Contents lists available at ScienceDirect

Chemical Geology



journal homepage: www.elsevier.com/locate/chemgeo

Geochemistry of the upper Han River basin, China 3: Anthropogenic inputs and chemical weathering to the dissolved load

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ARTICLE INFO

Article history: Received 22 December 2008 Received in revised form 10 February 2009 Accepted 24 February 2009

Editor: D.B. Dingwell

Keywords: Upper Han River Water geochemistry Chemical weathering CO₂ consumption

ABSTRACT

The study focuses on the chemical and trace element compositions of the dissolved load in the upper Han River, the water source area of the Middle Route of China's South-to-North Water Transfer Project. Water samples were collected in the high flow period and analyzed for cations by Inductively Coupled Plasma Atomic Emission Spectrometer and anions by ionic chromatography respectively, in order to understand the contributions of anthropogenic activities and rock weathering to river solutes, as well as the associated CO₂ consumption in the carbonate-dominated basin. The river waters have a mean T_Z^+ of 2674 µeq/l ranging from 1034.3 to 4611.6 µeq/l, which is significantly higher than that of the global river waters. Calcium and HCO₃⁻, followed by Mg²⁺ and SO₄²⁻, dominate the chemical composition of major species in the basin. There are three major reservoirs (carbonates, silicates and agriculture/urban effluents) contributing to the dissolved load in the river. Chemical weathering rate is approximately 53.1 t/km²/yr with respective carbonate and silicate weathering rates of 47.5 t/km²/yr (19.8 mm/kyr) and 5.6 t/km²/yr (2.1 mm/kyr). The CO₂ consumption is estimated to be 64.69 × 10⁹ mol/yr and 9.69 × 10⁹ mol/yr by carbonate and silicate weathering, respectively. The contribution of the anthropogenic inputs to the dissolved load is estimated to be 16.7%, demonstrating the strong impacts of human activities on water chemistry.

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1. Introduction

Weathering processes including chemical weathering of soils/ rocks and mechanical erosion supply dissolved and particulate loads to rivers. The products of chemical weathering affected by meteoric water and other factors such as wind and vegetation reveal the biogeochemical cycles of elements, as well as chemical compositions, weathering rates and CO₂ consumption (Gibbs, 1970; 1972; Hu et al., 1982; Stallard and Edmond, 1983; 1987; Meybeck, 1987; Sarin et al., 1989; Gaillardet et al., 1999; Chen et al., 2002; Chetelat et al., 2008). Since chemical weathering of carbonates dominates water chemistry of most of the world's major rivers (Hu et al., 1982; Gaillardet et al., 1999; Chen et al., 2002), characterization of water chemistry in carbonate-dominated drainage basin is of great importance for quantifying respective contributions of varying sources to river solutes, and estimating chemical weathering rates and associated CO₂ consumption.

The Han River, a main tributary of the Changjiang River, is the water source area of the Middle Route of China's South to North Water Transfer Project. Previous studies on the Han River have focused on water quality and its correlations with land use/land cove (Li et al.,

2008a, 2008b, 2008c, 2009a, 2009b), and the spatio-temporal pattern of major element concentrations and their controlling mechanisms (Li and Zhang, 2008a; Li and Zhang, *unpublished*), and revealed the main pollutants of organic matter and nitrogen, and significant anthropogenic additions to water chemistry. In this study, a systematic water sampling representing two main types of bedrock (silicates and carbonates), and between industrial and agricultural sections was carried out to identify and quantify each geochemical signature in order to determine rock weathering rates, associated CO₂ consumption and anthropogenic fluxes.

2. General setting

The upper Han River, with a length of 925 km, runs through Shanxi, He'nan and Hubei provinces. Its drainage basin is situated between 31°20'N–34°10'N and 106°E–112°E in a mountainous region with an elevation from 210 to 3500 m, and covers a total area of 95,200 km² (Fig. 1; Li et al., 2008a). The basin is subject to north sub-tropic monsoon climate, and annual mean temperature is 12 °C–16 °C. Average annual rainfall amount is 700–1800 mm with large intraannual and inter-annual variability. Floods in the basin are formed by storms concentrating between May and October, and this period accounts for about 80% of the annual total precipitation (Li et al., 2008a,b, 2009b). The field period (November in 2005) of the present



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^{0009-2541/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.chemgeo.2009.02.021



Fig. 1. Location of sampling sites in the upper Han River basin, China.

study belongs to the rainy season with the peak flow of 14,000 m³/s. The average runoff in the upper Han River is about 41.1×10^9 m³/yr, accounting for 70% of the total runoff of the entire basin (Li et al., 2008a, 2009b).

Vegetation covers approximately 77% of the surface area with higher vegetation covers in uplands (Li et al., 2008a, 2009b). Cultivated land, representing about 15% of the drainage area, is mainly located along the river networks, *i.e.*, the Hanzhong Plain in the headwater, the Ankang Plain in the middle section, and industrial centers in the Danjiangkou Reservoir region (Li et al., 2009b, Fig. 1). The strata exposed in the catchment are overlain by a sedimentary rocks composed of carbonates and silicates from Precambrian to Quarternary in age. Carbonate rocks are widely spread over the drainage basin, while silicates mainly exist in the upper reaches of the Han River (Chen et al., 2002; Li and Zhang, 2008a; Fig. 1).

