Environ Earth Sci (2015) 73:7505–7516
DOI 10.1007/s12665-014-3921-2

ORIGINAL ARTICLE

Major ion chemistry, chemical weathering and CO_2 consumption in the Songhua River basin, Northeast China

Yingjie Cao · Changyuan Tang · Xianfang Song · Changming Liu

Received: 8 April 2014 / Accepted: 24 November 2014 / Published online: 10 December 2014

Abstract A detailed analysis of the major ion chemistry, chemical weathering and CO_2 consumption was conducted in the Songhua River basin, which is the largest basin with a draining area of 557 thousand km^2 in Northeast China. The dataset used in this study included major ion concentrations came from 56 hydrological stations from the year of 1962 to 1984. The median of the total dissolved solid concentration of the Songhua River was 104.8 mg/L, about two times higher than the global average (65.0 mg/L), but lower than that of other Chinese Rivers. Prevalent ions were Na^+, Ca^{2+} and HCO_3^-, and the average Ca^{2+}/Na^+ and Mg^{2+}/Na^+ molar ratios were 0.70 and 0.42, which were close to silicate weathering end-member. Long-term trend analysis by seasonal MK test showed that from 1962 to 1984, Ca^{2+}, $Na^+ + K^+$ and HCO_3^- were significantly increasing, and the increasing rates calculated by linear fit slopes for Ca^{2+}, $Na^+ + K^+$ and HCO_3^- ions were 0.22, 0.63 and 2.35 mg/year, respectively. An inverse model showed that the dissolved loads primarily came from rock weathering (91.5 %), including silicate weathering (66.4 %) and a small portion from carbonates (16.1 %) and evaporites (9.0 %). Other origins consisted of anthropogenic inputs (5.3 %) and atmospheric inputs (3.2 %). Average silicate and carbonate weathering rates were estimated as 4.03 and 1.76 t km^{-2} year^{-1}, and CO_2 consumption rates of silicates and carbonates were 17.1 × 104 and 1.85 × 104 mol km^{-2} year^{-1}, respectively. These results are consistent with the lithologies of the study area, which mainly consisted of silicate rocks.

Keywords The Songhua River · Major ion chemistry · Long-term trends · Chemical weathering · CO_2 consumption

Introduction

From the view of the global carbon cycle, it has been recognized that the flux of CO_2 consumed by carbonate dissolution on the continents is balanced by the flux of CO_2 released into the atmosphere from the oceans by carbonate precipitation on the geological time scale (Berner et al. 1983). Chemical weathering of silicate rock acts as a net sink for atmospheric CO_2, and its rate and feedback mechanisms, which are controlled by climatic and geologic factors, function as regulators of atmospheric CO_2 levels over geologic time scales (Berner 1991; Edmond 1992; Raymo and Ruddiman 1992; Walker et al. 1981). Numerous studies on major ions and dissolved loads of larger rivers have been carried out in the Changjiang River (Chen et al. 2002; Ran et al. 2010), the Huanghe River (Zhang et al. 1995), the Pearl River (Xu and Liu 2010; Zhang et al. 2007), the Huai River (Zhang et al. 2011) and the rivers of the Qinghai-Tibet Plateau (Wu et al. 2008) to examine hydrochemical characteristics, chemical erosion and CO_2 consumption rates, and long-term climatic evolution of the Earth. A general conclusion of CO_2 consumption rate for

Y. Cao · C. Tang
School of Environmental Science and Engineering, Sun Yat-Sen University, No. 135, Xingang Xi Road, Guangzhou 510275, People's Republic of China

Y. Cao · C. Tang (✉)
Faculty of Horticulture, Graduate School of Horticulture, Chiba University, Matsudo 271-8510, Japan
e-mail: tangchangyuan@gmail.com

X. Song · C. Liu
Key Laboratory of Water Cycle and Related Land Surface Processes, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Datun Rd. A11, Chaoyang District, Beijing 100101, China

Chinese large rivers showed that it decreased from South China to North China due to climate and hydrological factors (Gaillardet et al. 1999).

The Songhua River as the largest tributary of the Heilong River is the largest basin with a drainage area of 557 thousand km^2 in Northeast China. Although the work of Gaillardet et al. (1999) gave an overall understanding on rock weathering and CO_2 consumption rates in the Heilong River basin, it was considered to be rough for the Songhua River basin due to rock weathering and associated CO_2 consumption rates varying with temperatures, runoff, geology and topographic relief. The average TDS, 55 mg/L for the Heilong River and 132 mg/L for the Songhua River, implies the hydrochemical difference of these two rivers. Consequently, a different weathering pattern in the Songhua River is expected compared to the overall weathering characteristics in the Heilong River.

In this study, the objectives are to (1) examine the characteristics of temporal and spatial distribution of major ion chemistry in the Songhua River basin, (2) identify the mechanisms controlling the major ion chemistry and determine the contributions of different end-members to the hydrochemical composition based on an inverse method, and (3) assess the chemical weathering rates of silicate, and carbonate and corresponding CO_2 consumption rates.

Study area

The Songhua River, located in Northeast China, is the largest tributary of Heilong River, flowing through the Jilin and Heilongjiang provinces (Fig. 1). The river originates in the Changbai Mountains, travels from southeast to

