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Geochemistry of the upper Han River basin, China
2: Seasonal variations in major ion compositions and contribution of precipitation chemistry to the dissolved load

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ABSTRACT

A total of 252 water samples were collected from 42 sites across the upper Han River basin during the time period from 2005–2006. Major ions (Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+}), Si, water temperature, pH, EC and TDS were determined and consequently correlation matrix, analysis of variance, factor analysis and principal component analysis were performed in order to identify their seasonal variations and atmospheric inputs into river solutes. The results reveal that pH, EC, TDS, Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+} and Mg^{2+}, K^+ and Si generally tend to show the minimum compositions in months belong to the rainy season, while the dry season for NO_3^- and Na^+. NO_3^-, Mg^{2+} and Si have the maximum concentrations in months belong to the rainy season. By comparing the major ions relating to hydrological regime, NO_3^-, contrary to other elements, has higher concentration in the rainy season. The overall water quality is non-polluted, while there are indications of enrichment of inorganic anions including NO_3^- causing water entrophication in the near future. The atmospheric inputs contribute to river solutes is limited with a mean inputs of approximate 1% in the basin. The understanding of the major ion dynamics would help water quality conservation in the basin for China's interbasin water transfer project.

1. Introduction

There is a worldwide deterioration of water quality due to natural processes (*e.g.*, hydrological features, climate change and precipitation) and human activities (*e.g.*, agricultural land use and sewage discharge) [1–5]. The major ion geochemistry study of river waters provides an insight of understanding the pattern and linkage between chemical weathering, evaporation, atmospheric deposition and anthropogenic processes in a basin [1,6,7]. Therefore, numerous geochemical studies on the major rivers in the world have been conducted for determining the mechanisms controlling water chemistry, weathering processes and stream characteristics, etc. [6,8–14].

In China, previous studies on major element chemistry have focused on large rivers such as the Changjiang (Yangtze River) and Yellow Rivers [1,7,9,15–17], and reported dramatic increase in Cl^- and SO_4^{2-} concentrations caused by anthropogenic inputs [1] and sensitiveness of major ions to human activities [7]. The Han River, a tributary of the Changjiang River, is a water source area of China's South to North Water Division Project, supplying water to North China including Bejing and Tianjin. Previous studies on the Han River reported the nutrient and slightly heavy metal contaminations [3–5,18–21], as well as the notable raising trend of NO_3^- [18], Cl^- and SO_4^{2-} concentrations [1]. In this study, a comprehensive and systematic study was completed to identify the temporal variations of major ions as a sequel to a previous studies dealing with the spatial distribution of major ions and their controlling factors [22], and chemical weathering rates, associated CO_2 consumption and anthropogenic inputs using one month data (November 2005) [23] in the upper Han River, as well as to determine the contribution of precipitation to dissolved solutes.

2. Materials and methods

2.1. Study area

The upper Han River basin with an elevation from 210 to 3500 m is situated between 31°20′N–34°10′N and 106°E–112°E in a mountainous region, and covers a total area of 95,200 km^2 (Fig. 1). Climate in the basin belongs to north sub-tropic monsoon, and annual mean temperature ranges between 12 and 16 °C. Average annual precipitation is 700–1800 mm with large intra-annual and inter-annual variabilities. Floods in the basin are generally formed by storms between May and October, and this period accounts about 80% of the annual total rainfall [3,5]. In the considered periods of the present study, August and November in 2005 and October in 2006

