

Rare Earth Element Patterns in the Karst Terrains of Guizhou Province, China: Implication for Water/Particle Interaction

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Received: 3 July 2008 / Accepted: 6 January 2009 / Published online: 30 January 2009
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Abstract The authors determine the concentrations of dissolved ($<0.22 \mu\text{m}$) rare earth elements (REE) and suspended particulate matter (SPM) of typical karst rivers in Guizhou Province, China during the high-flow period. The concentrations of acid-soluble REE extracted from SPM using diluted hydrochloric acid are also obtained to investigate water/particle interaction in the river water. The dissolved REE contents in the river water are extremely low in the rivers of the study. The dissolved REE distribution patterns normalized by the Post Archean Australia Shale (PAAS) in the karst rivers are not flat, show slight enrichment of heavy REE to light REE, and also have significant negative Ce and Eu anomalies. The acid-soluble REE appears to have similar distribution patterns as characterized by MREE enrichment and slight LREE depletion, with unremarkable Ce and Eu anomalies. The PAAS-normalized REE distribution patterns of SPM are flat with negative Eu anomalies. The contents and distribution patterns of REE in the SPM are closely related to the lithological character of the source rocks. The SPM contains almost all the REE produced in the process of surficial weathering. This demonstrates that particle-hosted REE are the most important form of REE occurrence. REE fractionation, which takes place during weathering and transport, leads to an obvious HREE enrichment in the dissolved loads relative to the SPM. Y/Ho ratio can be used to shed light on REE behaviors during water/particle interaction.

Keywords Karst · Rare earth elements (REE) · Water chemistry · Water/particle interaction · Y/Ho ratio

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1 Introduction

Rare earth elements (REE) are a collection of fifteen chemical elements that form a REE series from the lightest REE (La) to the heaviest REE (Lu) and whose bulk chemical properties change systematically. Yttrium is chemically similar to the lanthanides, so it is usually assimilated to lanthanides. REE geochemical behaviors have been well documented in the past decade, because elements in this group provide a series of geochemical indicators that can be used to constrain the processes in which the elements are mobilized during weathering and redistribution between suspended particulate matter (SPM) and dissolved phases in river waters (Goldstein and Jacobsen 1988; Sholkovitz 1992, 1993, 1995; Johannesson and Zhou 1999; Tricca et al. 1999; Takahashi et al. 2002; Tang and Johannesson 2003; Mayanovic et al. 2007). The behaviors of dissolved REE in river waters are controlled mainly by water/particle interaction and solution chemistry (e.g., organic and inorganic complexation, adsorption, and sediment resuspension, etc.).

In Han and Liu (2007), the authors investigated the dissolved REE in river waters in Guizhou Province, China. They did not, however, get sufficient SPM in the low-flow season. The aim of this study is to evaluate the behaviors of REE (including Y) during water/particle interaction in terms of REE abundances and distribution patterns of different loads (dissolved load, acid-soluble load and SPM) in the karst river. This study can help us to understand the fractionation of REE in karst rivers so as to constrain the water/particle interaction.

2 Geological Setting

Guizhou Province covers an area of $17.6 \times 10^4 \text{ km}^2$ from $24^\circ 37' \text{ N}$ to $29^\circ 13' \text{ N}$ and from $103^\circ 36' \text{ E}$ to $109^\circ 35' \text{ E}$. It is located in the center of the Southeast Asia Karst Region, which is the largest karst area in the world. The geological details of the province can be found in Han and Liu (2004).

The Wujiang River winds its way through the Yunnan–Guizhou Plateau and is the largest tributary of the upper reaches of the Yangtze River. Limestones are the major strata distributed in the upper reaches of the Wujiang River, while limestone, dolomite, and clastic rocks are distributed in the middle and lower reaches (Fig. 1a). The region is topographically complicated, with elevations ranging from 300 m to 2300 m, and is under a humid subtropical monsoonal climate with an annual-average temperature of $9\text{--}17^\circ\text{C}$ and an annual-average precipitation of 900–1400 mm.

The area along the upper reaches of the Wujiang River is covered mainly by calcareous soils and shrubs, and the rest of the area is covered with calcareous, yellow soils and arbor–shrub vegetation. The Yuanjiang River system is the second largest river in Guizhou, which consists of two branches (the Qingshuijiang River and the Wuyanghe River). The elevation of the Qingshuijiang River and the Wuyanghe River are very large, about 1275 m and 454 m above the sea level, respectively. Distributed in the middle and lower reaches of the Qingshuijiang River are mostly detrital sedimentary rocks, while dolomitic limestone strata are exposed in the upper and middle reaches of the Wuyanghe River.

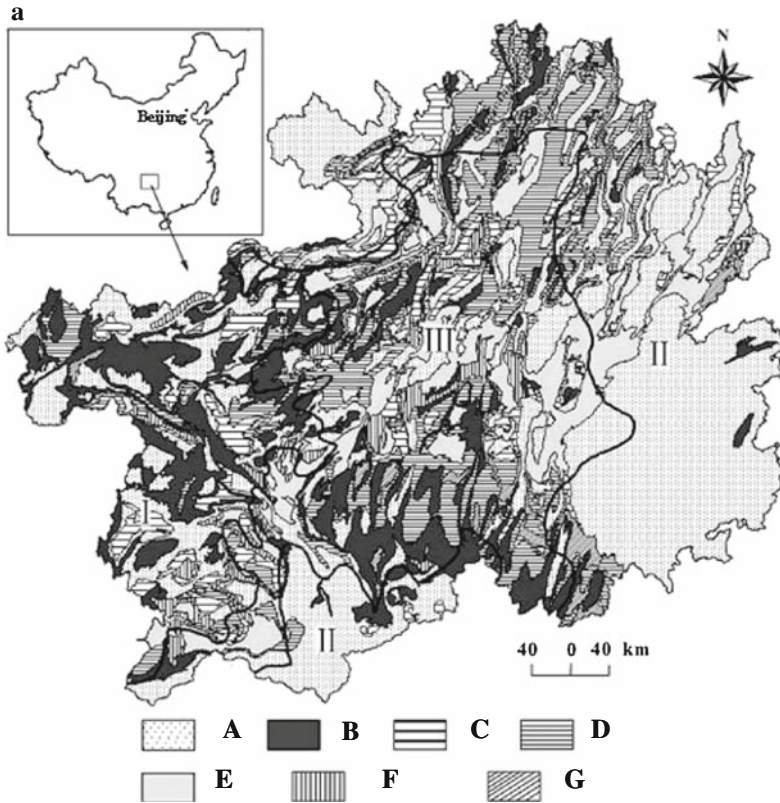


Fig. 1 **a** Sketch showing the lithology of Guizhou Province (reproduced from Wang et al. 2004). Zone I has an average altitude of more than 1500 m, zone II, less than 700 m, and zone III, 700–1500 m. *Legend* A stands for clastic sedimentary rocks. B, E, and G are consecutive carbonate rock assemblages (carbonate rocks account for more than 90%), respectively for limestone, dolomite and mixed assemblage of limestone and dolomite. C and F are assemblage of carbonate rocks interbedded with clastic rocks (carbonate rocks account for 70–90%), respectively for limestones and dolomites interbedded with clastic rocks. D stands for clastic rocks interbedded with limestone (carbonate rocks account for 30–70%). **b** Map showing sampling locations and sample numbers

3 Sampling Strategies and Analytical Methods

Sixty-one river water and SPM samples were collected during the high-flow season from August 4 to 29 of 1999. The sampling locations are shown in Fig. 1b. Water temperature, pH, and conductivity were measured at the sampling site with a portable pH and salt conductivity meter. HCO_3^- was titrated by hydrochloric acid standard solution on the spot. The REE concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS, ELEMENT) in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. ICP-MS instrumentation, operating conditions and data acquisition can be found in Su et al. (1998). Samples and procedural blank were accomplished in the Class-100 laboratory and Millipore-Q water (18.2 M Ω cm) and sub-boiling high-purity reagents were used. Each REE stock solution (1 mg/ml) was prepared by dissolving its high-purity oxide. The standard



Fig. 1 continued

solutions, which contained all REE at the same concentration, were prepared by diluting the stock solution to 1, 5 and 10 ng/ml with 5 ng/ml of internal standards, Rh, and 1% of HNO_3 (v/v). The following analyses were applied for every sample: first the blank was measured, then samples were taken, and at the end, the standard. Three continuous measurements were made on each solution. A 5% v/v HNO_3 solution was used to flush the introduction system between measurements to avoid any possible contamination and memory effect. The following masses were used for REE measurement: ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb , and ^{175}Lu . The interferences of BaO^+ on Eu and PrO^+ on Gd were corrected by measuring the signature Ba and Pr solutions. The procedural blanks were less than 5% for La, 10% for Ce, and 2–3% for other REE and Y of the samples. Each calibration curve was evaluated by analysis of these quality control (QC) standards before, during, and after the analysis of a set of samples. The accuracy of heavy REE and Y were better than $\pm 3\%$, and that of light REE were better than $\pm 5\%$ for the quality control standards.

