1 **Consumption of atmospheric CO₂ via chemical weathering in the**
2 **Yellow River basin: the Qinghai-Tibet Plateau is the main**
3 **contributor to the high dissolved inorganic carbon in the Yellow**
4 **River**

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15 **Abstract:** The high HCO₃⁻ concentrations in the Yellow River (China) are generally
16 believed to originate primarily from the carbonate-rich Loess Plateau as a result of
17 carbonate weathering reactions that consume atmospheric CO₂. We studied chemical
18 weathering across the entire Yellow River basin in 2007 and 2009 and found that the
19 amounts of CO₂ consumption by carbonate and silicate weathering were 87.61×10⁹
20 mol/a and 10.70×10⁹ mol/a, respectively. As the source of water for the Yellow River,
21 although the Qinghai-Tibet Plateau accounts for only 30% of the area of the basin, it
22 has a strong leaching effect and contributes a majority (61%) of the atmospheric CO₂
23 consumption of the entire basin and a majority of the riverine DIC flux (66%) to the
24 ocean. As a result, the dissolved inorganic carbon (DIC) concentrations in this river
25 are among the highest of the world's major rivers. In contrast, despite the abundant
26 carbonate mineral content in the Loess Plateau, the high ratio of evaporation to
27 precipitation (4.2) limits the weathering processes, and the low amount of runoff
28 restricts the transport of weathering products, which results in a relatively low
29 contribution (38%) to the basin-wide atmospheric CO₂ consumption, which is much
30 lower than was previously thought. The Qinghai-Tibet Plateau is the origin of the high
31 levels of HCO₃⁻ in and acts as the main DIC contributor to the Yellow River.

32 **Keywords:** Yellow River, Chemical weathering, HCO₃⁻ origin

33 **Introduction**

Chemical weathering is a key earth surface process that links geologic cycling of the solid earth to the atmosphere and oceans (Berner, 2003; Sun et al., 2010; Moquet et al., 2011). The global consumption of CO₂ by chemical weathering has been reported to range between 0.22-0.29 Gt/a (Gaillardet et al., 1999; Amiotte Suchet et al., 2003; Hartmann et al., 2009). Rock weathering processes transform atmospheric CO₂ and carbon that is locked in carbonate rocks into riverine HCO₃⁻ as dissolved inorganic carbon (DIC), and the lateral transport of DIC to the oceans is an integral component of the global carbon budget (Barnes and Raymond, 2009; Regnier et al., 2013). Global riverine transfers of DIC have been estimated to be between 0.38 and 0.41 Pg C/a (Amiotte Suchet et al., 2003; Mackenzie et al., 2004; Lerman et al., 2007; Cai et al., 2008), which accounts for approximately 40% of the overall riverine carbon flux (Amiotte Suchet et al., 2003). In this context, quantifying chemical weathering fluxes and clarifying the controlling factors are essential for understanding global carbon cycles.

The Yellow River, most of which is situated in arid and semiarid regions, has the highest HCO₃⁻ concentration of any river in the world (Meybeck and Ragu, 1997; Cai et al., 2008). It is generally admitted that the high levels of HCO₃⁻ in the Yellow River are a result of it flowing through the world's largest loess plateau. Cauwet and Mackenzie (1993) found that the DIC concentration in the Yellow River was high (29 mg/L), which reflects the high carbonate content of the eroded and leached soils in the Yellow River watershed. The high concentration of alkali earth elements (Ca, Mg), the high (Ca+Mg)/(Na+K) ratio (mean: 0.76) and the extreme alkalinity (mean: 3.1-3.5 meq/L) in the Yellow River demonstrate the importance of carbonate weathering and erosion in the river drainage basin (Zhang et al., 1990). Several studies have indicated that the carbonate content in the loess, which is widespread in the middle reach of the Yellow River, ranges between 10% and 20% (Zhang, 1995; Li et al., 2007). The high contents of evaporites and carbonates in the loess are also believed to be the leading cause of the high total dissolved solids (TDS) and HCO₃⁻ concentrations in the Yellow River; furthermore, HCO₃⁻ accounts for approximately 60% of the anions (Chen et al., 2003, 2005). In a comparative overview of weathering intensity and HCO₃⁻ flux in the world's major rivers, Cai et al. (2008) speculated that the weathering rate of the carbonates in loess must be particularly high to explain the extremely high levels of HCO₃⁻ in the Yellow River water because the carbonate content in loess is less than is expected for such a high HCO₃⁻ concentration in the

water. However, although the upper Yellow River basin, which is located in the Qinghai-Tibet Plateau, is rich in shale and contains relatively few carbonate minerals (Chen et al., 2005; Chen et al., 2006), carbonate weathering still dominates in this area (Wu et al., 2005; Wu et al., 2008a; Fan et al., 2014), which is probably due to the much faster kinetics of dissolution and the much greater solubility of carbonates compared to silicates (Liu and Dreybrodt, 1997; Kump et al., 2000; Jacobson et al., 2002). Compared with Zhang et al. (1990) and Zhang et al. (1995), Wu et al. (2005) concluded that the upper Yellow River supplies about 80% of the total riverine TDS flux and has higher chemical weathering rates per unit area than the basin as a whole. Fan et al. (2014) also concluded that the CO₂ consumption rate by carbonate weathering is highest in the upper Yellow River, reaching $304 \times 10^5 \text{ mol}/(\text{km}^2 \cdot \text{a})$. In addition, as the water source of the Yellow River, the Qinghai-Tibet Plateau supplies approximately 60% of the water to the Yellow River (Chen et al., 2005). Therefore, contributions from the Qinghai-Tibet Plateau to the high HCO₃⁻ levels in and DIC flux of the Yellow River cannot be neglected.

We use data from our two field investigations in the summers of 2007 and 2009 to study chemical weathering across the entire Yellow River basin. Based on identifying the contributions from different sub-basins, we examine the origin of the high HCO₃⁻ levels in the Yellow River and conclude that the Qinghai-Tibet is the major source of HCO₃⁻. Our work not only provides basic data that informs studies of the global carbon budget but also reveals the characteristics of chemical weathering and CO₂ consumption in arid and semiarid regions in the context of current climate changes and anthropogenic activities.

2. Materials and methods

2.1 Studying area

The Yellow River originates in the Yueguzonglie Basin on the Qinghai-Tibet Plateau at an elevation of 4500 m. It flows approximately 5464 km and drains an area of $75.2 \times 10^4 \text{ km}^2$ before discharging into the Bohai Sea. Shale is the main rock type in the region above the Lanzhou station, which is located in the transitional zone from the Qinghai-Tibet Plateau to the Loess Plateau (Fig. 1). The region between the Lanzhou and Huayuankou stations mainly contains loess (Fig. 1), which covers approximately 44% of the basin (Chen et al., 2005). Quartz, carbonate, feldspar and micas are the most important detrital minerals in the loess (Zhang et al., 1995). The potential source region of the loess on the Chinese Loess Plateau contains abundant

carbonate minerals (Li et al., 2007), which causes the carbonate content in the loess to range between 10% and 20% (Zhang et al., 1995; Li et al., 2007). Evaporite minerals are also very abundant in the loess (5%-10%) (Zhang et al., 1990; Zhang et al., 1995). Downstream from the Huayuankou station, the river is confined to a narrow basin that is characterized by a riverbed that has been raised up to 10 m above the surrounding area by severe siltation. Clays are dominant in this area (Fig. 1).

Fig. 1. Sampling stations and rock types in the Yellow River basin.

The figure is taken from Chen et al. (2005) and Chen et al. (2006). I, II and III stand for the Qinghai-Tibet Plateau sub-basin, the Loess Plateau sub-basin and the Lower sub-basin, respectively. DR: Dari; LJ: Lajia; GD: Guide; LIX: Liujiaxia; LZ: Lanzhou; DT: Datong River; HS: Huangshui River; TH: Taohe River; YC: Yinchuan; BT: Baotou; WJZ: Wanjiazhai; TG: Tongguan; SMX: Sanmengxia; XLD: Xiaolangdi; HYK: Huayuankou; KF: Kaifeng; HZ: Heze; DP: Dongping.