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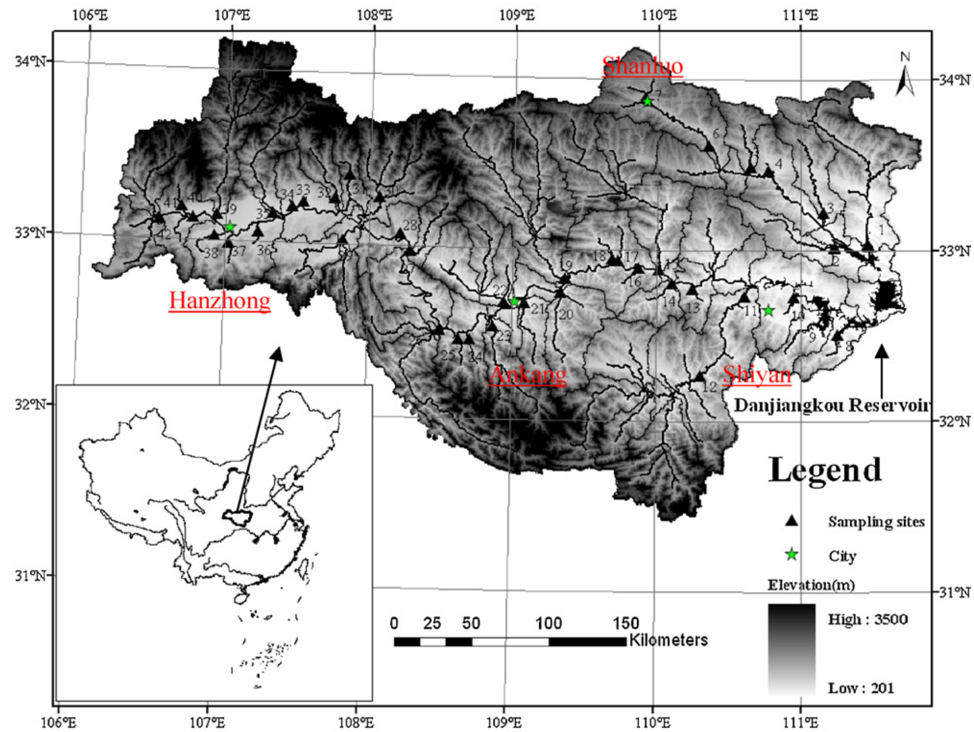

Fig. 1. The upper Han River basin showing the sampling sites, DEM and drainage system, China.

belong to rainy season, the rests (June 2005, April and June 2006) belong to dry season according to the hydrological routing in the region. The basement rocks are overlain by a sedimentary cover from Precambrian to Quarternary in age and carbonate rocks widely spread throughout the drainage basin [1,22].

Vegetation, the dominant land use, accounts for approximate 77% of the total surface area in the upper Han River. Agriculture and urban respectively representing about 15% and 0.5% of the total drainage area are located along the river networks [3; Fig. 1]. Industries mainly concentrate in the cities of Shiyan, Shangluo, Hanzhong and Ankang (Fig. 1)

2.2. Sampling and analysis

Field surveys were conducted in June, August, November 2005 and April, June, October 2006 from 42 sites representing major tributaries with varying landscape settings across the upper Han River basin (Fig. 1). Thus, a total of 252 grab samples were collected including 126 water samples in the rainy season (August and November 2005 and October 2006). Samples were collected at a depth of 10 cm, stored temporally in acid-washed high density polyethylene (HDPE) 1 l containers, and filtered through pre-washed 0.45 μm Millipore nitrocellulose filters on the same day. The initial portion of the filtration was discarded to clean the membrane and the following ones were stored using previously acid-washed HDPE bottles for analysis. The two aliquots, one acidified using ultra-pure concentrated nitric acid to pH 2 for cations determination and another non-acidified for the anions measurements were prepared. Simultaneously, five rainwater samples were collected in spring (April, 2006) in the Danjiangkou Reservoir, and their pretreatment and analysis procedures were the same to river waters.

Water temperature (*T*), pH, electrical conductivity (EC) and total dissolved solids (TDS) were determined *in situ* using YSI 6920 (YSI Incorporated, Yellow Springs, Ohio, USA) after calibrations. HCO_3^- was measured by titration using hydrochloric acid on the sampling day. Major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and Si concentrations were measured by Inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II XSP DUO, USA) with a precision better than 5%. Anions (Cl^-, NO_3^- and SO_4^{2-}) concentrations were determined by ionic chromatography (IC) (Dionex Corporation, Sunnyvale, CA, USA) with a precision of 5% [24].

2.3. Statistical analyses

Relationships using Pearson's correlation and analysis of variance (ANOVA) was performed to compare seasonal differences in major ion concentrations (least-significance difference, LSD), *p* values smaller than 0.05 were considered to be significant. Factor analysis and principal component analysis (PCA) with Varimax rotation were conducted for extraction and deriving factors, respectively. All the processes were performed using SPSS 15.0 for windows.

