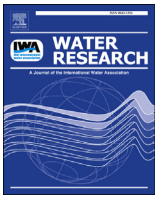
Water Research 93 (2016) 91–97

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres



Strontium concentrations and isotope ratios in a forest-river system in the South Qinling Mts., China

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ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form
27 January 2016
Accepted 30 January 2016
Available online 12 February 2016

Keywords:
Forested catchment
Sr
$^{87}Sr/^{86}Sr$
Ca/Na
Ca/K
Source contribution

ABSTRACT

The concentrations of dissolved strontium (Sr) and isotope ratios ($^{87}Sr/^{86}Sr$) in rainwater, river water, and water from forest soil are measured to investigate the contributions of these sources to a river during base flow conditions in the relatively pristine South Qinling Mountains, China. Dissolved Sr concentrations and $^{87}Sr/^{86}Sr$ ratios vary significantly between different water types ($p < 0.01$) suggesting that it is suitable for differentiating sources. Dissolved Sr is also positively correlated with most ions and a range of physicochemical parameters ($p < 0.01$ and $p < 0.05$ respectively) in water samples including Ca^{2+}, Mg^{2+}, EC, and TDS ($p < 0.001$) indicating their similarities in the drivers of biogeochemical processes and common origins. The correlations between Sr isotopes and Ca/Na, Ca/K, and 1000/Sr ratios suggest that three end-members of atmospheric inputs, carbonate and silicate weathering control the Sr water chemistry in the river water. Using the three-source mixing model, atmospheric inputs, carbonate, and silicate weathering contribute 74%, 20%, and 6% respectively to the dissolved Sr in the river water. This research has provided new insights into the contribution of sources of Sr to a river system in a mountainous catchment.

1. Introduction

Natural strontium (Sr) isotopes have been proved to be useful tools for tracing the past and for monitoring present-day environmental processes (Bain and Bacon, 1994; Åberg, 1995; Shand et al., 2009). The geochemical behaviour of Sr is generally similar to that of Ca (Aubert et al., 2002), but is different from that of the alkali elements K and Na. The Sr isotopic ratios ($^{87}Sr/^{86}Sr$) of natural materials reflect the sources of Sr available during their formation (Capo et al., 1998). Additionally, $^{87}Sr/^{86}Sr$ ratios are ideal source tracers because these isotopes have quite small fractionation during biogeochemical cycling (Pett-Ridge et al., 2009; Shand et al., 2009). One study found that the concentration of Sr varied from ~6 to 800 $\mu g\ L^{-1}$, and averaged ~60 $\mu g\ L^{-1}$ in a river water system (Stallard, 1985), whereas another study found that the global river average was 78 $\mu g\ L^{-1}$ (Palmer and Edmond, 1992). Strontium isotopic composition ($^{87}Sr/^{86}Sr$) from Canadian rivers in general has a high value of ~0.711 (Wadleigh et al., 1985). The global average river water value for the strontium isotope ratios ($^{87}Sr/^{86}Sr$) is 0.7119 (Palmer and Edmond, 1989, 1992).

The $^{87}Sr/^{86}Sr$ ratio in natural waters can also reflect the contributions made by various dissolved minerals (Clow et al., 1997). Strontium in river water is derived from two sources, the dissolved minerals in the river basin and atmospheric deposition following evaporation of seawater (Faure, 1986; Bain and Bacon, 1994; Aubert et al., 2002). Therefore, the ratio of $^{87}Sr/^{86}Sr$ reflects the contribution of two sources, bedrock weathering and atmospheric inputs (Capo et al., 1998). These ratios are relatively constant over time, another reason why they can be used to trace the transport of Sr through the ecosystem (Graustein, 1989; Bailey et al., 1996). When considered in conjunction with river water chemistry, the Sr isotopes provide a powerful tool for distinguishing among solute sources in rivers.