3.1 Dissolved REE

Samples were collected by using a 10-l nitric acid-cleaned polyethylene bucket. The samples used for determining the dissolved load REE were immediately filtered on site using 0.22 μm cellulose acetate filter membranes (Millipore). The solution that has passed through this filter is referred to as dissolved load, which consists of dissolved ions and colloids smaller than 0.22 μm in size. The filtrates were then acidified with ultra-purified hydrochloric acid until their pH values became less than 2 to prevent adsorption during

storage, and they were stored in 2 l high-density polyethylene bottles, which were cleaned with acid (2–3 N HCl) and rinsed with Milli-Q water and dried. All of the samples were stored at 4°C before being analyzed within 30 days.

The dissolved load REE concentrations are below the detection limit of the inductively coupled plasma mass spectroscopy (ICP-MS). We hence used the method of Shabani et al. (1990) to increase the concentration of the REE by at least a factor of 100. The procedure of determining the concentrations of dissolved load REE is similar to that described by Han and Liu (2007). The preconcentration of dissolved load REE concentration involves the following steps: REE were extracted from water samples with 65% HDEHP (2-ethylhexyl hydrogen phosphate) and 35% H₂MEHP (2-ethylhexyl dihydrogen phosphate) in heptane, then back-extracted with 6 N ultra-purified hydrochloric acid and transformed into nitrates of REE for ICP-MS analysis. Indium was used as the internal standard to monitor the chemical procedure on the quantitative basis.

3.2 Acid-Soluble Load REE

The unfiltered water samples were acidified to $\text{pH} < 2$ ($\text{pH} \approx 1.6$) using ultra-purified hydrochloric acid directly after their collection, and then filtered through 0.22- μm filter membranes after 2 weeks. The sample includes both the initially dissolved species (REE_{diss}) and the exchangeable REE initially adsorbed on particulate matter that can be desorbed by diluted hydrochloric acid (REE_{sorb}). The fraction is referred to as acid-soluble load. Numerous methods were used to extract different particle phases: one involves sequential removal of different phases, such as exchangeable, adsorbed, carbonate, and organic phase by using different chemical reagents (Tessier et al. 1979). A simpler method was adopted to extract the labile fraction or acid-soluble phase, including carbonates and coatings, from the SPM with acid (Sholkovitz et al. 1994; Negrel et al. 2000; Vesely et al. 2001).

3.3 REE of SPM

The filter membranes were dried and stored carefully for chemical digestions and determination of REE in SPM. The digestions of SPM were carried out in a sealed Teflon bomb at 120°C using a mixture of HCl, HNO₃, and HF. The bomb digestion was a procedure that involves two parts. The first treatment was effected with HCl and HNO₃ mixture, and the second treatment was effected with the addition of HF. Filter membrane blanks were also carried out through the digestions.

4 Results

REE concentrations of dissolved load, acid-soluble load, and SPM are listed in Table 1. Although most samples show differences in the absolute concentration of REE, they have similar relative concentration. Therefore, it is a common practice to normalize the concentrations of REE to the PAAS (PAAS data from Taylor and McLennan 1985). This allows one to identify, within the typical sedimentary REE patterns, an enrichment or deficiency of a single element or group of elements (Henderson 1984).

Table 1 The concentrations of REE in dissolved loads (ng/l), acid-soluble loads (ng/l) and suspended particulate matters (mg/kg) in the karst waters of Guizhou Province

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
<i>Dissolved loads</i>																			
Wujiang River system																			
The upper reaches of Wujiang River																			
990804-1	7.9	13.1	18.2	2.5	11.8	2.9	1.0	2.7	0.4	2.4	0.5	1.5	0.2	0.8	0.2	17.1	1.2	0.7	1.7
990804-2	8.2	7.6	10.5	1.8	8.2	2.4	0.3	2.2	0.3	2.5	0.4	1.2	0.2	0.8	0.2	20.6	0.7	0.7	0.6
990804-3	7.7	13.1	18.9	2.9	13.9	2.7	0.6	2.9	0.4	2.4	0.5	1.5	0.2	1.1	0.2	23.4	0.9	0.7	1.0
990804-4	8.0	14.1	15.6	2.7	13.7	2.5	0.5	2.5	0.3	2.1	0.5	1.3	0.1	0.9	0.1	20.9	1.2	0.6	0.9
990805-5	8.3	14.3	16.4	3.5	16.2	4.1	0.7	4.3	0.8	4.9	0.8	2.4	0.4	1.9	0.3	25.3	0.6	0.5	0.8
990805-6	7.9	9.4	9.3	1.5	7.0	1.2	0.1	1.3	0.2	1.0	0.3	0.6	0.1	0.6	0.1	10.8	1.2	0.6	0.4
990805-7	7.9	15.9	18.4	3.2	13.4	2.5	0.5	2.6	0.4	2.1	0.4	1.2	0.2	0.9	0.1	19.8	1.3	0.6	0.9
990805-8	8.2	20	30.2	4.4	15.9	3.9	1.2	3.3	0.8	2.8	0.6	1.6	0.3	1.2	0.3	23.2	1.2	0.7	1.6
990806-9	7.6	10.3	11.3	2.1	9.4	1.7	0.2	1.9	0.2	1.5	0.3	1.0	0.1	0.7	0.1	14	1.1	0.6	0.6
Average	8.0	13.1	16.5	2.7	12.2	2.7	0.6	2.6	0.4	2.4	0.5	1.4	0.2	1.0	0.2	19.5	1.0	0.6	0.9
The middle reaches of Wujiang River																			
990806-10	7.8	22.0	33.3	6.7	34.0	8.0	2.0	9.9	1.4	7.8	1.6	4.1	0.4	2.5	0.4	59.2	0.6	0.6	1.1
990806-11	8.1	6.9	11.7	1.3	5.9	1.3	0.2	1.5	0.2	1.1	0.2	0.6	0.1	0.5	0.1	7.5	1.0	0.9	0.7
990806-12	8.3	6.0	6.7	1.2	5.1	1.1	0.3	1.5	0.3	1.9	0.4	1.3	0.2	1.0	0.2	28.7	0.4	0.6	0.9
990814-13	8.0	5.1	9.5	1.2	5.0	1.2	0.1	1.0	0.2	0.9	0.3	1.0	0.1	0.9	0.2	7.7	0.4	0.9	0.6
990814-14	7.7	10.5	19.6	2.8	12.6	3.2	0.4	2.7	0.3	2.3	0.5	1.3	0.2	0.9	0.1	15.5	0.9	0.8	0.6
990814-15	7.9	9.4	13.6	2.4	10.8	1.9	0.5	2.1	0.3	2.2	0.6	1.8	0.2	1.7	0.3	16.9	0.4	0.7	1.2
990814-16	8.1	5.4	7.1	1.0	2.8	0.7	0.04	0.8	0.2	0.7	0.1	0.2	0.03	0.3	0.1	3.2	1.3	0.7	0.3
990814-17	8.0	38.9	66.6	11.6	54.6	11.0	1.7	11.2	1.5	8.4	1.7	4.8	0.6	3.5	0.6	72.7	0.8	0.7	0.7
990814-18	8.2	3.7	11.7	0.9	4.2	1.0	0.04	1.0	0.1	0.7	0.1	0.4	0.1	0.4	0.1	4	0.7	1.5	0.2
990815-19	7.9	7.2	9.2	1.9	9.4	1.8	0.2	2.1	0.3	2.2	0.5	1.5	0.2	1.4	0.2	20.3	0.4	0.6	0.6
990815-20	8.0	6.5	10.2	1.4	6.1	1.4	0.2	1.4	0.2	1.3	0.3	1.1	0.1	0.8	0.1	12.9	0.6	0.8	0.6
990816-21	7.8	26.6	15.6	1.3	6.9	1.2	0.1	1.8	0.2	1.3	0.3	1	0.2	0.9	0.3	12.5	2.2	0.5	0.3