3. Results

All the major ions display remarkable temporal differences except NO_3^- (Table 1). Generally, most of water variables tend to display the minimum concentrations in months of the rainy season, i.e., pH (8.08 ± 0.33), EC (236.08 ± 70.77 μS/cm), TDS (153.41 ± 46.00 mg/l), Cl^- (3.51 ± 1.82 mg/l), SO_4^{2-} (25.43 ± 12.71 mg/l), HCO_3^- (120.55 ± 42.43 mg/l), Ca^{2+} (33.55 ± 0.42 mg/l) and Mg^{2+} (6.69 ± 3.49 mg/l) in August, K^+ (0.71 ± 0.30 mg/l) and Si (2.83 ± 0.88 mg/l) in November, while NO_3^- (4.81 ± 3.47 mg/l) and Na^+ (0.67 ± 0.36 mg/l) in months of the dry season. The maximum concentrations of NO_3^- (7.10 ± 3.91 mg/l), Mg^{2+} (9.43 ± 4.24 mg/l) and Si (5.82 ± 2.03 mg/l) are observed in months of the rainy season, and other variables in the dry season (June 2005). As for the averages, NO_3^- is contrary to other elements, reaching the peak value in the rainy season (Table 1).

Factor analysis for major ion compositions indicates two components for June and November 2005, while three components are observed for other sampling times (Table 2). These significant fac-

Table 1
Temporal variations of main variables (*T*, pH, EC, TDS), Si and major ion compositions in the upper Han River basin, China (unit in mg/l except T in °C, EC in μS/cm and pH; The different letters indicate statistical difference among seasons at $p < 0.05$; LSD test).

