



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



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## ABSTRACT

The concentrations of dissolved strontium (Sr) and isotope ratios (<sup>87</sup>Sr/<sup>86</sup>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 <sup>87</sup>Sr/<sup>86</sup>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<sup>2+</sup>, Mg<sup>2+</sup>, 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.

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## 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 (<sup>87</sup>Sr/<sup>86</sup>Sr) of natural materials reflect the sources of Sr available during their formation (Capo et al., 1998). Additionally, <sup>87</sup>Sr/<sup>86</sup>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 µg L<sup>-1</sup>, and averaged ~60 µg L<sup>-1</sup> in a river water system (Stallard, 1985), whereas another study found that the global river average was 78 µg L<sup>-1</sup> (Palmer and Edmond, 1992). Strontium

isotopic composition (<sup>87</sup>Sr/<sup>86</sup>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 (<sup>87</sup>Sr/<sup>86</sup>Sr) is 0.7119 (Palmer and Edmond, 1989, 1992).

The <sup>87</sup>Sr/<sup>86</sup>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 <sup>87</sup>Sr/<sup>86</sup>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 <sup>87</sup>Sr/<sup>86</sup>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 <sup>87</sup>Sr/<sup>86</sup>Sr of parent

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alluvial sediment is relatively high, i.e. 0.7165 (Capo and Chadwick, 1999). Precambrian granitic bedrock derived from felsic rocks generally has high  $^{87}\text{Sr}/^{86}\text{Sr}$  values ( $>0.71$ ). In addition, strontium from current seawater has a fairly constant  $^{87}\text{Sr}/^{86}\text{Sr}$  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  $^{87}\text{Sr}/^{86}\text{Sr}$  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  $^{87}\text{Sr}/^{86}\text{Sr}$  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  $^{87}\text{Sr}/^{86}\text{Sr}$  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  $^{87}\text{Sr}/^{86}\text{Sr}$  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  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in different water types, this study attempts to reveal the characteristics of dissolved Sr and major ions, to find the evolution of  $^{87}\text{Sr}/^{86}\text{Sr}$  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<sup>2</sup> 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 Yangtze 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<sup>−1</sup>, 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.

