plotting of these equivalent ratios greatly above gypsum dissolution line suggested a minor contribution of gypsum to sulfate (Fig. 8d). The SO_4^{2-} signature in the Longchuanjiang River was, therefore, likely affected by anthropogenic emissions and pyrite oxidation.

Similar to SO_4^{2-} , Cl^- and Na^+ are often suspected to anthropogenic origin. Chen et al. (2002) concluded the contribution of cyclic salts to riverine dissolved solutes in the upper Changjiang River could be neglected. As there is no geological evidence of evaporites, particularly halite strata exposed in the drainage basin, we ascribed chloride to anthropogenic inputs ($Cl^-_{\text{anthropogenic}} = 0.253 \text{ mmol/l}$), i.e., domestic salt usage from more than 200,000 people in the upper Longchuanjiang River and in particular from the Chuxiong city. $Cl^-_{\text{anthropogenic}}$ was completely balanced by Na^+ ($Na^+_{\text{anthropogenic}} = 0.253 \text{ mmol/l}$).

5.2. Anthropogenic contribution to dissolved solutes

Part of the riverine Ca^{2+} and SO_4^{2-} is sourced from the dissolution of gypsums within the drainage basin in theory, and the gypsums

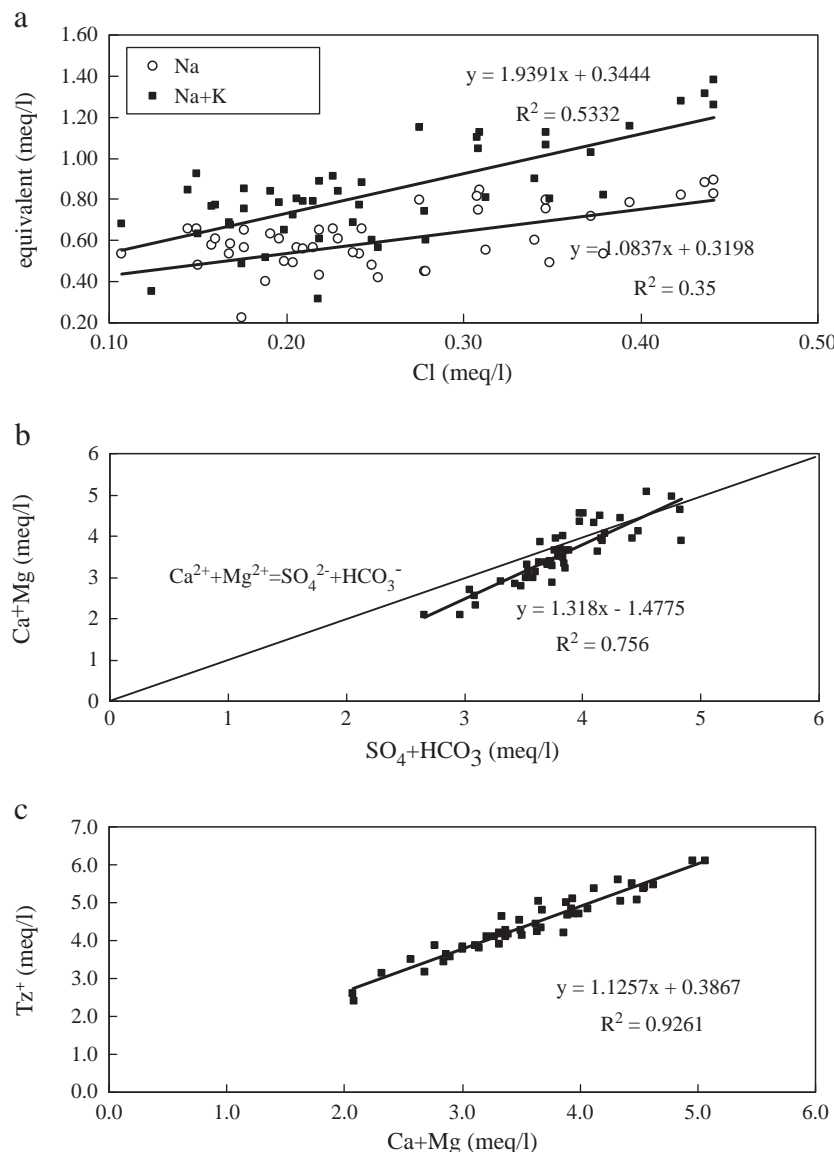


Fig. 8. Scatter plots of Na versus Cl^- , $Na^+ + K^+$ versus Cl^- (a), $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$ (b), Tz^+ versus $Ca^{2+} + Mg^{2+}$ (c), $(Ca^{2+} + Mg^{2+})/HCO_3^-$ versus SO_4^{2-}/HCO_3^- (d), Ca^{2+} versus HCO_3^- and Mg^{2+} versus Ca^{2+} (e) and Mg^{2+} versus SO_4^{2-} (f) in the Longchuanjiang River, China.