The average elevation of the upper Yellow River in the Qinghai-Tibet Plateau is about 3000 m. As a result, annual average temperature here is always below 0°C (the Dari station), and even achieves -4°C in the water resource region. In addition, temperature difference between day and night here is also very large (~20°C) (<http://cdc.nmic.cn/home.do>). The very low temperature leads to the fact that precipitation in the upper Yellow River basin is mainly in the form of ice and snow. As the result, melt ice-cover on the Qinghai-Tibet Plateau is the major source for river runoff (Chang et al., 2007; Wang et al., 2006). In the Loess Plateau, contributions from ice and snow melting to runoff is quite small. Except for upstream input, rainfall is the major factor for flow variation in the middle reach (Ma, 2005).

As the “Mother River” of China, the Yellow River is a major source of fresh water for approximately 107 million people within the river basin, which represents approximately 8.7% of the total population of China (Wang et al., 2006). Most of the people in the basin live downstream from the Lanzhou station. For example, the population density of Qinghai Province, which is located in the upper Yellow River

basin, is only 8.2 people per square kilometer (China Statistical Yearbook, 2013). In the Loess Plateau, agriculture is quite developed, and the area of farmland accounts for more than 90% of the total area of the Yellow River basin (<http://www.yellowriver.gov.cn>). However, the climate is arid and semi-arid; the annual precipitation and evaporation in the Loess Plateau over the last several decades have been estimated at 436 mm and 1850 mm, respectively (Yang et al., 2004). As a result, half of the agriculture farmland in the basin is irrigated by the Yellow River (Yang et al., 2004). The withdrawal of water for agricultural irrigation represents approximately 80%-90% of the total reduction in water discharge (Chen et al., 2003).

Based on the geographic features and rock types, the Yellow River basin is divided into three sub-basins in this study. The Qinghai-Tibet Plateau, or the upper basin (I), is located above the Lanzhou station, while the Loess Plateau, or the middle basin (II), is located between the Lanzhou station and the Huayuankou station. The area below the Huayuankou station is considered to be the lower sub-basin (III).

2.2 Sampling and analysis

Samples were collected from the main stream of the Yellow River between the water resource region and the mouth of the river during May and July of 2007 and 2009 (Table 1, Table 2, Fig. 1). These months are within the wet season of the Yellow River basin. Using floating bridges or boats, water samples were collected from approximately 1 m below the surface in the middle of the river. The water samples were first stored in pre-cleaned polyethylene bottles that were free of air and filtered through 0.45 μm cellulose acetate membrane filters in the temporary lab that night. The filtrate was separated into two parts; one part was acidified to $\text{pH} < 2$ with ultrapure 1:1 nitric acid for cation analysis (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), and the non-acidified part was used for anion determination (SO_4^{2-} , Cl^- , NO_3^-). Samples for DIC measurements were first filtered through a 0.45 μm cellulose acetate membrane into a 20 ml glass vial immediately after collection and poisoned with saturated HgCl_2 (final concentration $\sim 0.02\%$ by volume; Dickson and Goyet, 1994). The DIC samples were preserved at 4°C for future analysis, which was carried out within approximately 1 week.

The cation analysis (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) was performed with an atomic absorption spectrophotometer (AA240FS, Agilent Corporation, U.S.), while the anion determination (SO_4^{2-} , Cl^- , NO_3^-) was performed with ion chromatography (ICS3000, Dionex Corporation, U.S.). Dissolved silica was measured by spectrophotometric

measurements of the Mo blue complex. The analytical errors in the concentration measurements were estimated to be less than 1%. The pH was determined using an Orion 3-Star Plus pH benchtop meter with a Ross pH electrode (Thermo Fisher Scientific Inc., Beverly, MA, USA) that was calibrated according to the National Bureau Standards (NBS Standards) of 4.00, 6.86, and 9.18 at 25°C. The levels of precision were approximately ± 0.005 . The measurements were taken at a constant temperature of 25°C.

As described in [Zhang et al. \(2010\)](#) and [Zhang et al. \(2012\)](#), DIC was determined by acid extraction using a total organic carbon analyzer (TOC-VCPN, Shimadzu Corporation, Japan). The sample was acidified to $\text{pH} < 3$ in a syringe using 2 mol/L HCl and was then sparged for 1.5 min with a CO_2 -free carrier gas. After the inorganic carbon in the sample was converted to CO_2 , the CO_2 gas was carried into the cell of the NDIR gas analyzer by the carrier gas, where the CO_2 was detected. The coefficient of variance of the instrument is less than 1%. Measurements were calibrated against certified reference material (CRM, provided by A.G. Dickson from Scripps Institution of Oceanography) at a precision of approximately $\pm 5 \mu\text{mol/kg}$. This method has also been applied in carbon studies of the Changjiang River ([Zhang et al., 2014a](#)) and the Yellow River Estuary ([Liu et al., 2014](#)).

As in previous studies ([Karim and Veizer, 2000](#); [Oh and Raymond, 2006](#); [Liu et al., 2010](#)), we assume that the concentrations of HCO_3^- are equal to the DIC values. However, previous researches on the chemical weathering and geochemistry of the Yellow River also used acid titration to obtain alkalinity data ([Wu et al., 2005](#)) or HCO_3^- concentrations ([Chen et al., 2005](#); [Zhang et al., 1995](#)), and the analytical errors were less than 5% ([Zhang et al., 1995](#); [Ollivier et al., 2010](#); [Rai et al., 2010](#)). In the Mississippi River water ($\text{pH} \approx 8$), the average HCO_3^- concentration is about 99% of the average TAlk ([Cai, 2003](#)). In addition, the HCO_3^- concentration can also be determined by the charge balance from the other ions ([Wu et al., 2008a](#); [Goldsmith et al., 2010](#)). The errors are mainly from the precision of determining the ions and the omission of some trace ions. In this paper, the HCO_3^- concentration, DIC, and TAlk are not differentiated.

The riverbed sediment samples were measured by the Qingdao Institute of Marine Geology. The samples were first dried to a constant weight and ground to 160 meshes ([Wu et al., 2008a](#)). To remove carbonate minerals, the ground powders were

immersed in 1 mol/L HCl (Analytical reagent) for 4 h. The residues were then washed to neutrality with deionized water. These residues were put in acid mixtures ($\text{HNO}_3 + \text{HF} + \text{HClO}_4$) for digestion, and the solutions were analyzed for Na^+ , K^+ , Ca^{2+} and Mg^{2+} by ICP-AES (IRIS Intrepid II XSP, Thermo Fisher, USA). The relative standard deviation of the instrument is less than 1.5%. All of the acids that were used in the experiment were analytical reagents. For additional details, please refer to [Wu et al. \(2008a\)](#) and [Xin et al. \(2011\)](#).

3. Results

The Yellow River waters are weakly alkaline; the pH ranges between 7.68 and 8.85 ([Table 1](#), [Table 2](#)). The measured total dissolved cations ($\text{TZ}^+ = \text{K}^+ + \text{Na}^+ + 2\text{Ca}^{2+} + 2\text{Mg}^{2+}$) and total dissolved anions ($\text{TZ}^- = 2\text{SO}_4^{2-} + \text{HCO}_3^- + \text{Cl}^- + \text{NO}_3^-$) of all samples are well balanced; 28 of the 34 samples have normalized inorganic charge balances (NICBs) below 5%, and all of the samples have NICBs within 8%, which indicates that unanalyzed organic anions are only a minor component ([Table 1](#), [Table 2](#)). The TDS values have an average of 550 mg/L (256-751 mg/L), which is much higher than that of large rivers around the world (283 mg/L; [Han and Liu, 2004](#)) and the TDS values of the Yamuna (152 mg/L; [Dalai et al., 2002](#)), Indus (164 mg/L; [Karim and Veizer, 2000](#)), and Changjiang (224 mg/L; [Chetelat et al., 2008](#)) Rivers, which also originate in the Qinghai-Tibet Plateau. The TDS values of the Yellow River increase gradually from the upper to lower reaches ([Table 1](#), [Table 2](#)). We use the normalized Na molar ratios (Ca/Na , Mg/Na , HCO_3^-/Na) because the absolute concentrations are affected by dilution and evaporation processes. The best correlations between the elemental ratios were observed for Ca/Na vs. Mg/Na ($R^2=0.85$, $n=29$) and Ca/Na vs. HCO_3^-/Na ($R^2=0.95$, $n=29$). These correlations mostly reflect mixing between carbonates and silicates.