3. Sampling and analytical procedures

Water samples in the major tributaries representing various landscape settings across the upper Han River basin were collected in November 2005 during the high flow season, and the sampling locations are shown in Fig. 1. Samples were collected from approximately 10 cm below the water surface using previously acid-washed 5 l high density polyethylene (HDPE) containers, and filtered through pre-washed 0.45 μ m Millipore nitrocellulose filters on the sampling day. The first portion of the filtration was discarded to clean the membrane. The sampling waters were stored in pre-cleaned HDPE bottles. Filtered solution for cations and trace elements analyses were acidified to pH < 2 with ultra-purified 6 M HNO₃.

Water temperature (*T*), pH and electric conductivity (EC) were determined *in situ* using YSI 6920 (YSI Incorporated, Yellow Springs,

Ohio, USA) after calibrations. HCO_3^- was titrated by hydrochloric acid on the sampling day. Major cations and trace elements (Na⁺, K⁺, Ca²⁺, Mg²⁺, Si and Sr) concentrations were measured by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA) with a precision better than 10%. Anions (F⁻, Cl⁻, NO₃⁻ and SO₄²⁻) concentrations were determined by ionic chromatography (IC) (Dionex Corporation, Sunnyvale, CA, USA) with a precision of 5%. Reagent and procedural blanks were measured in parallel to the sample treatment using identical procedures. Each calibration curve was evaluated by analyses of these quality control standards before, during and after the analyses of a set of samples.

4. Results and discussions

4.1. Major ion compositions

Chemical compositions are presented in Table 1. The waters are slightly alkaline with pH values ranging from 7.41 (Site 41) to 8.79 (Site 33). The EC values vary from 122.9 (Site 40) to 445.3 (Site 6) μ S/cm with an average of 281.1 μ S/cm, and there is a strong correlation between EC, Tz⁺ (Tz⁺ = Na⁺ + K⁺ + 2 Mg²⁺ + 2Ca²⁺) and Tz⁻ (Tz⁻ = F⁻ + Cl⁻ + NO₃⁻ + 2SO₄²⁻ + HCO₃⁻) (*r*>0.94, *p*<0.01). The total cationic charge (Tz⁺) ranges between 1034.3 (Site 40) and 4611.6 (Site 2) μ eq/l with an average of 2674.6 μ eq/l, twice higher than world rivers' average (Tz⁺ = 1250 μ eq/l; Meybeck, 1981), while close to the average of the Changjiang River (2800 μ eq/l, Han and Liu, 2004), and the anionic charge (Tz⁻) ranges from 1397.9 (Site 40) to 5100.2 (Site 6) μ eq/l with an average of 3352.4 μ eq/l. Compared to the Wujiang River (Tz⁺ = 4140 μ eq/l; a tributary of the Changjiang River) draining the karst terrain with the dominance of carbonates (Han and Liu, 2004), the Han River has lower total cationic concentrations. The