		T	pH	EC	TDS	Cl^-	$NO_3{}^-$	$SO_4{}^{2-}$	$HCO_3{}^-$	Na^+	K^+	Ca^{2+}	Mg^{2+}	Si
June 2005	Minimum	19.78	6.64	136.10	88.50	1.26	1.15	10.36	48.80	1.24	0.38	21.88	2.27	
	Maximum	33.01	9.04	604.10	392.70	70.67	18.79	161.90	280.60	16.15	4.95	81.48	24.12	
	Mean	27.51 (a)	8.34 (a)	313.81 (a)	203.98 (a)	11.88 (a)	4.81 (a)	41.12 (a)	147.32 (ab)	5.93 (a)	1.57 (b)	46.27 (a)	8.60 (ab)	
	S.D.	3.14	0.50	106.93	69.50	15.40	3.47	28.05	50.20	3.58	0.88	13.02	4.49	
August 2005	Minimum	16.19	7.03	111.40	72.40	1.43	0.65	8.53	36.60	1.44	0.23	14.17	2.38	2.80
	Maximum	29.32	8.74	425.20	276.30	10.30	11.40	72.90	237.90	9.63	1.93	56.17	22.30	5.58
	Mean	20.67 (b)	8.08 (b)	236.08 (b)	153.41 (b)	3.51 (b)	5.09 (a)	25.43 (b)	120.55 (c)	3.41 (b)	0.81 (c)	33.55 (c)	6.69 (c)	4.01 (b)
	S.D.	3.38	0.33	70.77	46.00	1.82	2.14	12.71	42.43	1.62	0.43	10.42	3.49	0.72
November 2005	Minimum	12.38	7.41	122.90	79.70	1.05	1.78	8.20	54.90	1.07	0.29	13.41	2.89	0.65
	Maximum	18.40	8.79	445.30	289.40	55.70	20.10	95.90	256.20	6.45	1.68	54.14	24.34	5.16
	Mean	15.88 (c)	8.24 (ab)	281.17 (a)	182.72 (a)	5.59 (b)	7.10 (a)	29.05 (b)	150.32 (a)	2.35 (c)	0.71 (c)	35.37 (bc)	9.43 (a)	2.83 (c)
	S.D..	1.52	0.27	79.66	51.80	8.12	3.91	15.91	45.23	1.10	0.30	10.19	4.24	0.88
April 2006	Minimum	12.21	7.20	149.60	97.20	1.57	2.38	1.20	43.92	0.00	0.05	0.01	0.00	0.07
	Maximum	22.09	9.13	526.50	342.20	18.49	37.32	89.04	248.88	1.45	3.98	72.45	19.32	8.17
	Mean	16.31 (c)	8.12 (b)	287.95 (a)	187.23 (a)	5.57 (b)	6.55 (a)	30.05 (b)	130.89 (bc)	0.67 (d)	2.10 (a)	34.99 (c)	6.79 (c)	4.04 (b)
	S.D.	2.35	0.43	101.21	65.82	3.39	5.87	17.46	51.03	0.36	0.96	14.90	3.66	1.38
June 2006	Minimum	20.37	7.05	133.40	86.70	2.11	1.97	10.87	63.44	1.53	0.35	17.74	2.66	1.69
	Maximum	35.66	9.27	510.60	331.90	20.79	13.32	117.57	248.88	10.90	3.71	83.93	25.87	10.82
	Mean	26.72 (a)	8.16 (b)	307.10 (a)	199.61 (a)	6.34 (b)	5.14 (a)	32.83 (ab)	146.51 (ab)	4.08 (b)	1.29 (b)	40.43 (b)	8.94 (a)	5.28 (a)
	S.D.	3.61	0.43	84.40	54.86	3.71	2.92	21.78	41.43	2.12	0.76	12.83	4.19	1.69
October 2006	Minimum	16.35	6.73	122.40	79.60	0.65	0.73	9.82	48.80	1.44	0.56	15.75	1.89	2.26
	Maximum	25.05	8.74	544.50	353.90	37.01	61.54	135.30	244.00	16.33	7.31	58.35	24.81	11.77
	Mean	20.86 (b)	8.08 (b)	288.66 (a)	187.63 (a)	4.95 (b)	6.31 (a)	34.07 (ab)	136.12 (abc)	3.40 (b)	1.42 (b)	37.53 (bc)	7.09 (bc)	5.82 (a)
	S.D.	2.01	0.42	84.86	55.15	5.60	11.26	21.65	39.20	2.38	1.03	9.44	3.78	2.03
Dry season (June 2005, April 2006, June 2006)	N	124	124	124	124	124	122	124	124	123	123	123	123	84
	Minimum	12.21	6.64	133.40	86.70	1.26	1.15	1.20	43.92	0.00	0.05	0.01	0.00	0.07
	Maximum	35.66	9.27	604.10	392.70	70.67	37.32	161.90	280.60	16.15	4.95	83.93	25.87	10.82
	Mean	23.45	8.21	302.78	196.83	7.87	5.50	34.56	141.48	3.50	1.66	40.42	8.10	4.66
	S.D.	5.98	0.46	97.65	63.48	9.56	4.32	23.04	47.93	3.21	0.93	14.28	4.20	1.65
Rainy season (August 2005, November 2005, October 2006)	N	126	126	126	126	124	124	124	126	126	126	126	126	126
	Minimum	12.38	6.73	111.40	72.40	0.65	0.65	8.20	36.60	1.07	0.23	13.41	1.89	0.65
	Maximum	29.32	8.79	544.50	353.90	55.70	61.54	135.30	256.20	16.33	7.31	58.35	24.81	11.77
	Mean	19.14	8.13	268.64	174.59	4.70	6.18	29.58	135.66	3.05	0.98	35.48	7.74	4.22
	S.D.	3.34	0.35	81.43	52.93	5.85	7.04	17.45	43.76	1.83	0.73	10.08	4.01	1.82
ANOVA for dry and wet seasons	d.f.	1	1	1	1	1	1	1	1	1	1	1	1	1
	M.S.	1160.11	0.33	72844.13	30916.36	621.62	28.51	1538.01	2117.48	12.48	28.80	1519.81	8.18	9.89
	F	49.69	1.97	9.03	9.06	9.89	0.83	3.68	1.01	1.84	41.09	9.99	0.49	3.21
	P	0.000	0.161	0.003	0.003	0.002	0.362	0.056	0.317	0.177	0.000	0.002	0.486	0.075

S.D. = standard deviation; d.f. = degrees of freedom; M.S. = mean square.

Table 2
Factor analysis for water variables in each sampling time of the upper Han River basin, China.

	June 2005		August 2005			November 2005	
	1	2	1	2	3	1	2
Part (a)							
pH	**−0.689**	−0.276	0.247	0.032	−0.788	0.321	−0.512
EC	0.652	**0.736**	**0.938**	0.219	0.222	**0.924**	0.325
TDS	0.652	**0.737**	**0.938**	0.218	0.222	**0.925**	0.325
Cl^-	**0.740**	0.368	0.364	**0.653**	0.572	−0.007	**0.763**
NO_3^-	0.031	**0.651**	0.348	0.297	**0.727**	0.476	**0.625**
SO_4^{2-}	**0.785**	0.047	0.249	0.378	**0.713**	0.424	**0.520**
HCO_3^-	−0.066	**0.893**	**0.931**	−0.052	−0.050	**0.882**	−0.081
Na^+	**0.816**	0.266	0.322	**0.826**	0.303	0.300	**0.893**
K^+	**0.864**	−0.031	0.178	**0.900**	0.073	0.213	**0.778**
Ca^{2+}	0.418	**0.815**	**0.897**	0.087	0.062	**0.902**	0.102
Mg^{2+}	0.472	**0.687**	**0.805**	0.216	0.063	**0.851**	0.108
Si			−0.451	**0.583**	0.117	**−0.550**	0.511
Eigenvalues	6.310	1.721	5.932	2.643	1.069	5.635	2.745
Cumulative %	39.120	73.014	39.981	61.996	80.366	41.428	69.838