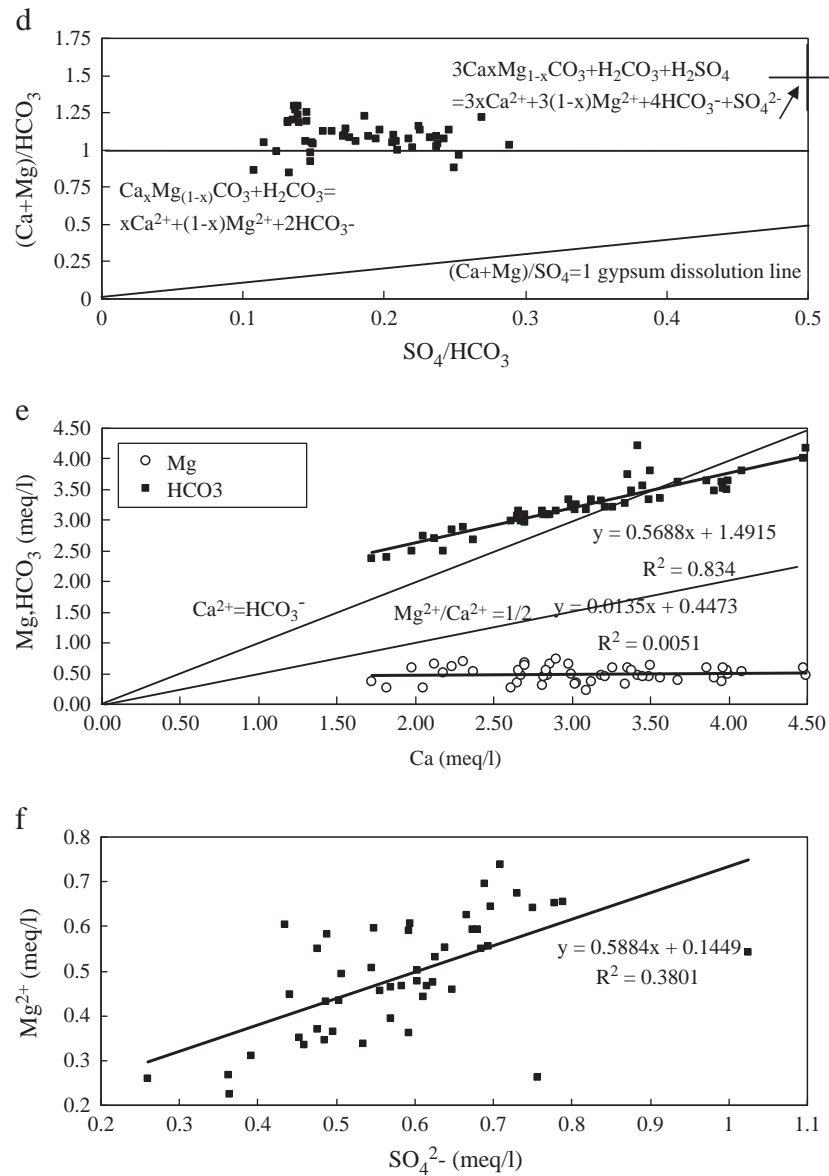


Fig. 8 (continued).

contributed to equal equivalent of Ca^{2+} and SO_4^{2-} (Stallard and Edmond, 1983). However, the SO_4^{2-} concentration varied from 12.5 to 49.2 mg/l (Table 1). We attributed this large variability to atmospheric acid deposition, waste discharge and oxidation of pyrite (the sum of the three items was the human activity-induced sulfuric acid). In fact, there are significant increases in Na^+ , Cl^- and SO_4^{2-} concentrations in the past two decades due to economic development and acid deposition associated with coal burning and the increase of domestic/urban industrial effluents in the Changjiang (including the Jinshajiang) basin (Table 2; Chen et al., 2002; Chetelat et al., 2008). The SO_4^{2-} concentration of 12.5 mg/l from the dissolution of gypsum was assumed ($\text{SO}_4^{2-}_{\text{gypsum}} = 0.130 \text{ mmol/l}$), and the SO_4^{2-} concentration from the human activities was then equal to the measured riverine SO_4^{2-} minus the $\text{SO}_4^{2-}_{\text{gypsum}}$, thus $\text{SO}_4^{2-}_{\text{anthropogenic}} = 0.162 \text{ mmol/l}$, which was balanced by Mg^{2+} due to their comparatively good association ($R^2 = 0.38$, $p < 0.01$; Fig. 8f). Therefore, anthropogenic inputs ($\text{Cl}^-_{\text{anthropogenic}} = \text{Na}^+_{\text{anthropogenic}} = 0.253 \text{ mmol/l}$; $\text{SO}_4^{2-}_{\text{anthropogenic}} = \text{Mg}^{2+}_{\text{anthropogenic}} = 0.162 \text{ mmol/l}$) contributed some 10.4% to dissolved solutes in the upper Longchuanjiang River. Our results were comparable with the mountainous rivers in the Changjiang systems such as Tongtianhe, Jinshajiang, Minjiang and Han Rivers (ca. 7–17%) (Qin et al., 2006; Wu et al., 2008b; Li et al., 2009a).

5.3. Chemical budget and chemical weathering rates

A forward mass-balance approach (Appendix A) suggests an X_{silicate} of 0–0.30, averaging 0.17, which is higher than the value in riverine waters dominated by carbonates (i.e., Wujiang; Han and Liu, 2004). The X_{dolomite} and $X_{\text{limestone}}$ were, on average, 0.18 and 0.65, respectively.

The average densities of silicates and carbonates are 2.7 and 2.4 g cm^{-3} , respectively (Galy and France-Lanord, 1999). Half of HCO_3^- originates from the atmosphere for carbonate dissolution (Roy et al., 1999). The carbonate and silicate weathering rates are 20.3 t/km²/yr and 5.75 t/km²/yr, respectively, within the range (1.6–71.9 t/km²/yr for carbonate and 1.2–9.1 t/km²/yr for silicate) of other Changjiang tributaries (Table 4; Appendix B). The total chemical denudation flux of the upper Longchuanjiang River is 26.1 t/km²/yr, very close to the global mean values of 26 t/km²/yr (Meybeck, 1979), 24 t/km²/yr (Gaillardet et al., 1999) and 21 t/km²/yr (Berner and Berner, 1996).

The estimation of CO_2 consumption by silicate weathering is $173.7 \times 10^3 \text{ mol/km}^2/\text{yr}$, lower than the values in the Jinshajiang while higher than that in the Changjiang River (Table 4). The estimation of

Table 4Chemical weathering and CO₂ consumption rates for the Longchuanjiang River, China, and comparison with other world rivers.

River	Discharge × 10 ⁹ m ³ /yr	Surface area × 10 ⁴ km ²	Carbonate weathering rate			Silicate weathering rate			Reference
			t/km ² /yr	mm/kyr	CO ₂ × 10 ³ mol/km ² /yr	t/km ² /yr	mm/kyr	CO ₂ × 10 ³ mol/km ² /yr	
Longchuanjiang	0.25	0.1788	20.3	8.46	202.9	5.75	2.13	173.7	This study
Tuotuo River	1.34	1.6	1.61	0.67	135	1.19	0.44	45.8	Wu et al., 2008b
Tongtian River	33.5	13.8	6.46	2.69	409	1.67	0.62	73	Wu et al., 2008b
Jinshajiang	39.4	23.3	18.1	7.5	190	9.1	3.4	370	Wu et al., 2008a
Lancang Jiang	29	8.9	59.3	24.7	610	4.1	1.5	70	Wu et al., 2008a
Nu Jiang	53.1	11	67.8	28.2	700	5.9	2.2	110	Wu et al., 2008a
Yalong Jiang	55.3	12.9	44.4	18.5	460	8	3	240	Wu et al., 2008a
Daduhe	61.6	8.9	71.9	29.9	740	8.3	3.1	180	Wu et al., 2008a
Minjiang	14.9	3.7	58.2	24.3	600	9	3.3	260	Wu et al., 2008a
Wujiang	32.7	6.7	65	33	682	6	2.4	98	Han and Liu, 2004
Upper Han River	41.1	9.52	47.5	19.8	679.5	5.6	2.1	101.8	Li et al., 2009a
Changjiang, Datong	899	170.5	14		378.9	2.4		112	Chetelat et al., 2008
Huang He	23.2	14.6	26.1	10.9	270	3	1.1	90	Wu et al., 2008a
Amazon	6590	611.2	11.08		105.37	13.04		52.36	Gaillardet et al., 1999
Mekong	467	69.5	637.4		588.5	16.4		279.14	Gaillardet et al., 1999
Brahmaputra	510	58	35.4	14.8	340	10.3	3.8	150	Gaillardet et al., 1999
Ganges	493	105	28	11.7	240	14	5.2	450	Gaillardet et al., 1999
Indus	90	91.6	13.8	5.7	90	3.8	1.4	60	Gaillardet et al., 1999