Table 1					
Chemical compositions	of rivers in	the upper	Han River	basin,	China

Sampling	Date and	W	Т	pН	EC	F^{-}	Cl-	NO_3^-	SO_{4}^{2-}	HCO_3^-	Na ⁺	K^+	Ca^{2+}	${\rm Mg}^{2+}$	Tz ⁺	Tz ⁻	NICB	Si	Sr
locations	sample number	m ^{3/} s	°C		µS/cm	μМ	μΜ	μМ	μМ	μΜ	μМ	μМ	μΜ	μΜ	μEq	μEq		μМ	μM
1	03/11/05-1	14.18	16.16	8.23	353.4	15.4	177.7	162.9	411.5	2700	165.5	29.1	1158.5	488.8	3489.1	3879	-0.112	94.1	3.1
2	03/11/05-2	5.25	15.91	8.08	421.9	10.1	127.6	103.4	176.0	4200	68.1	12.2	1251.5	1014.2	4611.6	4793.1	-0.039	74.0	2.5
3	03/11/05-3	17.92	15.84	8.41	348.6	9.9	167.9	156.1	269.8	2900	157.4	33.9	1016.0	659.2	3541.6	3773.5	-0.065	90.6	3.0
4	03/11/05-4	0.31	12.89	8.04	295.4	9.7	138.9	124.2	280.2	2500	171.5	26.3	929.8	345.7	2748.7	3333.2	-0.213	136.2	3.0
5	03/11/05-5	2.65	12.91	8.16	341.4	10.4	150.7	161.0	305.2	3300	156.4	28.3	1039.3	504.6	3272.4	4232.5	-0.293	100.9	3.1
6	03/11/05-6	30.24	13.03	8.1	445.3	17.5	231.5	317.7	466.7	3600	188.9	24.7	1353.5	692.1	4304.8	5100.2	-0.185	104.2	4.3
7	03/11/05-7	2.94	12.38	8.3	377.2	14.5	208.5	324.2	450.0	2700	186.8	22.2	1128.8	500.8	3468.2	4147.2	-0.196	101.1	4.9
8	11/11/05-51	0.92	18.27	8.6	172	6.4	135.5	84.0	279.2	1198.4	75.7	10.5	467.5	219.0	1459.1	1982.6	-0.359	92.4	1.7
9	11/11/05-50	0.11	18.37	8.07	191.9	8.4	146.5	63.2	438.5	1198.4	101.7	12.4	466.5	217.0	1481.3	2293.6	-0.548	128.9	1.9
10	11/11/05-49	1.02	18.4	7.81	327.7	11.1	1569.0	193.5	491.7	1800	280.3	42.9	728.0	380.8	2540.8	4557	-0.794	147.8	2.9
11	11/11/05-48	/	16.55	8.06	244.6	9.0	108.7	73.9	229.2	2200	56.2	10.5	753.8	336.4	2247	2849.9	-0.268	102.3	3.1
12	11/11/05-46	0.9	15.42	8.2	270.1	8.8	101.7	59.2	276.0	2400	52.1	9.8	849.8	402.2	2565.8	3121.8	-0.217	80.9	3.4
13	11/11/05-47	0.6	15.65	8.31	292.4	11.5	213.5	100.5	414.6	2300	102.9	22.9	875.8	372.1	2621.6	3454.6	-0.318	68.4	2.9
14	10/11/05-42	8.85	16.1	8.35	343.6	16.7	194.6	146.0	999.0	1600	140.0	20.6	959.3	513.8	3106.6	3955.3	-0.273	102.8	3.6
15	10/11/05-41	10	16.58	8.16	360.9	12.0	132.1	169.4	309.4	3300	94.0	17.8	1196.3	468.3	3440.9	4232.2	-0.23	123.3	3.7
16	10/11/05-40	2.43	14.89	8.3	391.9	13.0	1/4.4	187.1	510.4	3000	96.8	20.0	1345.8	511.7	3831.7	4395.3	-0.147	121.6	4.9
17	10/11/05-39	2.86	14.71	8.41	383.8	10.0	249.6	93.5	453.1	3000	107.2	8.2	1108.5	638.3	3609	4259.4	-0.18	27.7	4.3
18	10/11/05-38	3.47	15.15	8.34	337.6	8.4	113.5	70.5	297.9	2800	82.7	7.8	1006.0	642.9	3388.3	3588.2	- 0.059	23.1	3.2
19	09/11/05-37	18	16.04	8.31	349.6	11.8	122.0	131.9	446.9	3400	107.5	22.1	1060.8	607.9	3467	4559.4	- 0.315	81.6	4.2
20	09/11/05-36	24.75	16.03	8.58	236.5	12.2	91.8	84.0	305.2	2300	82.3	13.3	751.0	378.5	2354.5	3098.4	- 0.316	86.7	3.0
21	09/11/05-35	24.9	16.19	8.33	255.3	10.8	96.6	74.4	354.2	2300	84.2	12.1	727.0	368.5	2287.3	3190.1	- 0.395	82.8	3.0
22	09/11/05-33	10	15.77	8.13	333.5	13.3	185.4	183.9	288.5	2800	147.0	21.3	1041.8	372.7	2997.3	3759.6	-0.254	58.4	3.8
23	09/11/05-34	/	17.19	8.1	213.9	8.2	66.8	85.6	176.0	2300	46.7	11.3	702.0	246.3	1954.6	2812.6	-0.439	109.3	2.5
24	07/11/05-32	24	16.64	8.49	255.1	8.5	88.5	111.9	209.4	2400	64.3	13.9	854.0	300.4	2386.9	3027.7	-0.268	126.4	2.9
25	07/11/05-31	24	16.5	8.11	249.6	8.5	83.4	103.9	206.3	2300	61.7	14.1	840.3	283.2	2322.6	2908.3	-0.252	114.0	2.9
26	07/11/05-30	86.4	17.3	8.37	282.6	10.3	29.6	127.9	235.4	2700	87.0	16.6	965.8	345.5	2726.2	3338.6	-0.225	131.4	3.3
27	07/11/05-29	2.56	16.72	8.29	293.9	9.1	85.9	56.0	166.7	3000	79.7	22.1	1074.8	240.9	2733.1	3484.3	-0.275	94.2	3.6
28	07/11/05-28	2.84	17.56	8.38	327.5	11.8	94.9	60.3	274.0	3300	99.6	25.1	1086.8	414.3	3126.6	4015	-0.284	111.4	4.4
29	07/11/05-27	19.14	16.06	8.05	175.6	8.1	77.2	43.4	164.6	2800	73.4	7.3	973.3	327.7	2682.7	3257.8	-0.214	93.2	4.2
30	05/11/05-8	13.6	13.33	8.14	218	8.6	64.2	37.3	171.9	2200	59.6	26.0	736.8	224.8	2008.7	2653.9	-0.321	85.0	2.2
31	05/11/05-13	0.43	13.07	8.39	126.5	6.1	49.0	28.7	125.0	1100	46.7	17.0	419.8	120.2	1143.6	1433.8	-0.254	88.8	1.3
32	05/11/05-14	4.53	15.37	8.37	229.7	8.7	82.5	88.7	132.3	2600	76.3	16.2	899.8	229.7	2351.3	3044.6	- 0.295	115.9	2.8
33	05/11/05-15	2.25	18.14	8.79	224.1	9.7	81.1	135.6	159.4	2100	72.5	16.5	799.3	197.6	2082.7	2645.2	-0.27	122.6	2.4
34	05/11/05-16	2.5	16.76	8.16	376.1	13.7	129.3	141.8	506.3	3100	144.7	25.6	1212.8	477.9	3551.6	4397.3	-0.238	123.0	6.6
35	05/11/05-17	3.84	15.38	8.03	271.2	7.6	116.1	130.2	172.9	2500	66.2	15.3	940.3	258.3	24/8.7	3099.6	-0.25	74.9	3.5
36	07/11/05-26	7.2	14.86	7.7	130.4	7.7	91.3	116.8	107.3	1100	90.1	9.9	348.5	152.2	1101.3	1530.4	-0.39	184.3	2.0
37	06/11/05-25	5.28	16.92	8.6	211.2	7.5	88.7	58.1	85.4	2200	69.5	8.6	723.0	253.9	2031.8	2525.1	-0.243	101.8	3.0
38	06/11/05-24	8.9	16.63	8.57	217.7	8.0	111.5	101.5	120.8	2000	91.2	11.2	593.3	436.3	2161.4	2462.7	-0.139	116.1	1.7
39	06/11/05-23	12.3	17.06	8.56	272.7	8.9	102.8	95.5	252.1	3400	89.1	20.5	949.3	316.5	2641	4111.4	-0.557	77.7	3.2
40	06/11/05-22	2.38	16.03	7.64	122.9	6.7	73.2	63.7	177.1	900	68.7	12.6	335.3	141.2	1034.3	1397.9	-0.352	131.6	1.8
41	06/11/05-21	1.87	15.48	7.41	245.9	46.4	163.9	91.9	471.9	1400	128.0	25.8	626.0	382.0	2169.8	2646	-0.219	157.5	2.5
42	06/11/05-20	2.56	16.89	8.44	289.9	15.0	91.3	65.5	340.6	2600	69.9	15.7	842.3	520.0	2810.1	3453	-0.229	49.9	2.5
Mean			15.9	8.2	281.2	11.2	157.4	114.5	302.6	2464.2	102.1	18.1	884.2	393.0	2674.6	3352.4	-0.3	100.9	3.2