The ion concentrations in the upper basin are the lowest of the three sub-basins ([Table 1](#), [Table 2](#)). The average TDS at the Lanzhou station is 375 mg/L, which is similar to the result of 383 mg/L that was found by [Wu et al. \(2005\)](#). Ca^{2+} is the dominant cation in the waters and contributes 38.4% of the total cation concentration at the Lanzhou station ([Fig. 2a](#)). This value agrees closely with the historical data (40.7%; [Chen et al., 2005](#)), but is slightly higher than the value of 33.2% that was found by [Wu et al. \(2005\)](#). The average HCO_3^- concentration is 2.98 ± 0.05 mmol/L, which accounts for approximately 68.4% of the total anion concentration; both of these values are similar to the results of [Chen et al. \(2005\)](#) and [Wu et al. \(2005\)](#),

which are 2.87 mmol/L and 69.7% and 2.97 mmol/L and 65.3%, respectively. In addition, the (Ca+Mg)/(Na+K) ratios are quite high (~4), which indicates that carbonate weathering is dominant in this region.

After entering the Loess Plateau from the Lanzhou station, the ion concentrations in the river waters, especially Na^+ , Cl^- and SO_4^{2-} , increase. The TDS and HCO_3^- concentrations in the middle reach average 627 ± 28.1 mg/L and 3.40 ± 0.08 mmol/L, respectively. In addition, the NO_3^- concentrations increase significantly compared to those in the upper reach (Table 1, Table 2), which indicates large impacts from agricultural fertilization (De Jong et al., 2007). The cations and anions in this region plot near the apexes of $\text{Na}^+ + \text{K}^+$ and $\text{Cl}^- + \text{SO}_4^{2-}$ in the cation and anion ternary diagrams, respectively (Fig. 2a, Fig. 2b), which suggests that the water geochemistry in the region is significantly affected by evaporite dissolution. However, the average (Ca+Mg)/(Na+K) ratio in this region is still very high (0.7) and is similar to that found by Zhang et al. (1990), who suggested that the entire Yellow River basin is dominated by carbonate weathering. The analysis presented above suggests that the high HCO_3^- concentrations and (Ca+Mg)/(Na+K) ratios in the Loess Plateau are mainly a legacy effect from sub-basin I.

Fig. 2. Cation (a) and anion (b) ternary diagrams of the Yellow River (LZ indicates the Lanzhou station).

Generally, the ion concentrations in 2007 were higher than those in 2009 (Table 1, Table 2), which is probably due to the impact of precipitation. Although the total rainfall in the Yellow River basin was greater in 2009 (518 mm) than in 2007 (489 mm), the contributions from the sampling months (May to July) of these two years were the opposite (31% vs 42%; <http://cdc.cma.gov.cn/home.do>). The higher proportion of precipitation in the sampling months of 2007 would lead to stronger chemical weathering but was not high enough to cause a dilution effect. Water

258 discharges can directly reflect precipitation; the discharges were approximately 4%,
259 16% and 14% higher at the Lanzhou, Huayuankou and Lijin stations during the
260 sampling months in 2007 than in 2009 ([Yellow River sediment bulletin, 2007; 2009](#)).

Table 1. Dissolved chemical composition of the Yellow River basin in 2007.

Basin	Station	Lat. N	Lon. E	dd/mm/yy	pH	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NO ₃ ⁻	SO ₄ ²⁻	DIC	Si	Cl ⁻	TDS ^a (mg/L)	NICB ^b (%)
Qinghai-Tibet Plateau sub-basin I	Lajia	34°40'46"	100°38'23"	13/07/07	8.41	0.36	0.04	0.48	1.12	0.03	0.12	2.81	0.13	0.29	269	6.0
	Guide	36°03'31"	101°26'59"	14/07/07	8.43	0.62	0.04	0.60	1.16	0.05	0.28	2.98	0.14	0.51	316	0.8
	Liujiaxia	35°56'05"	103°20'43"	20/07/07	8.41	0.84	0.04	0.68	1.17	0.06	0.42	2.86	0.10	0.58	329	5.4
	Lanzhou	36°03'39"	103°48'55"	17/07/07	8.28	1.06	0.07	0.94	1.25	0.07	0.72	3.01	0.14	0.79	394	3.2
Loess Plateau sub-basin II	Yinchuan	38°21'5"	106°24'45"	18/07/07	7.88	3.28	0.11	1.15	1.48	0.18	1.24	3.52	0.17	2.37	606	1.3
	Wanjiazhai	39°54'30"	110°41'10"	20/06/07	8.14	4.17	0.12	1.23	1.22	0.23	1.37	3.30	0.13	3.07	642	-1.5
	Tongguan	34°36'47"	110°15'08"	17/06/07	7.68	4.83	0.14	1.53	1.63	0.24	1.41	3.99	0.16	3.65	751	5.4
	Sanmenxia	34°47'56"	111°12'16"	17/06/07	8.07	4.79	0.13	1.33	1.52	0.24	1.53	3.36	0.16	3.64	713	3.0
	Xiaolangdi	34°54'58"	112°20'56"	17/06/07	8.46	4.68	0.13	1.27	1.53	0.27	1.62	3.37	0.15	3.36	710	1.7
	Huayuankou	34°54'24"	113°41'18"	15/06/07	8.07	4.49	0.13	1.30	1.65	0.32	1.71	3.26	0.13	3.49	724	2.7
Lower sub-basin III	Kaifeng	34°54'30"	114°30'37"	16/06/07	8.18	4.53	0.13	1.34	1.64	0.31	1.70	3.52	0.12	3.21	724	1.7
	Heze	35°25'09"	115°07'03"	13/06/07	8.14	4.45	0.13	1.47	1.34	0.32	1.65	3.67	0.15	3.22	722	-3.1
	Dongping	36°02'39"	116°03'59"	13/06/07	8.23	4.48	0.13	1.33	1.61	0.32	1.65	3.73	0.11	3.20	730	-0.7
	Liji	37°30'54"	118°18'24"	25/06/07	8.29	4.51	0.14	1.35	1.36	0.30	1.41	3.54	0.13	3.44	692	-1.9
Tributary	Taohe	--	--	20/07/07	8.32	0.73	0.073	0.65	1.26	0.073	0.31	3.34	0.11	0.51	348	1.5
	Huangshui	36°20'05"	102°47'40"	16/07/07	8.30	2.86	0.083	1.06	2.00	0.21	1.85	3.05	0.17	1.92	630	2.1
	Datonghe	36°37'44"	102°47'08"	16/07/07	8.48	0.49	0.041	0.68	1.25	0.06	0.43	3.00	0.11	0.35	326	3.0

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^a TDS (total dissolved solids) = Na⁺ + K⁺ + Mg²⁺ + Ca²⁺ + Cl⁻ + SO₄²⁻ + HCO₃⁻ + NO₃⁻ + SiO₂;
^b NICB (Net Inorganic Charge Balance) = (TZ⁺-TZ⁻)/TZ⁺, TZ⁺ (total dissolved cations) = K⁺ + Na⁺ + 2Ca²⁺ + 2Mg²⁺, TZ⁻ (total dissolved anions) = 2SO₄²⁻ + HCO₃⁻ + Cl⁻ + NO₃⁻

Table 2. Dissolved chemical composition of the Yellow River basin in 2009.