the CO₂ consumption rates by carbonate weathering, 202.9×10^3 mol/km²/yr, is comparable with the range of values reported in other studies for the Changjiang's tributaries, i.e. $135\text{--}740 \times 10^3$ mol/km²/yr (Table 4).

The calculated results show that consumption of CO₂ by silicate and carbonate rock weathering for the Longchuanjiang basin is 3.11×10^8 mol/yr and 3.63×10^8 mol/yr, respectively, and accounts for 0.00358% and 0.00295% of the global CO₂ consumption fluxes by silicate and carbonate rocks (8700×10^9 mol/yr and $12,300 \times 10^9$ mol/yr, Gaillardet et al., 1999). However, the total CO₂ consumption per km² (376.6×10^3 mol/km²/yr) is higher than the world average (246×10^3 mol/km²/yr), indicating a more intense CO₂ consumption in this basin. We thus concluded that the higher uptake rate of atmospheric CO₂ by chemical weathering within the rivers originating from the Qinghai–Tibet Plateau regulated the atmospheric CO₂ level and played an important role in the global and local carbon budgets. Furthermore, chemical weathering rate will increase with global warming, thus rock chemical weathering process offers an important carbon sink potential.

5.4. Comparison with other tributaries in the upper Changjiang River basin

The surface water chemistry and river transport of dissolved materials are strongly influenced by the lithological composition of substrata, hydroclimatic conditions, plant coverage and human activities within the drainage basin (Stallard and Edmond, 1983; Probst et al., 1994). Generally, chemical weathering for carbonate rocks is more intense than silicates; humid hydroclimatic conditions also enhance mineral weathering. Examination of the major element chemistry demonstrated that the Longchuanjiang had a similar water chemistry to the two small tributaries Tuotuo and Tongtian in the Tibetan Plateau and also Minjiang (relatively large tributary) (Table 2). For example, TDS, HCO₃[−], and SO₄^{2−} concentrations were higher than the larger tributaries or the main channel, but lower than the Tibetan small rivers. Annual Na⁺, Cl[−] and SO₄^{2−} concentrations in the Tuotuo and Tongtian were much higher than in the Longchuanjiang and other larger tributaries, probably because of intense evaporation, high weathering rates and the dissolution of halite, and saline lakes and hot springs in the source areas of the Changjiang (Wu et al., 2008a, b). Concentrations of Na⁺ and Cl[−] in the Longchuanjiang were intermediate relative to the other larger rivers. Si and K⁺ concentrations were at the upper end of the

concentration ranges of the Tibetan rivers and the Minjiang River (drainage = 37,000 km²), due to abundant volcanic rocks and granites along the Longchuanjiang River. Ca²⁺ concentration in the Longchuanjiang was the highest among all the tributaries. In contrast, Mg²⁺ concentration was the lowest (Table 2). By comparing with other rivers originating from the Qinghai–Tibet Plateau (Table 2; Wu et al., 2008a), the Yalong Jiang and Daduhe, with higher proportion of granites and small proportion of carbonates, had the lowest dissolved solutes (Appendix C; Table 2).

The areal yield of dissolved load of the Longchuanjiang River was much lower than the Changjiang, Zhujiang and Amazon (Table 3). This could be explained by more abundance of carbonates in the Zhujiang and the middle and lower reaches of the Changjiang basin (Appendix C), while more humid hydroclimatic conditions could be responsible for higher solutes in the Amazon River with low importance of carbonates (3.9%) (Table 6). China's rivers lower areal yield of dissolved solutes occurred in the Yellow River (Table 3), which was strongly related to lithology and hydroclimatic conditions. For example, clastic rocks intercalated with volcanic rocks and evaporites are more important in the Yellow River basin. With much less precipitation (329 mm/yr) and colder temperatures, with 78–93% of the area underlain by permafrost, these factors were mainly responsible for the low areal yield of the Lena River. Also, the concentrations and areal yields of major elements were regulated by other physical characteristics such as land use/land cover, population density, etc. (Tables 6 and 7a, b). Forested land had low major ions, while anthropogenic activities such as urban expansion contributed to dissolved solutes, particularly SO₄^{2−} (Table 7a and b), which was consistent with the combustion of sulfur-rich coal and acid deposition worldwide. Though chemical weathering and associated CO₂ consumption were primarily controlled by lithology, land-use and population also contributed to atmospheric CO₂ uptake through rock chemical weathering (Table 7c). Forested land decreased CO₂ consumption rate, while population density and human activities, particularly cultivated land, significantly contributed to CO₂ consumption. The CO₂ consumed by silicate weathering was more susceptible to human activities.

The dilution effect for most cations and anions in the Longchuanjiang also occurred in most other smaller tributaries of the Changjiang (Tables 1 and 2), which resulted from the highest hydrological cycling in the high flow period (Anshumali and Ramanathan, 2007; Li and Zhang, 2009). The anomalous enrichment of Mg²⁺ and SO₄^{2−} during high flow conditions was opposite to what is found in most of the tributaries of the Changjiang (Tables 1

and 2). These trends may be related to Mg-containing mineral dissolution and other anthropogenic inputs in the upper basin, while enhanced diffuse input from the application of fertilizers and pesticides in farmland and urban areas could produce higher concentrations of SO_4^{2-} in the high flows.