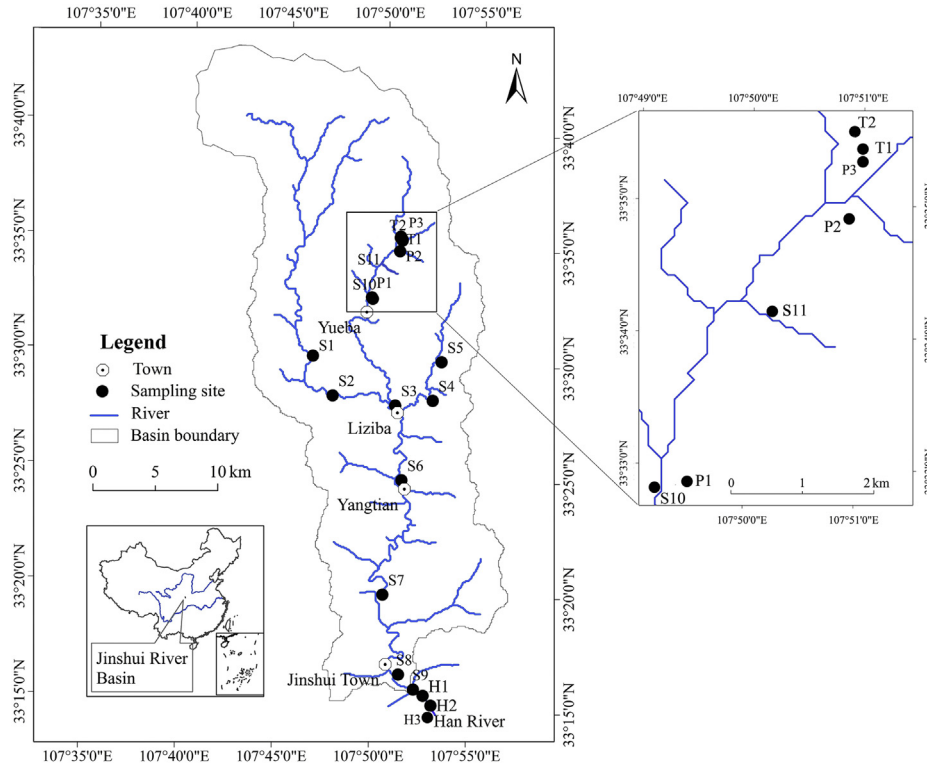
### 2.2. Sampling and analyses

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 ( $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{K}^{+}$ , and  $\text{Na}^{+}$ ) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (5300 DV, PerkinElmer), and anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^{-}$ , and  $\text{NO}_3^{-}$ ) were determined by ion chromatography (ICS-90, Dionex) (Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing). Detection limits were  $<0.1 \mu\text{g L}^{-1}$  for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Sr}^{2+}$  and  $0.1\text{--}1 \mu\text{g L}^{-1}$  for  $\text{Na}^{+}$  and  $\text{K}^{+}$ . Anions of  $\text{HCO}_3^{-}$  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<sup>−1</sup> 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<sup>−1</sup> 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<sup>−1</sup> HCl, the column was washed with 7 mL of 5 mol L<sup>−1</sup> HCl. Afterwards, the Sr fraction was stripped with 3.5 mL of 5 mol L<sup>−1</sup> 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<sup>®</sup> 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  $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$ . An international standard sample NBS-987



**Fig. 1.** The location and sampling sites of the Jinshui River basin in the South Qingling Mts., China. P1, P2, and P3 are rainwater samples, T1 and T2 are forest soil water samples, S1–S11 are river water samples in the Jinshi River, and H1–H3 are river water samples in the Han River, respectively.

was employed to evaluate instrument stability during the period of data collection. The mass spectrometer yielded a value of  $0.710258 \pm 0.000010$  ( $2\sigma$ ,  $n = 4$ ) for the NBS-987 Sr metal standard during the measurement period, in good agreement with the reported values (Li et al., 2012). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of samples were precise to within 0.000012 ( $2\sigma$ ).

### 2.3. Statistical analyses

The One-way ANOVA with Nonparametric Dunnett's C test was performed to analyze the differences in Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of different water types, since Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were abnormally distributed and had unequal variance (Bu et al., 2010, 2015). Correlation analysis was applied to explore correlations between dissolved Sr and major ions, which were expressed by Pearson's correlation coefficients at the  $p < 0.01$  and  $p < 0.05$  levels (two-tailed). Linear regression, based on  $p$ -value, was used to simulate the correlations between dissolved Sr and major ions to explain their characteristics in waters. All statistical analyses were performed using SPSS 13.0.

The contributions from three sources to a mixture were quantified using a three-source mixing model (Phillips and Gregg, 2001). For a three-end-member mixture, the three-source mixing model could be formulated from the following mass balance equations:

$$\begin{cases} f_A \bar{\delta}_A + f_B \bar{\delta}_B + f_C \bar{\delta}_C = \bar{\delta}_M \\ f_A \bar{\lambda}_A + f_B \bar{\lambda}_B + f_C \bar{\lambda}_C = \bar{\lambda}_M \\ f_A + f_B + f_C = 1 \end{cases} \quad (1)$$

where  $\bar{\delta}$  and  $\bar{\lambda}$  represent mean isotopic compositions for two elements, the subscripts refer to the three sources A, B, and C, and the mixture M, and  $f_A$ ,  $f_B$ , and  $f_C$  are the proportions of A, B, and C in M.