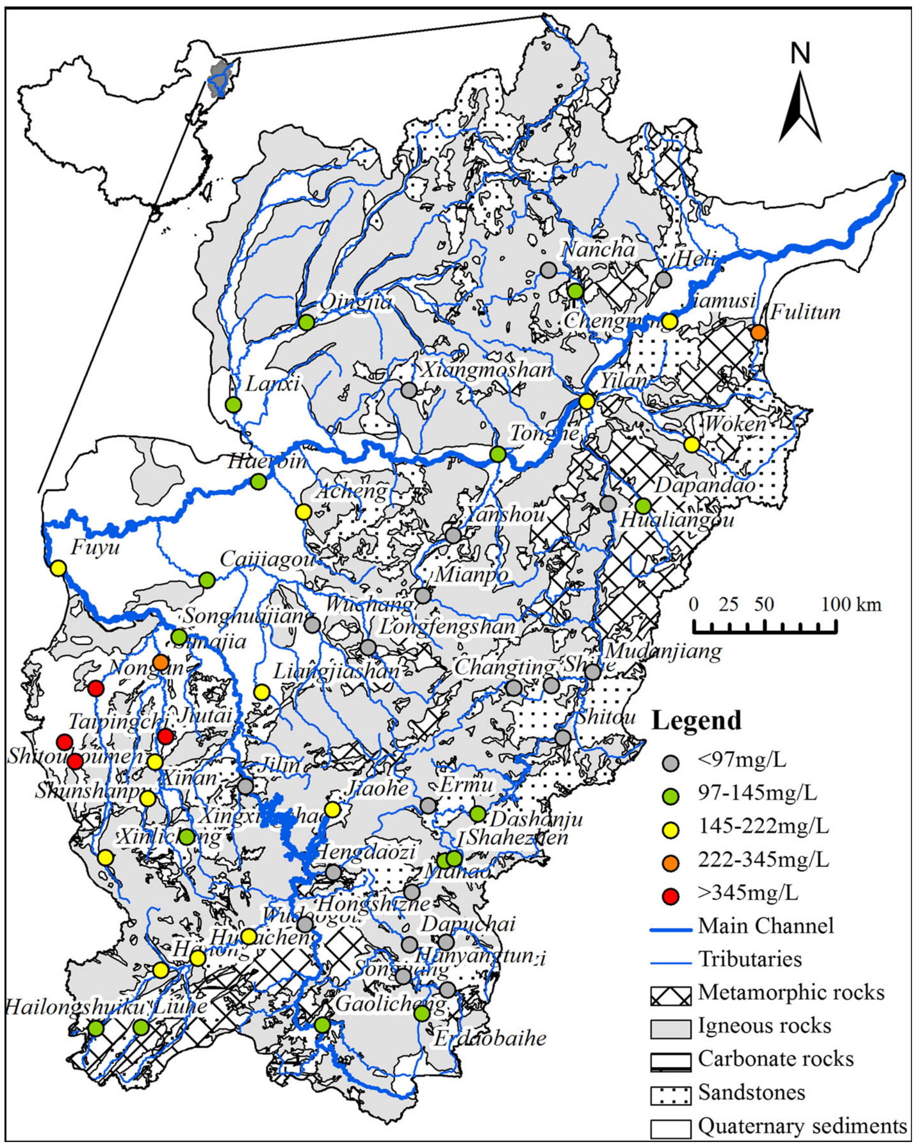

Fig. 1 Map of the study area, geology and monitoring stations in the Songhua River basin. The TDS range was divided by natural breaking method

Table 1 The mean values of the major element concentrations in main channel and major tributaries of the Songhua River basin

River	Station	*T* (°C)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	$K^+ + Na^+$ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	SiO_2 (mg/L)	TDS (mg/L)
Main channel	Gaolicheng	7.8	7.4	8.8	5.7	12.8	2.8	12.7	65.1	8.7	107.9
	Hongshizhe	7.8	7.0	10.5	4.3	10.2	3.8	8.8	60.3	10.1	97.8
	Jilin	9.0	6.9	11.9	3.8	8.4	3.9	9.2	57.3	5.9	94.5
	Songhuajiang	9.1	7.0	16.7	4.6	13.9	9.6	8.3	78.3	5.2	131.4
	Fuyu	9.7	7.2	19.3	6.0	18.1	9.1	14.9	96.4	9.9	163.5
	Haerbin	9.0	7.3	17.5	3.9	14.0	7.7	5.8	86.5	24.1	135.2
	Tonghe	8.8	7.1	17.0	3.9	14.0	7.7	6.2	84.0	28.2	132.9
	Yilan	10.2	7.2	18.8	5.2	22.1	9.0	9.6	107.6	5.2	171.7
	Jiamusi	10.1	7.2	17.5	5.0	21.6	8.4	9.1	102.2	5.5	163.3
Major tributaries											
Mudan R.	6 Stations	8.7	7.0	11.0	4.0	8.9	5.3	4.0	60.9	5.3	94.2
Huifa R.	4 Stations	10.8	7.1	20.2	8.7	11.8	7.1	13.0	105.8	5.6	166.6
Hulan R.	2 stations	8.6	7.0	15.8	3.6	12.4	5.4	2.7	84.1	19.9	123.9
Lalin R.	2 Stations	9.2	7.0	13.7	3.5	11.2	5.0	5.1	72.3	18.0	110.9
Mayi R.	2 Stations	9.5	6.9	11.1	2.5	8.8	6.7	3.4	52.1	16.1	84.6
Yinma R.	2 Stations	9.2	7.4	30.7	8.6	31.6	15.8	7.6	174.3	4.1	268.5
Tangwang R.	1 Station	7.7	6.9	14.0	4.2	15.3	9.0	8.4	72.3	7.2	122.2
Woken R.	1 Station	11.6	7.1	19.8	6.9	30.6	8.5	9.6	140.0	5.9	215.0

TDS was calculated by the sum of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^- and HCO_3^-

northwest until the Nenjiang River joins near Zhaoyuan city. Then it turns its direction toward the northeast, and finally flows into the Heilong River at Tongjiang city. The main channel of Songhua River, with a length of 1897 km, is connected by a large number of branches, including Mudan River, Huifa River, Hulan River, Lalin River, Mayi River, Yinma River, Tangwang River and Woken River (Table 1).

The Songhua River basin is located in the temperate continental monsoon zone with annual mean temperature ranging from 3 to 5 °C. Mean temperatures in July and January are 22.5 and −20 °C, respectively. Annual precipitation of the Songhua River basin is around 500 mm, and about 79 % occurs from June to September. The average annual runoff at the hydrological station Jiamusi near the outlet is about $6.32 \times 1{,}010\ m^3$ and the runoff from July to October takes up almost 60 % of the annual runoff.

The Songhua River basin is a Meso-Cenozoic sedimentary basin developed on a pre and upper Paleozoic basement (Fig. 1). The basement rocks, which mainly outcrop on the south and north-east edges of the basin, are composed of gneiss with inclusions of marble and metamorphic peridotite. Igneous rocks such as granite, diorite and basalt show banded distribution extending from the north to the south at the center of the basin. Sandstones scatter in the entire basin. Quaternary sediments are found in the northeast part of the basin with a thickness from 50 to 120 m. No significant outcrops of carbonates are observed in the Songhua River basin and they are mainly disseminated along with other rock types.

Materials and methods

Data sources

Since 1956, the Ministry of Water Resources of the People's Republic of China has established more than 900 hydrochemical stations along more than 500 rivers in China including the Songhua River to monitor major element concentrations, as well as other hydrological and water quality parameters (Chen et al. 2002). Available data of the Songhua River basin used in this study were from a total of 56 stations in the basin from 1962 to 1984. Among these stations, Gaolicheng, Hongshizhe, Jilin, Songhuajiang, Fuyu, Haerbin, Tonghe, Yilan and Jiamusi are located along the main channel from the upstream to downstream (Fig. 1; Table 1). Other stations are along the tributaries of the Songhua River. The data are given in the unit of both mg/L and meq/L, which are convenient for chemical stoichiometric calculations. In this study, only data with the charge balance ($\sum$cation − $\sum$anion)/$\sum$total ions) <5 % was accepted. Those that did not satisfy the criterion were taken as outliers due to misprint and excluded from following analysis. Analytical methods for major element were summarized as Ca^{2+} and Mg^{2+} by EDTA titration, Na^+ (K^+) by flame spectrometry, HCO_3^- by acid titration, SO_4^{2-} by $BaCl_2$ titration, Cl^- by $AgNO_3$ titration and SiO_2 by molybdenum blue method. TDS was calculated by the sum of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^- and HCO_3^-, and SiO_2 was not included due to too much missing values. Quality assurance and quality control information about the data sources was introduced and examined by Chen et al. (2002).