The small seasonal variability in the concentrations of TDS and major ions versus great variations in water discharge was similar to most Himalayan rivers (Galy and France-Lanord, 1999) and the Changjiang River and its tributaries, including the Jinshajiang River (Chen et al., 2002; Chetelat et al., 2008; Wu et al., 2008b; Li and Zhang, 2009), whereas very different from other world rivers such as the Amazon (Gibbs, 1972) and Lena (Gordeev and Sidorov, 1993), where dissolved load decreased significantly in the high flow period due to dilution from increased water discharge. The relatively slight decrease of dissolved load, particularly the concentrations of TDS, Ca^{2+} and HCO_3^- , compared to the drastic increase in discharge during the flood season implied that there existed additional dissolved salt sources in the river basin to balance the dilution effect, as suggested by the power equation (Fig. 5). Chen et al. (2002) ascribed this to the enhanced dissolution of carbonate rocks in the high flow period and the enhanced dissolution of detrital calcite because the suspended solid concentrations in the high flows (i.e., November) were the tens of times that in the low flows (i.e., Jan. and Feb.).

6. Conclusions

The total cationic charge (Tz^+) averages of 4.4 meq/l in the Longchuanjiang were 3.5 times the average for world rivers. The water of the River is characterized by mild alkalinity and high concentrations of Ca^{2+} and HCO_3^- , which in total account for approximately 78% of the total ionic budgets. All the chemical species show moderate variability compared to the considerable variations in water discharge, and most elements tend to show lower compositions in the high flow period. The dissolved flux, dominated by HCO_3^- and Ca^{2+} , has strong relationships with water flow rate.

Estimation of chemical weathering rates of the river catchments by both methods of stoichiometry and the chemical budget of the river waters indicates that carbonate weathering largely dominates the riverine water chemistry. Calculations demonstrate that 83% of cations in the Longchuanjiang River originate from carbonates, including 18% from dolomite and 65% from limestone, and 17% from silicates. As compared to most world rivers, the total chemical denudation fluxes are moderate (26.1 t/km²/yr) and are very close to the global average of approximately 24 t/km²/yr. The total CO_2 consumption rate by rock chemical weathering within the upper Longchuanjiang basin is 376.6×10^3 mol/km²/yr, higher than the world average of 246×10^3 mol/km²/yr. The CO_2 consumed by rock chemical weathering in the upper catchment of Changjiang basin constituted a significant part of global carbon budget. With global warming and rising CO_2 , the elevated rates of rock chemical weathering will increase its carbon sink potential, thus extra attention should be paid to rivers particularly from the Qinghai–Tibet Plateau.

Population density and human activities, particularly agricultural practices, largely contributed to major ions and associated CO_2 consumption worldwide. In the upper Longchuanjiang River, this anthropogenic contribution comprised some 10.4% of the dissolved solute.

Acknowledgements

This work was funded by grants from the National University of Singapore (R-109-000-086-646), the Asia Pacific Network (ARCP2006-06NMY, ARCP2007-01CMY, and ARCP2008-01CMY) and NSFC-Yunnan Foundation (U0933604 and 40872118). Andy Plater and two anonymous reviewers are thanked for their remarks to improve the quality of the manuscript.

Appendix A. Elemental mass balance estimates

The chemistry of rain waters primarily originates from sea water aerosols and dissolution of continental dust, while the marine influence diminishes inland (Stallard and Edmond, 1981; Galy and France-Lanord, 1999). Chen et al. (2002) reported that chloride in the Changjiang River did not decline with increasing distance from the sea. Moreover, the study area was located in the upper Changjiang River and seasonal variations (3.8–15.7 mg/l) in chloride showed weak relations with discharge ($R^2 = 0.1$), indicating the limited influence of marine aerosols on solute load. With this approach, weathering of mineral dust by rainwater may be relatively important. However, we have not carried out a systematic study on the chemistry of rainwater in the catchments. In the present study, rainwater data for the upper Longchuanjiang River was derived from Shigu town ($\text{Cl}^- = 1.8$, $\text{Ca}^{2+} = 2.5$, $\text{Mg}^{2+} = 1.0$, $\text{Na}^+ = 0.4$, $\text{K}^+ = 2.0$, $\text{SO}_4^{2-} = 5.2$ $\mu\text{mol/l}$, respectively; Wu et al., 2008a). The estimation for the cyclic input using atmospheric correction by Cl^- reference (Bernier and Bernier, 1996; Gaillardet et al., 1997) showed that corrections for sodium, potassium, calcium, magnesium, sulfate and chloride were close to 2.94% (1.73–8.48%), 0.02% (0.01–0.04%), 0.0025% (0.0016–0.0042%), 0.09% (0.054–0.018%), 0.039% (0.021–0.083%) and 0.80% (0.41–1.68%), respectively. Additionally, atmospheric dust inputs were calculated based on the X/Cl ratio of the rainwater data, and this rain correction also made little difference to river solutes. Thus, an atmospheric correction was ignored in the present study.

The mass balance equation in the direct/forward model for the element X (in molar concentration) in river waters can be expressed as follows (i.e., Meybeck, 1987; Galy and France-Lanord, 1999):

$$[\text{X}]_{\text{river}} = [\text{X}]_{\text{cyclic}} + [\text{X}]_{\text{carbonate}} + [\text{X}]_{\text{silicate}} + [\text{X}]_{\text{evaporite}} + [\text{X}]_{\text{anthropogenic}} \quad (2)$$

This model needs some simplification of assumptions. First, the atmospheric correction for cyclic salts was not conducted in the present study due to its minor contribution to solutes in the Longchuanjiang River, and all the chloride was considered to be from anthropogenic emissions and balanced by Na^+ , as discussed above. Second, sulfate sources were from both sulfide oxidation and anthropogenic inputs. Third, the contributions of anthropogenic sources to K^+ , Ca^{2+} and Mg^{2+} are negligible, since the anthropogenic contributions to these cations are minor. Fourth, the contributions of carbonates to Na^+ and K^+ are neglected (Dalai et al., 2002). With the above assumptions, the budget equation can be simplified as follows:

$$[\text{Cl}]_{\text{river}} = [\text{Cl}]_{\text{anthropogenic}} \quad (3)$$

$$[\text{SO}_4]_{\text{river}} = [\text{SO}_4]_{\text{sulfide}} + [\text{SO}_4]_{\text{anthropogenic}} \quad (4)$$

$$[\text{Na}]_{\text{river}} = [\text{Na}]_{\text{silicate}} + [\text{Na}]_{\text{anthropogenic}} = [\text{Na}]_{\text{silicate}} + [\text{Cl}]_{\text{anthropogenic}} \quad (5)$$

$$[\text{K}]_{\text{river}} = [\text{K}]_{\text{silicate}} \quad (6)$$

$$[\text{Ca}]_{\text{river}} = [\text{Ca}]_{\text{carbonate}} + [\text{Ca}]_{\text{silicate}} \quad (7)$$

$$[\text{Mg}]_{\text{river}} = [\text{Mg}]_{\text{carbonate}} + [\text{Mg}]_{\text{silicate}} \quad (8)$$