Basin	Station	Lat. N	Lon. E	dd/mm/yy	pH	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NO ₃ ⁻	SO ₄ ²⁻	DIC	Si	Cl ⁻	TDS (mg/L)	NICB (%)
Qinghai-Tibet Plateau sub-basin I	Dari	33°46'05"	99°39'20"	01/07/09	8.59	0.54	0.04	0.80	0.77	0.03	0.14	3.22	0.08	0.48	297	7.8
	Lajia	34°40'46"	100°38'23"	01/07/09	8.56	0.33	0.04	0.58	0.89	0.04	0.09	2.81	0.10	0.26	256	0.8
	Guide	36°03'31"	101°26'59"	30/06/09	8.34	0.59	0.04	0.68	1.08	0.05	0.33	3.04	0.10	0.47	317	2.2
	Liujiaxia	35°56'05"	103°20'43"	04/07/09	8.40	0.82	0.05	0.80	0.91	0.06	0.45	3.06	0.09	0.52	334	6.0
	Lanzhou	36°03'39"	103°48'55"	04/07/09	8.33	0.97	0.06	0.80	1.17	0.08	0.47	3.06	0.09	0.68	357	4.3
Loess Plateau sub-basin II	Yinchuan	38°21'5"	106°24'45"	03/07/09	7.91	1.59	0.07	0.88	1.12	0.12	0.64	3.53	0.10	1.18	437	8.0
	Baotou	36°03'39"	103°48'55"	02/07/09	8.37	3.04	0.09	1.32	1.17	0.14	1.16	3.36	0.09	2.17	558	1.4
	Tongguan	34°36'47"	110°15'08"	06/07/09	7.78	3.34	0.13	1.51	1.32	0.18	1.08	3.60	0.11	2.87	614	3.8
	Xiaolangdi	34°54'58"	112°20'56"	07/07/09	8.16	3.24	0.12	1.25	1.24	0.21	1.24	3.04	0.10	2.63	576	0.2
	Huayuankou	34°54'24"	113°41'18"	08/07/09	8.16	3.20	0.12	1.25	1.32	0.28	1.05	3.03	0.10	2.59	558	3.4
Lower sub-basin III	Lijin	37°30'54"	118°18'24"	27/05/09	--	3.65	0.13	1.32	1.51	0.29	1.42	3.18	0.09	2.79	634	3.6
	Kenli	37°36'18"	118°31'48"	26/05/09	8.38	3.97	0.13	1.35	1.45	0.29	1.61	3.30	0.09	3.31	683	4.2
	*D-LJ1	37°44'15"	118°45'29"	26/05/09	8.35	3.87	0.13	1.31	1.46	0.28	1.59	3.21	0.09	3.32	673	4.8
	*D-LJ2	37°47'8"	119°02'16"	26/05/09	8.39	3.92	0.13	1.34	1.51	0.28	1.65	3.19	0.09	3.31	681	3.7
	*D-LJ3	37°45'40"	119°09'20"	26/05/09	8.34	3.76	0.13	1.32	1.56	0.28	1.54	3.17	0.09	3.16	662	0.2
Tributary	Huangshui	36°20'05"	102°47'40"	03/07/09	8.43	2.35	0.09	0.92	1.01	0.13	1.01	2.87	0.16	1.45	461	2.9
	Wei River	--	--	06/07/09	8.85	4.79	0.22	1.27	0.75	0.10	1.42	2.50	0.05	3.26	593	4.0

*D-LJ represents sampling locations downstream of Lijin station.

4. Discussion

4.1 Sources of major ions

Dissolved major ions in rivers come from atmospheric inputs, the weathering of rocks and anthropogenic activities (Roy et al., 1999; Moon et al., 2007; Chetelat et al., 2008; Moquet et al., 2011; Moosdorf et al., 2011; Shin et al., 2011). The budget equation for any soluble element X in a river can be written as (Galy and France-Lanord, 1999):

$$[X]_{\text{riv}} = [X]_{\text{atm}} + [X]_{\text{ant}} + [X]_{\text{car}} + [X]_{\text{sil}} + [X]_{\text{eva}} + [X]_{\text{sul}} \quad (4)$$

where “riv” indicates river water, “atm” represents the atmospheric input, “ant” is the anthropogenic input, “car”, “sil” and “eva” denote the inputs from carbonate, silicate weathering and evaporite dissolution, respectively, and “sul” represents the contribution from sulfide oxidation.

(1) Atmospheric input

Atmospheric deposition is considered to be a non-negligible source to river water chemistry. Its contributions to river water elements mainly range between 5% and 20% and sometimes even reach 60% (Gaillardet et al., 1999; Moon et al., 2007; Moquet et al., 2011; Noh et al., 2009). Therefore, weathering results will be overestimated if this input is not considered.

Based on data of precipitation, runoff, and rainwater composition in the Yellow River basin, this paper adopts the correction from Moquet et al. (2011):

$$X_{\text{atm}} = (X/\text{Cl})_{\text{rain}} \times \text{Cl}_{\text{ave}} \times P/R \quad (5)$$

where X_{atm} refers to the corrected concentration derived from rainwater, $(X/\text{Cl})_{\text{rain}}$ denotes the ratio of measured ions to Cl^- in rainwater, Cl_{ave} stands for the Cl^- concentration in river water that is derived from rainwater, and P and R refer to precipitation and runoff, respectively.

Table 3. Ions in rainwater in the Yellow River basin.

Sub-basin	station	Rainwater (10^{-3} mmol/L)						reference
		Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	
I	Waliguan	17.0	6.0	8.7	3.8	6.1	12.0	Tang et al. (2000)
	Longmeng*	163.0	45.0	152.0	29.7	107.3	211.0	
II	Toudaoguai*	73.4	21.2	20.2	9.2	11.8	71.0	Zhang et al. (2015)
	Zhengzhou	188	47	79	37	427	195	

I and II denote the Qinghai-Tibet Plateau and the Loess Plateau, respectively. * refers to the average value calculated from Zhang et al. (2015).

However, the Yellow River basin covers a large area with elevation differences of up to 4000 m (Zhang et al., 2013). In addition, the ratio of evaporation to precipitation (Yang et al., 2004) and the composition of rainwater (Table 3) in the Qinghai-Tibet Plateau and Loess Plateau are quite different. Therefore, we corrected the atmospheric contributions separately for the different sub-basins.

The atmospheric input was corrected using equation 5, and the results showed that these inputs accounted for approximately 4.1% (3.0%-5.3%) and 7.6% (6.3%-13.7%) of the total riverine cations of the Qinghai-Tibet Plateau and the Loess Plateau, respectively. It is important to note that the following discussions of the other sources are based on this correction (indicated with *).

After this correction, we assume that all of the remaining Cl^- originates from evaporite minerals:

$$\text{Cl}^-_{\text{riv}} = \text{Na}^+_{\text{NaCl}} \quad (6)$$

(2) Silicate weathering

Silicate weathering mainly contributes Na^+ and K^+ cations from aluminosilicate weathering and Ca^{2+} and Mg^{2+} from calcium-magnesium silicate weathering to the dissolved load in river waters.