Strontium derived from the weathering of bedrock, such as Phanerozoic limestone and dolomite, has a relatively low $^{87}Sr/^{86}Sr$ ratio (~0.707–0.709; Burke et al., 1982). In contrast, the silicate ratio of dust ranges from 0.7109 to 0.7112, while the $^{87}Sr/^{86}Sr$ of parent

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http://dx.doi.org/10.1016/j.watres.2016.01.061

alluvial sediment is relatively high, i.e. 0.7165 (Capo and Chadwick, 1999). Precambrian granitic bedrock derived from felsic rocks generally has high $^{87}Sr/^{86}Sr$ values (>0.71). In addition, strontium from current seawater has a fairly constant $^{87}Sr/^{86}Sr$ ratio of 0.70916 (Beck et al., 2013). Due to these differentiations in ratios, apportioning the contributions of Sr from various sources to rivers could be calculated by using $^{87}Sr/^{86}Sr$ ratios.

Previous studies have demonstrated the usefulness of the Sr isotope technique in tracing the geochemical cycling processes of river water (Graustein and Armstrong, 1983; Bain and Bacon, 1994; Capo et al., 1998; Shand et al., 2009). By using $^{87}Sr/^{86}Sr$ ratios, Graustein and Armstrong (1983) traced the sources of strontium in natural waters, vegetation, and soil taken from watersheds in the Sangre de Cristo Mountains of New Mexico, and found that more than 75% of the strontium in the vegetation was derived from atmospheric sources, and less than 25% from weathering of the underlying bedrock. The $^{87}Sr/^{86}Sr$ ratio of rainwater, stream water, soils, and rocks were determined by Bain and Bacon (1994) to determine mineral weathering, and the origin of the solutes in the stream water in two Scottish catchments. Additionally, a number of case studies also highlighted that Sr isotopes represented a powerful tool in determining weathering processes and quantifying end-member mixing processes when combined with other hydrochemical data (Shand et al., 2009).

Our study examined the geochemistry and sources of Sr in a minimally disturbed watershed of the South Qinling Mountains (China). We investigated the concentrations of dissolved Sr and $^{87}Sr/^{86}Sr$ ratios of rainwater, forest soil water, and river water in a natural forest river system of the Jinshui River basin in subtropical area of central China. Based on major ion chemistry, Sr concentrations, and $^{87}Sr/^{86}Sr$ ratios in different water types, this study attempts to reveal the characteristics of dissolved Sr and major ions, to find the evolution of $^{87}Sr/^{86}Sr$ in different water types, and to determine the contributions of Sr from atmospheric and weathering end-members in river water of the river basin.

2. Materials and methods

2.1. Study area

The forest-river water system is entirely located within the Jinshui River basin (730 km^2 area) in the South Qinling Mountains, China (Fig. 1). The Jinshui River (33°16′–33°45′N, 107°40′–108°10′E) is a tributary of the Han River in the upper Yangtse River. It has a total length of 87 km and originates from the Foping National Nature Reserve at about 1500 m above sea-level, a conservation area for Qinling giant pandas, and finally discharges into the Han River at about 430 m sea-level.

The river basin has a humid monsoonal climate zone (Bu et al., 2010, 2015). The annual average air temperature in the basin is approximately 11.5 °C, while the highest is 21.9 °C in summer and the lowest −0.3 °C in winter. The rainfall varies between 924 and 1240 mm year^{-1}, and most of the rainfall occurs from June to August. The watershed is a typical mountainous catchment in the South Qinling Mts. of China. Forest and shrub lands, are the major land use types in the river basin covering 96.4% of the drainage area, with agricultural land only accounting for 2.2%. Additionally, 51.4% of total human population and 94.1% of the agricultural lands (principally crops) in the catchment are distributed in the lower reaches of the river, especially in Jinshui Town (Fig. 1). There is no industrial activity.