## 3. Results

### 3.1. Dissolved Sr concentrations in the river water system

The Sr concentrations were significantly different between each water type in the Jinshui River basin ( $F_{3,18} = 20.278$ ,  $p < 0.001$ ) (Table 1). The rainwater collected in open field had the lowest Sr concentration ranging from 37 to  $51 \mu\text{g L}^{-1}$ , with mean value of  $42 \mu\text{g L}^{-1}$  ( $n = 3$ ). The Sr concentrations in the Jinshui River ranged from 44 to  $120 \mu\text{g L}^{-1}$  with a mean value of  $77 \mu\text{g L}^{-1}$  ( $n = 11$ ), which is very close to the global river average of  $78 \mu\text{g L}^{-1}$  (Palmer and Edmond, 1992). Concentrations were higher in river water from the Han River, ranging from 124 to  $206 \mu\text{g L}^{-1}$  with a mean of  $172 \mu\text{g L}^{-1}$  ( $n = 3$ ). This is close to the mean Sr concentration of the Han River basin ( $179.6 \mu\text{g L}^{-1}$ ) studied by Xu et al. (2011). Water from forest soil had the highest Sr concentration of  $234 \mu\text{g L}^{-1}$ , and mean value of  $189 \mu\text{g L}^{-1}$  ( $n = 2$ ), while its lowest value is  $145 \mu\text{g L}^{-1}$ .

### 3.2. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the river water system

There were statistical differences in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the different water types ( $F_{3,18} = 23.010$ ,  $p < 0.001$ ) (Table 1). The Sr isotope ratios of river water in the Jinshui River ranged from 0.71070 to 0.71137, with a mean value of 0.71116 ( $n = 11$ ). The river water in the confluence of the Jinshui River and the Han River had the least non-radiogenic Sr isotope ratio of all the samples, i.e.  $0.71088 \pm 0.00018$  (mean  $\pm$  S.D.,  $n = 3$ ), with a range of 0.71067–0.71102. The average isotope ratio of rainwater was  $0.71116 \pm 0.00011$  ( $n = 3$ ). Water from forest soil was the most radiogenic compared with the other samples, which the mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is 0.71213 ( $n = 2$ ), ranging from 0.71209 to 0.71216.

**Table 1**

Dissolved Sr concentrations and isotopic composition, major ion concentrations, and physicochemical parameters (mean and S.D.) in different water type samples collected during May 2012 in the Jinshui River basin of the South Qingling Mts., China.

Parameter	River water (n = 11)		Han river water (n = 3)		Rainwater (n = 3)		Forest soil water (n = 2)	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Sr ( $\mu\text{g L}^{-1}$ )	77	27	172	43	42	8	189	63
$^{87}\text{Sr}/^{86}\text{Sr}$	0.711156	0.000230	0.710876	0.000181	0.711159	0.000112	0.712129	0.000049
Ca ( $\text{mg L}^{-1}$ )	21.19	8.36	44.48	8.58	10.28	3.28	37.41	9.17
Mg ( $\text{mg L}^{-1}$ )	3.43	1.59	8.53	2.52	1.26	0.77	9.14	3.90
Ba ( $\text{mg L}^{-1}$ )	0.03	0.01	0.04	0.01	0.03	0.01	0.10	0.02
K ( $\text{mg L}^{-1}$ )	1.61	0.42	1.80	0.38	4.50	3.46	17.92	0.89
Na ( $\text{mg L}^{-1}$ )	3.36	0.81	10.13	0.30	1.11	0.63	1.17	0.16
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	13.5	1.9	24.7	5.3	14.7	9.5	34.5	28.3
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	1.0	0.2	6.4	3.1	1.9	1.6	6.4	3.7
$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	4.4	1.5	9.5	2.0	0.8	0.1	45.3	24.1
$\text{HCO}_3^-$ ( $\text{mg L}^{-1}$ )	102.6	23.4	138.9	22.7	71.9	11.8	93.9	22.3
pH	7.7	0.5	7.5	0.2	7.0	0.3	7.0	0.3
EC ( $\mu\text{S cm}^{-1}$ )	150.1	54.8	345.3	86.8	81.9	42.5	207.4	149.3
TDS ( $\text{mg L}^{-1}$ )	76.9	25.8	164.9	42.1	44.0	21.6	151.4	58.1

### 3.3. Correlations between dissolved Sr and major ions and physicochemical parameters

Dissolved Sr in the river water system was significantly correlated with the ions,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  as well as EC, and TDS ( $p < 0.01$ ; Table 2) in correlation analysis. It was significantly correlated with  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{HCO}_3^-$  at  $p < 0.05$  level (Table 2). Dissolved Sr was also strongly correlated with Ca ( $r^2 = 0.883$ ,  $p < 0.001$ ), Mg ( $r^2 = 0.963$ ,  $p < 0.001$ ), EC ( $r^2 = 0.774$ ,  $p < 0.001$ ), and TDS ( $r^2 = 0.950$ ,  $p < 0.001$ ) in a regression analysis (Fig. 2).