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
990816-22	7.9	10.1	11	1.9	9.7	2.3	0.4	2.6	0.3	2.3	0.5	1.5	0.2	1.0	0.1	23	0.7	0.6	0.7
990816-23	8.0	7.7	10.4	1.4	6.3	1.3	0.2	1.4	0.2	1.5	0.4	1.0	0.1	1.0	0.1	14.1	0.6	0.7	0.5
990816-24	8.5	4.4	7.6	1.3	5.8	1.5	0.2	1.6	0.2	1.6	0.3	1.0	0.1	0.7	0.2	11.8	0.5	0.7	0.5
990816-25	8.1	4.2	6	1.2	4.2	0.9	0.1	1.0	0.2	0.8	0.2	0.7	0.1	0.6	0.1	9.0	0.5	0.6	0.3
990819-35	8.0	6.4	8.3	1.7	8.3	1.7	0.3	2.2	0.4	2.4	0.6	1.8	0.2	1.7	0.3	24.7	0.3	0.6	0.8
990819-36	8.2	5.7	6.8	0.7	2.9	0.6	0.03	0.7	0.1	0.7	0.1	0.4	0.04	0.4	0.1	4.0	1.1	0.8	0.2
990819-37	7.7	12.5	26.5	3.4	15.5	3.8	0.7	4.6	0.6	3.6	0.9	2.3	0.3	2.1	0.3	26.6	0.4	0.9	0.8
Average	8.0	10.5	15.3	2.4	11.1	2.4	0.4	2.7	0.4	2.3	0.5	1.5	0.2	1.2	0.2	19.7	0.7	0.7	0.6
The lower reaches of Wujiang River																			
990816-26	8.1	13	11.5	1.8	8.4	1.9	0.4	2.5	0.5	2.4	0.5	1.6	0.3	1.5	0.2	23.5	0.6	0.5	0.8
990816-27	7.5	8.4	15.7	2.4	14.2	4.5	0.9	5.1	0.7	4.6	0.9	2.4	0.3	1.7	0.2	34.4	0.4	0.8	0.9
990816-28	7.8	4.5	10.4	1.1	4.9	1.2	0.2	1.5	0.2	1.2	0.3	0.8	0.1	0.7	0.1	8.9	0.5	1.1	0.7
990817-29	7.9	21.5	18.9	7.4	29.0	4.6	0.7	4.1	0.5	2.8	0.5	1.5	0.2	1.1	0.2	29.3	1.4	0.3	0.8
990817-30	7.9	8.6	7.4	1.0	5.0	1.1	0.2	1.2	0.3	2.4	0.4	0.9	0.1	0.8	0.2	13.4	0.8	0.6	0.7
990817-31	8.2	6.9	9.9	1.3	8.5	1.7	0.5	1.9	0.3	2.5	0.4	1.5	0.3	1	0.2	16.5	0.5	0.8	1.3
990817-32	8.1	2.8	5.7	0.6	3.0	0.7	0.1	0.7	0.1	0.9	0.1	0.4	0.1	0.8	0.2	3.9	0.3	1.0	0.6
990817-33	8.0	7.3	10.8	1.6	7.4	2.9	0.4	1.8	0.3	1.9	0.5	1.5	0.2	1.2	0.2	17.4	0.4	0.7	0.8
990817-34	7.6	6.1	9.7	1.4	7.2	1.5	0.2	1.8	0.3	1.8	0.4	1.3	0.2	1.1	0.2	18.9	0.4	0.8	0.6
Average	7.9	8.8	11.1	2.1	9.7	2.2	0.4	2.3	0.4	2.3	0.4	1.3	0.2	1.1	0.2	18.5	0.6	0.7	0.8
Yuanjiang River system																			
Qingshuijiang River																			
990826-38	7.6	11.2	24.9	3.3	16.2	3.9	0.5	4	0.6	3.8	0.8	2.1	0.3	1.7	0.3	26.3	0.5	0.9	0.6
990826-39	7.7	32.2	55.2	9	39.6	8.6	1.6	8	1.1	6.5	1.3	3.7	0.4	2.4	0.4	52.6	1.0	0.8	0.9
990826-40	7.8	22.2	16.3	3.2	16.7	3.2	0.6	3.7	0.5	3.1	0.6	1.8	0.2	1.4	0.2	25.3	1.2	0.4	0.9

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
990827-41	6.8	37.2	56.3	8.8	38	8.2	1.6	8.4	1.1	5.9	1.1	2.6	0.3	1.8	0.3	30.2	1.5	0.7	0.9
990827-42	7.5	24.7	54.7	6.4	28.9	6.5	0.6	6.6	0.9	5.0	0.8	2.2	0.3	1.5	0.2	27.1	1.2	1.0	0.4
990827-43	7.7	14.8	14.1	4.0	19.1	4.1	0.5	4.0	0.6	3.3	0.7	2.0	0.2	1.5	0.2	25.1	0.7	0.4	0.6
990827-44	7.6	16.8	32.1	5.2	24.3	5.7	1.0	4.9	0.7	3.8	0.8	2.2	0.3	1.7	0.3	27.8	0.7	0.8	0.9
990827-45	7.6	20.3	32.4	4.6	19.7	4.5	0.7	4.4	0.6	3.1	0.6	1.4	0.2	1.2	0.2	17.7	1.2	0.8	0.7
990827-46	6.7	55.3	118.9	14.2	60.5	12.7	2.3	10.5	1.3	6.5	1.2	2.9	0.3	2.4	0.4	32.7	1.7	1.0	0.9
990828-47	7.0	49.1	90.6	12.3	49.5	10.2	1.9	8.8	1.2	6.5	1.2	3.2	0.4	2.4	0.4	37.1	1.5	0.9	1.0
990828-48	7.0	86.7	85.7	11.2	49.1	10.5	2.1	8.1	1.3	6.4	1.4	3.8	0.5	2.6	0.4	33	2.5	0.6	1.1
990828-49	7.7	16.3	21.7	4.0	18.7	4.3	0.7	4.1	0.6	2.9	0.6	1.5	0.2	1.2	0.2	20.6	1.0	0.6	0.8
990828-50	7.6	53.6	74.3	10.7	45.5	9.5	1.8	8.4	1.2	6.1	1.1	2.8	0.3	1.9	0.3	33.3	2.1	0.7	1.0
990828-51	7.7	39.5	33.3	5.6	25.3	6.3	1.0	6.5	1.0	5.7	1.2	3.6	0.5	3.1	0.5	53.8	0.9	0.5	0.7
990828-52	8.0	14.8	19.2	4.5	21.6	4.9	0.9	5.3	0.8	5.2	1.2	3.3	0.4	2.3	0.4	53.7	0.5	0.5	0.8
990828-53	6.4	65.9	78.0	10.9	45.2	9.6	1.6	8.3	1.1	5.6	1.0	2.8	0.4	2.1	0.3	30.2	2.3	0.7	0.9
Average	7.4	35.0	50.5	7.4	32.4	7.0	1.2	6.5	0.9	5.0	1.0	2.6	0.3	2.0	0.3	32.9	1.3	0.7	0.8
Wuyanghe River																			
990829-54	7.9	9.5	8.5	2.2	9.6	2.6	0.4	2.5	0.4	2.0	0.5	1.2	0.2	1.1	0.2	20.6	0.6	0.4	0.8
990829-55	7.7	13.4	12.2	1.2	5.4	1.3	0.3	2.1	0.2	1.4	0.3	0.9	0.1	0.7	0.1	12.3	1.4	0.6	0.7
990829-56	7.9	7.4	6.5	1.6	8.2	2.2	0.3	2.2	0.4	2.2	0.5	1.3	0.2	1.1	0.2	22.2	0.5	0.4	0.7
990829-57	8.0	8.7	12.0	3.5	9.7	2.7	0.6	2.8	0.5	2.9	0.7	1.9	0.3	1.6	0.2	30.8	0.4	0.5	1.0
990829-58	7.9	8.1	7.2	1.7	8.3	2.2	0.5	2.7	0.4	2.9	0.6	2.0	0.3	1.5	0.2	29.4	0.4	0.4	0.9
990829-59	8.1	9.9	9.4	1.0	4.6	1.4	0.1	1.4	0.2	1.4	0.3	0.7	0.1	0.7	0.1	11.4	1.0	0.6	0.5
990829-60	8.1	9.4	11.9	2.1	9.6	2.3	0.4	2.4	0.4	2.6	0.6	1.7	0.3	1.5	0.2	26.6	0.5	0.6	0.9

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
990829-61	8.0	9.1	11.1	1.9	8.4	1.9	0.3	2.2	0.4	2.5	0.5	1.6	0.2	1.3	0.2	19.4	0.5	0.6	0.7
Average	8.0	9.4	9.9	1.9	8.0	2.1	0.4	2.3	0.4	2.2	0.5	1.4	0.2	1.2	0.2	21.6	0.7	0.5	0.8
<i>Acid-soluble loads</i>																			
Wujiang River system																			
The upper reaches of Wujiang River																			
990804-1	878	2293.8	272.7	1193.5	277.2	63.1	247.4	33.0	157.3	26.5	61.5	7.0	37.9	4.8	753.7	1.7	1.1	1.1	1.1
990804-2	471	1214.4	148.6	672	173.6	37.7	162.4	23.9	121.3	21.8	53	6.2	35.4	4.7	686.4	1.0	1.1	1.1	1.1
990804-3	6451.1	15875.4	1870	7732.5	1642.4	380.8	1454.4	200.6	991.2	168	392.1	44.2	230.2	28.5	4774.6	2.1	1.1	1.2	1.2
990804-4	6027.9	15026.9	1771	7241.8	1606.8	370.2	1390.4	194.1	964.1	161.4	389	46.9	267.9	33.8	4517	1.7	1.1	1.2	1.2
990805-5	1235.8	2969.5	349.6	1438	318.2	69.1	280.7	39.8	199.7	34.5	82.5	9.9	55.0	7.3	980.6	1.7	1.0	1.1	1.1
990805-6	1125.7	2970.8	305.5	1294	294.4	66.4	266.4	39.2	209.5	38.6	98.1	12.3	72.9	9.7	1270.5	1.1	1.2	1.1	1.1
990805-7	4057.8	10819.6	1307	5489.5	1339	314	1165.6	163.9	812.6	134.3	326.6	41	248.4	32.6	3783.4	1.2	1.1	1.2	1.2
990805-8	2072.4	4880.2	560.9	2257.9	468.8	100	395.4	54.3	268.7	45.4	108.7	13.3	78.5	10.2	1259	1.9	1.0	1.1	1.1
990806-9	103.7	240	30.8	126.2	29.5	6.1	26.0	3.6	16.6	2.9	7.1	0.8	4.7	0.6	90.3	1.6	1.0	1.0	1.0
Average	2491.5	6254.5	735.1	3049.5	683.3	156.4	598.7	83.6	415.7	70.4	168.7	20.2	114.5	14.7	2012.8	1.6	1.1	1.1	1.1
The middle reaches of Wujiang River																			
990806-10	362.8	929.3	124.7	574.1	144.5	32.7	140.0	19.2	90.5	14.9	34.1	3.8	20.7	2.7	424.8	1.3	1.0	1.1	1.1
990806-11	555.3	1861.2	154.6	636.4	139.3	27.0	123.1	17.2	88.2	15.9	40.3	4.8	28.1	3.9	499.2	1.5	1.5	1.0	1.0
990806-12	504.4	1177.3	132.6	537.6	128.2	29.9	132.3	22.1	123.2	22.8	56.8	7.2	42.4	5.7	954	0.9	1.1	1.1	1.1
990814-13	46.8	190.7	12.1	47.8	10.5	2.1	9.9	1.4	7.3	1.4	3.8	0.5	2.9	0.4	43.4	1.2	1.9	1.0	1.0
990814-14	2242.8	5028	645.9	2643.3	573.5	127.7	494.4	68.7	338.8	57.1	137.6	16.5	94.8	12.6	1597.2	1.7	1.0	1.1	1.1
990814-15	129.5	321.7	38.9	158.6	34.2	5.4	26.4	3.7	17.9	3.0	7.7	1.0	5.8	0.9	89.9	1.6	1.0	0.9	0.9
990814-16	479.2	1561.1	130.1	517.9	111.4	21.9	100.1	14.3	71.6	12.8	32.0	4.0	24.2	3.3	375.7	1.5	1.4	1.0	1.0
990814-17	1394.5	3402.6	458.6	1899.4	384.1	52.9	302.8	37.2	164	26.7	63.3	7.0	41.0	5.5	794.2	2.5	1.0	0.7	0.7
990814-18	312.9	1050.7	80.4	317.2	73.7	14.7	71.8	10.9	58.1	10.6	27.1	3.5	21.4	2.9	306.9	1.1	1.5	1.0	1.0