To facilitate the calculation of equations of (7) and (8), the molar ratios of $\text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{K}^+$ for the silicate-weathering end-member must be determined. Silicate weathering mainly contributes to Na^+ and K^+ from their silicates such as sodium-feldspar and potassium-feldspar weathering, and Ca^{2+} and Mg^{2+} from calcium-magnesium silicate weathering (Mortatti and Probst, 2003). However, there is a large variability of the molar ratios of $(\text{Ca}^{2+}/\text{Na}^+)_{\text{silicate}}$ and $(\text{Mg}^{2+}/\text{K}^+)_{\text{silicate}}$ from silicate weathering because of the varied lithologies in the drainage basin (Table 5). Since the drainage basin has

Table 5End-members composition of $\text{Ca}^{2+}/\text{Na}^+$, $\text{Mg}^{2+}/\text{K}^+$ and $\text{Mg}^{2+}/\text{Na}^+$ for silicates.

River	$\text{Ca}^{2+}/\text{Na}^+$	$\text{Mg}^{2+}/\text{K}^+$	$\text{Mg}^{2+}/\text{Na}^+$	Reference
Longchuanjiang	0.40	0.80		This study
Changjiang	0.35	1.18	0.2	Chetelat et al., 2008
Minjiang	0.7		0.3	Qin et al., 2006
Minjiang	0.32	0.60		Wu et al., 2008a
Hanjiang	0.33	0.5	0.2	Li et al., 2009b
Wujiang	0.2	0.5		Han and Liu, 2004
Seven rivers in the upper Changjiang River ^a	0.17–0.58	0.42–0.88		Wu et al., 2008a
Tongtian and Jinshajiang Rivers	0.42–0.84		0.18–0.43	Wu et al., 2008b
Zhujiang	0.4		0.2	Zhang et al., 2007
Himalaya	0.18–0.3	0.5 ± 0.2		Galy and France-Lanord, 1999
Yamuna basin	0.7 ± 0.3, 0.35 ± 0.15		0.3	Dalai et al., 2002
Hong River	0.44	0.16		Moon et al., 2007
Global rivers	0.35		0.24	Gaillardet et al., 1999

^a Seven rivers include the Jinshajiang, Yalong Jiang, Minjiang, Daduhe, Lancang Jiang, Nu Jiang and Huang He originating in the Qinghai–Tibet Plateau.

a mixed lithology it is difficult to estimate the $\text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{K}^+$ ratios using the present chemical data. In the present study, the ratios of $\text{Ca}^{2+}/\text{Na}^+$ (0.4) and $\text{Mg}^{2+}/\text{K}^+$ (0.8) in silicate fractions of the riverbed sediments in the Jinshajiang River were adopted (Table 5; Blum et al., 1998). The end-member for $\text{Ca}^{2+}/\text{Na}^+$ was comparable to other rivers and also close to the value defined for silicate on a global scale (Gaillardet et al., 1999), while $\text{Mg}^{2+}/\text{K}^+$ was more closely aligned to that in the Changjiang River (Table 5). Thus, Eqs. (7) and (8) can further be made:

$$[\text{Ca}]_{\text{river}} = [\text{Ca}]_{\text{carbonate}} + 0.4[\text{Na}]_{\text{silicate}} \quad (9)$$

$$[\text{Mg}]_{\text{river}} = [\text{Mg}]_{\text{carbonate}} + 0.8[\text{K}]_{\text{silicate}} \quad (10)$$

We can then calculate the silicate to carbonate budget using the ratio of dissolved cations originating from silicates over the sum of dissolved cations from silicates and carbonates. This was described by Galy and France-Lanord (1999) using the ratio of equivalent cationic charge:

$$X_{\text{sil}} = \frac{([\text{Na}]_{\text{silicate}} + [\text{K}]_{\text{silicate}} + 2 \times [\text{Ca}]_{\text{silicate}} + 2 \times [\text{Mg}]_{\text{silicate}}) / ([\text{Na}]_{\text{silicate}} + [\text{K}]_{\text{river}} + 2 \times [\text{Ca}]_{\text{river}} + 2 \times [\text{Mg}]_{\text{river}})}{(1.8 \times [\text{Na}]_{\text{silicate}} + 2.6[\text{K}]_{\text{silicate}}) / ([\text{Na}]_{\text{silicate}} + [\text{K}]_{\text{river}} + 2 \times [\text{Ca}]_{\text{river}} + 2 \times [\text{Mg}]_{\text{river}})} \quad (11)$$

Then we can further determine the proportions of cations from limestone and from dolomite. In this work, the ratios of $\text{Mg}^{2+}/\text{Ca}^{2+}$ from limestone (0.1) and dolomite (1.1) are assigned following the carbonate-dominated river water (Wujiang, Han and Liu, 2004).

$$X_{\text{silicate}} + X_{\text{dolomite}} + X_{\text{limestone}} = 1 \quad (12)$$

$$[\text{Mg}/\text{Ca}]_{\text{dolomite}} = 1.1 \quad (13)$$

$$[\text{Mg}/\text{Ca}]_{\text{limestone}} = 0.1 \quad (14)$$

Appendix B. Calculation of chemical weathering and CO_2 consumption rate

Roy et al. (1999) expressed the calculations for the silicate and carbonate weathering rates in basins. The carbonate weathering rate (CWR) is quantified using dissolved concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- from carbonate weathering:

$$\text{CWR} = (\text{Ca}_{\text{carbonate}} + \text{Mg}_{\text{carbonate}} + 1/2\text{HCO}_{3\text{carbonate}}) \times \text{discharge/drainage area} / \text{density of carbonates} \quad ([\text{HCO}_3]_{\text{carbonate}} = 2[\text{Ca}]_{\text{carbonate}} + 2[\text{Mg}]_{\text{carbonate}}) \quad (15)$$

The silicate weathering rate (SWR) is determined as follows:

$$\text{SWR} = (\text{Na}_{\text{silicate}} + \text{K}_{\text{silicate}} + \text{Ca}_{\text{silicate}} + \text{Mg}_{\text{silicate}} + \text{SiO}_{2\text{silicate}}) \times \text{discharge/drainage area/density of silicates} \quad (16)$$