Statistical methods

One-way analysis of variance (ANOVA) was performed to compare seasonal differences in major ion concentrations by IBM SPSS 18.0 for windows, and p values smaller than 0.05 were considered significant. The long-term trend analysis of major ion concentrations was performed using the seasonal Mann–Kendall trend analysis, following the approaches of Hirsch and Slack (1984). Trends were considered statistically significant when $p < 0.01$. When there was a statistically significant trend, the changing rate was quantified by linear fit. The seasonal Mann–Kendall trend test was performed by statistical software R.

Result

Spatial distribution

Mean values of physical and hydrochemical parameters for the main channel of Songhua River and its seven major tributaries are shown in Table 1. In the Songhua River basin, pH ranged from 6.5 to 7.8, with an average of 7.1. TDS varied from less than 50.0 mg/L to higher than 300.0 mg/L. The median of TDS was 104.8 mg/L which was higher than the world median (65.0 mg/L) (Meybeck and Helmer 1989) and lower than other major rivers in China such as the Changjiang River (205.9 mg/L), the Yellow River (486.4 mg/L), the Pearl River (192.0 mg/L) and the Huai River (214.2 mg/L). The highest TDS was found in the Yinma River on the southwest corner of the Songhua River basin (Fig. 1).

Prevalent cations were $K^+ + Na^+ > Ca^{2+} > Mg^{2+}$, and these chemical features showed a typical cationic composition of rivers draining silicate bedrocks. Na^+ (plus K^+) and Ca^{2+} were the most abundant cations with concentrations of 8.4–31.6 and 8.8–30.7 mg/L, respectively. HCO_3^- was the most abundant anion; and its concentration ranged from 60.3 to 174.3 mg/L. Cl^-, as the second most abundant anion, varied from 2.8 to 15.8 mg/L. SO_4^{2-} ranging from 2.7 to 14.9 mg/L was the least abundant anion among the anions. Similar with TDS, the highest cations and anions were observed in the southwest of the study area.

Variations of TDS values and hydrochemical pattern along the main channel of Songhua River are shown in

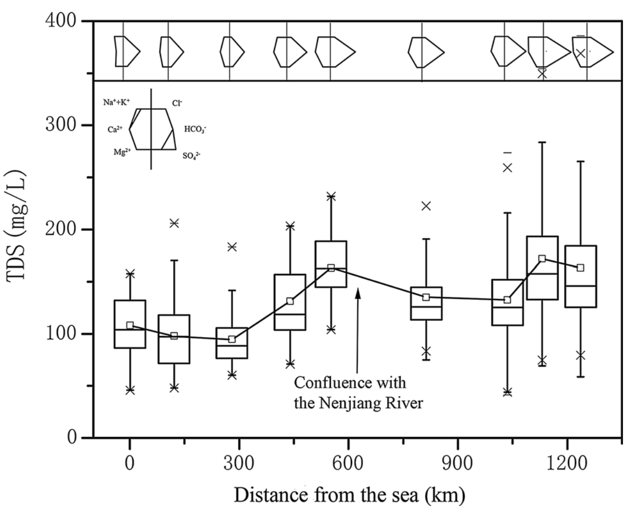

Fig. 2 The variations of TDS and hydrochemical pattern along the main channel. The *boxplot* showed the TDS ranges of each station. *White square* gave the mean value of TDS, *upper* and *lower edge* of the box showed the 25th and 75th percentiles of TDS. The *line in the box* gave the median of TDS. The *whiskers* are determined by the 5th and 95th percentiles. The *asterisk* showed the "outliers"

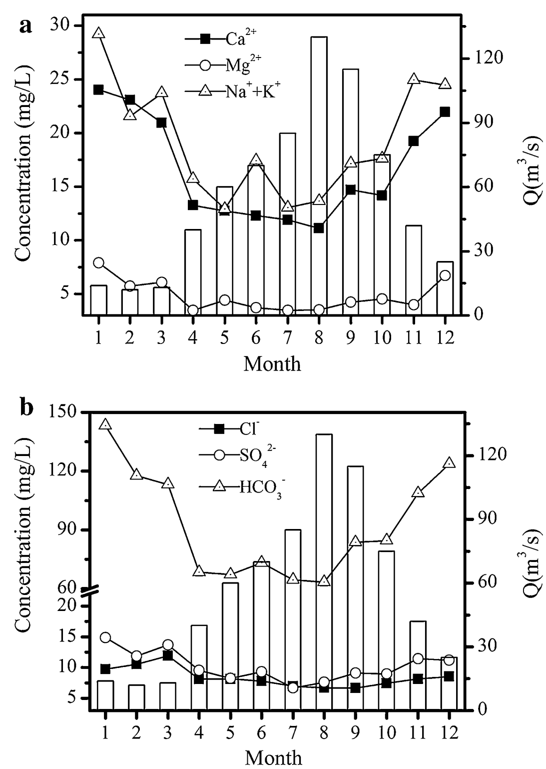

Fig. 3 Seasonal variations of the major ions at the Jiamusi station. **a** showed the variations of major cations, and **b** showed the variations of major anions. The VF of runoff was 10.83, much higher than the VFs of ions, and it implies that rock weathering enhanced with increasing water discharge

Fig. 2. For convenience, the Gaolicheng station and the Jiamusi station were set as the starting and ending point, respectively, along the main channel in this paper. TDS was less than 100 mg/L in the upstream with mountains and increased up to 300 mg/L after the Yinma tributary joins about 400 km downstream from the Gaolicheng station. A sudden decrease of TDS was observed after the Nenjiang River flows in before the Haerbin station. Then TDS increased again at the lower reach until the river flows through the Jiamusi station. The increasing trend along the river shows the tributaries had substantial contributions to the increased TDS of the main channel; and this trend does not seem to be consistent with trends observed in the Changjiang River and Huai River, where the TDS concentrations of the main channel showed a general decreasing trend due to dilution effect by large tributaries