K^+

The K^+ in river waters originates from silicate weathering, atmospheric inputs and agricultural contributions (Chetelat et al., 2008); silicate weathering is the dominant source (Gaillardet et al., 1999; Dalai et al., 2002; Han and Liu, 2004; Moon et al., 2007; Moquet et al., 2011). The impacts of anthropogenic inputs (e.g., fertilizer) must also be considered, especially in well-developed agricultural regions (Chetelat et al., 2008). The source region of the Yellow River, which is defined in this study as the area above the Lajia station, is one of the least populated areas of the Yellow River basin with farmland accounting for less than 0.5% of the entire area (<http://www.yellowriver.gov.cn>). In addition, the average NO_3^- concentration in the water is only 0.03 ± 0.002 mmol/L. Therefore, we assume that almost all of the K^+ in the water resource region of the Yellow River originates from silicate weathering. In contrast, agriculture is well developed in other parts of the Yellow River basin and especially in sub-basin (II), which includes more than 80% of the farmland in the basin. Due to the wide application of fertilizers, the concentrations of NO_3^- and K^+ increase greatly from the upper to lower reaches (Table 1, Table 2). According to the

China Statistical Yearbook (2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011), the application ratio of nitrogenous and potassic fertilizers, which are considered as NO_3^- and K^+ , respectively, in the Yellow River basin is approximately 4.6 (mol/mol). However, based on utilization ratios of 0.35 and 0.48 for these two types of fertilizers, respectively (Chen et al., 1998), large amounts of these fertilizers cannot be consumed, and the ratio of the residues of these two fertilizers (NO_3^-/K^+) is approximately 5.4 (mol/mol). Given that the soils in the Loess Plateau are slightly alkaline (Zhang et al., 1990), some of the nitrogenous fertilizers will be lost in the form of ammonia, which will decrease this ratio. In addition, the large area of farmland (13% of the entire country), the different types of crops in the Yellow River basin and the different cycling rules for each element can cause large uncertainties in determining this ratio. In this study, we used a NO_3^-/K^+ ratio of 5 to correct the agricultural input of K. Thus, the K^+ that originates from silicate weathering (K^+_{sil}) in the Yellow River basin can be expressed as follows:

$$\text{K}^+_{\text{sil}} = \text{K}^+_{\text{riv}} - \text{K}^+_{\text{agr}} = \text{K}^+_{\text{riv}} - 1/5 \text{NO}_3^- \quad (7)$$

The NO_3^-/K^+ ratio that is used in this study is different from that applied in the Changjiang River basin (Chetelat et al., 2008); this is probably due to the different fertilizer utilization ratios for various crops, such as wheat and rice (Chen et al., 1998). Na^+

After correcting for the atmospheric inputs, the Na^+ in the river waters is derived mainly from evaporite dissolution (NaCl , Na_2SO_4) and silicate weathering. For a region in which NaCl is the only type of evaporite ($\text{Na}^+_{\text{Na}_2\text{SO}_4} = 0$), the Na^+ from silicate weathering (Na^+_{sil}) can be calculated as the difference between the total Na^+ in the river (Na^+_{riv}) and that from NaCl dissolution ($\text{Na}^+_{\text{NaCl}}$) (Moon et al., 2007; Noh et al., 2009):

$$\text{Na}^+_{\text{sil}} = \text{Na}^+_{\text{riv}} - \text{Na}^+_{\text{NaCl}} - \text{Na}^+_{\text{Na}_2\text{SO}_4} = \text{Na}^+_{\text{riv}} - \text{Cl}^-_{\text{riv}} \quad (8)$$

However, loess is widely distributed across the middle Yellow River basin (Fig. 1), and the contribution from Na_2SO_4 , which is a major type of evaporite in loess, prevents using equation 8 to obtain Na^+_{sil} ($\text{Na}^+_{\text{Na}_2\text{SO}_4} \neq 0$). However, when K^+_{sil} values are available, Na^+_{sil} can be obtained through the $(\text{K}^+/\text{Na}^+)_{\text{sil}}$ ratios. For example, Gaillardet et al. (1999) used a $(\text{K}^+/\text{Na}^+)_{\text{sil}}$ ratio of 0.1 to study global chemical weathering. The $(\text{K}^+/\text{Na}^+)_{\text{sil}}$ ratio in the Guayana Shield, which is typical of silicate draining waters, mainly ranged between 0.3 and 0.8 (Edmond et al., 1995), while the

ratios in the Mackenzie River basin were between 0.1 and 0.25 (Millot et al., 2003). Chetelat et al. (2008) used a $(K^+/Na^+)_{sil}$ ratio of 0.17, which is similar to that deduced by Millot et al. (2003) and observed in rivers that drain silicates (Meybeck, 1986), to study chemical weathering in the Changjiang River basin.

The water source region of the Yellow River (above the Lajia station) is mainly composed of shale and is not significantly influenced by loess (Fig. 1); the SO_4^{2-} concentrations in the river waters are very low (Table 1, Table 2). As a result, the Na^+ from silicate weathering in the water resource region can be calculated using equation 8. Combined with the K^+_{sil} calculated using equation 7, we conclude that the ratio of $(K^+/Na^+)_{sil}$ in the water resource region of the Yellow River ranges between 0.31-0.43 and has an average value of 0.37 ± 0.03 . Therefore, we utilize a $(K^+/Na^+)_{sil}$ ratio of 0.37 for the other parts of the Yellow River basin (downstream of the Lajia station, where loess is widespread) to calculate the Na^+_{sil} in the river waters. However, two uncertainties must be considered. First, the $(K^+/Na^+)_{sil}$ ratio can be calculated by assuming that halite is the only type of evaporite in the water source region. However, Na_2SO_4 still contributes to riverine Na^+ in this area, even though the amount is very small. This will cause the $(K^+/Na^+)_{sil}$ ratio to be underestimated, which will overestimate the CO_2 consumption by chemical weathering. Second, applying the $(K^+/Na^+)_{sil}$ ratio from a sub-basin to the entire basin will over- or under-estimate the results. However, instead of using the ratio from typical silicate draining waters, we prefer to consider the Yellow River as a whole and apply the ratio of 0.37 to obtain Na^+_{sil} .

$$Ca^{2+}_{sil} \quad Mg^{2+}_{sil}$$

Ca^{2+} in river waters is derived from carbonates, evaporites and silicates, whereas carbonates and silicates are the sources of Mg^{2+} . In river waters, Ca^{2+} and Mg^{2+} that are derived from silicate weathering (Ca^{2+}_{sil} and Mg^{2+}_{sil}) can be written as (Galy and France-Lanord., 1999):

$$Ca_{sil} = Na^+_{sil} \times (Ca^{2+}/Na^+)_{sil} \quad (9)$$

$$Mg_{sil} = K^+_{sil} \times (Mg^{2+}/K^+)_{sil} \quad (10)$$

where $(Ca^{2+}/Na^+)_{sil}$ and $(Mg^{2+}/K^+)_{sil}$ are the molar ratios released to river waters from silicates in the drainage basins during chemical weathering.

Galy and France-Lanord (1999) applied $(Ca^{2+}/Na^+)_{sil}$ and $(Mg^{2+}/K^+)_{sil}$ values of 0.18-0.3 and 0.5 ± 0.2 , respectively. These values are based on the (Ca^{2+}/Na^+) ratios in whole rock silicate compositions that are representative of the Higher Himalaya and

Lesser Himalaya and in plagioclase of the High Himalaya crystalline rocks. Based on the $(\text{Ca}^{2+}/\text{Na}^+)$ ratios of Lesser Himalaya granites/gneisses, soil profiles and rivers that predominantly drain silicates, [Krishnaswami et al. \(1999\)](#) used $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ and $(\text{Mg}^{2+}/\text{Na}^+)_{\text{sil}}$ values of 0.7 ± 0.3 and 0.3 ± 0.2 , respectively. In the Hong River drainage basin, [Moon et al. \(2007\)](#) used $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ and $(\text{Mg}^{2+}/\text{Na}^+)_{\text{sil}}$ ratios of 0.44 and 0.16, respectively. Riverbed sand samples are believed to be representative of unweathered bedrock from the watershed ([Blum et al., 1998](#); [Wu et al., 2008a](#)). By attributing Ca^{2+} in proportion to the $\text{Ca}^{2+}/\text{Na}^+$ ratio of plagioclase to the weathering of anorthite to kaolinite, the ratios of $\text{Ca}^{2+}/\text{Na}^+$ can be calculated from the silicate fraction of the riverbed sediment as $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ because plagioclase dominates the Ca^{2+} and Na^+ budgets of the silicate fraction. Similarly, the contribution of Mg_{sil} from silicate in rivers can also be obtained by multiplying the K^+ value in the river by the $(\text{Mg}^{2+}/\text{K}^+)_{\text{sil}}$ ratio of the silicate fraction of the riverbed sediments ([Blum et al., 1998](#)). In a chemical weathering study of the seven Chinese rivers that originate in the Qinghai-Tibet Plateau, [Wu et al. \(2008a\)](#) applied the $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ and $(\text{Mg}^{2+}/\text{K}^+)_{\text{sil}}$ ratios of the riverbed sand to obtain $\text{Ca}^{2+}_{\text{sil}}$ and $\text{Mg}^{2+}_{\text{sil}}$, respectively.