extent of Tz^+ – Tz^- charge imbalance, characterized by the normalized inorganic charge balance (NICB = (Tz^+ – Tz^-)/ Tz^+), is related to the contribution of other cations.

Calcium is the dominant cation with concentrations ranging from 335.3 (Site 40) to 1353.5 (Site 6) μ mol/l and accounts for 62.8%–83.5% of the total cations. Magnesium concentrations range from 120.2 (Site 31) to 1014.2 (Site2) μ mol/l, accounting from 11.2% to 31.8% of the total cations. Na concentrations fall within a range of 6.7 (Site 23) and 280.3 (Site 10) μ mol/l with a mean value of 102.1 μ mol/l, while between 7.3 (Site 29) and 42.9 (Site 10) μ mol/l for *K* with an average of 18.1 μ mol/l. All the major cation compositions generally increase from upstream to downstream.

 $\rm HCO_3^-$ is the dominant anion for the samples, ranging from 900 (Site 40) to 4200 (Site 2) µmol/l with a mean value of 2464.2 µmol/l. SO₄²⁻ is next in abundance to $\rm HCO_3^-$, ranging from 85.4 (Site 37) to 999.0 (Site 14) µmol/l. With an exception of Site 10 (70%), $\rm HCO_3^-$ and $\rm SO_4^{2-}$ together account for 88%–97% of the total anions. There are large variations for Cl⁻ and $\rm NO_3^-$, varying from 29.6 (Site 26) to 1569.0 (Site 10) µmol/l and 28.7 (Site 31) to 324.2 (Site 7) µmol/l respectively. Generally, both of them display increasing concentrations from upstream to downstream. F⁻ concentrations are less variable, ranging from 6.1 (Site 31) to 17.5 (Site 6) µmol/l when site 41 (46.4 µmol/l) is excluded.

The dissolved Si concentrations present a range from 23.1 (Site 18) to 184.3 (Site 36) μ mol/l with a mean value of 100.9 μ mol/l, lower

than the world average of 145 μ mol/l (Meybeck, 2003), and decrease from upstream to downstream. The strontium concentrations vary between 1.3 (Site 31) and 6.6 (Site 34) μ mol/l with an average of 3.2 μ mol/l, much higher than the estimated average value of 0.89 μ mol/l of global rivers (Palmer and Edmond, 1992).

4.2. Long-term evolution of the solute concentrations in the Han River

Chen et al. (2002) have compiled major element concentrations of the rivers in the Changjiang basin including 11 sites in the upper Han River and reported a long-term increase in SO₄²⁻ and Cl⁻ concentrations as a consequence of anthropogenic impacts during the period of 1958–1990. This study revels that Ca^{2+} and Mg^{2+} concentrations remain roughly at the same level whereas Cl^- and SO_4^{2-} follow the same increasing trend. The increase of Cl⁻ concentrations, particularly its peak value occurring in the industrial areas (e.g., Shiyan City) seems to be attributable to industrial and domestic sewages. The SO_4^{2-} concentration in the present study is twice higher than those in the previous study (Chen et al., 2002; Table 2), confirming the observation of persistent increase and the rise of acid deposition (Chen et al., 2002), and also implying increasing discharge of industrial and domestic effluents. The NO_3^- concentration rises sharply compared to its concentration in 1997 (Liu et al., 2003; Chen et al., 2000), which could be ascribed to nitrogen-fertilizer applications in the basin.

