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Relationship between water discharge and sulfate sources of the Yangtze River inferred from seasonal variations of sulfur and oxygen isotopic compositions

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ABSTRACT

Resolving sulfate sources in river systems and thus to the global ocean is important for understanding the sulfur biogeochemical cycle. The Yangtze River is one of most important large rivers connecting land and sea, showing a trend of acidification characterized by persistently increasing SO_4^{2-} concentration. A weekly sampling campaign from the middle Yangtze River in Wuhan was conducted, over a 1-year period in 2011, to systematically examine the effects of seasonality and associated water discharge on the balance of sulfate sources of the Yangtze River. The SO_4^{2-} concentrations varied from 8.6 to 55.4 mg/L with a discharge-weighted average of 30.0 mg/L, while the SO_4^{2-} fluxes varied from 103.2 to 1257.6 kg/s with an annual average of 532.5 kg/s. The $\delta^{34}S_{SO4}$ values ranged between 6.7‰ and 16.2‰ with a discharge-weighted average of 10.4‰, while the $\delta^{18}O_{SO4}$ values ranged between 1.6‰ and 10.5‰ with a discharge-weighted average of 5.1‰. In comparison to the low water discharge period, the period of high water discharge of the Yangtze River in Wuhan is characterized by 1) a doubling in water discharge with higher water level by 5–10 m; 2) a concomitant doubling in SO_4^{2-} flux without substantial change in SO_4^{2-} concentration; 3) a systematic increase of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values; 4) a significant increase of sulfate contribution from evaporites dissolution. From the observed seasonal variation of sulfur and oxygen isotopic composition of sulfate, a relationship between the dynamic water discharge and dominant sulfate sources of the Yangtze River was inferred. During the period of low water discharge in January–mid May, the sulfur and oxygen isotopic compositions of sulfate had averaged values of 8.3 ± 0.4‰ for $\delta^{34}S_{SO4}$ and 4.9 ± 0.7‰ for $\delta^{18}O_{SO4}$, suggesting the riverine SO_4^{2-} of the Yangtze Riveris derived from sulfide oxidation, atmospheric deposition and evaporite dissolution; whereas during the period of low water discharge in December, the contribution of anthropogenic sulfate could be important, indicated by relatively higher $\delta^{34}S_{SO4}$ (10.5 ± 1.5‰) and $\delta^{18}O_{SO4}$ (9.6 ± 1.0‰) values. In contrast, during the period of high water discharge in June-September, the dual-isotope compositions were characterized by 14.7 ± 0.7‰ for $\delta^{34}S_{SO4}$ and 8.1 ± 0.7‰ for $\delta^{18}O_{SO4}$, indicating sulfate from dissolution of evaporites would be a dominant source. The jump event of dual-isotopic composition between low and high water discharge occurred when a half-year drought suddenly turned into the flood season. Due to the water storage dispatch of the Three Gorge Dam, the Hanjiang River could make a greater impact on the variation of water discharge and thus sulfate sources of the Yangtze River during the transition from high to low water discharge in October–November. However, the relationship between water discharge and sulfate sources of the Yangtze River need s to be confirmed by additional years of observation. Further studies on the mechanisms of water discharge controlling sulfate sources of the Yangtze River is urgently required, as well as a mixing model to calculate the contribution of different sulfate sources.

1. Introduction

River systems, especially large rivers connecting land and sea, play a key role in the global biogeochemical cycle. Knowledge of the terrestrial discharge of bio-essential element fluxes from large rivers is important for understanding estuarine ecology and coastal environments (Gao and Wang, 2008; Seitzinger et al., 2010; Siswanto et al., 2008). Sulfur is an essential biological element, an important electron acceptor and electron donor for metabolic processes, which undergo redox cycling in earth surface environments and intimately linked with redox cycles of oxygen, carbon, nitrogen and iron (Turchyn and Schrag, 2006). Dissolved sulfate (SO_4^{2-}) is a major form of sulfur and ubiquitous in most natural environments. Throughout the last few decades, SO_4^{2-}

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concentration of rivers have received considerable attention, due to its dominant role in anthropogenic acidification of surface waters, and the importance for understanding the role of sulfuric acid in chemical weathering of carbonate rocks and its effect on the global carbon cycle (Calmels et al., 2007; Spence and Telmer, 2005; X.D. Li et al., 2011).

Global river systems provide the largest source of sulfate to the ocean and thus are critical in the marine biogeochemical sulfur cycle (Meybeck, 1979). Resolving the source of sulfate to river systems, and thus to the global ocean is important, but remains a difficult task. Riverine SO_4^{2-} often originates from the oxidative weathering of sulfide bearing minerals, dissolution of evaporite minerals, atmospheric deposition and anthropogenic sources. Microbial sulfate reduction process leads to the production of ^{34}S-depleted sedimentary sulfide minerals and concomitantly enriches evaporite sulfate in ^{34}S (Krouse and Mayer, 2000; Nightingale and Mayer, 2012). In turn, oxidation of reduced sulfur involves little S isotopic fractionation but controls the oxygen isotopic composition of sulfate formed during weathering (e.g. Krouse and Mayer, 2000; Van Stempvoort and Krouse, 1994). This leads to potentially distinctive sulfur and oxygen isotopic compositions associated with different sulfate sources such as natural geologic and anthropogenic sources (e.g. Samborska et al., 2013), and thus sulfur and oxygen isotopic composition can be used as a fingerprint of different sulfate sources.