In a large basin such as the Yellow River basin, it is appropriate to analyze riverbed sand samples from different reaches. The $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ ratio of the riverbed sand in the Yellow River basin ranges between 0.24-0.31 and has an average value of 0.27 ± 0.02 , while the $(\text{Mg}^{2+}/\text{K}^+)_{\text{sil}}$ ratio ranges between 0.57-0.85 and has an average value of 0.68 ± 0.05 ([Table 4](#)). Previous studies of the Yellow River also calculated similar ratios. [Wu et al. \(2008a\)](#) calculated $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ and $(\text{Mg}^{2+}/\text{K}^+)_{\text{sil}}$ ratios of the Yellow River of 0.26 and 0.67, respectively, and [Wu et al. \(2005\)](#) assumed that the $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ ratio in the upper Yellow River ranged between 0.2 and 0.5. Considering the length of the Yellow River, we apply the $(\text{Ca}^{2+}/\text{Na}^+)_{\text{sil}}$ and $(\text{Mg}^{2+}/\text{K}^+)_{\text{sil}}$ ratios from the nearest station with riverbed sand data to obtain $\text{Ca}^{2+}_{\text{sil}}$ and $\text{Mg}^{2+}_{\text{sil}}$.

Table 4. Silicate compositions of the riverbed sand in the Yellow River basin.

Station	Ca^{2+}	Mg^{2+}	Na^+	K^+	$\text{Ca}^{2+}/\text{Na}^+$	$\text{Mg}^{2+}/\text{K}^+$
	(μmol/g)					
Dahejia*	149	324	567	483	0.26	0.67
Baotou	202	418	806	489	0.25	0.85
Tongguan	250	340	797	468	0.31	0.73
Huayunkou	254	295	816	517	0.31	0.57
Ljin	196	285	806	496	0.24	0.57

*Data quoted from [Wu et al. \(2008a\)](#)

(3) Evaporite dissolution

The Yellow River flows through the largest and deepest loess plateau in the world, and its basin has one of the highest evaporite contents in the world (Zhang et al., 1990; Zhang et al., 1995). As a result, the contributions from evaporite dissolution accounted for approximately 43.5%-54.7% of the ions in the Yellow River (Li and Zhang, 2005; Gaillardet et al., 1999), which is much higher than the global average of 13.6% (Gaillardet et al., 1999). The cations that are derived from evaporite dissolution are mainly Na^+ , Ca^{2+} and Mg^{2+} .

As discussed above, the Na^+ in river waters is derived mainly from evaporite dissolution and silicate weathering (Moon et al., 2007; Moquet et al., 2011). Therefore, Na^+ from evaporite dissolution (Na^+_{eva}) can be calculated as follows:

$$\text{Na}^+_{\text{eva}} = \text{Na}^+_{\text{Na}_2\text{SO}_4} + \text{Na}^+_{\text{NaCl}} = \text{Na}^+_{\text{riv}} - \text{Na}^+_{\text{sil}} \quad (11)$$

The Ca^{2+} and Mg^{2+} from evaporite dissolution ($(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{eva}}$) come from CaSO_4 and MgSO_4 , and the amount of Ca^{2+} and Mg^{2+} is equal to the amount of SO_4^{2-} . However, SO_4^{2-} is also derived from the dissolution of Na_2SO_4 and the oxidation of pyrite (Torres et al., 2014). The SO_4^{2-} concentrations in the water resource region of the Yellow River are very low (0.08 mmol/L). After the Yellow River flows through the loess-like soil area and is affected by high SO_4^{2-} tributaries (Fig. 1, Table 1, Table 2), the SO_4^{2-} concentration reaches 0.6 mmol/L. The high levels of SO_4^{2-} at the Lanzhou and Huayuankou stations are the result of the world's largest and deepest loess plateau. The loess originates from the northern margin of the Tibetan Plateau (Li et al., 2007), which does not have favorable mineralogic conditions for pyrite. Furthermore, the SO_4^{2-} and Cl^- levels in the Yellow River water correlate very well with each other ($R^2=0.93$, $n=29$), which indicates that the SO_4^{2-} and the Cl^- in the Yellow River originate mainly from evaporite dissolution (Huh et al., 1998). Li and Zhang (2005) also concluded that almost all of the SO_4^{2-} in the Yellow River was contributed by evaporite minerals. However, pyrite oxidation, which releases CO_2 while supplying H_2SO_4 for weathering, could also be a source of SO_4^{2-} . Furthermore, CO_2 is released during carbonate weathering with sulfuric acid, which leads to the underestimation of CO_2 consumption by chemical weathering. In this study, we assume that all of the SO_4^{2-} in the Yellow River originates from evaporite dissolution (Na_2SO_4 , CaSO_4 and MgSO_4). Based on this assumption, $(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{eva}}$ can be calculated as follows:

$$(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{eva}} = \text{SO}_4^{2-}_{\text{riv}} - \text{SO}_4^{2-}_{\text{Na}_2\text{SO}_4} \quad (12)$$

Combined with (8) and (11), equation (12) can be written as:

$$(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{eva}} = \text{SO}_4^{2-}{}_{\text{riv}}^* - (\text{Na}^+_{\text{riv}}{}^* - \text{Cl}^-_{\text{riv}}{}^* - \text{Na}^+_{\text{sil}})/2 \quad (13)$$

(4) Carbonate weathering

Carbonate weathering mainly provides $\text{Ca}^{2+}_{\text{car}}$ and $\text{Mg}^{2+}_{\text{car}}$ cations to river waters. Based on the discussion presented above, we subtract the Ca^{2+} and Mg^{2+} that originates from silicate weathering and evaporite dissolution from the total and calculate the values of Ca^{2+} and Mg^{2+} from carbonate weathering ($(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{car}}$) as:

$$\begin{aligned} &(\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{car}} \\ &= (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{riv}}^* - (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{sil}} - (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{eva}} \end{aligned} \quad (14)$$

4.2 Contributions from different rock types and sub-basins to cations in the Yellow River

Concentrations of the cations that are generated from rock weathering and evaporite dissolution all increase from upstream to downstream in the Yellow River basin (Fig. 3a). However, the variations from rock weathering are much smaller than those from evaporite dissolution. For example, from the Qinghai-Tibet Plateau to the Loess Plateau, the average values of cations that are derived from carbonate weathering increase from 1.43 ± 0.03 mmol/L to 1.77 ± 0.08 mmol/L, whereas the cations from evaporates increase sharply from 0.87 ± 0.15 mmol/L to 3.91 ± 0.44 mmol/L.

Fig. 3. Cation concentrations from different rock types and their contributions to the total (average values of 2007 and 2009). I, II and III denote the Qinghai-Tibet Plateau, the Loess Plateau and the lower basin, respectively.