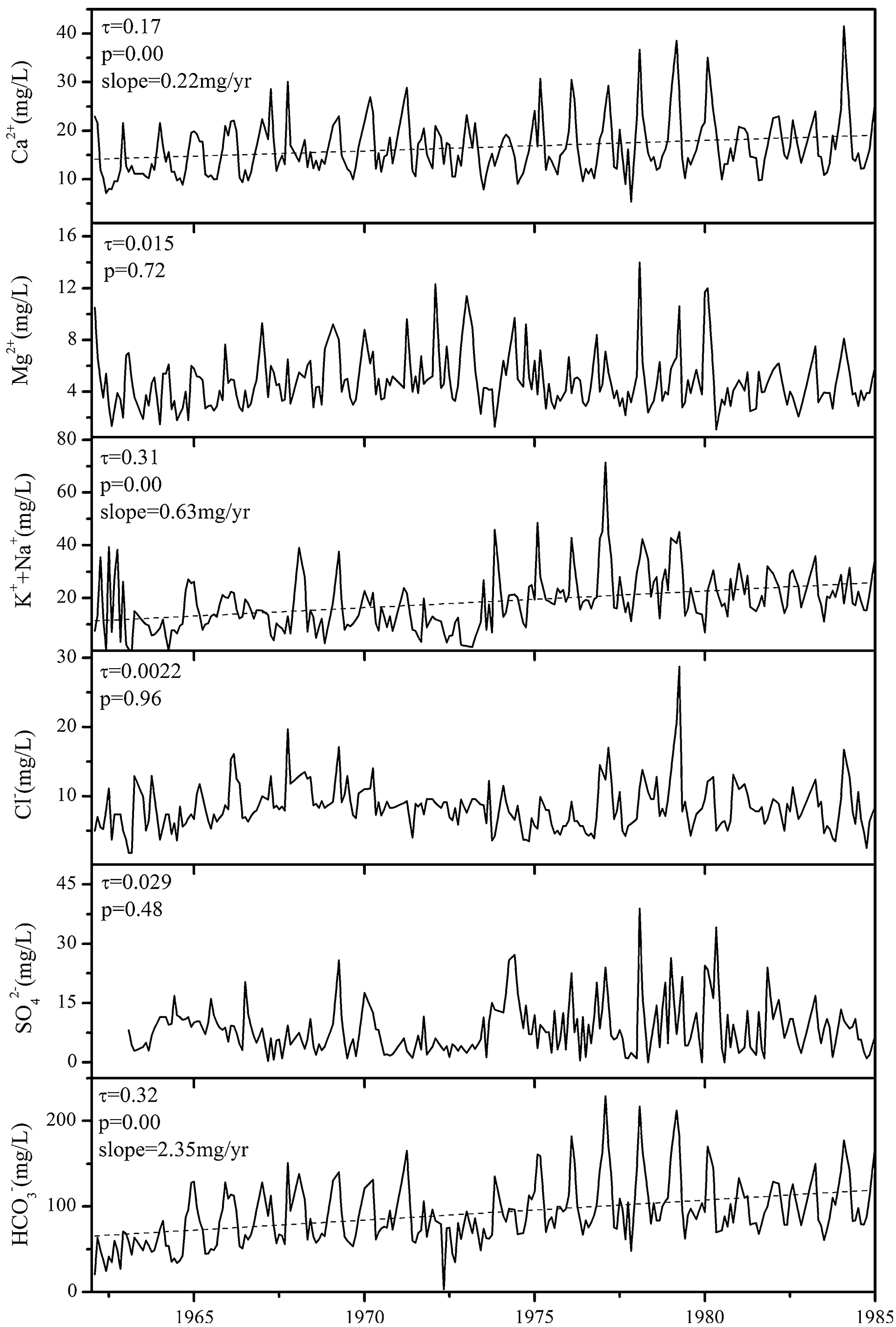

Fig. 4 Long term trends of major ions at Jiamusi station. Trends were considered statistically significant when $p < 0.01$. When there was a statistically significant trend, the changing rate was quantified by linear fitting slope

(Chen et al. 2002). Hydrochemical pattern changed from Ca–Na–HCO_3 type in the headwater to Ca–HCO_3 type in the middle and upper reaches.

Temporal variations

Seasonal variations of major ions were illustrated by the monthly averaged hydrochemistry data at the Jiamusi station (Fig. 3). All the ions showed significant seasonal variations, with variation factors (VF: the ratio of the highest to the lowest value during a year) for Ca^{2+}, Mg^{2+}, $Na^+ + K^+$, Cl^-, SO_4^{2-} and HCO_3^- being 2.16, 2.28, 2.26, 1.78, 2.23, and 2.61, respectively. All the ions showed significant decreases in wet season due to dilution, which was similar to Amazon River (Gibbs 1972) and the Lena River (Gordeev and Sidorov 1993), but different from the Changjiang River where the major element did not vary greatly in different seasons (Chen et al. 2002).

Furthermore, the time series data from 1962 to 1984 at the Jiamusi station were used to evaluate the long-term trend of major ions (Fig. 4). Ca^{2+}, $Na^+ + K^+$ and HCO_3^- showed significant increasing trends during this period. No significant trends were detected for other ions. The increasing rates calculated by linear fit for Ca^{2+}, $Na^+ + K^+$ and HCO_3^- ions were 0.22, 0.63 and 2.35 mg/year, respectively. The long-term variations observed in the Songhua River basin were different from the Changjiang River with significant increasing trend of Cl^- and SO_4^{2-} due to intensified acid deposition caused by increases in coal consumptions (Chen et al. 2002).

Discussion

Statistical difference for seasonal change of major ions

The one-way ANOVA procedure of pairwise multiple comparisons was used to examine the seasonal differences of major ions (Table 2). In spring, major ions were significantly higher than that in summer but lower than that in winter except for SO_4^{2-}, and not statistically differed from fall except for Cl^- and SO_4^{2-}. In summer, all the ions had the lowest concentrations due to dilution effect. The ion concentrations between summer and winter had a large gap, and the values of the deviation were −10.11, −2.62, −10.20, −55.44, −4.28 and −3.45 mg/L for Ca^{2+}, Mg^{2+}, $Na^+ + K^+$, HCO_3^-, Cl^- and SO_4^{2-}, respectively. The concentrations of the major ions in fall were similar with that in spring, significantly higher than that in summer and lower than that in winter. Moreover, all the ions showed strong condensed features in winter, contrary to the dilution effect in summer.

Table 2 Result of one-way ANOVA for pairwise multiple comparisons to discriminate the major ion differences in different seasons

Season		Spring	Summer	Autumn	Winter
Spring (Mar.–May.)	Ca^{2+}		2.44*	−0.08	−7.66*
	Mg^{2+}		1.06*	0.14	−1.56*
	$Na^+ + K^+$		2.52*	1.16	−7.68*
	HCO_3^-		12.96*	−0.20	−42.48*
	Cl^-		1.98*	1.52*	−2.30*
	SO_4^{2-}		2.57*	1.49*	−0.88
Summer (Jun.–Aug.)	Ca^{2+}	−2.44*		−2.53*	−10.11*
	Mg^{2+}	−1.06*		−0.91*	−2.62
	$Na^+ + K^+$	−2.52*		−1.36	−10.20*
	HCO_3^-	−12.96*		−13.16*	−55.44*
	Cl^-	−1.98*		−0.46	−4.28*
	SO_4^{2-}	−2.57*		−1.08*	−3.45*
Autumn (Sep.–Nov.)	Ca^{2+}	0.09	2.53*		−7.57*
	Mg^{2+}	−0.14	0.91*		−1.71*
	$Na^+ + K^+$	−1.16	1.36		−8.83*
	HCO_3^-	0.20	13.16*		−42.28*
	Cl^-	−1.52*	0.46		−3.82*
	SO_4^{2-}	−1.49*	1.08*		−2.37*
Winter (Dec.–Feb.)	Ca^{2+}	7.66*	10.11*	7.57*	
	Mg^{2+}	1.56*	2.62*	1.71*	
	$Na^+ + K^+$	7.68*	10.20*	8.83*	
	HCO_3^-	42.48*	55.44*	42.28*	
	Cl^-	2.30*	4.28*	3.82*	
	SO_4^{2-}	0.88	3.45*	2.37*	