### 3.4. Correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ and Ca/Na ratios, Ca/K ratios, and 1000/Sr in the river water system

The strontium isotope ratios,  $^{87}\text{Sr}/^{86}\text{Sr}$  were plotted against Ca/Na ratios (Fig. 3a) and Ca/K ratios (Fig. 3b). There was separation between all water sample groups. Forest soil water with the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios also had the highest Ca/Na ratios and the lowest Ca/K ratios. Rainwater had a much lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio with Ca/Na ratios  $> 8$  and Ca/K ratios lower than 4. The Han River water samples with the highest Ca/K ratios and the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Ca/Na ratios. The Jinshui River water had Ca/Na ratios between 4 and 8, but relatively high Ca/K ratios ranging from 9 to 16.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were plotted against the reciprocal of the Sr concentrations (1000/Sr) for all water samples in river water

system and there was a high level of separation between the sample types (Fig. 4a). Forest soil water had much higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr concentrations than the other water samples. The Han River water had lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios but higher Sr concentrations, while rainwater had lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr concentrations. The Jinshui River water samples fell between the Han River waters and rainwaters. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio vs. 1000/Sr was also plotted as mean  $\pm$  2S.E. values for the different water types also showing the three end-members of river water: Atmospheric inputs, carbonate and silicate weathering (Fig. 4b).

### 3.5. Source contributions of the three end-members in the river water system

According to Eq. (1), the mean proportion of each end-member in the Jinshui River water was calculated based on the concentrations and isotope ratios of Sr using the equations:

$$\begin{cases} f_a(^{87}\text{Sr}/^{86}\text{Sr})_a + f_c(^{87}\text{Sr}/^{86}\text{Sr})_c + f_s(^{87}\text{Sr}/^{86}\text{Sr})_s = (^{87}\text{Sr}/^{86}\text{Sr})_R \\ f_a(\text{Sr})_a + f_c(\text{Sr})_c + f_s(\text{Sr})_s = (\text{Sr})_R \\ f_a + f_c + f_s = 1 \end{cases} \quad (2)$$

where  $(^{87}\text{Sr}/^{86}\text{Sr})$  is the mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and (Sr) is the mean concentration; the subscripts of a, c, and s refer to the three sources

**Table 2**

Correlation coefficients among dissolved Sr and major ion concentrations, and physicochemical parameters.

	Sr	Ca	Mg	Ba	K	Na	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{HCO}_3^-$	pH	EC	TDS
Sr	1												
Ca	0.940**	1											
Mg	0.981**	0.957**	1										
Ba	0.750**	0.566*	0.728*	1									
K	0.477*	0.274	0.444	0.873**	1								
Na	0.516*	0.696**	0.539*	-0.127	-0.354	1							
$\text{SO}_4^{2-}$	0.800**	0.690**	0.818**	0.699**	0.539*	0.261	1						
$\text{Cl}^-$	0.871**	0.778**	0.863**	0.647**	0.499*	0.445	0.888**	1					
$\text{NO}_3^-$	0.703**	0.478*	0.674**	0.897**	0.809**	-0.127	0.770**	0.670**	1				
$\text{HCO}_3^-$	0.519*	0.567**	0.546*	0.110	-0.177	0.641**	0.387	0.478*	0.125	1			
pH	0.003	0.248	0.049	-0.263	-0.393	0.338	-0.227	-0.294	-0.348	-0.003	1		
EC	0.880**	0.939**	0.900**	0.404	0.074	0.777**	0.725**	0.788**	0.357	0.672**	0.194	1	
TDS	0.975**	0.970**	0.983**	0.645**	0.358	0.624**	0.805**	0.866**	0.585**	0.596**	0.078	0.949**	1