Table 2

 $Comparison \ of \ the \ major \ chemical \ species \ in \ the \ upper \ Han \ River \ with \ those \ in \ the \ Changjiang \ River \ and \ its \ tributaries \ (unit \ in \ \mu mol/l).$

	Na ⁺	K ⁺	Ca ²⁺	Mg^{2+}	Cl-	NO_3^-	SO_{4}^{2-}	HCO ₃	SiO ₂
This work	102.1	18.1	884.2	393	157.4	114.5	302.6	2464.2	100.9 ^f
Han River ^a	$10.6 (Na^+ + K^+ mg/l)$		920.0	345.8	93.0	74.2 ^e	114.6	2555.7	115.0
ChangJiang ^a	$9.7(Na^+ + K^+ mg/l)$		807.5	345.8	160.6		177.1	2109.8	103.3
Yangtze ^b	222	36	973	292	151		164	2311	108
Jinsha jiang ^c	2391	58.5	1100	533	1269	8.9	388	3858	105
Lancang Jiang ^c	306	25.1	1445	458	184	19.2	279	3466	126
Nu Jiang ^c	137	26.9	1088	409	21	14.4	220	2728	115
Yalong Jiang ^c	241	29.7	815	425	22		192	2318	111
Dadu He ^c	102	35.4	828	304	11	15.5	92	2198	107
Min Jiang ^c	417	53.1	1228	393	100	107	302	2901	135
Wujiang ^d	300	50	1560	340	140	110	640	2780	90
Huang He ^c	700	30.3	1210	617	369	44.8	255	3535	107
Brahmaputra ^b	91	100	350	156	31		104	951	130
Ganges ^b	417	67	580	267	143		83	1951	128
Indus ^b	1370	112	958	374	931		436	2130	233

^a Chen et al., 2000.

^b Gaillardet et al., 1999.

^c Wu et al., 2008.

^d Han and Liu, 2004.

^e Liu et al., 2003.

f Dissolved silica.

The increase of solute concentrations from upper basin downward implies the contributions of anthropogenic inputs. The rises of major chemical species, especially Cl⁻, SO₄²⁻, NO₃⁻ from upstream to downstream, are related to the releases from agricultural and industrialized areas along the river network. The decrease of Si concentrations downward is linked to the abundance of silicate rocks in the head water of the basin (Fig. 1; Li and Zhang, 2008a). Therefore, there is a raising trend of solute concentrations, and there is a great possibility of enrichment in Cl⁻, SO₄²⁻ and NO₃⁻ contents due to the increasing anthropogenic perturbances in the drainage basin. Also, NO₃⁻ is distinctly higher than those in the Changjiang's main tributaries and other rivers originating from the Qinghai–Tibet Plateau, and Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻ and HCO₃⁻ concentrations are remarkably higher than those in Brahmaputra and Ganges (Table 2; Gaillardet et al., 1999).

4.3. Sources of solute and characterization of the end-members

The major chemical species of waters originate from weathering of rocks and minerals in the drainage basin, atmospheric deposition and anthropogenic inputs. Previous studies have reported the river water chemistry dominated by carbonate weathering (Li and Zhang, 2008a) and atmospheric inputs using Cl⁻ reference (Li and Zhang, *unpublished*). In the following discussion, we attempt to quantify the contribution of the anthropogenic and rock weathering sources of dissolved solutes to the river waters.

4.3.1. Atmospheric inputs

Li and Zhang (*unpublished*) have evaluated the contribution of precipitation to river dissolved load in the upper Han River basin. In this study, we estimate the Cl⁻ concentration originating from the atmosphere of 34.7 μ mol/l, 1.91 μ mol/l, 29.8 μ mol/l, 0.69 μ mol/l, 0.69 μ mol/l, and 3.64 μ mol/l for SO₄²⁻, Na⁺, K⁺, Ca²⁺, and Mg²⁺, respectively. Thus, atmospheric corrections for the elements except Cl⁻ and Na⁺ are ignored in the present work.

4.3.2. Anthropogenic inputs

The large variable of EC concentrations, reflecting dissolved solutes, is related to lithologies, land use and human activities in the basin (Li and Zhang, 2008a; Li et al., 2008b). Sharp increases in major chemical species are primarily observed in the upper Dan River and rivers in the industrialized areas (Table 1; Fig. 1). Also the Cl^-/Na^+ molar ratios with large variability (0.3–5.6) and more than 90%

samples with the equivalent mole ratios of Cl^-/Na^+ greater than 1 and the wide range of 0.15–0.78 for Sr (Table 1) reflect the impacts of anthropogenic activities on river water chemistry (Grosbois et al., 2000, 2001). In addition, there is no geological evidence for the exposure of evaporite strata in the river basin (Chen et al., 2002; Li and Zhang, 2008a). Therefore, we may assume that the excess of Cl^- over the atmospheric origin (34.7 µmol/l) is attributable only to human activities including industrial and agricultural inputs. Past studies also reported the sensitiveness of HCO_3^- , SO_4^{2-} , K^+ , Ca^{2+} and Mg^{2+} concentrations to human activities (Chen et al., 2002; Qin et al., 2006; Chetelat et al., 2008).

4.3.3. Chemical weathering inputs

Studies have reported major chemical species mainly originating from carbonates (Li and Zhang, 2008a), indicating by the plotting of



Fig. 2. Scatter plot of $\rm HCO_3^-$ with $\rm Ca^{2+}$ and $\rm Ca^{2+} + Mg^{2+}$ in the upper Han River basin, China.