* The mean difference is significant at the 0.05 level

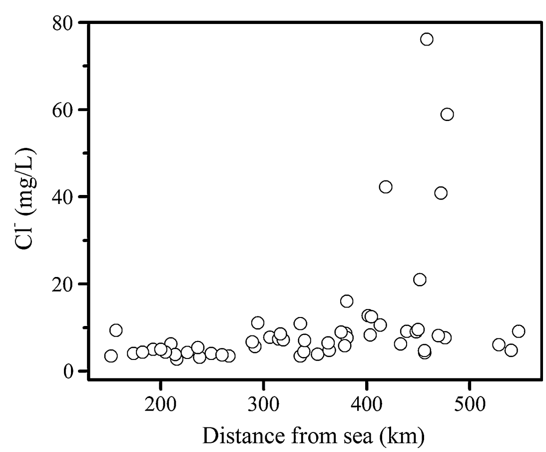

Fig. 5 The concentration of Cl^- vs. distance from sea

Mechanisms controlling the major ion chemistry

Atmospheric inputs

Rainwater has been recognized as an important source of dissolved species (major ions) in surface waters (Appelo and Postma 2005; Gibbs 1970; Stallard and Edmond 1981). The contribution of Cl^- to dissolved salt loads in rivers is expected to decrease with increasing distance from the sea when there are no terrestrial sources effects (Stallard and Edmond 1981). However, in the Songhua River basin, elevated Cl^- concentrations were found in some inland stations located in the southwest rather than in the seaward stations (Fig. 5), implying that in addition to precipitation inputs other origins such as weathering of evaporite rocks or anthropogenic inputs existed in the study area.

Contributions from precipitation inputs can be estimated as Cl^-, which behaves conservatively through the hydrological cycle (Appelo and Postma 2005; Ollivier et al. 2010). Li et al. (2010) reported chemical data of precipitation at the Longfengshan station located around the center of the study area. It was found that the SO_4^{2-}/Cl^- molar ratio in precipitation was about 3.65, showing a sulfate enrichment of rainwater with respect to sea origin salt ($SO_4^{2-}/Cl^- = 0.05$). The Ca^{2+} and Mg^{2+} also suggested terrestrial sources with a high Cl-normalized ratio (1.75 and 0.49, respectively) compared to sea origin salt (0.02 and 0.01, respectively).

Runoff coefficient of the Songhua River was about 0.21 (Song et al. 2010); therefore, the evaporation factor (the reciprocal of the runoff coefficient) of the major ions was 4.72. Accordingly, major ions came from precipitation and their contributions to river chemical compositions were estimated. It was found that as a whole the atmospheric inputs contributed 16.5 % of Ca^{2+}, 8.9 % of Mg^{2+}, 11.6 % of $K^+ + Na^+$ and 17.3 % of Cl^- in the Songhua River basin.

Anthropogenic inputs

The major ion chemistry can also be affected by a variety of human activities (Meybeck and Helmer 1989), which have become particularly important in China due to drastically intensified industrial and agricultural activities (Chen et al. 2002). Based on the Cl-normalized ratio of precipitation, it was found that the atmospheric loading in the Songhua River had a significant terrestrial component, especially for SO_4^{2-} as a result of extensive and intensive use of S-enriched coal and power production via coal combustion in the study area. In addition, Cl^- is also considered to be an indicator of the impact of land use and human activity on water chemistry. In this study, three reservoirs were considered for Cl^- as atmospheric inputs, anthropogenic inputs and evaporite weathering, and two reservoirs were considered for SO_4^{2-} as cyclic salt origin from sea and anthropogenic inputs from coal combustion. The contribution of anthropogenic inputs was calculated by deducting the TDS came from other sources from the total TDS.

Rock weathering inputs

Ternary diagrams were employed to develop an overall understanding of the water–rock reactions which control the major chemical compositions of river water in the study area (Fig. 6). Samples defined a narrow range on the cation ternary diagram, and most clustered in the center of the plot which implied that chemical weathering of silicates dominated in the study area. The dominance of silicate rock weathering is not surprising, given the fact that silicate rocks are well-spread in the Songhua River basin (Fig. 1). Outcrops of carbonate rocks sporadically existed; therefore, it was reasonable to recognize the contribution of the carbonate rock weathering to the river chemical compositions. In addition, evaporites were also considered to

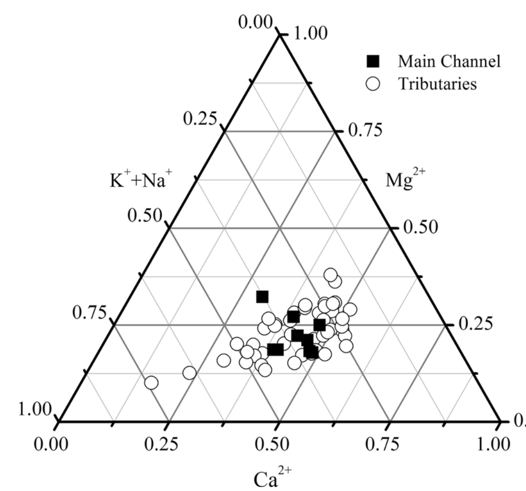

Fig. 6 Ternary diagrams showing the relative abundances (in meq/L) of major cations (Ca^{2+}, Mg^{2+} and $Na^+ + K^+$) for the main channel and tributaries in the Songhua River basin

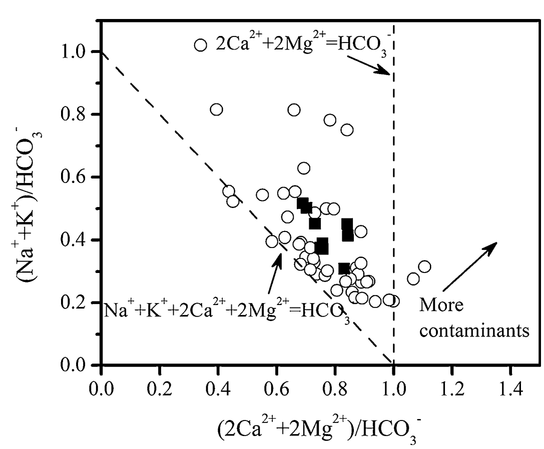

Fig. 7 Relative contributions from silicate and carbonate weathering to waters by carbonic acid based on stoichiometry. The cation concentrations (mmol/L) used was all corrected by eliminating the precipitation inputs

contribute the chemical compositions of the river due to only 17.3 % of Cl^- explained by atmospheric inputs.

Beside the ternary diagram, the plot of the relation between the molar ratio of $(Na^+ + K^+)/HCO_3^-$ and $(2Ca^{2+} + 2Mg^{2+})/HCO_3^-$ also showed the dominance of silicate dissolution in the Songhua River basin (Fig. 7). The line of $Na^+ + K^+ + 2Ca^{2+} + 2Mg^{2+} = HCO_3^-$ reflects the contributions of silicate weathering to water chemistry (Li et al. 2009). Obviously, river water samples fall into the section between the silicate weathering line and the carbonate weathering line, and had a tendency to be close to the silicate weathering line.