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

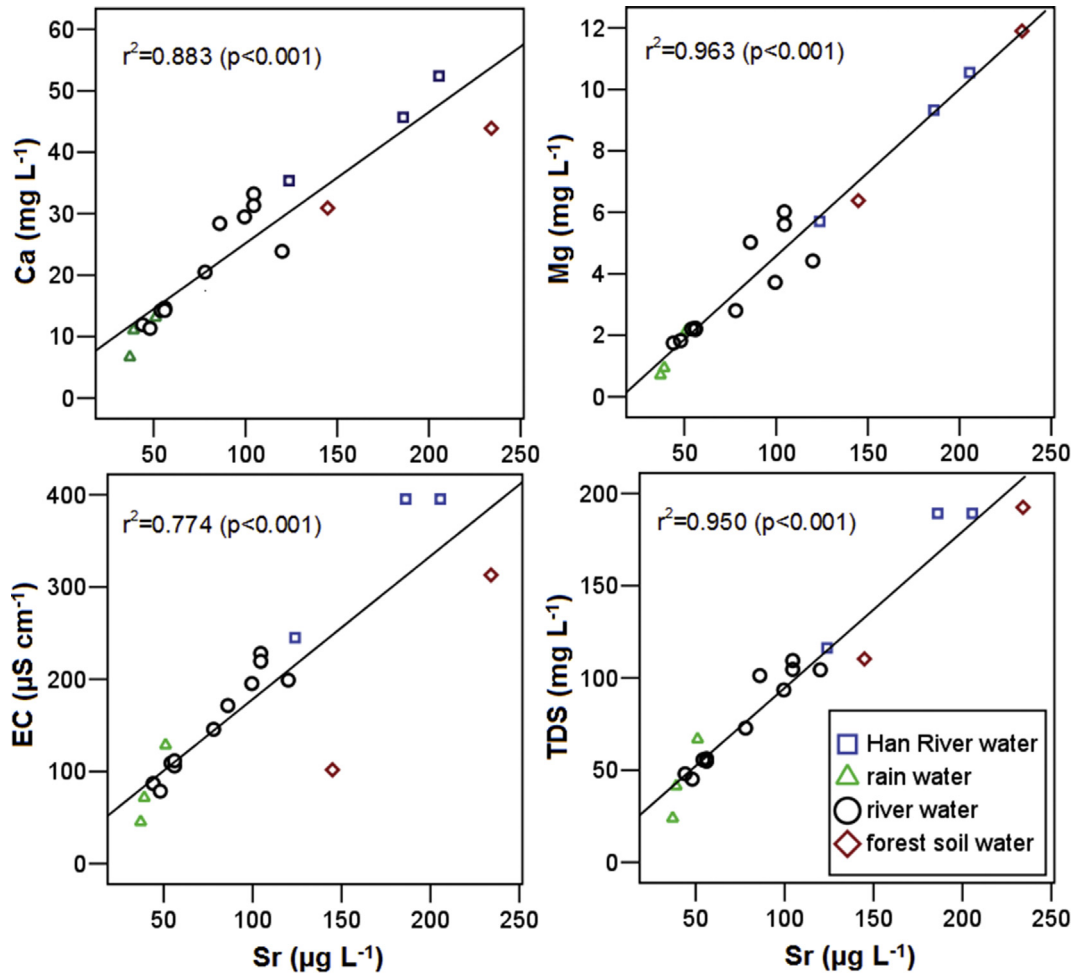


Fig. 2. Correlations between Ca, Mg, EC, and TDS and Sr concentrations for water samples collected during May 2012 in the Jinshui River basin of the South Qingling Mts., China.