Fig. 3. Relative contributions from silicate and carbonate weathering to waters by carbonic acid based on stoichiometry.

equivalent mole concentrations of HCO_3^- vs. Ca^{2+} and HCO_3^- vs. $(Ca^{2+}+Mg^{2+})$ (Fig. 2), with Ca^{2+} , on average balancing more than 70% of HCO_3^- , and $(Ca^{2+}+Mg^{2+})$ basically balancing with HCO_3^- . The second contribution through chemical weathering to solutes is silicates, while the contribution of evaporates is omitted because of the climate and lithology in the basin (Li and Zhang, 2008a). Covariation of $[Na^+ + K^+]/[HCO_3^-]$ versus $[Ca^{2+} + Mg^{2+}]/[HCO_3^-]$ also show the dominance of carbonate dissolution in the drainage basin (Fig. 3). The river waters fall into the second quadrant and along the line of $[Na^+ + K^+ + Ca^{2+} + Mg^{2+}] = [HCO_3^-]$, reflecting the contributions of silicate weathering to water chemistry The waters plot in the first quadrant, showing the excess of $[Ca^{2+} + Mg^{2+}]$ over $[HCO_3^-]$, is attributable to anthropogenic sources, such as agricultural fertilizes.

4.3.4. The end-member chemical compositions

The dissolved load is composed by the mixes of rock weathering and human activities after subtracting the rainwater contribution to river waters. To evaluate anthropogenic contributions and chemical weathering to the dissolved load, industrial, agricultural and rock weathering end-member chemical compositions need to be constrained.

4.3.4.1. Constrains from associations between elemental ratios. The covariation of Mg^{2+}/Ca^{2+} and Na^+/Ca^{2+} molar ratios in the upper Han River is similar to those of the surface waters of the Wujiang River (Han and Liu, 2004; Fig. 4). Three end-members including limestone, dolomite and silicate sources are recognizable according to the chemical weathering of minerals. Previous studies on the Wujiang draining carbonate-dominated terrain indicates that the limestone end-member has an Mg^{2+}/Ca^{2+} molar ratio of 0.1, Na^+/Ca^{2+} molar ratio of 0.02, and Mg^{2+}/Ca^{2+} molar ratio of 1.1 and Na^+/Ca^{2+} molar ratio of 0.02 respectively for dolomite end-member (Han and Liu, 2004). The corresponding ratio of the carbonate rocks in the upper



Fig. 4. Plots showing variations of Mg^{2+}/Ca^{2+} versus Na^+/Ca^{2+} molar ratio in the upper Han River basin, China.

Han River are $Mg^{2+}/Ca^{2+} = 0.22-0.81$, $Na^+/Ca^{2+} = 0.05-0.39$ (Fig. 4). We term the dolomitic limestone end-member according to the molar ratio of Mg^{2+}/Ca^{2+} (averaged ~0.5), thus the molar ratio of HCO_3^-/Ca^{2+} is close to 3 for carbonate end-member in this study area after ignoring silicate-source for HCO_3^- . For the Na^+/Ca^{2+} ratio, we refer to the estimation of previous studies on the Changjiang and its tributaries (Han and Liu, 2004; Chetelat et al., 2008), reporting a value of ~0.02 of Na^+/Ca^{2+} ratio for carbonate end-member (Table 3).

The averaged molar ratio of 0.1 for Na⁺/Ca²⁺ in silicate-dominated catchment is significantly lower than the values reported by other studies (Grosbois et al., 2000, 2001; Han and Liu, 2004; Chetelat et al., 2008), which is contributable to the low dissolution rate of silicates and chemical weathering of carbonates in the catchment. The controlling processes for Ca²⁺/Na⁺/Mg²⁺ compositions relating to the bedrocks are complicated (Han and Liu, 2004), and there is a considerable variability of Ca²⁺/Na⁺ and Mg²⁺/Na⁺ associated with silicate weathering (Gaillardet et al., 1999; Wu et al., 2008). In the present study, we adopt 3 to be the Na⁺/Ca²⁺ molar ratio for the silicate end-member (Chetelat et al., 2008), ~0.6 for the Mg²⁺/Ca²⁺ molar ratio (Han and Liu, 2004), and SO₄²⁻, Cl⁻ and NO₃⁻ concentrations are minimal (Table 3).

For the Mg^{2+}/K^+ ratio, we refer to the estimation of Han and Liu (2004) reporting Mg^{2+}/K^+ ratio of 0.5 for silicate-weathering endmember because of their similar lithology though there is a large variability from 0.12 (Meybeck, 1986) to 0.5 (Galy and France-Lanord, 1999; Han and Liu, 2004).

4.3.4.2. Constrains from waters draining monolithological terrains. Generally, Cl⁻, NO₃⁻ and SO₄²⁻ mainly originate from anthropogenic inputs (Grosbois et al., 2000, 2001; Chetelat et al., 2008). The study area is a less developed mountainous region with rock-dominated water chemistry, so we neglect the contributions to Ca²⁺, Mg²⁺ and K⁺ of anthropogenic source. Second, we assume that the dissolution of carbonates does not contribute to Na⁺ and K⁺.

To estimate the composition of the urban end-member we refer to the analysis of the polluted river waters (Sites 7, 10 and 14). Industrial and domestic sewages discharge directly to the three rivers and they have the highest concentrations in fluoride, chloride, nitrate and sulphate. Thus, the maximum concentrations of $[Cl^-]_{urban}$, $[NO_3^-]_{urban}$ and $[SO_4^2^-]_{urban}$ are assumed to be 1569, 324 and 999 µmol/l, respectively (Table 3). The agricultural end-member was defined by rivers (sites 22, 32–35) distributing in concentrations of sulphates and nitrates, consistent with other reports (Table 3; Grosbois et al., 2000, 2001; Chetelat et al., 2008).