Rock weathering inputs were evaluated in terms of mixing between three main end-members corresponding to the weathering products of carbonates, silicates and evaporites (Gaillardet et al. 1997; Negrel et al. 1993; Ollivier et al. 2010). The approach used by Ollivier et al. (2010)

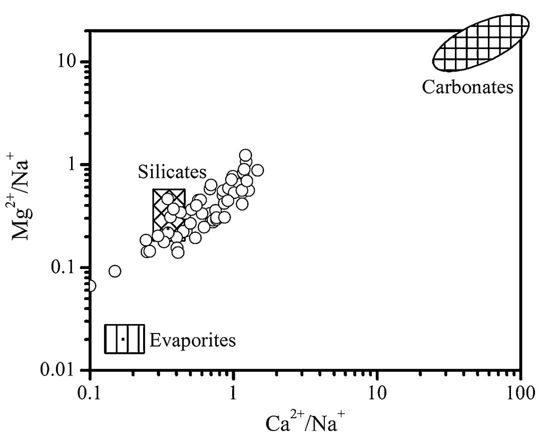

Fig. 8 Mixing diagrams using the end-members of carbonates silicates and evaporites expressed by Na-normalized molar ratios. The molar concentrations used in the ratio calculation were corrected by eliminating the precipitation inputs

Table 3 Summary of the rock weathering contributions to Ca^{2+}, Mg^{2+} and Na^+

	Carbonates (%)	Silicates (%)	Evaporates (%)
Ca^{2+}			
Mean	30.7	63.2	6.2
Max	73.9	100	43.9
Min	0	22.5	0
Mg^{2+}			
Mean	18.8	79.5	1.7
Max	56.0	100	11.8
Min	0	42.8	0
Na^+			
Mean	0.4	84.4	15.3
Max	1.5	100	67.8
Min	0	31.9	0

was followed to determine rock weathering contributions to major cations (Na^+, Ca^{2+} and Mg^{2+}). The end-members and samples expressed by Na-normalized molar ratios (Ca^{2+}/Na^+ and Mg^{2+}/Na^+) are showed in Fig. 8. Carbonate end-member was characterized with high ratios of Ca^{2+}/Na^+ and Mg^{2+}/Na^+ in the top-right corner of Fig. 8. In the Songhua River basin, the highest values of Ca^{2+}/Na^+ and Mg^{2+}/Na^+ were 2.03 and 1.56, much less than the Na-normalized molar ratios of carbonate end-member due to no tributaries flow through purely carbonate-dominated area. The influence of silicate weathering end-member was reflected by lower Ca^{2+}/Na^+ and Mg^{2+}/Na^+ ratios compared to the carbonate and it was found that most of the samples located around the silicate end-member. Evaporite end-member was usually difficult to be constrained due to the diversity of salt rock types, but it is recognized that this end-member was reflected by the lowest Ca^{2+}/Na^+ and Mg^{2+}/Na^+ ratios. In this study, the molar ratios of Ca^{2+}/Na^+ and Mg^{2+}/Na^+ for the three end-members were selected as 55 and 15 for carbonates, 0.35 and 0.24 for silicates and 0.17 and 0.02 for evaporites, respectively.

Chemical budget and CO_2 consumption

Contributions of different end-members

Contributions of weathering to major cations (Na^+, Ca^{2+} and Mg^{2+}) were estimated followed by the method used by Ollivier et al. (2010), and the chemical budget estimation for other elements (anions and silica) was calculated by using a forward method based on stoichiometry.

The proportions of Ca^{2+}, Mg^{2+} and Na^+ originating from different rock weathering reservoirs are given in Table 3. Overall, in the Songhua River Basin, the dissolved cation load of rivers was dominated by silicate weathering, and specifically 63.2 % of Ca^{2+}, 79.5 % of Mg^{2+} and 84.4 % of Na^+ came from silicates weathering. Carbonates contributed to Ca^{2+} and Mg^{2+} with a value of 30.7 and 18.8 % in the dissolved cation load. Evaporites weathering contribute 6.2 % of Ca^{2+}, 1.7 % of Mg^{2+} and 15.3 % of Na^+.

The contributions of atmospheric inputs, anthropogenic inputs, and rock weathering (sum of carbonates, silicates and evaporites) to the total TDS for all the stations were shown in Fig. 9. Here, chemical budget calculated according to the hydrochemistry data at the Jiamusi station (the basin outlet station) was used to give an overall understanding. Generally, rock weathering contributed 91.5 % of the total TDS including 66.4 % from silicates, 16.1 % from carbonates and 9.0 % from evaporites. About 5.3 % of the TDS came from anthropogenic inputs, and atmospheric inputs only contributed 3.2 % of the TDS. The significant dominance of silicate weathering with an

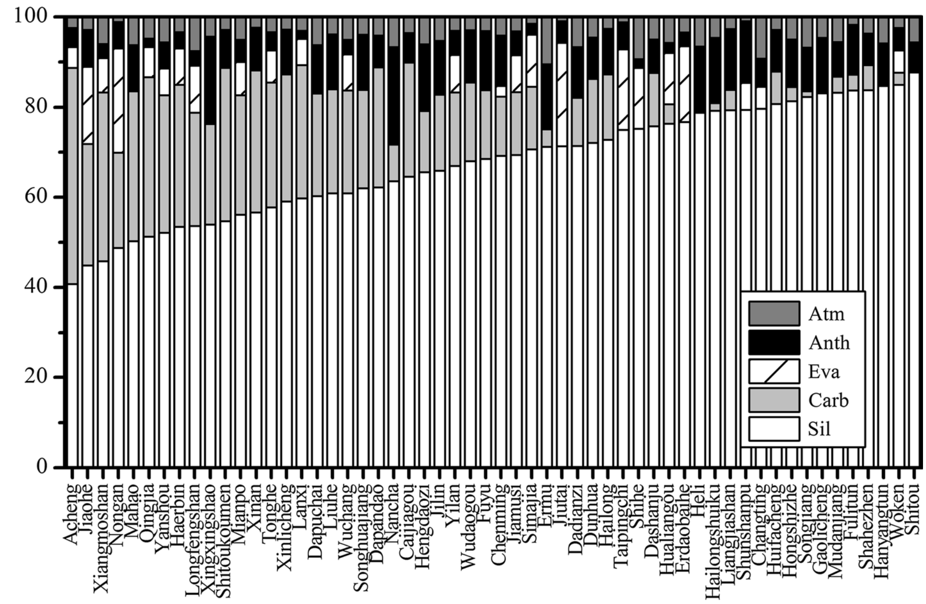

Fig. 9 Calculated contributions (%) of carbonate, silicate and evaporite weathering, anthropogenic inputs and atmospheric inputs to the total TDS (mg/L) in the Songhua River basin. The result was sorted by ascending order of silicate weathering contribution from *left* to *right*

average of 66.4 % was quite higher than the global silicate weathering proportions (<40.0 %) (Gaillardet et al. 1999).