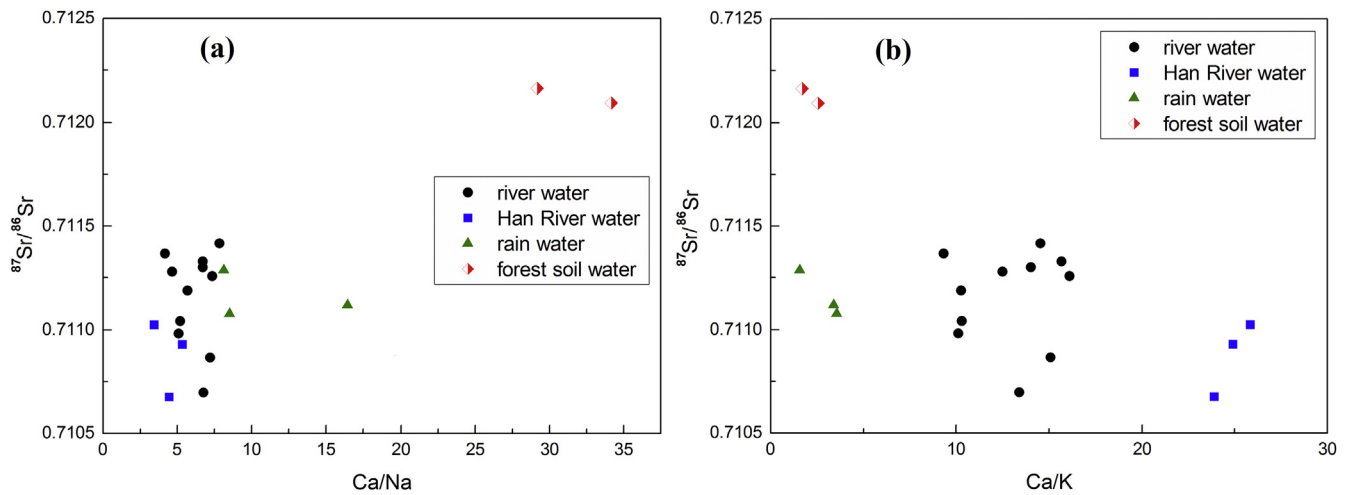


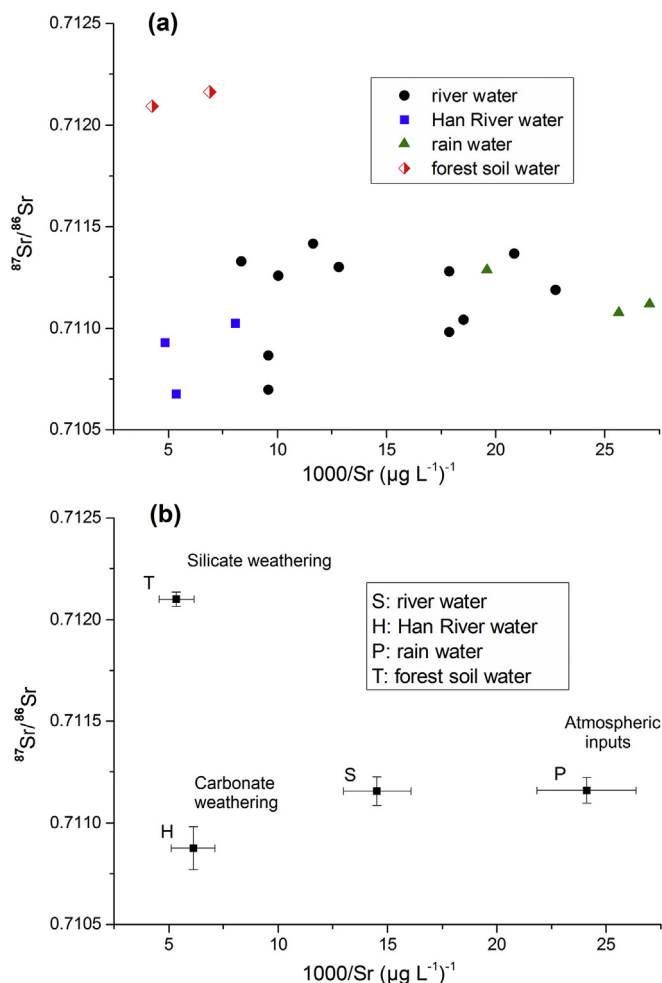
Fig. 3. a) Correlations between  $^{87}\text{Sr}/^{86}\text{Sr}$  and Ca/Na ratios (in mg/mg); b) Correlations between  $^{87}\text{Sr}/^{86}\text{Sr}$  and Ca/K ratios (in mg/mg) for different water types collected in the Jinshui River basin of the South Qinling Mts., China.

