



# Characteristics of carbonate, evaporite and silicate weathering in Huanghe River basin: A comparison among the upstream, midstream and downstream



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## ABSTRACT

To systematically study chemical weathering in the entire Huanghe River basin, we divided the basin into three parts with significant differences in geology and climate. We collected 38 water samples from the main channel and its main tributaries, spread between the upstream (above Lanzhou), midstream (from Lanzhou to Huayuankou) and downstream (from Huayuankou up to river mouth) segments of the river. The concentrations of major elements and H, O isotopic compositions were obtained from the samples, and the total dissolved solids (TDS) and, CO<sub>2</sub> consumption budget were calculated from the aggregated data of each of the three segments. The results demonstrate that: the TDS are mainly derived from carbonate weathering in upper Huanghe River; evaporite dissolution is predominately occurred in the midstream; and there is almost no additional contribution from rock weathering in the downstream. An increasing trend of CO<sub>2</sub> consumption rate by silicate weathering is observed, from  $0.14 \times 10^5$  mol/km<sup>2</sup>/yr in the upstream to  $5.62 \times 10^5$  mol/km<sup>2</sup>/yr in the downstream, and the budget of CO<sub>2</sub> consumption by silicate weathering is estimated to be  $26.2 \times 10^9$  mol/yr. In contrast, the CO<sub>2</sub> consumption rate by carbonate weathering decreases from  $3.04 \times 10^5$  mol/km<sup>2</sup>/yr in the upstream to near zero in the downstream, and the budget of CO<sub>2</sub> consumption is estimated to be  $100.5 \times 10^9$  mol/yr. As a whole, in the entire Huanghe River basin, the CO<sub>2</sub> consumption budget and TDS yield are estimated to be  $126.7 \times 10^9$  mol/yr, and  $27.5 \times 10^6$  t/yr, respectively. These results indicate that evaporite dissolution in the midstream is responsible for the high TDS in the Huanghe River basin, while carbonate weathering in the upstream plays the most significant role in CO<sub>2</sub> consumption.

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## 1. Introduction

Continental weathering is thought to play an important role in the long-term carbon cycle, and thus to regulate global climate on geological time scales through consumption of atmospheric CO<sub>2</sub> (Bernier et al., 1983; Dessert et al., 2003; Gaillardet et al., 1995; Meybeck, 1987; Raymo et al., 1988). Weathering is also a key process controlling the geochemical cycle of elements, because many elements are released in abundance during rock weathering (Gaillardet et al., 1995; Gardner et al., 1981; Gibbs, 1972; Huh et al., 1998; Zhang et al., 1995). Silicate, carbonate and evaporite rocks weather differently and each displays a different role in

carbon cycles and riverine chemical compositions. During silicate weathering, which is accompanied by CO<sub>2</sub> consumption and thought to be the dominant long-term sink of atmosphere CO<sub>2</sub>, primary minerals are decomposed and then converted to residue clays, dissolved loads, and silica. Carbonate weathering is not accompanied by secondary mineral formation, and has an effect on the CO<sub>2</sub> cycle only on a short time scale, though the dissolution rate of carbonate is thought to be much faster than that of silicate. However, carbonate weathering is considered to be more important than the weathering of silicate minerals in controlling river water chemistry (Fairchild et al., 1994; Han and Liu, 2004). The dissolution of evaporite minerals does not consume CO<sub>2</sub>, but it does exert an important role in chemical composition of river waters, even if evaporite outcrops are rather rare in the watershed (Meybeck, 1987; Ryu et al., 2008), because evaporite is more

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susceptible to weathering compared with silicate and carbonate, and such dissolution can generate K, Na, Ca, Mg, Cl and  $\text{SO}_4$ .

Rivers carry the products of chemical weathering in dissolved phases or in solid form, and transport these products seaward. Rivers, particularly large rivers, are of great importance for substance circulation. The 30 largest rivers of the world are thought to represent half of the total runoff to the ocean (Gaillardet et al., 1999). To gather the fundamental information about the evolution of the Earth's surface, geologists have paid much attention to large rivers (Chetelat et al., 2009, 2008; Gaillardet et al., 1995, 1999; Galy et al., 1999). For instance, one of the world's largest rivers, the Amazon River, has been investigated since 1903 (Gaillardet et al., 1997; Gibbs, 1972). Generally, the geochemical investigation of large rivers allows us to obtain important information about weathering processes, matter cycles in the continent–river–ocean system, and  $\text{CO}_2$  consumption associated with the weathering of continental rocks. In an extremely large watershed the lithology of the drainage basin is complex, and it is important to distinguish the sources of geochemical weathering along different reaches of the river system.

The Huanghe River (Yellow River), one of the world's largest rivers, transports approximately  $14.8 \times 10^9 \text{ m}^3/\text{yr}$  of water and about  $2.88 \times 10^{11} \text{ kg}/\text{yr}$  of suspended sediment, on average, to seaward (1987–2010 data from <http://www.yellowriver.gov.cn/nish-agonggao/2012/index>, in Chinese). It accounted for a large part of the world sediment load input to ocean, and the River is the most important water source for northern China, so it has received significant attention from geologists since the 1980s (Wang et al., 2012, 2006; Wu et al., 2005; Zhang et al., 1995, 1990a). However, most of previous research on chemical weathering in the Huanghe River basin was based on samples near its mouth (Wang et al., 2012) or near its headwater (Wu et al., 2005), with few studies based on sampling throughout the whole basin (Zhang and Wen, 2009). As a result, the knowledge of chemical weathering in the entire Huanghe River basin is limited.