Chemical weathering and CO_2 consumption rates

Chemical weathering and CO_2 consumption rates of silicates and carbonates were estimated by mass budget, surface area and runoff of the basin. The calculation method of silicates weathering (R_{sil}) and carbonates weathering (R_{carb}) rates were followed from the work of Xu and Liu (2010). Because no data for K was available, the equation was slightly modified by eliminating the K item as follows:

$$R_{sil} = (Na_{sil} + Ca_{sil} + Mg_{sil} + SiO_{2sil}) \times Q_{annual}/A$$

$$R_{carb} = (Ca_{carb} + Mg_{carb} + 1/2HCO_{3carb}) \times Q_{annual}/A$$

where X_{sil} (X refers to Na, Ca, Mg and SiO_2) is the composite came from silicate weathering and Y_{carb} (Y refers to Ca, Mg and HCO_3^-) is the composite came from carbonate weathering. Q_{annual} is the annual runoff and A is the draining area of the station.

The equations describing the calculation of CO_2 consumption rates of silicates (ΦCO_{2sil}) and carbonates (ΦCO_{2carb}) were shown as follows.

$$\Phi CO_{2sil} = (Na_{sil} + 2Ca_{sil} + 2Mg_{sil}) \times Q_{annual}/A$$

$$\Phi CO_{2carb} = (Ca_{carb} + Mg_{carb}) \times Q_{annual}/A$$

where the symbols are the same with the above equations.

The results of chemical weathering and CO_2 consumption rates for main channel and tributaries, grouped based on lithology, are listed in Table 4. In the Songhua River basin, the average silicate (R_{sil}) and carbonate weathering (R_{carb}) rates at the river outlet station Jiamusi were 4.03 and 1.76 t km^{-2} $year^{-1}$, respectively; and the corresponding CO_2 consumption rates for silicates and carbonates were 17.1 × 104 and 1.85 × 104 mol km^{-2} $year^{-1}$. It is obvious that lithology plays an important role in chemical weathering by comparing chemical weathering rates among the tributaries with different lithology (Table 4). Igneous rocks had the highest R_{sil} with an average of 7.61 t km^{-2} $year^{-1}$ than other rocks. Quaternary sediment had the highest R_{carb} with an average of 4.19 t km^{-2} $year^{-1}$. The area covered by sandstones showed the lowest R_{carb} with an average of 0.50 t km^{-2} $year^{-1}$ due to carbonates deficiency. In addition, the climatic influence (here mainly refer to runoff) to the silicate weathering in the Songhua River basin was illustrated by Fig. 10. The log–log correlation plot gave a positive correlation trend between R_{sil} and runoff, which agreed with the silicate weathering rate law of other world rivers.

In comparison with other Chinese rivers (Table 5), for R_{sil}, the Songhua River was the same as the Lancang Jiang (4.1 t km^{-2} $year^{-1}$), but lower than most of other Chinese rivers such as the Changjiang, the Xijiang and the five rivers originating in the Qingha-Tibet. Only the Huanghe had a lower R_{sil} (3.0 t km^{-2} $year^{-1}$) than the Songhua River due to its small runoff. For R_{carb}, the Songhua River was one order of magnitude lower than other Chinese rivers because of little carbonate outcrops in this study area. In addition, cold temperature (3–5 °C) and low annual precipitation (500 mm) also have a strong influence on the rock weathering rate. For the CO_2 consumption rates, the Songhua River had a higher ΦCO_{2sil} than the Changjiang, Huanghe, Xijiang and Jinsha Jiang Rivers, but

Table 4 Chemical weathering and CO_2 consumption rates for 25 stations for which runoff data are available

Station	Draining area ($10^3 km^2$)	Annual runoff (mm $year^{-1}$)	Weathering rate (t km^{-2} $year^{-1}$)		CO_2 consumption (10^4 mol km^{-2} $year^{-1}$)	
Main channel			Silicates	Carbonates	Silicates	Carbonates
Jiamusi	527.7	120	4.03	1.76	17.1	1.85
Tonghe	450.4	100	4.40	2.75	7.98	2.78
Haerbin	390.5	103	3.95	3.15	7.43	3.09
Fuyu	77.4	184	7.75	3.12	30.4	3.74
Songhuajiang	51.5	262	7.45	4.98	30.9	5.88
Jilin	44.1	297	6.51	3.16	25.2	3.55
Tributaries						
Metamorphic rocks						
Woken	4.2	112	5.95	0.41	26.91	0.44
Hengdaozi	0.5	140	3.04	1.04	9.75	1.19
Dapandao	3.2	153	4.00	3.30	14.97	3.56
Igneous rocks						
Chenming	18.9	269	8.32	2.94	32.49	3.40
Dunhua	2.2	223	5.35	2.39	25.41	2.62
Ermu	0.8	488	6.31	0.61	21.70	0.67
Mianpo	2.3	248	7.99	4.33	11.01	4.30
Changting	2.4	446	7.00	0.00	19.56	0.00
Longfengshan	1.7	571	10.81	5.79	11.48	4.57
Wuchang	6.4	208	7.49	3.05	8.62	2.86
Sandstones						
Shihe	3.6	369	4.85	0.00	12.66	0.00
Shitou	21.9	140	3.57	0.00	14.22	0.00
Dashanju	8.1	256	5.74	2.02	26.74	2.16
Heli	0.5	220	3.64	0.00	19.23	0.00
Mudanjiang	21.9	230	5.45	0.49	22.24	0.52
Quaternary						
Lanxi	27.3	131	6.19	4.13	11.30	3.99
Qingjia	9.6	196	3.94	4.73	10.51	4.39
Caijiagou	18.3	177	5.51	4.22	20.68	4.50
Yanshou	5.0	206	3.84	3.68	10.09	3.65

The tributaries are grouped based on the lithology of its draining area

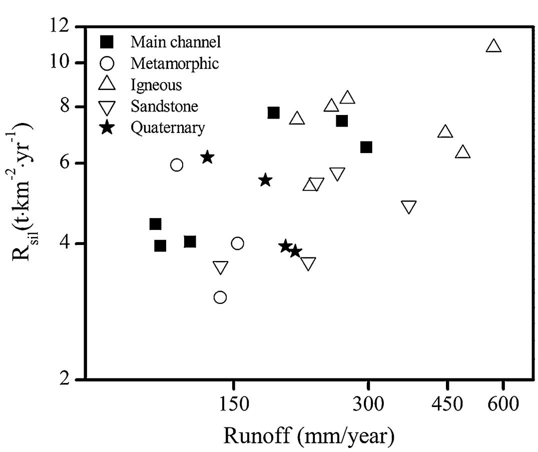

Fig. 10 *Scatter plots* of silicate weathering rates versus runoff, which indicate that the R_{sil} in the Songhua River basin is closely related to global weathering rate laws

a lower ΦCO_{2carb} than all the Chinese rivers. In addition, compared to the result of the Heilong River (Gaillardet et al. 1999), the Songhua River basin showed a higher silicate and a lower carbonate weathering rate, and this further indicates that the spatial heterogeneity of the lithology and climatic factors such as runoff and temperature have a strong influence on the chemical weathering of rivers.