from rain water, carbonate rock weathering, and silicate rock weathering, and  $R$  refers to river water as the mixture;  $f_a$ ,  $f_c$ , and  $f_s$  are the proportions of  $a$ ,  $c$ , and  $s$  in  $R$ .

Using the Eq. (2), the proportion of atmospheric input end-member was  $74 \pm 8\%$  (mean  $\pm$  S.E.), and carbonate and silicate

rock weathering respectively contributed  $20 \pm 10\%$  and  $6 \pm 7\%$  to Sr concentrations of the Jinshui River water.





**Fig. 4.** Correlations between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $1000/\text{Sr}$  concentrations ( $\mu\text{g L}^{-1}$ ) for the forest river water system collected in the Jinshui River basin of the South Qinling Mts., China. a) Values for all data to show their positions; b) mean  $\pm 2\text{S.E.}$  for different water types to show the end-members.

## 4. Discussion

### 4.1. Characteristics of dissolved Sr and major ions in the river water system

In our study, dissolved Ca and  $\text{HCO}_3^-$  concentrations accounted for over 75% of the molar concentrations of all major ions in all water types (Table 1), except forest soil water. Other studies have shown that carbonate in a river water system can be dominated by rock weathering, e.g. Ganga headwater basins, India (Tripathy et al., 2010). Additionally, in our study  $\text{Ca}^{2+} + \text{Mg}^{2+}$  concentrations dominated about 80% of the cations in the Jinshui River water and the Han River water, showing that the natural sources of isotopic composition of Sr for river water in the forested watershed were mainly from atmospheric inputs and carbonate weathering inputs (Bailey et al., 1996). The results confirmed the findings from Xu and his coworkers who showed that the Han River is a typical carbonate-dominated river (Xu et al., 2011).

The dissolved Sr in different water types showed significant positive correlations with major ions and physicochemical parameters during the sampling period (Table 2). These findings indicated their similar geochemical and biological processes in waters (Aubert et al., 2002) and common origins (Shand et al.,

2009), which control the weathering of Sr. Moreover, the dissolved Sr firmly linked with  $\text{NO}_3^-$  in the river water system, which may be partly induced by consumption of plants or algae during the sampling season (Bu et al., 2015).

The dissolved Sr strongly covaried with Ca, Mg, EC, and TDS in the river water system. The linear correlation between Sr concentrations and both Ca and Mg in all water types suggests that Sr can be used as an analogue for tracing sources and cycling processes of dissolved Ca and Mg (Capo et al., 1998; Aubert et al., 2002). This correlation also indicates that rock weathering is an important source for dissolved Sr (Wu et al., 2009) in different water types in the Jinshui River basin. Dissolved Sr has a slightly higher correlation with Mg than with Ca. This suggests that carbonate from limestone is not the major contributor to dissolved Sr in the river water system, but shale and/or sandstone are more important ones. This is similar to the findings of Löfvendahl et al. (1990). The dissolved Sr concentrations also correlated with EC and TDS in all water samples, suggesting that the dissolved Sr in the river water system was controlled by similar hydrochemical processes to EC and TDS, such as colloid destabilization or sedimentary inputs (Bu et al., 2015). Thus, the correlations between Sr and major ions and physicochemical parameters, have given insights into hydrological and geochemical processes, as well as deducing sources of Sr (Shand et al., 2009).

