



Chemical balance of the Yellow River source region, the northeastern Qinghai-Tibetan Plateau: Insights about critical zone reactivity

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ABSTRACT

Rivers play a vital role in geochemical processes of the critical zone. As the Third Pole, the geochemical processes of the Qinghai-Tibetan Plateau are vital to global element cycles. The Yellow River source region is located in the northeastern Qinghai-Tibetan Plateau, yet there has been little research concerning water chemistry in this region. In this study, river water and rain samples were collected to analyze the stable isotopes and major ion chemistry in the Yellow River source region. The $\delta^{18}\text{O}$ and δD values ranged from -12.9‰ to -4.5‰ and from -95.7‰ to -36.7‰ , respectively. The stable isotopic values of tributaries were lower than those in the main stream, and the construction of the dam could result in the enrichment of $\delta^{18}\text{O}$ and δD . The stable isotopic values showed that precipitation was the main source of river water. The total dissolved solids (TDS) in river water ranged from 214.9 to 563.2 mg/L, and calcium and bicarbonate were the dominant ions. The average contributions of atmospheric input, evaporites, silicates, and carbonates to the dissolved load of river water were 1.8%–12.5%, 12.4%–15.9%, 18.1%–18.4%, and 56.7%–64.3%. The silicate and carbonate weathering rates were 2.3–2.5 t/km²/yr and 17.4–19.6 t/km²/yr, respectively. The chemical denudation rate in the study area was about 23.0–26.8 t/km²/yr, comparable to the world average value. The CO₂ consumption rates by silicate and carbonate weathering were $91\text{--}94 \times 10^3$ mol/km²/yr and $185\text{--}208 \times 10^3$ mol/km²/yr, respectively. The TDS flux in the study area was 6.1×10^9 kg/yr, which accounted for 38–47% of that of the Yellow River into the sea. This study showed that although as an alpine arid area, the Yellow River source region had a comparable chemical denudation rate to the world average value, and even higher CO₂ consumption rates by silicate and carbonate weathering than some of the large rivers in the world.

1. Introduction

Rivers are vital channels that connect the continent and sea and carry inland materials, including suspended sediments and solutes, into the ocean. In addition, rivers are important sources for domestic, industrial, and ecological water use and systems to remove anthropogenic pollutants. Research on water chemistry of rivers is of great significance to water environment management and protection and can provide crucial insights to biogeochemical cycles of elements in the critical zone (Zhang et al., 1995; Chen et al., 2002). Compared with trace elements, the major ion compositions in river water are more related to lithology environment and erosion conditions across the drainage basin (Zhang et al., 1990), and the major ion chemistry of waters is controlled by a series of biogeochemical conditions. Terrestrial chemical weathering is an important part of global geochemical cycles that includes dissolution and hydroxylation of inorganic materials. These processes require

atmospheric CO₂ and supply alkalinity for rivers, thus representing vital sinks of atmospheric CO₂ (Gaillardet et al., 1999; Mortatti and Probst, 2003). Hence, terrestrial chemical weathering could affect atmospheric CO₂ concentration and further exert great impact on global climate change, and many studies regarding river geochemistry have focused on the estimation of inorganic denudations of the continents and their atmospheric CO₂ consumption (Gaillardet et al., 1999; Galy and France-Lanord, 1999; Mortatti and Probst, 2003; Wu et al., 2008; Hren et al., 2007). Meanwhile, terrestrial chemical weathering could be affected by climate factors, such as temperature and moisture (Grosbois et al., 2000). Therefore, research on the major ion chemistry of rivers is also helpful to understand the interaction between global climate change and terrestrial weathering processes (Walker et al., 1981; Garrels, 1983; Berner, 1994, 2006).

Stable hydrogen and oxygen isotopes are ideal tracers of water sources and movement because they are integral constituents of water

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molecules. Waters are often uniquely labeled by their isotopic compositions, allowing the separation of waters from different sources (Kendell, 1998). Phase changes and simple mixing are the main processes that affect the hydrogen and oxygen isotopic compositions of waters in a catchment. Meanwhile, the hydrogen and oxygen isotopic compositions of water samples are useful to evaluate biogeochemical cycles of elements that are dependent on the water cycle; integration of isotopic and hydrochemical methods can provide a better explanation for geochemical characteristics of rivers (Michener and Lajtha, 2008; Li et al., 2015).

The Qinghai-Tibetan Plateau, the Third Pole of the Earth, is located in the hinterland of Asia, with an average altitude of over 4000 m. It plays a crucial role in atmospheric circulation in the mid-latitudes of the Northern Hemisphere. Affected by its topography, the Qinghai-Tibetan Plateau not only shapes the distribution of temperature and precipitation in China, but also forms unique regional climate. The Qinghai-Tibetan Plateau is sensitive to global climate change, and the geochemical processes here have attracted much interest. The Qinghai-Tibet Plateau holds the headwaters of many large Asian rivers. Among them, the Brahmaputra (Huang et al., 2009), the Yamuna River (Dalai et al., 2002), the source region of the Yangtze River (Jiang et al., 2015), and the Lancang River (Wu et al., 2008) have been studied for the major ion chemistry. However, little research has been reported regarding the source region of the Yellow River. Most of available research on the major ion chemistry of the Yellow River (Hu et al., 1982; Zhang et al., 1995, 2015; Chen et al., 2005; Li and Zhang, 2005) has mainly focused on the middle and lower reaches, with limited sampling sites in the source region. Meanwhile, many studies have investigated the stable hydrogen and oxygen isotopic compositions of rivers and their controlling factors in the western and southern Qinghai-Tibetan Plateau (Tian et al., 2001; Hren et al., 2009; Yao et al., 2009; Wen et al., 2012). However, few studies for the northeastern Qinghai-Tibetan Plateau have been reported such as for the Yellow River source region; there are only a few studies of the Yellow River (Su et al., 2004; Li et al., 2015), and those included only two or three sampling sites in the source region.