Table 3

Chemical compositions of the different end members in upper Han River and their comparisons with other rivers (unit in μ mol/l).

		${ m Mg^{2+}}/{ m Ca^{2+}}$	Na ⁺ / Ca ²⁺	$\frac{\rm Mg^{2+}}{\rm K^{+}}$	HCO_3^-/Ca^{2+}	Cl ⁻	NO_3^-	SO ₄ ²⁻
Silicate	This work	0.6	3	0.5		0	0	0
	Changjiang ^a	0.57	~3	~ 1.17				
	Orleans ^b	1.07	0.86	2.14	2.86	100	0	0
Carbonate	This work	0.5	0.02		3	0	0	0
	Changjiang ^a	0.38	0.02					
	Orleans ^b	0.05	0.001	0.8	2	300	0	0
	Brehemont ^c	0.07	0.013	0.83	2	500	10	10
Urban	This work					1569	324	999
	Changjiang ^a	0.25	0.125	1.25				
	Orleans ^b	0.1	0.3	0.33		1100	0	0
	Brehemont ^c	0.3	2.67	1.5		3700	600	1100
Agriculture	This work					185	184	510
	Orleans ^b	1	2.4	6.67	0.2	500	0	0
	Brehemont ^c	40	120	2.67	1	880	500	660

^a Chetelat et al., 2008.

^b Grosbois et al., 2000.

^c Grosbois et al., 2001.

4.4. Dissolved fluxes in the upper Han River

The inputs of the different end-members to the dissolved load are calculated using the above estimation of the chemical signature of the pure end-members. These contributions of silicate, carbonate, anthropogenic including urban and agriculture are calculated following the mass balance equation:

$$[X]_{\text{river}} = [X]_{\text{silicate}} + [X]_{\text{carbonate}} + [X]_{\text{urban}} + [X]_{\text{agriculture}}$$
(1)

With the above assumption and discussions, the above equation can be simplified as follows:

$$[Cl^{-}]_{\text{residue}} = [Cl^{-}]_{\text{anthropogenic}}$$
(2)

$$[F^{-}]_{\text{river}} = [F^{-}]_{\text{anthropogenic}} \tag{3}$$

$$\left[SO_4^{2-}\right]_{\text{river}} = \left[SO_4^{2-}\right]_{\text{anthropogenic}} \tag{4}$$

$$[NO_3^-]_{river} = [NO_3^-]_{anthropogenic}$$
(5)

$$\begin{bmatrix} K^+ \end{bmatrix}_{\text{river}} = \begin{bmatrix} K^+ \end{bmatrix}_{\text{silicate}}$$
(6)

$$\left[\mathrm{Na}^{+}\right]_{\mathrm{corrected}} = \left[\mathrm{Na}^{+}\right]_{\mathrm{silicate}} + \left[\mathrm{Na}^{+}\right]_{\mathrm{anthropogenic}}$$
(7)

$$\left[Mg^{2+}\right]_{river} = \left[Mg^{2+}\right]_{carbonate} + \left[Mg^{2+}\right]_{silicate}$$
(8)

$$\left[Ca^{2+}\right]_{river} = \left[Ca^{2+}\right]_{carbonate} + \left[Ca^{2+}\right]_{silicate}$$
(9)

In order to simplify the calculations, we rewrite Eq. (8) where all species are in $\mu mol/l$:

$$\left[Mg^{2+}\right]_{river} = \left[Mg^{2+}\right]_{carbonate} + \left[K^{+}\right]_{silicate} \times 0.5$$
(10)

We can calculate the contributions of carbonates, silicates and anthropogenic inputs to dissolved load (Table 4). The carbonate fluxes (including the atmospheric CO₂ inputs) dominate the water chemistry in the study area, representing 73.7% of the total dissolved flux. Anthropogenic fluxes including urban and agriculture contribute 16.7% to the total solutes. With the discharge of 1.01×10^9 t/yr for

industrial water in the basin (Li and Zhang, 2008b), the urban fluxes (171.7×10^3 t/yr for the sum of Cl⁻, NO₃⁻ and SO₄²⁻) represent 10.3% of the anthropogenic additions, about 1.7% of the total annual dissolved load. Agriculture and silicate fluxes contribute 15% and 9.6% to the chemical budgets.

4.5. Chemical weathering and CO₂ consumption rate

The carbonate weathering rate (CWR) is quantified using dissolved concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- for carbonate weathering (Roy et al., 1999):

$$CWR = \left(Ca_{carb}^{2+} + Mg_{carb}^{2+} + 1/2HCO_{3carb}^{-}\right) \times discharge$$

$$\div drainage area / density of carbonates$$
(11)

The silicate weathering rate (SWR) is determined as follows (Roy et al., 1999):

$$SWR = \left(Na_{sil}^{+} + K_{sil}^{+} + Ca_{sil}^{2+} + Mg_{sil}^{2+} + SiO_{2sil}\right) \times discharge$$

$$\div drainage area / density of silicates$$
(12)

The CO₂ consumption rates from silicates (CO_{2sil}) and carbonates (CO_{2carb}) are calculated as follows (Wu et al., 2008):

$$CO_{2carb} = 1/2HCO_{3carb}^{-} \times discharge / drainage area$$
 (13)

$$CO_{2sil} = HCO_{3sil} \times discharge / drainage area$$
 (14)