	April 2006			June 2006			October 2006		
	1	2	3	1	2	3	1	2	3
Part (b)									
pH	0.077	0.002	**−0.859**	−0.070	−0.064	**−0.798**	−0.097	0.040	**−0.859**
EC	**0.889**	0.394	0.174	**0.820**	0.507	0.197	0.569	**0.816**	0.037
TDS	**0.889**	0.393	0.174	**0.820**	0.507	0.197	0.569	**0.816**	0.037
Cl^-	0.378	**0.766**	0.212	0.248	0.837	0.160	**0.887**	0.218	0.260
NO_3^-	0.447	0.212	**0.601**	0.561	0.131	**0.594**	**0.660**	0.364	0.270
SO_4^{2-}	0.112	**0.761**	−0.019	0.155	**0.691**	−0.118	**0.530**	0.331	−0.149
HCO_3^-	**0.955**	0.015	0.119	**0.929**	−0.035	0.170	0.147	**0.894**	−0.025
Na^+	0.391	**0.803**	0.201	0.238	**0.887**	0.130	**0.916**	0.193	0.269
K^+	0.153	**0.813**	0.185	0.107	**0.858**	0.116	**0.924**	0.028	0.180
Ca^{2+}	**0.872**	0.295	0.278	**0.852**	0.232	0.332	0.277	**0.876**	−0.145
Mg^{2+}	**0.796**	0.253	−0.111	**0.774**	0.208	−0.206	−0.030	**0.877**	0.085
Si	0.204	0.264	**0.797**	0.091	**0.472**	0.371	0.294	−0.006	**0.772**
Eigenvalues	6.501	1.649	1.379	6.087	1.895	1.048	6.252	2.397	1.022
Cumulative %	37.203	62.588	79.403	33.465	63.107	75.249	33.659	66.980	80.591

Bold values present high loadings.

tors (*i.e.*, Eigenvalues >1) account for more than 70% of the total variability (Table 2). Overall, EC, TDS, HCO_3^-, Ca^{2+} and Mg^{2+} are in the same component in the both seasons.

Correlation analysis for hydrological regime (rainy and dry seasons) data of major ions demonstrates EC and TDS have positive relationships with the rest variables in the dry season, while Si excluded in the rainy season (Tables 3 and 4). There are significant associations among Ca^{2+}, Mg^{2+} and HCO_3^- ($r > 0.6$, $p < 0.01$), and positive correlations among Cl^-, SO_4^{2-}, Na^+ and K^+ in the both seasons. Moreover, Na^+, K^+ and Si in the rainy season tend to show relatively better correlations than in the dry season.

Component principal analysis for the two seasons indicates the first component in the rainy and dry seasons, accounting for more than 35% of the total variability, including the same variables such as EC, TDS, HCO_3^-, Ca^{2+} and Mg^{2+}, and the first two and four components accounting for 68% and 80% of the total variability in the rainy and dry seasons, respectively (Table 5).

4. Discussion

4.1. Seasonal characteristics of major ions

The first component from factor analysis shows the strong geochemical relationships among EC, TDS, HCO_3^-, Ca^{2+} and Mg^{2+} in the rainy season (Table 5), representing the carbonate dissolution [1,2], as suggested by the dominated carbonate lithologies in the basin [22]. Cl^-, Na^+, K^+ and Si in the second component appear to indicate the mixed sources of silicates and evaporites for Na^+ and K^+. NO_3^- and SO_4^{2-} represent weak associations with the two significant factors, implying their variable sources especially diffuse caused by runoff in the rainy season [2]. Similar to the rainy season, the first component in the dry season indicates the strong associations between EC, TDS, HCO_3^-, Ca^{2+} and Mg^{2+}, reflecting the contribution from weathering of carbonate mineral [1,2]. The second and third components include Cl^-, SO_4^{2-}, Na^+, K^+ and Si, reflecting weathering of alkaline silicates and evaporites. The last component shows the dominant nature of pH and NO_3^-, which accounts for anthropogenic inputs and mineralization (Table 5; [2]).