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
990815-19		122.8	447.9	33.7	136.1	30.6	5.2	25.9	3.7	20.1	3.6	9.3	1.2	7.2	1.1	112.6	1.3	1.6	0.9
990815-20		239.74	616.98	67.46	270.26	58.25	12.08	51.35	7.36	36.92	6.65	16.43	2.07	12.51	1.74	200.48	1.4	1.1	1.0
990816-21		354.5	947.2	100.4	407.3	93.7	18.3	79.3	11.7	59.1	10.4	25.9	3.2	19.2	2.6	311.7	1.4	1.2	1.0
990816-22		340.8	882.4	99.1	429.5	107.4	21.7	102.7	15.6	82.4	15.1	37.7	4.8	28.5	3.8	463.9	0.9	1.1	1.0
990816-23		334.8	886.9	96.2	384.1	89.4	17.8	77.2	11.3	57.5	10.3	25.3	3.0	17.1	2.3	300.2	1.4	1.1	1.0
990816-24		106.7	310.5	35.3	158.9	46.6	9.0	40.8	6.4	33.5	6.0	14.5	1.8	10.4	1.5	179.8	0.8	1.2	1.0
990816-25		294.7	725.5	84.4	342.5	81.1	16.4	70.5	10.0	50.2	8.7	21.0	2.6	15.4	2.2	253.5	1.4	1.1	1.0
990819-35		1415.3	3644.5	416.7	1714	401.9	77.9	367.3	56.9	298.3	55.6	141.8	17.7	101.8	13.9	1673.5	1.0	1.1	1.0
990819-36		127.1	427.4	37.5	160.7	40.0	8.0	38.6	5.8	30.3	5.3	13.1	1.7	9.6	1.3	159.1	1.0	1.4	1.0
990819-37		1167.4	3507.2	353	1520.4	430.8	84.4	433.9	69.3	365.9	67.1	165.3	20.0	112.8	14.9	1911.8	0.8	1.3	0.9
Average		554.3	1469.4	163.2	676.6	156.8	30.8	141.5	20.7	104.9	18.6	45.9	5.6	32.4	4.4	560.6	1.3	1.2	1.0
The lower reaches of Wujiang River																			
990816-26		239.8	693.2	72.9	310.8	79.4	15.6	72.5	10.9	55.2	10.0	24.9	2.9	16.4	2.2	296.9	1.1	1.2	1.0
990816-27		728.8	2133.5	269.1	1274.7	411.4	84.4	408.7	60.1	303.3	52.5	124.7	14.7	78.7	10	1484.3	0.7	1.1	1.0
990816-28		1006.6	2505.7	241.7	959.6	193.7	37.8	169.5	22.5	112.1	20.2	49.3	6.1	35.2	4.8	608.5	2.1	1.2	1.0
990817-29		361.8	735.4	90.9	359.2	69.9	11.3	56.0	7.2	33.4	5.9	14.1	1.7	9.8	1.4	193.3	2.7	0.9	0.9
990817-30		822.5	2258.6	249.4	1060.2	263.1	53.1	234.3	34.3	173.7	30.6	73.7	9.1	51.8	7.1	882	1.2	1.1	1.0
990817-31		824.9	2180.8	240.9	1016.1	245.3	49.2	216.8	31.7	158.1	28.3	67.9	8.3	46.2	6.1	801.2	1.3	1.1	1.0
990817-32		238	587.4	62	257.8	58.3	9.9	48.9	7.0	35.4	6.2	15.9	1.9	11.6	1.6	187.5	1.5	1.1	0.9
990817-33		73.4	200.4	22.1	93.7	23.7	4.7	21.2	3.1	15.5	2.7	6.6	0.8	4.5	0.6	77.3	1.2	1.1	1.0
990817-34		448.9	1260.1	138.2	604.4	157.4	31.6	143.4	21.2	107.2	18.6	45.7	5.5	31.6	4.3	539.1	1.0	1.2	1.0
Average		527.2	1395.0	154.1	659.6	166.9	33.1	152.4	22.0	110.4	19.4	47.0	5.7	31.8	4.2	563.3	1.4	1.1	1.0

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
Yuanjiang River system																			
Qingshuijiang River																			
990826-38		6212.3	20178.5	2358.5	10944.5	3157.4	621.3	2995.7	454.8	2319.8	416.9	1032	126.4	690	89.7	11690.9	0.7	1.2	1.0
990826-39		14762.6	43914.5	5357.7	24151.9	6383.1	1159.4	5421.5	788.6	3809.8	656.5	1570	185.4	1020.1	135.3	18901.5	1.1	1.1	0.9
990826-40		3181.1	9678.1	1173.8	5238	1369.2	270.8	1317.0	188.2	942.8	166.6	405.6	48.0	268.7	35.9	4842.7	0.9	1.1	1.0
990827-41		2331.8	5222.8	612.2	2480.1	554.7	106.3	497.0	71.7	345.2	55.1	122.2	13.4	73.9	9.2	1552.7	2.3	1.0	1.0
990827-42		1540.5	4651.7	566.3	2492.1	667.3	127.6	614.8	85.4	426.0	74.4	181.2	22.0	128.8	17.3	2134.7	0.9	1.1	0.9
990827-43		5347.5	16379.1	1958.8	8801.6	2299.7	429.3	2059.2	293.3	1445.6	254.2	610.4	71.3	385.4	50.1	6919	1.0	1.1	0.9
990827-44		7791	23397	2802.7	12415	3248.5	601.8	2875.6	404.6	1984.4	345.8	834.3	97.9	545.4	72.1	9258.8	1.1	1.1	0.9
990827-45		5207.7	16483.3	1963.8	8712.1	2195.7	403.1	1911	266.3	1290.7	223.1	526.1	61.4	339.6	45.4	5989.9	1.1	1.2	0.9
990827-46		349.8	989.6	86.0	345.9	70.8	12.9	59.9	7.7	37.3	6.4	15.0	1.9	11.1	1.6	181.4	2.3	1.3	0.9
990828-47		1006.6	2505.7	241.7	959.6	193.7	37.8	169.5	22.5	112.1	20.2	49.3	6.1	35.2	4.8	608.5	2.1	1.2	1.0
990828-48		933.4	2044.7	215.3	842.2	162.9	31.4	137.2	19.4	91.2	15	34.3	3.7	21.3	2.6	448.6	3.2	1.1	1.0
990828-49		3412.8	9546.5	1153	4978.6	1259.2	237.6	1106.1	162.2	797.8	138.2	334.4	39.6	219.4	28.8	3879.1	1.1	1.1	1.0
990828-50		3354.8	9531.6	1053.1	4375.8	1040.6	195.2	891.3	127.6	623.4	106.6	249.8	29.1	167.7	22.2	3012.2	1.5	1.2	1.0
990828-51		588.9	1483.8	171.6	710.7	178.4	34.4	156.6	23.8	121.4	21.8	54.2	6.6	38.4	5.2	689.6	1.1	1.1	1.0
990828-52		2020.0	5413.4	676	2849	690.6	131.5	600.8	86.8	434.4	75.5	181.5	21.1	116.6	15.5	2262.8	1.3	1.1	1.0
990828-53		1948.8	4695.8	472.3	1856.7	377.1	68.1	316.4	42.0	206.7	36.4	88.3	10.5	60.8	8.1	924.8	2.4	1.1	0.9
Average		3749.4	11007.3	1303.9	5759.6	1490.6	279.3	1320.6	190.3	936.8	163.3	393.0	46.5	257.7	34.0	4581.1	1.5	1.1	0.9
Wuyanghe River																			
990829-54		225.4	578.6	63.3	259.6	65.2	12.2	55.9	8.3	41.6	7.1	17.3	2.1	12.2	1.6	216.8	1.4	1.1	1.0
990829-55		135.9	325.5	35.2	141.9	34.1	6.7	30.6	4.6	23.2	4.2	9.9	1.3	7.1	1	125.8	1.4	1.1	1.0
990829-56		215.2	517.1	57.6	243.3	61.6	11.7	54.7	7.9	39.3	7.0	17.5	2.1	12.3	1.7	204.4	1.3	1.1	1.0
990829-57		328.1	874.0	91.3	375.8	95.5	18.8	86.5	13.0	63.7	11.4	28.1	3.2	19.2	2.5	318.9	1.3	1.2	1.0
990829-58		728.3	1672.2	200.0	854.3	220.2	41.9	205.1	28.9	144.5	24.6	58.9	7.0	39.7	5.3	690.4	1.4	1.0	0.9