The average densities of 2.7 and 2.4 g cm⁻³ for silicates and carbonates are applied respectively (Galy and France-lanord, 1999). Half of HCO₃⁻ produced by carbonate dissolution originates from the atmosphere (Roy et al., 1999). The calculated results are listed in Table 4. The carbonate and silicate weathering rates are 47.5 t/km²/yr and 5.6 t/km²/yr, respectively, within the range (18.1–71.6 t/km²/yr for carbonate and 3–9.1 t/km²/yr for silicate) of other Changjiang's tributaries (Table 4; Wu et al., 2008). The total chemical denudation fluxes of the upper Han River is 53.1 t/km²/yr, higher than 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 CO₂ consumption by silicate weathering is $101.8 \times 10^3 \ mol/km^2/yr$, close to the studies on the Changjiang and the Han River (Table 4). The estimation of the CO₂ consumption rates by

Table 4

River	Discharge×	Surface	Carbonate we	eathering rate		Silicate weathering rate			
	10 ⁹ m ³ /yr	area 10 ⁴ km ²	t/km²/yr	mm/kyr	CO ₂ 10 ³ mol/ km ² /yr	t/km²/yr	mm/kyr	CO ₂ 10 ³ mol/ km ² /yr	
Upper Han River	41.1	9.52	47.5	19.8	679.5	5.6	2.1	101.8	
Han River, Wuhan ^a	1306 m ³ /s	15.9	9		261.0	2.45		119.5	
Changjiang, Datong ^a	27429 m ³ /s	170.5	14		378.9	2.4		112.0	
Wujiang ^b	32.7	6.7	65	33	682	6	2.4	98	
Jinsha jiang ^c	39.4	23.3	18.1	7.5	190	9.1	3.4	370	
Lancang Jiang ^c	29.0	8.9	59.3	24.7	610	4.1	1.5	70	
Nu Jiang ^c	53.1	11.0	67.8	28.2	700	5.9	2.2	110	
Yalong Jiang ^c	55.3	12.9	44.4	18.5	460	8.0	3.0	240	
Dadu He ^c	61.6	8.9	71.9	29.9	740	8.3	3.1	180	
Min Jiang ^c	14.9	3.7	58.2	24.3	600	9.0	3.3	260	
Huang He ^c	23.2	14.6	26.1	10.9	270	3.0	1.1	90	
Brahmaputra ^d			35.4	14.8	340	10.3	3.8	150	
Ganges ^d			28.0	11.7	240	14.0	5.2	450	
Indus ^d			13.8	5.7	90	3.8	1.4	60	

The discharge is the average annual discharge.

^a Chetelat et al., 2008.

^b Han and Liu, 2004.

^c Wu et al., 2008.

^d Gaillardet et al., 1999.

carbonate weathering, $679.5 \times 10^3 \text{ mol/km}^2/\text{yr}$, is higher than the previous published results in the Han River, but comparable with the reports in the Changjiang's tributaries, i.e., $190-700 \times 10^3 \text{ mol/km}^2/\text{yr}$ (Table 4; Wu et al., 2008).

From our calculations, we estimate CO_2 consumption of 9.69×10^9 mol/yr and 64.69×10^9 mol/yr by silicate and carbonate rock weathering in the upper Han River basin, accounting for 0.11% and 0.53% of the global CO_2 consumption fluxes by silicate and carbonate rocks (8700×10^9 mol/yr and 12300×10^9 mol/yr, Gaillardet et al., 1999), respectively. The area of the upper basin is about 95,200 km² which accounts for 0.063% of the global continental area of 150×10^6 km², indicating a much intense CO_2 consumption in this basin.

5. Conclusions

 Ca^{2+} , followed by Mg^{2+} , is the dominant cation, accounting for more than 62% of the total cations. Bicarbonates, followed by SO_4^{2-} , are the dominant anions, and together account for 88% to 97% of the total anions. All the major species display increasing concentrations from upstream to downstream.

The geochemical study on the dissolved load shows the three major reservoirs including carbonates, silicates and agriculture/urban effluents contributing to the dissolved solutes. The total chemical denudation fluxes are about 53.1 t/km²/yr with carbonate and silicate weathering rates of 47.5 t/km²/yr or 19.8 mm/kyr and 5.6 t/km²/yr or 2.1 mm/kyr, respectively, remarkably higher than the global average of approximately 24 t/km²/yr, which suggests a relatively intense chemical weathering regime in the upper Han River basin. The contribution of the anthropogenic inputs to the dissolved load is estimated to be 16.7%, demonstrating the strong impacts of human activities on water chemistry.

Chemical weathering of the drainage basin consumes the atmospheric CO_2 of 74.38×10^9 mol/yr (64.69×10^9 mol/yr for carbonate and 9.69×10^9 mol/yr for silicate, respectively), accounting for 0.64% of the global total consumption fluxes, and reflecting a very big percentage considering the small area in the world.

Acknowledgements

The research is jointly supported by the National Key Sciences Research Program of China (2008CB418000), the "Hundred-talent Project" of the Chinese Academy of Sciences (0629221C01), and the Chinese National Natural Science Foundation (40773077). We would like to thank Sheng Gu, Jia Li, Lianfa Li, Sha Mu and Yiping Wang for their help during the samples collection, and Hongyin Han of the Chinese University of Geosciences for the assistance on the major ion analysis. We also thank Dr. Donald B. Dingwell and other two anonymous reviewers for their comments and suggestions.

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