By comparing the two seasonal geochemical signatures (Table 1), inputs mainly from precipitation and bedrock weathering in the rainy season with the highest of the hydrological cycle and dilution can explain the low cations, Cl^- and SO_4^{2-} concentrations [2,25,26], while higher NO_3^- concentrations in the rainy season are contrary to studies by Anshumali and Ramanathan [2] and Grosbois et al. [25], and similar to the Changjiang River [18]. This can be explained as the contributions of agricultural diffuses due to rain runoff and easily soil loss, and less uptaking of atmospherically deposited N due to fast flow rates in the flood season [1,5,27]. In the dry season, inputs mainly from carbonate (ground or surface water) and sewage can explain higher concentrations of cations, Cl^-, SO_4^{2-} and Si concentrations. Also, no significant differences in compositions of Si and NO_3^- (Table 1) between the rainy and dry seasons imply the little contributions of diatom bloom, and algae consumption and non bioavailability of the both chemical species in soils [26].

TDS and major ions in fluvial system vary greatly with varying hydrological routing due to dilution [2,6], i.e., Amazon with sharply decreasing TDS and major ions in the rainy season [6]. The variation factors (i.e., the ratio of average values in each month) for TDS and major ions are smaller than 1.5 in the upper Han River, similar to the

Table 3
Pearson correlation coefficients among the water physicochemical parameters in the rainy season of the upper Han River basin, China.

	T	pH	EC	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	Si
T	1.00												
pH	0.06	1.00											
EC	−0.04	0.02	1.00										
TDS	−0.04	0.02	**1.00**[a]	1.00									
Cl^-	−0.05	**−0.24**[a]	**0.42**[a]	**0.42**[a]	1.00								
NO_3^-	**−0.25**[a]	−0.15	**0.55**[a]	**0.55**[a]	**0.47**[a]	1.00							
SO_4^{2-}	0.00	−0.11	**0.57**[a]	**0.57**[a]	**0.36**[a]	**0.34**[a]	1.00						
HCO_3^-	−0.12	**0.19**[b]	**0.81**[a]	**0.81**[a]	0.13	**0.33**[a]	**0.18**[b]	1.00					
Na^+	**0.26**[a]	**−0.27**[a]	**0.51**[a]	**0.51**[a]	**0.63**[a]	**0.60**[a]	**0.45**[a]	0.17	1.00				
K^+	**0.25**[a]	**−0.23**[b]	**0.45**[a]	**0.45**[a]	**0.55**[a]	**0.50**[a]	**0.37**[a]	0.14	**0.81**[a]	1.00			
Ca^{2+}	0.00	0.14	**0.85**[a]	**0.85**[a]	0.17	**0.38**[a]	**0.40**[a]	**0.77**[a]	**0.32**[a]	**0.26**[a]	1.00		
Mg^{2+}	−0.09	0.09	**0.74**[a]	**0.74**[a]	**0.20**[b]	**0.26**[a]	**0.29**[a]	**0.71**[a]	**0.18**[b]	0.02	**0.62**[a]	1.00	
Si	**0.32**[a]	**−0.40**[a]	0.05	0.05	0.16	**0.22**[b]	**0.18**[b]	**−0.20**[b]	**0.43**[a]	**0.51**[a]	−0.02	**−0.20**[b]	1.00

Bold values represent correlation with significance.
[a] Significance at the 0.01 probability level.
[b] Significance at the 0.05 probability level.

Table 4
Pearson correlation coefficients among the water physicochemical parameters in the dry season of the upper Han River basin, China.