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
990829-59		463.0	1036.5	110.6	447.7	127.3	25.3	124.3	18.1	94.3	17.3	43.7	5.4	32.8	4.4	512.2	1.0	1.1	1.0
990829-60		91.4	179.2	18.9	74.7	17.0	3.2	15.8	2.5	14.3	2.9	7.3	1.0	5.8	0.8	90.4	1.2	1.0	0.9
990829-61		169.8	447.4	44.2	178.9	41.9	7.9	37.0	5.7	29.2	5.4	13.4	1.6	10.3	1.4	148.3	1.2	1.2	1.0
Average		294.6	703.8	77.6	322.0	82.9	16.0	76.2	11.1	56.3	10.0	24.5	3.0	17.4	2.3	288.4	1.3	1.1	1.0
<i>Suspended particulate matters</i>																			
Wujiang River system																			
The upper reaches of Wujiang River																			
990804-1		64.5	146.3	16.6	66.1	13.8	3.2	12.5	1.7	10.3	1.8	4.5	0.7	4.1	0.6	50.7	1.2	1.0	1.2
990804-2		30.2	60.1	6.9	26.0	5.8	1.1	5.0	0.7	4.5	0.8	2.3	0.3	2.1	0.3	24.7	1.1	1.0	1.0
990804-3		84.4	165.5	21.9	88.0	18.2	4.0	15.7	2.1	12.5	2.4	6.8	1.0	6.3	0.9	71.7	1.0	0.9	1.1
990804-4		73.4	147.7	18.8	76.1	15.9	3.5	14	2.0	12.1	2.2	6.3	0.9	5.6	0.8	62.0	1.0	0.9	1.1
990805-5		80.6	172.2	18.4	71.1	14.2	3.1	12.7	1.9	11.1	2.1	6.1	0.8	5.3	0.8	60.1	1.1	1.0	1.1
990805-6		83.2	179.2	18.8	71.1	14.1	3.1	13.6	1.9	12.2	2.3	6.7	0.9	6	0.9	70.9	1.0	1.1	1.1
990805-7		102.3	214.2	24	95.2	18.6	4.1	17.0	2.3	14.3	2.7	7.3	1.0	6.4	0.9	75.5	1.2	1.0	1.1
990805-8		87.2	185.9	19.9	74.5	14.8	3.0	12.3	1.8	11.4	2.1	5.8	0.9	5.5	0.8	60.0	1.2	1.0	1.1
990806-9		8.0	17.3	1.9	7.0	1.7	0.3	1.2	0.2	1.2	0.2	0.5	0.1	0.4	0.1	6.0	1.5	1.0	0.9
Average		68.2	143.2	16.4	63.9	13.0	2.8	11.6	1.6	10.0	1.8	5.1	0.7	4.6	0.7	53.5	1.1	1.0	1.1
The middle reaches of Wujiang River																			
990806-10		21.0	53.3	7.0	29.9	7.6	1.7	7.8	0.9	4.6	0.8	2.0	0.2	1.3	0.2	19.9	1.2	1.0	1.0
990806-11		41.2	101.6	9.1	33.8	6.7	1.3	6.0	0.8	5.0	1.0	3.0	0.4	2.8	0.4	29.9	1.1	1.2	0.9
990806-12		27.4	63.6	6.4	24.3	5.9	1.2	6.2	0.9	5.4	1.1	2.6	0.3	1.9	0.3	36.3	1.1	1.1	0.9
990814-13		0.5	1.1	0.1	0.3	0.1	0.01	0.1	0.01	0.1	0.02	0.04	0.008	0.1	0.007	0.5	0.4	1.2	0.6
990814-14		43.1	96.1	10.5	39	7.8	1.6	7.1	1.0	5.9	1.1	3.0	0.4	3.0	0.4	31	1.1	1.0	1.0
990814-15		5.4	11.7	1.0	2.6	0.9	0.03	0.8	0.1	0.6	0.1	0.4	0.1	0.4	0.05	3.5	1.0	1.1	0.2
990814-16		26.7	59.4	5.5	19.5	4.1	0.6	3.9	0.5	3.5	0.7	2.0	0.3	1.8	0.3	19.1	1.1	1.1	0.7

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
990814-17		139.4	334.5	40.1	163.7	31.8	4.4	26.9	3.2	16.3	2.6	6.8	0.9	5.4	0.8	74.1	1.9	1.0	0.7
990814-18		13.3	34.1	2.9	9.5	2.3	0.3	2.2	0.3	2.2	0.4	1.1	0.2	1.1	0.2	10.7	0.9	1.3	0.7
990815-19		16.3	34.6	3.4	11.1	2.4	0.3	2.5	0.3	1.9	0.4	1.1	0.2	1.1	0.2	10.9	1.1	1.1	0.5
990815-20		29.1	62.7	6.5	23	5.6	0.9	4.4	0.6	4.1	0.7	2.2	0.3	1.9	0.3	20.5	1.1	1.1	0.8
990816-21		9.5	20.7	2.1	7.8	1.7	0.3	1.5	0.2	1.3	0.2	0.7	0.1	0.7	0.1	6.9	1.0	1.1	0.8
990816-22		10.8	20.4	2.4	9.1	1.9	0.3	1.8	0.2	1.7	0.3	0.9	0.2	0.9	0.1	10.1	0.9	0.9	0.8
990816-23		11.1	24.1	2.5	9.4	2.0	0.3	1.8	0.3	1.6	0.3	0.8	0.1	0.7	0.1	8.4	1.2	1.1	0.8
990816-24		3.8	7.8	0.7	2.2	0.5	0.03	0.4	0.04	0.4	0.1	0.2	0.03	0.2	0.03	2.1	1.4	1.1	0.3
990816-25		73.7	156	17.5	63.3	14.2	2.2	12.2	1.6	10.4	2.0	5.6	0.8	5.1	0.8	57	1.1	1.0	0.8
990819-35		5.9	12.2	1.2	4.0	0.9	0.1	0.7	0.1	0.7	0.1	0.4	0.1	0.4	0.1	3.8	1.1	1.1	0.5
990819-36		65	140.6	13.2	46.1	9.8	1.3	9.2	1.2	8.8	1.7	4.7	0.8	4.6	0.7	46.5	1.0	1.1	0.6
990819-37		44.8	97.7	9.7	36.3	7.1	1.4	7.1	0.9	6.1	1.2	3.3	0.5	3.2	0.5	32.2	1.0	1.1	0.9
Average		30.9	70.1	7.5	28.2	6.0	1.0	5.4	0.7	4.2	0.8	2.1	0.3	1.9	0.3	22.3	1.1	1.1	0.7
The lower reaches of Wujiang River																			
990816-26		11.0	24	2.3	8.2	1.6	0.2	1.2	0.2	1.2	0.2	0.6	0.1	0.6	0.1	6.3	1.4	1.1	0.8
990816-27		54.9	107.5	11.1	40.3	7.4	1.2	5.9	0.8	5.2	1.0	3.0	0.4	2.8	0.4	29.8	1.4	1.0	0.9
990816-28		10.7	24.7	2.4	8.9	2.2	0.3	1.9	0.3	1.8	0.3	1.1	0.2	1.3	0.2	10	0.6	1.1	0.7
990817-29		36.6	92.7	8.9	30	7.6	0.7	6.0	0.8	4.4	0.6	1.6	0.2	1.5	0.2	19.7	1.8	1.2	0.5
990817-30		43.6	90.7	9.8	36.3	7.2	1.4	6.2	0.8	5.5	1.0	3.0	0.4	2.8	0.4	29.7	1.1	1.0	1.0
990817-31		13.1	27.2	2.8	11.7	3.1	0.4	2.2	0.2	1.6	0.3	0.9	0.2	0.8	0.1	8.6	1.2	1.0	0.6
990817-32		12.7	27.8	2.6	8.9	1.9	0.2	1.6	0.2	1.3	0.2	0.7	0.1	0.6	0.1	6.9	1.6	1.1	0.6
990817-33		39.0	80.6	8.5	31.6	6.1	1.1	5.4	0.7	4.4	0.9	2.5	0.4	2.4	0.4	25.3	1.2	1.0	0.9
990817-34		59.3	119.3	12.6	46.8	8.9	1.6	7.7	1.0	6.8	1.3	3.6	0.5	3.5	0.5	37.3	1.3	1.0	0.9
Average		31.2	66.1	6.8	24.7	5.1	0.8	4.2	0.6	3.6	0.6	1.9	0.3	1.8	0.3	19.3	1.3	1.1	0.8