The CO_2 consumption rates from silicates ($\text{CO}_{2\text{silicate}}$) and carbonates ($\text{CO}_{2\text{carbonate}}$) are calculated as follows (Wu et al., 2008a):

$$\text{CO}_{2\text{carbonate}} = 1/2\text{HCO}_{3\text{carbonate}} \times \text{discharge/drainage area} \quad (17)$$

$$\begin{aligned} \text{CO}_{2\text{silicate}} &= \text{HCO}_{3\text{silicate}} \times \text{discharge/drainage area} \\ &= ([\text{Na}]_{\text{silicate}} + [\text{K}]_{\text{silicate}} + 2 \times [\text{Ca}]_{\text{silicate}} + 2 \times [\text{Mg}]_{\text{silicate}}) \times \text{discharge/drainage area} \\ &= (1.8 \times [\text{Na}]_{\text{silicate}} + 2.6[\text{K}]_{\text{silicate}}) \times \text{discharge/drainage area} \end{aligned} \quad (18)$$

Appendix C. River basin physical characteristics in Tables 2 and 3

Lithological characteristics are given below and other physical characteristics are shown in Tables 6 and 7.

The Tuotuo River: clastic rocks and Quaternary fluvial deposits;

The Tongtianhe: low-grade metamorphic rocks, clastic rocks and Quaternary fluvial deposits with little granitoids;

The Minjiang: clastic rocks, limestones, low-grade metamorphic rocks, granitoid intrusive rocks and Quaternary deposits;

The Lancang Jiang: its upper basin contains clastic rocks, limestones and volcanic rocks; its downstream reaches are low-grade metamorphic rocks, granitoid intrusive rocks, clastic rocks and limestones;

The Daduhe: clastic rocks, limestones, low-grade metamorphic rocks, basalts and granites;

The Nu Jiang: clastic rocks, limestones, low-grade metamorphic rocks, granitoid intrusive rocks and Precambrian high-grade metamorphic rocks;

The Yalong Jiang: the source area contains clastic rocks, volcanic rocks and Quaternary deposits. Other areas include ophiolites, granites and volcanic rocks;

The Jinshajiang (upper Shigu): source areas contain evaporite-bearing Quaternary deposits, clastic rocks and limestones; downstream reaches are granitoid intrusive rocks, ophiolitic melanges, volcanic rocks, clastic rocks and lower-grade metamorphic rocks;

The Jinshajiang (whole catchment): upper reaches are Triassic low-grade metamorphic rocks, Palaeozoic carbonate rocks and clastic rocks, Neoproterozoic meta-volcanic rocks and crystalline limestones; the reaches from Shigu to Panzhihua are Permian clastic rocks, continental basalts, Triassic carbonate rocks, Quaternary fluvial deposits, Precambrian granitoids and high-grade metamorphic rocks; and carbonate rocks and clastic rocks from Panzhihua to Yibin;

Table 6

Comparison of land use, population density, T and precipitation in the Longchuanjiang and other rivers.

	Land use/land cover composition (%)						Population density people/km ²	Temperature °C	Precipitation mm
	Forest	Grass, savanna and shrub	Wetlands	Cropland	Irrigated cropland	Urban			
Longchuanjiang	31.4	54.9	0	11.4	4.1	1.8	113	15.6	825
Changjiang	6.3	28.2	3	47.6	7.1	3	226	4 source area; others 16–18	1100
Huang He	1.5	60	1.1	29.5	7.2	5.9	156	– 11 (winter); 11 (summer)	430
Pearl River	9.6	6.1	1.3	66.5	5.2	5.3	194	14–22	1200–2200
Ganges–Brahmaputra	9.8	25.6	18.9	55.6	15.3	4.8	316	0–30	2650 (1750–6400)
Brahmaputra	18.5	44.7	20.7	29.4	3.7	2.4	182		
Ganges	4.2	13.4	17.7	72.4	22.7	6.3	401		
Amazon	73.4	10.2	8.3	14.1	0.1	0.6	4	25–27	1500–3000
Congo	44	45.4	9	7.2	0	0.2	15	24	1500–3000
Lena	84.7	11.4	0.6	1.7	0	0.4	1	– 40–20	329 (800–1000)

Land use/land cover composition (%) (Longchuanjiang excluded) originated from <http://earthtrends.wri.org/> (read on 2 Nov., 2010).

The Changjiang basin: mainly underlain by sedimentary rocks composed of marine carbonates, evaporites and alluvium from Precambrian to Quaternary in age. Carbonate rocks are widely spread over the basin and are particularly abundant in the southern part (Yunnan, Guizhou and western Hunan Provinces) and the sub-basin of the Hanjiang. Evaporites are mainly present in the upper reach of the Changjiang;

The Yellow River: comprised mainly of limestones, low-grade metamorphic rocks, clastic rocks intercalated with volcanic rocks and evaporates;

The Pearl River: various source rocks from Precambrian metamorphic rocks to Quaternary fluvial sediments. Carbonates are widely distributed in the basin, accounting for 39% of the total. Also, granites and pyrites concomitant with high sulfur content coal are exposed, and minor evaporites are scattered in its upper reaches;

The Amazon basin: dominated by silicate terrains (96.1% of the total area). In detail, the contribution of each main lithology is as

follows: 16.7% sands and sandstones, 50.7% shales, 26.8% plutonic and metamorphic rocks, 1.9% volcanic acid rocks and 3.9% carbonate rocks;

The Congo River: 49% of the total area is occupied by sandy rocks (Mesozoic to Quaternary sandstones), 42% by crystalline and metamorphic rocks (Precambrian), and only 9% by carbonate rocks (upper Precambrian);

The Ganges–Brahmaputra River: composed primarily of Palaeozoic–Mesozoic carbonate and clastic sediments, ortho- and paragneisses, migmatites and highly meta-morphosed marbles, metamorphosed Precambrian sediments, quartzo-pelitic schists, quartzites, and dolomitic carbonates. Mio-Pliocene detrital sediments accumulated in the former Gangetic plain;

The Lena River: carbonate, occasionally halogenous and gypsum-bearing Palaeozoic rocks. Carbonate, gypsum-bearing and halogenous rocks predominate. Approximately 78–93% of the area is underlain by permafrost.

Table 7

Influences of some basin physical characteristics on major ions and chemical weathering (indicated by Pearson R correlation using rivers in Table 6).