	T	PH	EC	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	Si
T	1.00												
pH	**0.30**[a]	1.00											
EC	0.06	**−0.33**[a]	1.00										
TDS	0.06	**−0.33**[a]	**1.00**[a]	1.00									
Cl^-	0.15	**−0.32**[a]	**0.58**[a]	**0.58**[a]	1.00								
NO_3^-	**−0.23**[b]	**−0.29**[a]	**0.49**[a]	**0.49**[a]	0.16	1.00							
SO_4^{2-}	**0.19**[b]	**−0.19**[b]	**0.52**[a]	**0.52**[a]	**0.45**[a]	0.14	1.00						
HCO_3^-	0.05	−0.09	**0.74**[a]	**0.74**[a]	**0.27**[a]	**0.38**[a]	−0.08	1.00					
Na^+	**0.59**[a]	−0.09	**0.50**[a]	**0.50**[a]	**0.68**[a]	0.03	**0.44**[a]	**0.29**[a]	1.00				
K^+	**−0.24**[a]	**−0.28**[a]	**0.43**[a]	**0.43**[a]	**0.39**[a]	**0.22**[b]	**0.34**[a]	0.09	**0.26**[a]	1.00			
Ca^{2+}	0.16	−0.23	**0.89**[a]	**0.89**[a]	**0.46**[a]	**0.45**[a]	**0.38**[a]	**0.81**[a]	**0.48**[a]	**0.25**[a]	1.00		
Mg^{2+}	0.15	−0.18	**0.74**[a]	**0.74**[a]	**0.42**[a]	**0.28**[a]	**0.39**[a]	**0.59**[a]	**0.40**[a]	**0.18**[b]	**0.61**[a]	1.00	
Si	**0.27**[a]	**−0.28**[a]	**0.36**[a]	**0.36**[a]	**0.30**[a]	**0.30**[a]	0.26	**0.29**[a]	**0.51**[a]	0.16	**0.46**[a]	**0.26**[b]	1.00

Bold values represent correlation with significance.
[a] Significance at the 0.01 probability level.
[b] Significance at the 0.05 probability level.

Changjiang River [1], reflecting an additional and significant contributions (enhanced carbonate rock dissolution) to the dissolved salts in the drainage basin responsible for compensating their dilutions in the rainy season. Moreover, study has reported that authigenic source especially in the dry season has important impact on dissolved calcium and carbonate species [26], which appears to cause remarkable variations in dominant ions such as Ca^{2+} and HCO_3^- between the rainy and dry seasons. Our results show the little variability for HCO_3^- (Table 1), also supporting their increasing sources in the rainy season [1].

By comparing with guidelines for drinking water of the World Health Organization [28] and Chinese State Standards [29], there exists NO_3^- in the rainy season beyond the safe limit of 50 mg/l (Table 1). Past report demonstrated 3.0 mg/l for Cl^- and 10.5 mg/l for SO_4^{2-} using the data during 1958–1990 [1], our results are therefore similar to the conclusion of persistent increases in Cl^- and SO_4^{2-} concentrations ([1]; Table 1), and NO_3^- concentration also rises sharply in the recent 10 years (i.e., 4.6 mg/l in 1997) [18,19]. Thus, there is a possible enrichment of inorganic anions and water eutrophication as the increasing anthropogenic activities, and some measurements should be introduced to mitigate chemical inputs to rivers.

4.2. Precipitation contribution to dissolved load

Chloride has been used as a reference of atmospheric contribution to the chemical composition of river waters because of its conservative behavior through the hydrological cycle, and Grosbois et al. [25] reported the precise correction method and their calculations. The reference of Cl^- (Cl_{ref}) was calculated using Cl^- concentration in rainwater (Cl_{rain}) multiplied by the evapotranspiration factor relating to the rainfall (P, in mm) and the evapotranspiration (E, in mm).

$$F = \frac{P}{(P - E)} \qquad (1)$$

Table 5
Factor analysis for some variables in the rainy and dry seasons of the upper Han River basin, China.

	Rainy season		Dry season			
Component	1	2	1	2	3	4
pH	0.246	−0.529	0.014	−0.035	−0.148	**−0.838**
EC	**0.931**	0.328	**0.872**	0.411	0.170	0.148
TDS	**0.931**	0.328	**0.872**	0.410	0.170	0.148
Cl^-	0.248	**0.667**	0.349	**0.723**	0.330	0.143
NO_3^-	0.424	0.593	0.468	0.240	−0.158	**0.616**
SO_4^{2-}	0.432	0.469	0.120	**0.738**	0.308	−0.110
HCO_3^-	**0.902**	−0.091	**0.956**	−0.073	0.062	0.104
Na^+	0.278	**0.853**	0.244	0.184	**0.859**	−0.090
K^+	0.184	**0.844**	0.100	**0.806**	−0.138	0.212
Ca^{2+}	**0.882**	0.094	**0.876**	0.208	0.193	0.224
Mg^{2+}	**0.840**	−0.075	**0.767**	0.091	0.279	−0.160
Si	−0.228	**0.687**	0.198	0.088	**0.707**	0.445
Eigenvalues	5.480	2.650	5.773	1.484	1.272	1.113
Cumulative %	39.030	67.754	35.442	53.866	67.892	80.352

Bold values present high loadings.