The Qinling Mountains were formed mainly during the early Mesozoic Orogeny when the Yangtze Block of South China collided with North China (Mattauer et al., 1985). The Jinshui River basin was formed the hills by movements of Yanshan Mountains uplifting and Himalayan Mountains rising in China's tectono-geomorphic types. The rock of the upper river basin is mainly composed of felsic and mafic granulites, granitoids, gneissic granite, metamorphic schist, limestone, shale, conglomerate, and sandstone (Zhai et al., 1998; Xu et al., 2011). In the lower reaches of the river, the low mountain areas are mainly sandstone, shale, conglomerate, red clay, and gravel accumulated by river terraces and underground portion of terraces. The soil is vertically distributed from the high to low elevations, including dark brown, brown, yellow brown, brown, and paddy soils.

2.2. Sampling and analyses

Rainwater, river water, and water from forest soil were collected in May 2012 under base flow conditions to characterize the Sr isotopic composition (Fig. 1). Rainwater (P1, P2, and P3) and water from the forest soil (T1 and T2) were sampled at an elevation above 1100 m in the source area of the Jinshui River. Rainwater was sampled in open field. Water from forest soil was collected from two pairs of suction lysimeters at depths from 20 to 30 cm in the oak forest zone. River water samples (S1–S11) were collected from the source area to the mouth of the Jinshui River. Three river water samples (H1, H2, and H3) were also collected in the confluence with the Han River. All water samples were filtered through MF-Millipore membrane filters (0.45 μm pore size and 47 mm diameter, USA). A part of each filtered sample was acidified with high-purity nitric acid and stored in pre-rinsed polyethylene bottles for cation analysis. Filtrate without acidification was also stored for anion analysis.

Cations (Sr^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, K^+, and Na^+) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (5300 DV, PerkinElmer), and anions (SO_4^{2-}, Cl^-, and NO_3^-) were determined by ion chromatography (ICS-90, Dionex) (Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing). Detection limits were <0.1 μg L^{-1} for Ca^{2+}, Mg^{2+}, Ba^{2+}, and Sr^{2+} and 0.1–1 μg L^{-1} for Na^+ and K^+. Anions of HCO_3^- were determined using titration methods (NEPB, 2002). The electrical conductivity (EC), total dissolved solid concentrations (TDS), and pH in water samples were determined in situ by using conductometer (YSI Incorporated, Yellow Springs, OH, USA).

Samples were pretreated prior to measurement for Sr isotopes using the water Sr isotopic analysis method (Li et al., 2012). Approximately 5–8 g of water samples were weighed into Savillex 15 mL Teflon-PFA vials. The samples were dried on a hotplate at 100 °C. Then, the samples were re-dissolved using 1.1 mL of 2.5 mol L^{-1} HCl. The sample solution was cooled to room temperature for 1 h before centrifugation for 8 min at 5000 rpm. Then, the supernatant was collected from centrifuge tubes and dried on a hotplate. Next, the samples were re-dissolved with 1.0 mL of 2.5 mol L^{-1} HCl. Then, the sample solution was loaded onto the pre-conditioned resin column with 2 mL of AG50W × 12 (200–400 mesh) for the separation of Sr from the sample matrix. After rinsing four times with 0.5 mL of 2.5 mol L^{-1} HCl, the column was washed with 7 mL of 5 mol L^{-1} HCl. Afterwards, the Sr fraction was stripped with 3.5 mL of 5 mol L^{-1} HCl. Finally, the Sr fraction was evaporated to dryness for analysis by thermal ionization mass spectrometry (TIMS). The blank for this procedure was lower than 300 pg for Sr.

The Sr isotopic measurements were performed on a Finnigan MAT 262® multi-collector mass spectrometer (Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing). A double Re filament configuration was used to determine Sr. Sr isotopic data was acquired in the static collection mode. The mass fractionation of Sr was corrected using the exponential law with $^{88}Sr/^{86}Sr = 8.375209$. An international standard sample NBS-987