For his study, we used a synoptic-sampling approach to examine the qualitative and quantitative estimations of the TDS yield and  $\text{CO}_2$  flux from the contribution of silicate, carbonate and evaporite weathering in the upstream, midstream and downstream of the Huanghe River. In particular, we aimed to characterize the aqueous geochemistry and its controlling factor(s) along different reaches of the river, and to get a clear understanding of the role of the three kinds of rock in the basin.

## 2. Geography, climate and lithology of the drainage catchments

The Huanghe River (basin surface area =  $752,000 \text{ km}^2$ ) located in northwestern China, flows from its source in high mountainous areas in the northeast of Tibet at about 5000 m elevation to its outlet into the Bohai Sea (Fig. 1). The basin displays complex features in lithology and topography, covered all kinds of rocks from Cambrian to Quaternary period. The source areas of the Huanghe River, from Lanzhou city upward with elevation of 2000–4000 m, is mainly comprised of detrital rocks of late Palaeozoic age to Mesozoic age, including coal bearing formations and red-beds, and limestones. The midstream segment of the river (from Lanzhou to Huayuankou) drains the Loess Plateau, which accounts for 44% of the total watershed area. Erosion on the Loess Plateau leads to extremely high sediment yield, and a large amount of unconsolidated sediment spread downstream (Saito et al., 2001; Wu et al., 2005; Zhang et al., 1995).

Except for the source area, which is characterized by high elevation and cold climate, the main body of the Huanghe River basin is subjected to a warm climate, with mean annual temperature of 1–8 °C in the upstream segment, 8–14 °C in the midstream

segment, and 12–14 °C in the downstream segment. Mean annual rainfall in the watershed is 476 mm, and is unevenly distributed, increasing from 150 mm for upstream and midstream to 900 mm for downstream. The Huanghe River basin also suffers strong surface evaporation of about 1100 mm annually (Chen and Wang, 2006; Zhang and Wen, 2009).

## 3. Materials and analytical methods

### 3.1. Sampling

Samples were collected from the Huanghe River, divided among its three main parts: upstream (above Lanzhou, samples MH01, MH02, M1–M5), midstream (from Lanzhou to Huayuankou, samples M6–M19) and downstream (Huayuankou to Dongying, samples M20–M23). These divisions were based on differences in the geologic and climatic factors. Samples were collected in August 2012 along the Huanghe River main channel and its main tributaries (Fig. 1). Between 15 and 20 L of river water was collected and filtered within a few hours after collection through  $0.45 \mu\text{m}$  cellulose acetate filters. The first liter was discarded and the following liters were stored in acid-washed polyethylene bottles, for analysis after acidification to pH-2 with double-distilled HCl. Two aliquots were prepared: one acidified for cations analysis, and another non-acidified for the anions determination.

### 3.2. Analytical methods

The temperature, pH and electric conductivity (EC) were measured in field. Alkalinity was determined with the Gran titrating method using 0.02 M HCl. Concentrations of cations and anions for the water samples were determined in the State Key Laboratory of Environmental Geochemistry using ICP-OES and Ion Chromatography with uncertainties of 5% and 8%, respectively.

Stable  $\delta^{18}\text{O}$  and  $\delta\text{D}$  were determined by Liquid–Water Isotope Analyzer in the State Key Laboratory of Environmental Geochemistry. The precision of chemical analyses was estimated through repeated determinations of standards. The external precision for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  were 0.07‰ and 0.12‰, respectively.

## 4. Results

### 4.1. Hydrogeochemistry

Hydrological parameters (pH, T and EC), concentrations of major elements and O, H isotope compositions of the water samples are presented in Table 1. The pH of river water samples range from 7.42 to 9.82, with a mean value of 8.02. The highest pH values are observed for a headwater tributary (MH02, pH = 9.82) and a tributary in the mainstream (T4, pH = 9.48). The EC values vary from 0.6 to 11,440  $\mu\text{S}/\text{cm}$ . The water temperature generally increase from upstream (9.6 °C, M2) to downstream (29.1 °C, M18) along the Huanghe River main channel, controlled by the progression to lower elevation and warmer climate of the sampling sites. The total cationic concentrations (in meq/L,  $\text{TZ}^+ = \text{Na}^+ + \text{K}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+}$ ) for most water samples range from 3 to 10 meq/L, except for five samples with much higher values (11–151 meq/L) in the tributaries.  $\text{TZ}^+$  is much higher than the average value of the world's rivers (1.25 meq/L, Meybeck, 1981). The total dissolved cations are mostly balanced with the total dissolved anions ( $\text{TZ}^- = \text{Cl}^- + 2\text{SO}_4^{2-} + \text{HCO}_3^-$ ) within 5%. Compared with the world's major rivers (Gaillardet et al., 1999), the Huanghe River samples have the highest values in terms of TDS, varying from 261.5 to 9177 mg/L, with an average of 557 mg/L. The

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