	Land use/land cover composition (%)						Population density
	Forest	Grass, savanna and shrub	Wetlands	Cropland	Irrigated cropland	Urban	People/km ²
<i>(a) Concentrations of major elements and some basin physical characteristics</i>							
Na ⁺	−0.431	0.599	−0.366	0.028	0.195	0.584	0.133
K ⁺	−0.490	0.760	−0.369	0.002	0.186	0.234	0.267
Ca ²⁺	−0.565	0.556	−0.525	0.194	0.336	0.473	0.413
Mg ²⁺	−0.548	0.623	−0.334	0.127	0.320	0.643	0.276
Cl [−]	−0.337	0.608	−0.371	−0.081	0.130	0.488	0.049
SO ₄ ^{2−}	−0.473	0.701	−0.350	0.006	0.264	0.571	0.193
HCO ₃ [−]	−0.622	0.555	−0.519	0.254	0.383	0.593	0.448
SiO ₂	0.113	−0.403	0.513	0.205	0.087	−0.378	0.143
TDS	−0.578	0.671	−0.475	0.132	0.342	0.612	0.340
<i>(b) Areal yields of major elements and some basin physical characteristics</i>							
Na ⁺	−0.494	−0.481	−0.065	0.852	0.378	0.701	0.545
K ⁺	−0.598	0.035	0.583	0.743	0.659	0.699	0.664
Ca ²⁺	−0.456	−0.528	0.165	0.839	0.491	0.426	0.676
Mg ²⁺	−0.551	−0.457	0.372	0.893	0.673	0.529	0.799 ^b
Cl [−]	−0.210	−0.343	−0.369	0.406	0.161	0.450	0.258
SO ₄ ^{2−}	−0.651	−0.234	0.458	0.877	0.886	0.671	0.933 ^a
HCO ₃ [−]	−0.458	−0.549	0.159	0.858	0.497	0.465	0.677
SiO ₂	0.298	−0.630	0.523	0.154	−0.034	−0.219	−0.067
TDS	−0.386	−0.587	0.292	0.822	0.506	0.420	0.647
<i>(c) CO₂ consumption impacted by some basin physical characteristics</i>							
CO ₂ by carbonate	−0.782	0.323	0.133	0.429	0.176	0.323	0.495
CO ₂ by silicate	−0.430	−0.319	0.511	0.775	0.926 ^a	0.598	0.864 ^b
Total CO ₂ consumption	−0.781	−0.079	0.486	0.864 ^b	0.846 ^b	0.662	0.972 ^a

^a Significance at the 0.01 level.^b Significance at the 0.05 level.