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
Yuanjiang River system																			
Qingshuijiang River																			
990826-38	73.6	149.8	16.6	64.6	13.2	2.0	12.4	1.7	10.4	1.9	5.5	0.8	5.2	0.8	54	1.0	1.0	0.8	0.8
990826-39	112.6	232.9	31.6	130.8	29.5	5.3	25.5	3.2	19.1	3.2	8.6	1.3	7.2	1.1	97.1	1.2	0.9	0.9	0.9
990826-40	46.2	99.9	11.2	44.4	9.4	1.6	8.5	1.2	7.0	1.3	3.5	0.5	3.2	0.5	36.4	1.1	1.0	0.8	0.8
990827-41	17.7	38.9	4.2	15.9	3.5	0.6	3.4	0.5	3.6	0.7	2.1	0.3	2.2	0.4	20.3	0.6	1.0	0.8	0.8
990827-42	52.9	115.3	12.3	46.5	9.8	1.6	8.4	1.1	6.7	1.2	3.3	0.5	3.1	0.5	36.5	1.3	1.0	0.8	0.8
990827-43	81.6	154.4	20.3	81.4	17.4	3.1	16.2	2.1	13.3	2.3	6.8	1.0	6.2	0.9	69.7	1.0	0.9	0.9	0.9
990827-44	70.9	150.2	18	73.1	17.1	3.0	14.4	1.9	11.3	2.1	6.0	0.9	5.1	0.8	62.2	1.0	1.0	0.9	0.9
990827-45	38.6	88.6	10.6	43.2	10	1.8	8.7	1.1	6.8	1.2	3.4	0.5	3.0	0.5	35.6	0.9	1.0	0.9	0.9
990827-46	14.5	35.9	3.3	11.9	2.9	0.4	2.6	0.3	2.5	0.5	1.4	0.2	1.6	0.3	13.2	0.7	1.2	0.8	0.8
990828-47	10.7	24.7	2.4	8.9	2.2	0.3	1.9	0.3	1.8	0.3	1.1	0.2	1.3	0.2	10.0	0.6	1.1	0.7	0.7
990828-48	13.9	30.3	3.3	12	2.4	0.4	2.2	0.3	1.7	0.3	0.9	0.1	0.7	0.1	9.1	1.5	1.0	0.9	0.9
990828-49	52.2	114.9	13	52.5	11.3	2.0	10.3	1.4	8.5	1.5	4.5	0.7	4.1	0.6	46.7	0.9	1.0	0.9	0.9
990828-50	25.6	52.7	5.9	23.2	4.9	1.0	4.4	0.7	3.8	0.8	2.2	0.4	2.3	0.4	21.1	0.8	1.0	1.0	1.0
990828-51	14.9	29.1	3.3	11.8	2.6	0.4	2.2	0.3	2.1	0.4	1.2	0.2	1.1	0.2	12.4	1.0	1.0	0.9	0.9
990828-52	5.8	12.5	1.2	4.2	1.0	0.2	0.9	0.1	0.8	0.2	0.5	0.1	0.5	0.1	4.6	0.9	1.1	1.0	1.0
990828-53	6.4	13.6	1.4	5	1.2	0.2	1.1	0.2	1.1	0.2	0.6	0.1	0.6	0.1	5.9	0.8	1.1	0.7	0.7
Average	39.9	84.0	9.9	39.3	8.7	1.5	7.7	1.0	6.3	1.1	3.2	0.5	3.0	0.5	33.4	1.0	1.0	0.8	0.8
Wuyanghe River																			
990829-54	8.7	17.9	1.9	6.6	1.5	0.2	1.4	0.2	1.1	0.2	0.7	0.1	0.7	0.1	6.7	0.9	1.0	0.7	0.7
990829-55	7.3	15.6	1.7	6.1	1.5	0.2	1.3	0.1	1.1	0.2	0.6	0.1	0.5	0.1	5.9	1.1	1.0	0.7	0.7
990829-56	10.9	21.8	2.4	8.2	2.0	0.3	1.9	0.3	1.6	0.3	0.9	0.1	0.8	0.1	8.9	1.0	1.0	0.7	0.7
990829-57	12.7	25.3	2.8	9.6	1.9	0.3	1.8	0.3	1.8	0.4	1.0	0.2	1.1	0.2	10.1	0.9	1.0	0.8	0.8
990829-58	14	27.4	3.0	10.6	2.2	0.3	2.3	0.3	1.9	0.4	1.1	0.2	1.2	0.2	11.2	0.9	1.0	0.7	0.7

Table 1 continued

Date and sample number	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	(La/Yb) _N	Ce anomaly	Eu anomaly
990829-59		9.0	16.9	1.7	5.7	1.4	0.1	1.3	0.1	1	0.2	0.6	0.1	0.5	0.1	5.1	1.3	1.0	0.4
990829-60		2.3	4.2	0.4	1.3	0.3	0.03	0.3	0.04	0.3	0.1	0.2	0.02	0.2	0.02	1.5	0.8	1.0	0.5
990829-61		6.6	14.1	1.3	4.3	1.1	0.1	1.0	0.1	1	0.2	0.6	0.1	0.6	0.1	5.5	0.8	1.1	0.4
Average		8.9	17.9	1.9	6.6	1.5	0.2	1.4	0.2	1.2	0.3	0.7	0.1	0.7	0.1	6.9	1.0	1.0	0.6
Standards																			
BCR-1 (basalt) (n = 4)		26.0 ± 1.3	53.3 ± 1.8	6.75 ± 0.21	28.2 ± 1.1	6.66 ± 0.14	1.89 ± 0.04	6.63 ± 0.21	1.07 ± 0.04	6.69 ± 0.09	1.36 ± 0.05	3.74 ± 0.13	0.52 ± 0.04	3.60 ± 0.11	0.53 ± 0.04	36.5 ± 1.5			
BCR-1 Certified		24.9	53.9	6.8	28.8	6.59	1.98	6.68	1.05	6.34	1.26	3.63	0.56	3.38	0.51	38			
GSR-6 (limestone) (n = 4)		13.7 ± 0.2	27.9 ± 0.6	3.25 ± 0.08	12.0 ± 0.4	2.31 ± 0.02	0.50 ± 0.01	1.91 ± 0.08	0.31 ± 0.01	1.77 ± 0.08	0.35 ± 0.01	0.95 ± 0.01	0.14 ± 0.01	0.81 ± 0.03	0.14 ± 0.01	9.38 ± 0.24			
GSR-6 Certified		14.6	25.4	3.4	12	2.4	0.51	1.9	0.35	1.6	0.33	1.1	0.17	0.9	0.14	9.1			

Ce anomaly = $2(\text{Ce}/\text{Ce}^*)/(\text{La}/\text{La}^* + \text{Pr}/\text{Pr}^*)$, Eu anomaly = $2(\text{Eu}/\text{Eu}^*)/(\text{Sm}/\text{Sm}^* + \text{Gd}/\text{Gd}^*)$, where Ce*, La*, Pr*, Eu*, Sm* and Gd* represent the concentrations of the respective REE in the PAAS

REE standards concentrations in mg/kg; GSR-6: Chinese geochemistry reference material

4.1 Dissolved Load REE

4.1.1 Variation of Dissolved Load REE

From Table 1, we can see that the dissolved load REE contents of these rivers are very low. Although the samples were collected during high-flow season, the concentrations of dissolved load REE in these rivers are similar to those samples collected in winter during low-flow season by Han and Liu (2007). The concentrations of most of the dissolved load REE from the Wujiang River and the Wuyang River are lower than 100 ng/l, while the concentrations of most samples from the Qingshuijiang River are higher than those from the Wujiang River and the Wuyanghe River.

4.1.2 LREE/HREE Fractionation

The PAAS-normalized REE patterns for the dissolved load are characterized by distinct negative Ce and Eu anomalies (Fig. 2a). It is clear that these water samples do not show a flat PAAS-normalized REE pattern. The shale-normalized ratio of La/Yb is a common indicator to demonstrate the enrichment of light REE (LREE) over heavy REE (HREE). From Table 1, it can be seen that the $(La/Yb)_N$ ratios for the water samples collected from the upper reaches of the Wujiang River vary from 0.6 to 1.3, averaging 1.0, and most of samples show slight HREE depletion with $(La/Yb)_N > 1$. The $(La/Yb)_N$ ratios vary from 0.3 to 2.2, averaging 0.7 for the samples collected from the middle reaches of the Wujiang River, while the $(La/Yb)_N$ ratios for the samples collected from the lower reaches of the Wujiang River vary from 0.2 to 1.5, averaging 0.6. So, the LREE/HREE fractionation of the dissolved load is characterized by HREE enrichment from the upper-to-lower reaches of the Wujiang River. Water samples from the Wuyanghe River also show HREE enrichment patterns, with $(La/Yb)_N = 0.4\text{--}1.4$, averaging 0.7. As compared to those samples from the Wujiang and Wuyanghe rivers, water samples from the Qingshuijiang River that winds its way through a clastic terrain have lower pH values, and most of samples from the Qingshuijiang River show LREE enrichment patterns, with $(La/Yb)_N = 0.5\text{--}2.3$, averaging 1.3.