Conclusions

In this study, the major ions chemistry, chemical weathering rates and CO_2 consumption rates in the Songhua River basin were examined. Main conclusions are provided as follows:

Table 5 Comparison of chemical weathering and CO_2 consumption rates in the Songhua River basin with other Chinese rivers

Rivers	R_{sil} (t km^{-2} year^{-1})	R_{Carb} (t km^{-2} year^{-1})	ΦCO_2sil (10^4 mol km^{-2} year^{-1})	ΦCO_2carb (10^4 mol km^{-2} year^{-1})
Songhua R.	4.0	0.93	17	1.9
Heilong R.[a]	1.2	3.88	1.8	3.5
Changjiang[a]	5.3	56.1	5.9	55
Huanghe[b]	3.0	24.1	9.0	27
Xijiang[c]	7.5	78.5	15	81
Jinsha Jiang[b]	9.1	14.8	13	29
Lancang Jiang[b]	4.1	54.7	52	46
Nu Jiang[b]	5.9	62.5	59	65
Yalong Jiang[b]	8.0	40.2	38	49
Dadu He[b]	8.3	68.4	68	60
Min Jiang[b]	9.0	52.1	48	18

[a] Came from (Gaillardet et al. 1999) and recalculated the data with drainage areas of the rivers

[b] Came from (Wu et al. 2008)

[c] Came from (Xu and Liu 2010)

1. The Songhua River had a low TDS with a median of 104.8 mg/L, and the prevalent ions were $Na^+ + K^+$ and Ca^{2+} for cations, and HCO_3^- for anions. All the ions showed significant seasonal variations with a decrease in wet seasons and an increase in dry seasons. From 1962 to 1984, Ca^{2+}, $Na^+ + K^+$ and HCO_3^- showed significant increasing trends in the study area. Increasing rates for Ca^{2+}, $Na^+ + K^+$ and HCO_3^- ions were 0.22, 0.63 and 2.35 mg/year, respectively. No significant long-term trends were detected for other ions.
2. The major ion chemistry was dominated by silicate dissolution in the Songhua River basin. The average Ca^{2+}/Na^+ and Mg^{2+}/Na^+ molar ratios were 0.70 and 0.42, respectively, which were close to silicate weathering end-member. Generally, rock weathering contributed 91.5 % of the total TDS including 66.4 % from silicates, 16.1 % from carbonates and 9.0 % from evaporites. About 5.3 % of the TDS can be attributed to anthropogenic inputs, and atmospheric inputs only contributed 3.2 % of the TDS in the Songhua River basin.
3. The average silicate (R_{sil}) and carbonate weathering (R_{carb}) rates of the Songhua River basin were 4.03 and 1.76 t km^{-2} year^{-1}, respectively. The CO_2 consumption rates of silicate and carbonate were 17.1 × 104 and 1.85 × 104 mol km^{-2} year^{-1}, respectively. Both of the weathering and CO_2 consumption rates for carbonates were lower than other Chinese Rivers.

Acknowledgments This work was funded by the Main Direction Program of Knowledge Innovation of Chinese Academy of Sciences: Study on water cycle, water resource carrying capacity and optimization configuration (No. KZCX2-YW-Q06-1). The authors wish to thank Dr. Long Di for the suggestions to this paper.

References

Appelo C, Postma D (2005) Geochemistry, groundwater and pollution. Taylor & Francis, London

Berner RA (1991) A model for atmospheric CO_2 over phanerozoic time. Am J Sci 291(4):339–376

Berner RA, Lasaga AC, Garrels RM (1983) The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. Am J Sci 283(7):641–683

Chen J, Wang F, Xia X, Zhang L (2002) Major element chemistry of the Changjiang (Yangtze River). Chem Geol 187(3–4):231–255

Edmond JM (1992) Himalayan tectonics, weathering processes, and the strontium isotope record in marine limestones. Science (New York, NY) 258(5088):1594–1597

Gaillardet J, Dupre B, Allegre CJ, Négrel P (1997) Chemical and physical denudation in the Amazon River Basin. Chem Geol 142(3):141–173

Gaillardet J, Dupré B, Louvat P, Allegre CJ (1999) Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. Chem Geol 159(1):3–30

Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 170(3962):1088–1090

Gibbs RJ (1972) Water chemistry of the Amazon River. Geochim Cosmochim Acta 36(9):1061–1066

Gordeev VV, Sidorov IS (1993) Concentrations of major elements and their outflow into the Laptev Sea by the Lena River. Mar Chem 43(1–4):33–45

Hirsch RM, Slack JR (1984) A nonparametric trend test for seasonal data with serial dependence. Water Resour Res 20(6):727–732

Li S, Xu Z, Wang H, Wang J, Zhang Q (2009) Geochemistry of the upper Han River basin, China: 3 Anthropogenic inputs and chemical weathering to the dissolved load. Chem Geol 264(1–4):89–95

Li Y, Yu X, Cheng H, Lin W, Tang J, Wang S (2010) Chemical characteristics of precipitation at three Chinese regional background stations from 2006 to 2007. Atmos Res 96(1):173–183

Meybeck M, Helmer R (1989) The quality of rivers: from pristine stage to global pollution. Global Planet Change 1(4):283–309

Negrel P, Allegre CJ, Dupre B, Lewin E (1993) Erosion sources determined by inversion of major and trace element ratios and strontium isotopic ratios in river water: the Congo Basin case. Earth Planet Sci Lett 120(1–2):59–76

Ollivier P, Hamelin B, Radakovitch O (2010) Seasonal variations of physical and chemical erosion: a three-year survey of the Rhone River (France). Geochim Cosmochim Acta 74(3):907–927

Ran X, Yu Z, Yao Q, Chen H, Mi T (2010) Major ion geochemistry and nutrient behaviour in the mixing zone of the Changjiang (Yangtze) River and its tributaries in the Three Gorges Reservoir. Hydrol Process 24(17):2481–2495

Raymo ME, Ruddiman WF (1992) Tectonic forcing of late Cenozoic climate. Nature 359(6391):117–122

Song X, Mu X, Gao P, Wang F, Wang S (2010) Analysis on historical evolution and driving force of rainfall and runoff of Harbin Station in Songhua River. Sci Soil Water Conserv 8(2):46–51

Stallard RF, Edmond JM (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

Walker JCG, Hays PB, Kasting JF (1981) A negative feedback mechanism for the long-term stabilization of the Earth's surface temperature. J Geophys Res 86(C10):9776–9782

Wu W, Xu S, Yang J, Yin H (2008) Silicate weathering and CO_2 consumption deduced from the seven Chinese rivers originating in the Qinghai-Tibet Plateau. Chem Geol 249(3–4):307–320

Xu Z, Liu CQ (2010) Water geochemistry of the Xijiang basin rivers, South China: chemical weathering and CO_2 consumption. Appl Geochem 25(10):1603–1614

Zhang J, Huang W, Letolle R, Jusserand C (1995) Major element chemistry of the Huanghe (Yellow River), China-weathering processes and chemical fluxes. J Hydrol 168(1–4):173–203

Zhang S, Lu X, Higgitt DL, Chen C, Sun H, Han J (2007) Water chemistry of the Zhujiang (Pearl River): natural processes and anthropogenic influences. J Geophys Res 112(F1):F01011

Zhang L, Song X, Xia J, Yuan R, Zhang Y, Liu X, Han D (2011) Major element chemistry of the Huai River basin China. Appl Geochem 26(3):293–300