There are a number of glaciers, permafrost and wetlands in the source region of the Yellow River, which have great influence on the water cycle and water chemistry processes in this region. In addition, the Yellow River is the northernmost large river in the Qinghai-Tibetan Plateau; its climatic conditions are different from those of other rivers. Therefore, the water chemistry of the Yellow River source region might be different from other rivers in the Qinghai-Tibetan Plateau.

Therefore, this research aimed to study the water chemistry characteristics of the Yellow River source region. The main objectives of this study were to: (1) investigate the characteristics of stable hydrogen and oxygen isotopes as well as the composition and features of the major ions in the river water, (2) analyze the main factors that dominate the major ion chemistry, (3) quantitatively estimate the contributions of various sources to the major ions of river water, and (4) calculate the chemical weathering rates, CO₂ consumption rates, and total dissolved solid (TDS) fluxes.

2. Materials and methods

2.1. Study area

The Yellow River source region (32°09'–36°33' N, 95°53'–103°25' E) refers to the area above the Longyangxia reservoir. The river length is 1687 km with an average gradient of 1.51%. The source region, with a drainage area of 131,400 km², represents 16.5% of the total drainage area of the Yellow River, but its discharge represents 38.6% of the total discharge. It is joined by many tributaries in this stretch, among them are 12 tributaries with discharge areas greater than 3000 km² (Li et al., 2010). The mean altitude of the Yellow River source region is above 3000 m, and the main rock type is shale. The climate, affected by

topography and geomorphology, has the characteristics of strong solar radiation, long sunshine time, low temperature, low humidity and strong wind power. The annual mean precipitation is around 530 mm, and about 75% of the total annual precipitation falls between June and September. The precipitation in the region has the characteristics of covering large areas (> 100,000 km²), long duration (10–30 days), and low intensity (< 50 mm/day). Precipitation tends to decrease from southeast (800 mm) to northwest (300 mm). The annual mean evaporation ranges from 800 to 1200 mm (Zheng et al., 2007; Hu et al., 2012). The river runoff mainly derives from the Darlag to the Jungong interval, the discharge of which accounts for 66.6% of the measured runoff at the Tangnag hydrological station, while the discharge above the Madoi station accounts for only 3.6%. The major vegetation is alpine meadow, and the main land use type in the study area is grassland which accounts for 53.52% of the study area, followed by forest land at 10.03%, and cultivated land at only approximately 5.19% (Du et al., 2015).

2.2. Sampling and analytic methods

The rainwater samples were collected from the four meteorological stations (Fig. 1) weekly from April to October in 2016; the samples were filtered with 0.45- μ m polyethersulfone membranes and were preserved in the refrigerator at 4 °C until analysis. The snowmelt samples were collected in the Amne Machin Mountains in August of 2016. The river water samples were collected from 12 sites along the main stream and 16 sites in the large tributaries (Fig. 1) from 5/30/2016–6/15/2016 (spring) and 7/30/2016–8/15/2016 (summer). During each sampling, river water samples were collected at 20 cm under the surface at each sampling site. The water temperature, pH, dissolved oxygen (DO), electric conductivity (EC), and oxidation-reduction potential (ORP) were measured in situ with a portable multi-parameter tester (SG78-FK-CN, METTLER TOLEDO). Water samples were filtered with 0.45- μ m polyethersulfone membranes on site within 24 h; the membranes were collected, and the filtered water was stored in clean polyethylene bottles after filtration. Section samples collected for cation analysis were acidified to pH < 2 with H₂SO₄. All samples were preserved in a cooler and transported to the laboratory as soon as possible, after which the samples were preserved in the refrigerator at 4 °C until analysis.

Cations (Na⁺, Mg²⁺, K⁺, and Ca²⁺) and anions (Cl⁻ and SO₄²⁻) in river water and rainwater samples were analyzed with ion chromatography (ICS1100, Dionex Corporation, US). Dissolved silica was determined by the molybdenum blue method. The precisions of ions and dissolved silica were within 5%. The analysis of alkalinity (expressed as HCO₃⁻) was performed with a total organic carbon analyzer (TOC-L_{CPN}, Shimadzu Corporation, Japan) with a precision of 1.5%. δ D and δ^{18} O were determined using a water isotope analyzer; the precisions of δ D and δ^{18} O were 0.5‰ and 0.1‰, respectively. The riverbed samples were dried to a constant weight and ground to 160 mesh (Wu et al., 2008). To remove carbonate minerals, the ground powders were immersed in 1 M HCl (analytical reagent) for 4 h. The residues were washed to neutrality with deionized water and then placed in an acid mixture (HNO₃ + HF + HClO₄, guaranteed reagent) for digestion. The cations (Na⁺, Mg²⁺, K⁺, and Ca²⁺) of solutions were measured by ICP-AES (SPECTRO ARCOS, USA) to prevent the digested solution from damaging chromatography column; the precision is 1.5%.

All statistical analyses were performed with SPSS 19, and plotting was performed by Origin 9. One-way ANOVA analysis was carried out to test the differences between each pair of compared groups. The difference was considered significant when the significance level was less than 0.05. The Pearson correlation coefficient was calculated and used to test the significance of the correlation between each pair of variables.

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