4.1.3 Ce and Eu Anomalies

Due to their special electron configuration in the outer shell, Ce and Eu occur as Ce(IV) and Eu(II). In general, the Eu anomaly of river water is determined by the petrogenesis of the rocks in the drainage basin, and the oxidation of Ce(III) to Ce(IV) does occur during weathering. The deviation of Ce and Eu relative to the neighboring elements is usually defined as Ce and Eu anomaly. Ce and Eu anomaly (DeBaar et al. 1985; Elderfield 1988; Sholkovitz et al. 1994) is defined as follows:

$$\text{Ce anomaly} = 2(\text{Ce}/\text{Ce}^*)/(\text{La}/\text{La}^* + \text{Pr}/\text{Pr}^*),$$

$$\text{Eu anomaly} = 2(\text{Eu}/\text{Eu}^*)/(\text{Sm}/\text{Sm}^* + \text{Gd}/\text{Gd}^*),$$

where Ce^* , La^* , Pr^* , Eu^* , Sm^* , and Gd^* represent the concentrations of the respective REE in the average shale. Negative and positive Ce(Eu) anomalies are defined as values of less and greater than 1, respectively.

Most of the calculated Ce anomalies of our samples are negative (<1 ; Table 1, Fig. 3c). Water samples from the Wuyanghe River have the highest pH value with the most

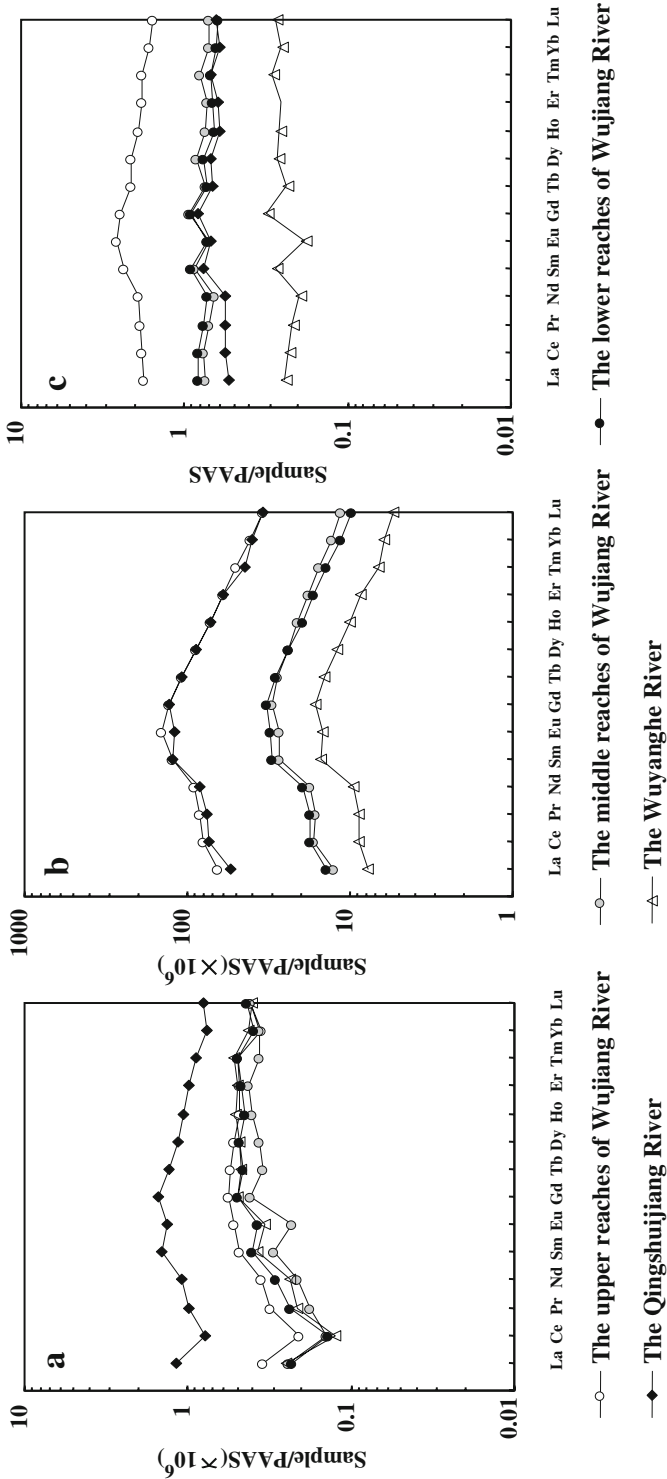


Fig. 2 Average of **a** dissolved load, **b** acid-soluble load, and **c** SPM REE abundance normalized to the PAAS patterns in different reaches of the Wujiang River, the Wuyanghe River and the Qingshuijiang River, respectively

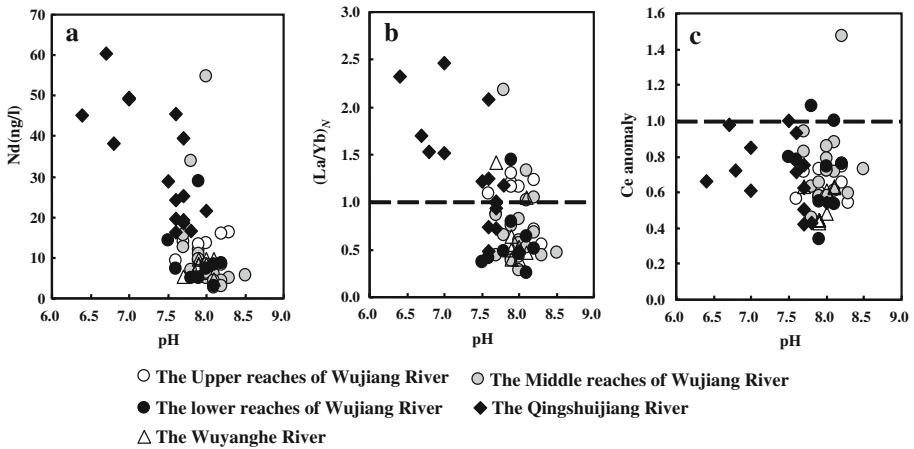


Fig. 3 a Nd concentrations, b $(La/Yb)_N$ ratios, and c Ce anomaly in the dissolved loads versus pH. Dashed line indicates crustal

remarkable negative Ce anomaly (Ce anomaly = 0.5). Negative Eu anomalies were also found in water samples from these three rivers. Most of water samples collected from the upper reaches of the Wujiang River show negative Eu anomalies, ranging from 0.4 to 1.7, averaging 0.9. The negative Eu anomalies vary from 0.2 to 1.2 (averaging 0.6) for the samples collected from the middle reaches of the Wujiang River, while the anomalies vary from 0.6 to 1.3 (averaging 0.8) for the samples collected from the lower reaches of the Wujiang River. Water samples from the Wuyanghe River also show negative Eu anomalies, with negative Eu = 0.4–1.1, averaging 0.8. Water samples from the Qingshuijiang River have negative Eu = 0.5–0.9, averaging 0.8.

4.2 Acid-Soluble Load REE

4.2.1 Variation of Acid-Soluble Load REE

Table 1 shows that the concentrations of acid-soluble load REE have a sharp increase, which is 6 to 634 times higher than that of dissolved load REE. The middle REE (MREE, from Sm to Dy) concentrations are preferentially increased. In comparison with those samples among the three rivers, the samples collected from the upper reaches of the Wujiang River and the Qingshuijiang River show the largest MREE enrichment in acid-soluble load, while those from the Wuyanghe River show the smallest MREE enrichment in acid-soluble load.

4.2.2 LREE/HREE Fractionation

The PAAS-normalized REE patterns for the acid-soluble load are shown in Fig. 2b. Clearly, the acid-soluble load REE fractionation has similar REE distribution pattern in the studied rivers. Water samples of acid-soluble load from these three rivers show the REE distribution patterns characterized by MREE and slight LREE enrichment.

4.2.3 Ce and Eu Anomalies

Most of the calculated Ce anomalies of acid-soluble load in these three rivers are a little positive (>1 ; Table 1) or without anomalies, except for one sample (990817-29). Most of the water samples have no Eu anomalies, except for those from the Qingshuijiang River. This is because negative Eu anomalies occur less often in leachates than in SPM.

4.3 REE of SPM

4.3.1 Variation of REE Concentration in SPM

Distribution coefficients of 100,000 to 1,000,000 for REE partitioning between dissolved load and SPM in our study. SPM derived from weathering of the rocks contains almost all of the REE in river water. The total amount of REE in SPM samples collected from the Wujiang and Qingshuijiang rivers is more than 100 mg/kg, exceeding that of the average upper continental crust (UCC) (Taylor and McLennan 1985). The concentrations of REE in SPM from the Wuyanghe River vary from 9 to 65 mg/kg, with an average of 42 mg/kg, lower than those of SPM from the Wujiang and Qingshuijiang rivers. This is consistent with the fact that the Wuyanghe River winds its way through the strata composed of dolomitic limestones.