Given that the absolute concentrations are related to dilution and evaporation processes, the contributions from different rock types to the total cations are compared in the different sub-basins (Fig. 3b). Although the cation concentrations from

carbonate weathering and evaporite dissolution in the upper reach are both lowest along the Yellow River, their contributions to the total cations are completely different. The cations that are derived from carbonate weathering contribute 46% to 77% (average of 61%) of the total cations in the river waters. In contrast, evaporite dissolution contributes only 16% to 48% (average of 34%). These results are similar to those of [Wu et al. \(2005\)](#) in the upper Yellow River basin. In the middle reach, the contributions from evaporite dissolution increase to 66% (49%-73%) ([Fig. 3b](#)). On the whole, cations from carbonate weathering and evaporite dissolution account for more than 90% of the total due to the high contents of evaporite ([Zhang et al., 1990; Zhang et al., 1995](#)) and carbonate ([Zhang, 1995; Li et al., 2007](#)) minerals in loess. Silicate weathering in the Yellow River basin is very weak; its contribution to the cations is only 1%-6%. It is worthy noting that uncertainties on amount and proportions of cations derived from evaporite dissolution increased substantially from the Lanzhou station, where the Loess Plateau starts. Based on the discussion above on the difference of ion concentrations between 2007 and 2009 (Section 3), we speculate that the inter-annual difference of sampling (mainly precipitation) is the main reason leading to these big uncertainties.

The HCO_3^- concentrations were also determined by charge balance from the other ions; they averaged at 3.30 ± 0.07 mmol/L, which is very similar to the measured concentration (3.27 ± 0.05 mmol/L). Based on the contributions of cations from different rock types, we conclude that approximately 90% of the HCO_3^- in the Yellow River is derived from carbonate weathering (half from the atmosphere and half from carbonate minerals), and the remaining 10% comes from silicate weathering (all from the atmosphere). Carbonate weathering is dominant across the entire Yellow River basin.

It is important to note that the Yellow River water is alkaline, and the concentrations of HCO_3^- and Ca^{2+} are high. Thus, calcite is supersaturated in both the upper basin ([Wu et al., 2005](#)) and the lower mainstream ([Liu et al., 2014](#)); calcite precipitation contributes to chemical weathering. However, we cannot use only the calcite saturation index to quantitatively assess the impact of carbonate precipitation because this chemical process is also affected by dissolved Mg^{2+} , PO_4^{3-} , and organic carbon ([Inskeep and Bloom, 1986](#)). Calcite precipitation would cause the standing stock of Ca^{2+} to be smaller than the value it should be, and lead to the underestimation of CO_2 consumption.

4.3 CO₂ Consumption by chemical weathering in the Yellow River basin

Many geologic, climatic or topographic variables control the physical denudation and chemical weathering of the continents. In addition, many large rivers flow through several regions with complex lithological distributions (Bluth and Kump, 1991; Moosdorf et al., 2010; Hartmann and Moosdorf, 2012). The most downstream sampling station of a river will give the accumulated results of the entire basin but cannot reflect the contributions of each sub-basin with different lithologic features. To do so, a river basin can be divided into several sub-basins with similar rock types. Quantifying chemical weathering in different sub-basins not only demonstrates their contributions to the entire basin but also reveals the impacts of climate, topography, geology and human activities on chemical weathering.

Based on the lithologic distributions, a river basin can be divided into several sub-basins with similar rock types. The cations in a sub-basin mainly originate from chemical weathering in the sub-basin and input from the upstream sub-basins, and the output of these cations flows downstream; this assumes that all of the cations are conserved in the river (Fig. 4).

Fig. 4. CO₂ consumption by chemical weathering in different sub-basins.

Generally, the CO₂ consumption fluxes and rates by silicate and carbonate chemical weathering can be calculated as follows:

$$F_{\text{CO}_2, \text{sil}} = (\text{Na}^+_{\text{sil}} + \text{K}^+_{\text{sil}} + 2\text{Ca}^{2+}_{\text{sil}} + 2\text{Mg}^{2+}_{\text{sil}}) \times Q_n \quad (15)$$

$$\Phi_{\text{CO}_2, \text{sil}} = F_{\text{CO}_2, \text{sil}} / S \quad (16)$$

$$F_{\text{CO}_2, \text{car}} = (\text{Ca}^{2+}_{\text{car}} + \text{Mg}^{2+}_{\text{car}}) \times Q_n \quad (17)$$

$$\Phi_{\text{CO}_2, \text{car}} = F_{\text{CO}_2, \text{car}} / S \quad (18)$$

According to these equations, the chemical weathering in the sub-basins can be expressed as:

$$F_{\text{CO}_2, i} = F_{\text{CO}_2, \text{out}, i} - F_{\text{CO}_2, \text{in}, i} \quad (19)$$

$$F_{\text{CO}_2} = \sum F_{\text{CO}_2, i} \quad (20)$$

$$\Phi_{\text{CO}_2} = F_{\text{CO}_2} / S \quad (21)$$

where sil and car stand for silicate and carbonate, respectively, F_{CO_2} and Φ_{CO_2} denote the CO_2 flux and rate consumed by chemical weathering, respectively, S represents the basin area, Q_n denotes natural discharge, i stands for the number of the sub-basin, and “out” and “in” represent the river outlet and inlet of the sub-basin, respectively.

F_{CO_2} for the entire Yellow River basin is calculated as 98.31×10^9 mol/a (Table 5), which is slightly higher than the value calculated by Li and Zhang (2005) (90.5×10^9 mol/a). Gaillardet et al. (1999) concluded that approximately 92×10^9 mol/a of CO_2 was consumed by carbonate and silicate weathering in the Yellow River basin. For different rock types, carbonate and silicate weathering contribute approximately 89% and 11% of the total CO_2 consumption in the Yellow River basin, respectively. Although sub-basin (I) accounts for only 30% of the basin area, F_{CO_2} of sub-basin (I) is more than 61% of the total, to which carbonate weathering contributes 90%. In contrast, only 38% of the total CO_2 is consumed in sub-basin (II), which covers nearly 70% of the entire basin. The area of sub-basin (III) is very small (3%), and it mainly consists of clastic and clay (Fig. 1); thus, its contribution to the total F_{CO_2} is quite small and can be ignored.

Table 5. CO_2 consumption by carbonate and silicate weathering in the Yellow River basin (averages of 2007 and 2009).

Basin	Area (10^4 km ²)	Natural discharge (km ³ /a)	Sub-basin flux		CO_2 consumption rate	
			F_{CO_2sil} (10^9 mol/a)	F_{CO_2car}	Φ_{CO_2sil} (10^3 mol/km ² ·a)	Φ_{CO_2car}
I	22.26	36.19±1.56	5.64±0.04	53.99±3.40	25.35±0.20	242.56±15.28
II	50.75	48.50±0.51	4.79±1.11	32.50±4.98	9.43±2.20	64.03±9.80
III	2.18	49.64±1.28	0.27±0.08	1.12±0.16	12.32±3.70	51.30±7.26
Entire basin	75.19	49.64±1.28	10.70±1.15	87.61±1.73	14.23±1.53	116.52±2.30

I, II and III denote the Qinghai-Tibet Plateau, the Loess Plateau and the lower basin, respectively. Natural discharge data are taken from the Yellow River Water Resources Bulletin, while the area data are taken from Yang et al. (2004). Natural discharge is defined as discharge without human disturbance and is equal to the sum of the actual discharge, water consumption and reservoir variations (Wang et al., 2006).

It is important to note that approximately 2 times more water than the discharge at the downstream Lijin station is diverted in the Yellow River basin (Yellow River Water Resources Bulletin, 2005, 2006, 2007, 2008, 2009, 2010), and approximately 80%-90% of the total reduction in water discharge is due to water withdrawals for agricultural irrigation (Chen et al., 2003). This human activity not only takes water away from rivers, but also ions originating from rock weathering, which are the two major elements for chemical weathering study. As a result, usage of actual discharge in rivers like the Yellow River will cause underestimation of the weathering results,

and natural discharge is more appropriate (Li and Zhang, 2005; Wu et al., 2005; Wu et al., 2008a). In addition, due to evaporation and precipitation, frequent sampling is needed to minimize the effect of this subtraction method.