Table 6
The contribution of precipitation to river solutes in the upper Han River basin, China (%).

	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Solutes
June 2005	10.37	0.45	11.57	1.72	0.06	1.02	0.84
August 2005	35.09	0.72	20.13	3.36	0.08	1.31	1.13
November 2005	22.05	0.63	29.22	3.83	0.08	0.93	0.94
April 2006	22.12	0.61	100.00	1.29	0.08	1.29	1.02
June 2006	19.44	0.56	16.83	2.10	0.07	0.98	0.91
October 2006	24.91	0.54	20.17	1.91	0.07	1.23	0.97
Dry season	15.66	0.53	19.60	1.63	0.07	1.08	0.92
Rainy season	26.21	0.62	22.47	2.77	0.08	1.13	1.00

$$\mathrm{Cl}_{\mathrm{ref}} = \sum_{i=1}^{n} \mathrm{Cl}_{\mathrm{rain}\,i} \times F_i \times \mathrm{Area}_i\% \qquad (2)$$

where $\mathrm{Cl}_{\mathrm{rain}\,i}$, F_i and Area_i% correspond to Cl concentration, evapotranpiration factor and the proportion of each region, i corresponds to divisions (from 1 to n) of a study area.

Unfortunately, we have not carried out a systematic study on the rainwater chemistry in the upper Han River, we therefore cannot divide the basin into several regions for calculation. In the present work, the rainfall and evapotranspiration are respectively 1200 mm and 850 mm [24], thus, F is equal to 3.4 according to Eq. (1). The atmospheric inputs were estimated in a less development basin (pristine areas) using one rainwater station with five samples collected in a spring non affected by human activities. The reference of Cl^- concentration representing the highest Cl^- concentration in the rainwater input to the river was estimated at 34.7 μmol/l [24]. Consequently the estimate of the precipitation contribution to river solutes is calculated based on seawater (Table 6). The main atmospheric correction is for sodium with an input of 22.47% in the rainy season, with 19.60% in the dry season, ranging from 11.57% (June 2005) to 29.22% (November 2005). Correction for chloride is similar to sodium, varying from 10.37% (June 2005) to 35.09% (August 2005) with a mean contribution of 26.21% in the rainy season and 15.6% in the dry season, respectively. The atmospheric correction for potassium is 2.77% and 1.63% in the rainy and dry seasons respectively and ranging from 1.72% (June 2005) to 3.83% (November 2005). Corrections for calcium, magnesium and sulfate are similar in monthly scale, close to 0.07%, 1.1% and 0.58%, respectively. Overall, precipitation has greater contribution in the rainy season than in the dry season, contributing approximately 1% to the river solutes, less than the world's average atmospheric contribution of 3% [30], which is consistent the previous result of rock weathering-dominated rivers in the Han River basin [22].

There are large spatial variability in the chemistry of rainwater and evapotranspiration in the upper Han River basin with a vast area of 95,200 km^2 Also, the estimation based on seawater may be underestimated considering the anthropogenic contributions to rainwater chemistry. Further study should be carried out through basin divisions and systematic rainwater analysis for estimating the chemistry of precipitation to river solutes.

5. Conclusions

All the major ions demonstrate remarkable temporal variations except NO_3^-. Most of water variables tend to display the minimum concentrations in month of the rainy season, such as pH, EC, TDS, Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+} and Mg^{2+} in August, K^+ and Si in November, while NO_3^- and Na^+ in month of the dry season. The maximum concentrations of NO_3^-, Mg^{2+} and Si are observed in months of rainy season, and others are opposite. All the ions show higher concentrations in the dry season except NO_3^- relating to hydrological regime. Inorganic species such as Cl^-, SO_4^{2-} and NO_3^- increase greatly compared to the past 10 years, thus, there is a possibility of water eutrophication in the near future.

The precipitation contributes more to river solutes in rainy season than in dry season, i.e., 26.21% and 15.66% for chloride, 0.62% and 0.53% for sulfate, 22.47% and 19.60% for sodium, 2.77% and 1.63% for potassium, 0.08% and 0.07% for calcium, and 1.13% and 1.08% for magnesium, respectively. Overall, the precipitation constitutes 1% of the river major ions.

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