References

- Amiotte-Suchet, P., Probst, J.L., 1993. Modelling of atmospheric CO₂ consumption by chemical weathering of rocks: application to the Garonne, Congo and Amazon basins. *Chem. Geol.* 107, 205–210.
- Anshumali, Ramanathan, A.L., 2007. Seasonal variation in the major ion chemistry of Pandoh Lake, Mandi District, Himachal Pradesh, India. *Appl. Geochem.* 22, 1736–1747.
- Berner, K.E., Berner, R.A., 1996. *Global Environment: Water, Air, and Geochemical Cycles*. Prentice Hall, Upper Saddle River, N. J.
- Berner, R.A., Kothavala, Z., 2001. GEOCARB III: a revised model of atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.* 301, 182–204.
- Blum, J.D., Gazis, C.A., Jacobson, A.D., Chamberlain, C.P., 1998. Carbonate versus silicate weathering in the Raikhot watershed within the High Himalayan Crystalline Series. *Geology* 26, 411–414.
- Chen, J., Wang, F., Xia, X., Zhang, L., 2002. Major element chemistry of the Changjiang (Yangtze River). *Chem. Geol.* 187, 231–255.
- Chen, J., Wang, F., Meybeck, M., He, D., Xia, X., Zhang, L., 2007. Spatial and temporal analysis of water chemistry records (1958–2000) in the Huanghe (Yellow River) basin. *Global Biogeochem. Cycles* 19, GB3016.1–GB3016.24.
- Chetelat, B., Liu, C., Zhao, Z., Wang, Q., Li, S., Li, J., Wang, B., 2008. Geochemistry of the dissolved load of the Changjiang Basin rivers: anthropogenic impacts and chemical weathering. *Geochim. Cosmochim. Acta* 72, 4254–4277.
- Dalai, T.K., Krishnaswami, S., Sarin, M.M., 2002. Major ion chemistry in the headwaters of the Yamuna river system: chemical weathering, its temperature dependence and CO₂ consumption in the Himalaya. *Geochim. Cosmochim. Acta* 66, 3397–3416.
- Ding, W.R., Zhou, Y., Zeng, H.P., 2009. Relationships between land use and soil erosion in the Longchuanjiang River, China. *Yangtze River* 40, 33–35 (in Chinese, with English Abstr.).
- Gaillardet, J., Dupré, B., Allègre, C.J., Nègre, P., 1997. Chemical and physical denudation in the Amazon River Basin. *Chem. Geol.* 142, 141–173.
- Gaillardet, J., Dupré, B., Louvat, P., Allègre, C.J., 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30.
- Galy, A., France-Lanord, C., 1999. Weathering processes in the Ganges–Brahmaputra basin and the riverine alkalinity budget. *Chem. Geol.* 159, 31–60.
- Gao, Q.Z., Tao, Z., Huang, X.K., Nan, L., Yu, K.F., Wang, Z.G., 2009. Chemical weathering and CO₂ consumption in the Xijiang River basin, South China. *Geomorphology* 106, 324–332.
- Gibbs, R.J., 1970. Mechanisms controlling world water chemistry. *Science* 170, 1088–1090.
- Gibbs, R.J., 1972. Water chemistry of the Amazon River. *Geochim. Cosmochim. Acta* 36, 1061–1066.
- Gordeev, V.V., Sidorov, L.S., 1993. Concentrations of major elements and their outflow into the Laptev Sea by the Lena River. *Mar. Chem.* 43, 33–45.
- Han, G., Liu, C., 2004. Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. *Chem. Geol.* 204, 1–21.
- <http://www.cxz.gov.cn/> (read on 28 Oct. 2010).
- <http://earthtrends.wri.org/> (read on 2 Nov. 2010).
- Hu, M., Stallard, R.F., Edmond, J.M., 1982. Major ion chemistry of some large Chinese rivers. *Nature* 298, 550–553.
- Huh, Y., Panteleyev, G., Babich, D., Zaitsev, A., Edmond, J.M., 1998. The fluvial geochemistry of the rivers of Eastern Siberia: II. tributaries of the Lena, Omoloy, Yana, Indigirka/Kolyma, and Anadyr draining the collisional/accretionary zone of the Verkhoyansk and Cherskiy ranges. *Geochim. Cosmochim. Acta* 62, 2053–2075.
- Li, J., Zhang, J., 2005. Chemical weathering processes and atmospheric CO₂ consumption of Huanghe River and Changjiang River Basins. *Chin. Geogr. Sci.* 15, 16–21.
- Li, S.Y., Zhang, Q.F., 2008. Geochemistry of the upper Han River basin, China, 1: spatial distribution of major ion compositions and their controlling factors. *Appl. Geochem.* 23, 3535–3544.
- Li, S.Y., Zhang, Q.F., 2009. Geochemistry of the upper Han River basin, China, 2: Seasonal variations in major ion compositions and contribution of precipitation chemistry to the dissolved load. *J. Hazard. Mater.* 170, 605–611.
- Li, S.Y., Xu, Z.F., Wang, H., Wang, J.H., Zhang, Q.F., 2009a. Geochemistry of the upper Han River basin, China, 3: Anthropogenic inputs and chemical weathering to the dissolved load. *Chem. Geol.* 264, 89–95.
- Li, W., Zeng, H., Chen, G.R., Yang, Y.M., Xiao, Q.Q., 2009b. Analysis on landscape pattern characteristics of Land Use and Cover Change (LUCC) of Longchuan River Based on ASTER Image Data Sources, China. *Guizhou Agric. Sci.* 37, 162–165 (in Chinese, with English Abstr.).
- Lu, X.X., 2005. Spatial variability and temporal change of water discharge and sediment flux in the lower Jinsha tributary: impact of environmental changes. *River Res. Applic.* 21, 229–243.
- Meybeck, M., 1979. Concentrations des eaux fluviales en éléments majeurs et apports en solution aux océans. *Rev. Geol. Dyn. Geogr. Phys.* 21 (3), 215–246.
- Meybeck, M., 1981. Pathways of major elements from land to ocean through rivers. In: Martin, J.M., Burton, J.D., Eisma, D. (Eds.), *River Inputs to Ocean Systems*. United Nations Press, New York, pp. 18–30.
- Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am. J. Sci.* 287, 401–428.
- Meybeck, M., 2003a. Global analysis of river systems: from Earth system controls to Anthropocene syndromes. *Philos. Trans. R. Soc. London Ser. B* 358, 1935–1955.
- Meybeck, M., 2003b. Global occurrence of major elements in rivers. In: Drever, J.I. (Ed.), *Treatise on Geochemistry, Surface and Ground Water, Weathering, and Soils*. Elsevier, pp. 207–223.
- Meybeck, M., Helmer, R., 1989. The quality of rivers: from pristine stage to global pollution. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 75, 283–309.
- Moon, S., Huh, Y., Qin, J., Pho, N.V., 2007. Chemical weathering in the Hong (Red) River basin: rates of silicate weathering and their controlling factors. *Geochim. Cosmochim. Acta* 71, 1411–1430.
- Mortatti, J., Probst, J.L., 2003. Silicate rock weathering and atmospheric/soil CO₂ uptake in the Amazon basin estimated from river water geochemistry: seasonal and spatial variations. *Chem. Geol.* 197, 177–196.
- Probst, J.L., Mortatti, J., Tardy, Y., 1994. Carbon river fluxes and weathering CO₂ consumption in the Congo and Amazon River basins. *Appl. Geochem.* 9, 1–13.
- Qin, J.H., Huh, Y., Edmond, J.M., Du, G., Ran, J., 2006. Chemical and physical weathering in the Min Jiang, a headwater tributary of the Yangtze River. *Chem. Geol.* 227, 53–69.
- Roy, S., Gaillardet, J., Allègre, C.J., 1999. Geochemistry of dissolved and suspended loads of the Seine river, France: anthropogenic impact, carbonate and silicate weathering. *Geochim. Cosmochim. Acta* 63, 1277–1292.
- Sarin, M.M., Krishnaswamy, S., Dilli, K., Somayajulu, B.L.K., Moore, W.S., 1989. Major ion chemistry of Ganga–Brahmaputra river system: weathering processes and fluxes of the Bay of Bengal. *Geochim. Cosmochim. Acta* 53, 997–1009.
- Stallard, R.F., Edmond, J.M., 1981. Geochemistry of the Amazon 1. precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge. *J. Geophys. Res.* 86 (C10), 9844–9858.
- Stallard, R.F., Edmond, J.M., 1983. Geochemistry of the Amazon 2. the influence of geology and weathering environment on the dissolved load. *J. Geophys. Res.* 88 (C14), 9671–9688.
- Stallard, R.F., Edmond, J.M., 1987. Geochemistry of the Amazon 3. weathering chemistry and limits to dissolved inputs. *J. Geophys. Res.* 92 (C8), 8293–8302.
- Wu, L., Huh, Y., Qin, J., Du, G., Van Der Lee, S., 2005. Chemical weathering in the Upper Huang He (Yellow River) draining the eastern Qinghai–Tibet Plateau. *Geochim. Cosmochim. Acta* 69, 5279–5294.
- Wu, W., Xu, S., Yang, J., Yin, H., 2008a. Silicate weathering and CO₂ consumption deduced from the seven Chinese rivers originating in the Qinghai–Tibet Plateau. *Chem. Geol.* 249, 307–320.
- Wu, W., Yang, J., Xu, S., Yin, H., 2008b. Geochemistry of the headwaters of the Yangtze River, Tongtian He and Jinsha Jiang: silicate weathering and CO₂ consumption. *Appl. Geochem.* 23, 3712–3727.
- Xu, Z., Liu, C., 2007. Chemical weathering in the upper reaches of Xijiang River draining the Yunnan–Guizhou Plateau, Southwest China. *Chem. Geol.* 239, 83–95.
- Zhang, S.R., Lu, X.X., Higgitt, D.L., Chen, C.T.A., Sun, H.G., Han, J.T., 2007. Water chemistry of the Zhujiang (Pearl River): natural processes and anthropogenic influences. *J. Geophys. Res.* 112, F01011. doi:10.1029/2006JF000493.
- Zhu, Y.M., Lu, X.X., Zhou, Y., 2007. Suspended sediment flux modeling with artificial neural network: an example of the Longchuanjiang River in the Upper Yangtze Catchment, China. *Geomorphology* 84, 111–125.
- Zhu, Y.M., Lu, X.X., Zhou, Y., 2008. Sediment flux sensitivity to climate change: a case study in the Longchuanjiang catchment of the upper Yangtze River, China. *Global Planet. Change* 60, 429–442.