4.4 High chemical weathering rate in the Qinghai-Tibet Plateau

CO₂ consumption by carbonate weathering in the Yellow River basin is higher than the average of other large rivers around the world, while CO₂ consumption by silicate weathering is smaller (Fig. 5). Although shale is the main rock type in the upper Yellow River basin, the chemical weathering rate of this region is the highest of the entire basin, especially for carbonate (Table 5). Previous studies in this region also observed high chemical weathering rates and DIC concentrations as well as the dominance of carbonate weathering (Wu et al., 2005; Wu et al., 2008a; Fan et al., 2014), which is probably due to the much faster dissolution kinetics and the much greater solubility of carbonates compared to silicates (Liu and Dreybrodt, 1997; Blum et al., 1998; Kump et al., 2000; Jacobson et al., 2002). In addition, the upper basin is the water source region and supplies more than 60% of the water to the Yellow River (Chen et al., 2005). Even more important, due to the high elevation and low temperature, averaging at about 3000 m and 0°C, respectively, the precipitation in the Qinghai-Tibet Plateau is mainly in the form of ice and snow. Therefore, waters that are involved in chemical weathering are mostly from ice and snow melting. Moreover, due to the many tall ice-covered mountains and deep valleys, with reliefs of 1000-2000 m (Cheng and Jin, 2013) and the widely distributed streams, lakes (Zhang et al., 2014b) in the Qinghai-Tibet Plateau, water from ice and snow melting may need to travel long distances and go through several leaching and oozing processes before flowing into the river, and the relationships between recharge and discharge of groundwater and surface waters can be reversed (Cheng and Jin, 2013), resulting in intense rock-water interactions. Although the low temperatures in the region may have negative impacts on rock weathering (Gaillardet et al., 1999), but due to the large temperature differences between day and night (<http://www.yellowriver.gov.cn>), the freezing and thawing processes may lead to higher physical weathering rates and result in intense chemical weathering (Huh and Edmond, 1999). All of these factors provide favorable conditions for rock weathering in the upper Yellow River basin.

Rock weathering is considered to be one of the most important inputs of riverine DIC (Barnes and Raymond, 2009; Regnier et al., 2013). Based on the natural

discharges and DIC at the Lanzhou station, which represents sub-basin (I), and the Lijin station, which stands for the entire Yellow River basin, we conclude that the DIC flux from the Qinghai-Tibet Plateau during our two field investigations is $(110 \pm 5.7) \times 10^9$ mol/a, which represents approximately 66% of the total riverine DIC flux $((167 \pm 13.3) \times 10^9$ mol/a). Therefore, the Qinghai-Tibet Plateau is considered as the main DIC contributor to the Yellow River.

Fig. 5. Comparison of the fluxes of consumed CO_2 in rivers that originate in the Qinghai-Tibet Plateau and other large rivers. The data are taken from Gaillardet et al. (1999) and Wu et al. (2008). UYR denotes the Upper Yellow River basin.

Previous studies of the chemical weathering of rivers that originate in the Qinghai-Tibet Plateau also found that the CO_2 consumption rates in these rivers are much higher than in other large rivers (discharges greater than $200 \text{ km}^3/\text{a}$) even with similar runoffs (Fig. 5). CO_2 consumption rates by silicate weathering in the Yamuna River, which originates in the Himalayas in the Qinghai-Tibet Plateau, are as high as $700 \times 10^3 \text{ mol}/(\text{km}^2 \cdot \text{a})$, which causes the high alkalinity at the Batamandi station (2.37-2.90 mmol/L) (Dalai et al., 2002). Intense chemical weathering in the Lancangjiang, which is the upper reach of the Mekong River, leads to a carbonate weathering CO_2 consumption rate of $590 \times 10^3 \text{ mol}/(\text{km}^2 \cdot \text{a})$ and an HCO_3^- concentration of 3.54 mmol/L (Wu et al., 2008a). Similarly, the high DIC concentrations of between 3 and 5 mmol/L in the mainstream and tributaries of the Changjiang River in the Qinghai-Tibet Plateau have been attributed to intense carbonate weathering (Wu et al., 2008b). The CO_2 consumption rate in the Changjiang River basin reached $397 \times 10^3 \text{ mol}/(\text{km}^2 \cdot \text{a})$, and the DIC concentrations in the upper reach were much higher, while they decreased in the lower reach due to dilution from Dongting Lake and Poyang Lake (Chetelat et al., 2008). Based on data collected from several field investigations

and other studies, [Zhang et al. \(2014a\)](#) concluded that the upper Changjiang basin contributed most to the riverine DIC flux.

In summary, rivers that originate in the Qinghai-Tibet Plateau always have high chemical weathering rates and high HCO_3^- concentrations.

4.5 Limitations on chemical weathering in the Loess Plateau

The middle basin of the Yellow River is located in arid and semiarid regions, where the annual evaporation (1850 mm) greatly exceeds the annual precipitation (436 mm) ([Yang et al., 2004](#)). The ratio of evaporation to precipitation (E/P) has reached 4.58 in recent decades ([Table 6](#)), which has caused very short water-rock interaction times and weak chemical weathering processes.

Table 6. Decadal averages of precipitation and evaporation in the Yellow River.

Decade	Qinghai-Tibet Plateau			Loess Plateau		
	P (mm/a)	E (mm/a)	E/P	P (mm/a)	E (mm/a)	E/P
1951-1960	424.6	1521	3.58	452.5	1823	4.03
1961-1970	459.5	1410	3.07	468.7	1908	4.07
1971-1980	456.0	1383	3.03	427.7	1930	4.51
1981-1990	470.0	1301	2.77	436.3	1774	4.07
1991-2000	434.7	1377	3.17	396.9	1816	4.58

P denotes the annual precipitation, E denotes the annual evaporation, and E/P is the ratio of evaporation to precipitation, which indicates the dryness of the climate. The data are taken from [Yang et al. \(2004\)](#).

In addition, because precipitation (mostly rainfall) is the main source of water in sub-basin (II), the increasing ratio of evaporation to precipitation will limit water and material transport from the land to the river. As a result, some chemical weathering products in this region are not reflected in the river waters. This is probably the main reason for the small increase of DIC and cations that are derived from rock weathering compared with those in sub-basin (I) ([Fig. 3](#)), even though the loess has a very high carbonate content ([Zhang, 1995; Li et al., 2007](#)). In contrast, although the annual precipitation in sub-basin (I) is only 450 mm and the average ratio of evaporation to precipitation is 3.1 ([Table 6](#)), the input of water from snow and ice melting generates a large total water supply and high chemical weathering rates ([Table 5](#)). In conclusion, sub-basin (II) area is large and contains abundant carbonate minerals, but the high ratio of evaporation to precipitation limits the chemical weathering processes, and the small amount of runoff restricts the transport of the chemical weathering products to the river.

Previous studies of chemical weathering in the Yellow River basin found that the high DIC concentrations in the Yellow River were caused by carbonate weathering in the Loess Plateau ([Zhang et al., 1995; Chen et al., 2003; Chen et al., 2005; Cai et al.,](#)

2008). However, these studies were either carried out only in sub-basin (I) (Wu et al., 2008a) only in sub-basins (II and III) downstream of the Lanzhou Station (Zhang et al., 1995; Chen et al., 2003; Chen et al., 2005) or the in the estuarine zone (Cauwet and Mackenzie, 1993). In addition, this long-held view was a qualitative conclusion that was based on the high carbonate content of the loess, but no quantitative correlation or mass balance calculation was reported to support it.

5. Conclusions

The amount of CO₂ consumption by chemical weathering in the Yellow River basin is 98.31×10^9 mol/a, of which 87.61×10^9 mol/a and 10.70×10^9 mol/a are contributed by carbonate and silicate weathering, respectively. As the water source region of the Yellow River, the Qinghai-Tibet Plateau experiences a strong leaching effect and has the highest CO₂ consumption rate among all the sub-basins. In the Loess Plateau, high ratios of evaporation to precipitation limit the chemical weathering processes, and the small amount of runoff restricts the transport of the chemical weathering products. Therefore, the Qinghai-Tibet Plateau is the origin of the high levels of HCO₃⁻ in the Yellow River and contributes approximately 66% of the riverine DIC flux. The contribution from the Loess Plateau has been overestimated in previous studies.

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