### 4.2. Evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ in the river water system

Our study showed that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in rainwater samples were significantly different to other water types, consistent with previous studies (Aubert et al., 2002). Clearly, rainwater, as the beginning in a river water system (Clow et al., 1997), contributes to river systems, and therefore isotopic composition of rainwater is a contributor (Bailey et al., 1996). The average isotope ratio of the Jinshui River water was generally similar to that of rainwater, suggesting the importance of wet deposition. This has also been demonstrated by Gosz and Moore (1989) and Aubert et al. (2002).

Overall, the mean value of Sr isotope ratios in the Jinshui River water was slightly lower than the global river average of 0.7119 (Palmer and Edmond, 1989, 1992) and higher than that of global seawater ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70916$ ; Beck et al., 2013), but close to the Sr from Canadian rivers with value of  $\sim 0.711$  (Wadleigh et al., 1985), reflecting weathering and erosion of continents which are influenced by sea level and climatic change (Palmer and Edmond, 1989; Capo et al., 1998).

In water cycle processes in a forested watershed, the chemistry of river water is the result of a combination of processes that occur in the atmosphere, vegetation, soil, and aquatic environments. Precipitation represents the beginning of the hydrologic cycle (Clow et al., 1997), thus, the rainwater data in this study are a useful chemical reference point to describe the effects of geochemical processes on natural waters in the forested watershed. Our rainwater samples had relatively low  $^{87}\text{Sr}/^{86}\text{Sr}$  and relatively high Ca/Na ratios ( $>8$ ), suggesting that most of the Sr in rain water was derived from airborne carbonate dust (Åberg, 1995). The higher Ca/Na ratios in rainwater also indicate that carbonate minerals in the atmosphere have important influence on the chemistry of rainwater. Forest soil water samples, whose dominant mineral is silicate, were more strongly influenced by granitoids, metamorphic schist, and calcite weathering, as indicated by much higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and Ca/Na ratios compared to rainwater. Overall, this study showed that the river water Sr is controlled by the three end-members: atmospheric inputs, and carbonate and silicate weathering. Based on our analyses, it also appears that the water leached from forest soil was not a dominant input to the Jinshui River water.

The sources of dissolved Sr in the river water system are further

distinguished. Analysis of the Sr isotopes, and Sr and ion concentrations showed that the dissolution of carbonate rocks (like limestone) with low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $<0.71$ ) made a substantial contribution to the Sr of the Han River system (Goldstein and Jacobsen, 1987; Xu et al., 2011). Therefore, the Han River water was used to represent the carbonate weathering end-member. Forest soil water had the most radiogenic Sr with high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, which could be regarded as silicate weathering end-member. Additionally, the rainwater with low concentrations and isotope ratios of Sr was the atmospheric input end-member in the river water system.

#### 4.3. Atmospheric and weathering end-members in the river water system

It is assumed that the Sr related processes measured in our study are representative of the system in the longer term as the South Qinling Mts. have relatively little human activities or natural disturbances (Pett-Ridge et al., 2009). The ultimate sources of Sr to an undisturbed forested watershed are atmospheric deposition, which includes wet and dry deposition, and weathering of local bedrock minerals (Åberg, 1995; Clow et al., 1997). In the Jinshui River basin, the wet deposition dominated since the river is in a humid monsoon climate zone. The dry deposition is generated through settling of particulates transported by wind. Indeed, our study demonstrated that atmospheric inputs accounted for a substantial proportion ( $74 \pm 8\%$ ) for the river water system in the watershed. Carbonate rock weathering contributed  $20 \pm 10\%$  to the river water, while silicate rock weathering ( $6 \pm 7\%$ ) was not a major input to the Jinshui River water.

## 5. Conclusions

This study investigates the dissolved Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of rain water, river water, and water from forest soil in a forest-river water system of the South Qinling Mts., China under base flow conditions. Concentrations and stable isotope ratios of dissolved Sr differed between water types. The dissolved Sr concentrations also correlated with Ca and Mg concentrations as well as EC, and TDS in the river water system meaning that Sr concentrations can be a useful proxy to understand processes associated with these parameters. Three end-members of atmospheric inputs, carbonate and silicate weathering are identified to control the Sr water chemistry in the river water system, and their contributions are 74%, 20%, and 6% to the river water, respectively.

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