Riverine SO_4^{2-} may retain the sulfur isotopic signatures of its sources due to minimal isotopic fractionation during sulfur transformations under aerobic conditions (e.g., Tuttle et al., 2009) such as soil adsorption/desorption, mineral precipitation/dissolution, plant assimilation, mineralization of organic sulfur, and oxidation of reduced sulfur. The measured $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values from global rivers have large ranges that vary with geology, land use, and anthropogenic impact from human activities (Brenot et al., 2007; Rock and Mayer, 2009; Szynkiewicz et al., 2011). Sulfur and oxygen isotopes are powerful tools for resolving the sources of sulfate to rivers (Cortecci et al., 2002; Otero et al., 2007; Rock and Mayer, 2009). However, a snapshot sampling strategy would probably fail to capture important signals during seasonal events which can produce an important effect on change of sulfate sources. It is necessary, therefore, to systematically examine the effects of seasonality and associated water discharge on the balance of sulfate source in a major, globally significant, river system.

The Yangtze River is not only the longest river in China, but also the second largest river in the world in terms of dissolved salt fluxes to the sea (Chen et al., 2002). A weekly sampling campaign of river SO_4^{2-} was first conducted from the middle Yangtze River in the city of Wuhan over a 1-year period of 2011, with detailed chemical and isotopic analysis and river discharge data. The main objectives of this study were a) to characterize seasonal variation of SO_4^{2-} concentration and its dual isotopic composition of the Yangtze River; b) to determine a relationship between periods of high and low water discharge, SO_4^{2-} flux and sulfate isotope composition; c) to identify dominant sulfate sources in the Yangtze River, and to examine the effects of the seasonality and water discharge on the balance of sulfate sources.

2. Study area

The Yangtze River, with a length of 6300 km, originates from main peak of the Tanggula Mountains in the Qinghai–Tibet Plateau, flows across 11 provinces in central and eastern China, and empties into the East China Sea (Fig. 1), the longest in Asia and the third longest in the world. Its drainage basin is located between 24°30′–35°45′N and 90°33′–122°25′E, and covers a total area of 1.8×10^6 km^2, with an annual average discharge of 960 km^3/a (Chen et al., 2008). The Yangtze River basin is located in a region with a subtropical monsoon climate, with an average annual precipitation of 1100 mm. The period from May to August accounts for 50–65% of the annual total precipitation (Chen et al., 2001). The river discharge changes with precipitation (Xu et al., 2008).

The Yangtze River is geographically divided into upper, middle and lower reaches by Yichang in Hubei province and Hukou in Jiangxi province (Fig. 1), respectively. The uppermost reach, above Yibin in Sichuan province, is called Jinshajiang River, and its major tributaries are the Yalongjiang and Minjiang Rivers. The upper reach of the Yangtze River receives water from two major tributaries of Jialingjiang and Wujiang Rivers, and the middle reach flows through the Dongting Lake basin, the Hanjiang River basin, and the Poyang Lake basin.

The Yangtze River basin contains sedimentary rocks composed of marine carbonates, evaporites and alluvium of Precambrian to Quaternary in age (a simplified geological map shown in Fig. 1). Carbonate rocks, which have a dominant influence on chemical weathering in the Yangtze River basin, are widely distributed, especially in the southern area of the upper and middle reaches (Chen et al., 2002). The Dongting Lake basin is almost covered by sedimentary rocks (mainly limestone) and metamorphic rocks, while the Poyang Lake basin drain mainly metamorphic rocks. Coal strata of the YRB are rich in sulfides and are inter-bedded with carbonates, especially in the southern basin; whereas evaporites are mainly present in the upper Yangtze River and its main tributaries (Yalongjiang, Minjiang and Jialingjiang) (Chetelat et al., 2008). In terms of land use structure, the Yangtze River basin is dominated by forest (38.59%), arable land (29.46%), and grassland (24.47%) (Gao et al., 2010).

As a large river, the Yangtze River is experiencing drastic hydrological changes, especially after the construction and operation of the Three Gorges Dam (TGD) (Jiang et al., 2014; Sun et al., 2012; Zhang et al., 2006). The TGD, located near Yichang between the upper and the middle reaches of the Yangtze River (Fig. 1), was completed in 2003, and is the largest water-engineering project in the world. It has a total storage capacity of 39.3 billion m^3 and a flood control capacity of 22.15 billion m^3 with a water elevation of 175 m. The dispatch modes for the TGD are as follows (Ou et al., 2012): (1) pre-discharge dispatch, water release in late May–early June to empty the flood control capacity (water level falls to 145 m); (2) flood-control dispatch, flow regulation in June–September (water level maintains at 145 m for preventing flood); (3) water-storage dispatch, water impounding in October–December and its water level can rise to 175 m; and (4) water-supplement dispatch, water release in January–April (water level falls but is higher than 155 m).

3. Sampling and methods

3.1. Local climate events during sampling year

During the sampling year, an extreme climate event occurred in the Yangtze River basin characterized by severe drought from January to May and drought–flood abrupt alternation in early June (Shen et al., 2012). Precipitation in the middle and lower reaches of the Yangtze River basin in the period from January to May 2011 reduced noticeably and triggered the most serve drought in recent decades, with an average rainfall of 260.9 mm that was 51% lower than that in the same period in previous years (533.3 mm) (Chen et al., 2014). In contrast, continuous heavy rainstorms pounded the Yangtze River basin in the whole June, which triggered a flood in the middle and lower reaches of the Yangtze River basin.

3.2. Sampling

The Yangtze River's longest tributary, Hanjiang River, enters in the middle reaches of the YRB where Wuhan, the capital of Hubei Province, is located. To monitor the Yangtze River at Wuhan, a hydrological station (No. 60270) is located there. Water and sulfate samples of the Yangtze River were collected weekly during 2011 from the sampling site that is located at 700 m upstream of the hydrological station after the junction of the Hanjiang River (Fig. 1). The data of water discharge and water level at the sampling site during sampling period were retrieved from the hydrological station (No. 60270) accessible at the website of http://www.cjh.com.cn/.