4.3.2 LREE/HREE Fractionation

The PAAS-normalized REE patterns for the SPM are shown in Fig. 2c. Clearly, samples from the upper reaches of the Wujiang River show flat REE distribution patterns, with an average $(La/Yb)_N = 1.1$ (from 0.96 to 1.2). The $(La/Yb)_N$ ratios vary from 0.6 to 1.9 (averaging 1.1) in samples from the middle reaches, and vary from 1.2 to 1.8 (averaging 1.4) in samples from the lower reaches of the Wujiang River. The SPM samples from the Wuyanghe River also show flat REE distribution patterns, with $(La/Yb)_N = 0.8$ –1.4 (averaging 1.0). Most SPM samples from the Qingshuijiang River, which winds its way through a clastic terrain, show flat REE distribution patterns also, with $(La/Yb)_N = 0.6$ –1.4 (averaging 0.96).

4.3.3 Ce and Eu Anomalies

All of the calculated Ce anomalies of SPM in these three rivers are not so remarkable. The REE distribution patterns of SPM show remarkable negative Eu anomalies (Fig. 2c), except for the upper reaches of the Wujiang River.

5 Discussion

5.1 Average REE Pattern of Dissolved Load

In comparison to the rivers in other parts of the world, the dissolved load REE concentrations of the studied rivers are apparently lower; in particular, they are lower than those of the Amazon River (Fig. 4). The Amazon River has the Rio Negro as a major tributary. The Rio Negro is very acidic as it is a black water river with high concentrations of humic organic matter. Thus, the Rio Negro helps to keep the Amazon pH low (averaging

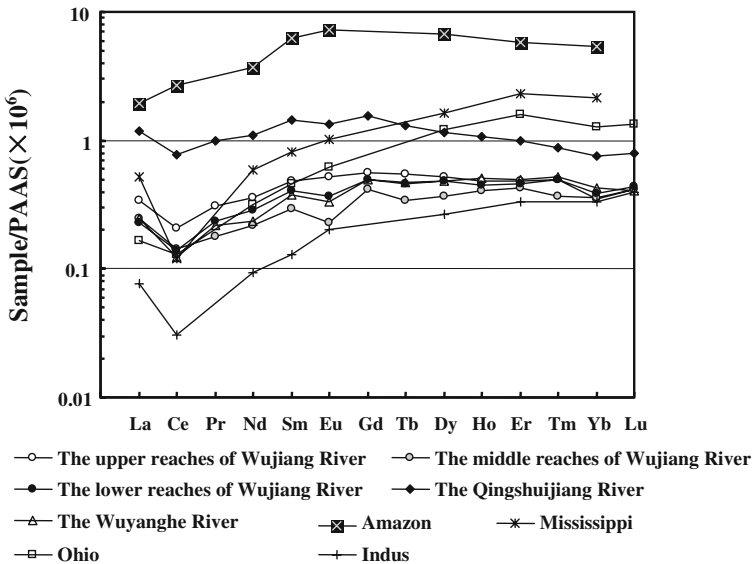


Fig. 4 PAAS-normalized REE patterns of dissolved loads in the river waters. Also shown are dissolved REE of the larger rivers in the world for comparison. The data for the Amazon, Mississippi, Ohio, and Indus rivers are taken from Goldstein and Jacobsen (1988)

pH = 6.6) and its concentrations of dissolved load REE are one order of magnitude higher than those in other rivers. The pH values of the three rivers in our study vary from 6.4 to 8.5, higher than 7.9 for most river samples. The mean pH values of the Wujiang River and the Wuyanghe River are 8.0 and 7.9, respectively, higher than the average pH value of the Qingshuijiang River (pH = 7.4). From Fig. 4, it is clear that the dissolved load REE concentrations of the Qingshuijiang River are apparently higher than those of the Wujiang River and the Wuyanghe River. Similar phenomena were observed in the Ohio River and Mississippi River in the United States and in the Indus River in Pakistan (Fig. 4), where the pH values are high, but the levels of dissolved load REE are relatively low (Goldstein and Jacobsen 1988). The reason may be that the high pH values make the content of colloidal particles decrease sharply in river water. Based on the observation that much of the REE pool in rivers is colloidal, the dissolved load REE concentrations are very low in alkaline river waters from the Wujiang River and the Wuyanghe River draining the karstic terrains.

From Figs. 3a, b, it can be seen that pH is a major factor controlling both the absolute abundances of the LREE in solution and relative REE patterns of dissolved load. There is an inverse relationship between the concentrations of Nd and pH: the higher the pH value, the lower the REE concentrations of dissolved load. Meanwhile, high-pH river water is enriched in HREE relative to LREE. This may be explained by the formation of carbonate and hydroxide complexes in mild alkaline solution. As compared with the LREE, the HREE can form stronger complexes than the LREE with such inorganic ions as CO_3^{2-} , OH^- , and F^- (Turner et al. 1981; Cantrell and Byrne 1987; Lee and Byrne 1993). Phosphate complexes might also potentially complex with the lanthanides in aqueous solution; however, in all of the river water samples there is no detectable PO_4^{3-} . It can also be found that there is more distinct trend in the Qingshuijiang River, the lower pH river, which drains through a clastic terrain.

The dissolved load REE patterns of the rivers of this study show significant negative Ce anomalies compared to the suspended load (Fig. 2). The Ce anomalies of dissolved load in rivers are, however, not that strongly controlled by pH (Fig. 3c). This behavior might be explained by the redox behavior of Ce, by contrast with the other REE. Since Ce anomaly is usually controlled by redox equilibrium between the dissolved Ce^{3+} and Ce^{4+} species (Elderfield and Sholkovitz 1987; Goldstein and Jacobsen 1988; Liu et al. 1989; Dia et al. 2000), the preferential removal of dissolved Ce(III) is ascribed to of redox reaction. In addition, the abiotic oxidation of Ce(III) on the surface of manganese oxides has also been reported from laboratory experiments in which synthetic minerals were used (Koeppenkastrup and De Carlo 1992; De Carlo et al. 1998).

In general, Eu anomaly is strongly lithology-dependent (Tricca et al. 1999; Möller et al. 2004). Thus, waters originating from source rocks with positive Eu anomalies have similarly positive anomalies whereas waters from source rocks with negative anomalies have also negative Eu anomalies. From Fig. 2, it can be seen that the PAAS-normalized REE patterns between dissolved load and acid-soluble load and SPM having similar negative or positive Eu anomalies. These samples originating from the upper reaches of Wujiang River are characterized by positive Eu anomalies, whereas the samples from other rivers are characterized by negative Eu anomalies (Fig. 2). This fact illustrates that Eu anomaly is not controlled by physico-chemical parameters such as pH but by the REE characteristics of the source rocks in the drainage basin itself. The Eu negative anomalies found in samples from the rivers of this study are attributed to carbonate rocks. The source rocks show negative Eu anomalies (Li et al. 1998), which is consistent with the fact that the river water draining Permian and Triassic carbonate terrains.

5.2 Average REE Pattern of Acid-Soluble Load

The LREE concentrations of acid-soluble load are 5–713 times higher than those of dissolved load. Water samples of dissolved load from these three rivers show the REE distribution patterns characterized by LREE depletion, whereas those of acid-soluble load show the REE distribution patterns characterized by slight LREE enrichment (Fig. 2a, b). This indicates that the rate at which the LREE are released into solution is different from that at which the MREE and HREE are released into solution. All the acid-soluble loads REE have experienced large-scale fractionation characterized by MREE enrichment (Fig. 2b). The MREE enrichment patterns of acid-soluble load are similar to those observed in the leached solutions (Hannigan and Sholkovitz 2001), mildly acidic surface water (Hoyle et al. 1984; Sholkovitz 1995), and acidic lake water (Johannesson and Lyons 1995; Johannesson and Zhou 1999). This shows that either the MREE were preferentially removed from the rocks as compared to the LREE and HREE, or rocks in the catchment basin contain readily leachable or acid-soluble MREE-rich minerals and/or amorphous phases. The PAAS-normalized REE patterns of SPM (Fig. 2c) are almost flat. So we believe that the MREE can be preferentially released from the sediments into solution phase as compared to the LREE and HREE. Water/particle interaction may also be an important factor affecting the REE fractionation between dissolved load and SPM. It shows that the PAAS normalized REE patterns of acid-soluble load are enrichment of LREE and MREE relative to HREE in Fig. 2b. This implies that more MREE and LREE relative to HREE exist in the exchangeable phase because the particle-absorbed phase is often significantly enriched in LREE (Sholkovitz et al. 1993). The LREE and MREE are easier to

absorb in particles than HREE in rivers during the water/particle interaction processes, resulting in the phenomenon of LREE depletion in REE patterns of dissolved load.

5.3 Partition Behavior of the REE Between Dissolved Load and SPM

A major conclusion has been drawn from the studies of REE in river water, indicating that chemical weathering on continents leads to extensive fractionation between the dissolved load in river water and that of SPM and continental crust (Goldstein and Jacobsen 1987, 1988; Elderfield et al. 1990; Sholkovitz 1992, 1995). The normalization of the dissolved load REE to SPM REE can remove variations in relative REE abundance that originate in the source rocks in a drainage area, and allow REE fractionation caused by the weathering process to be examined. A measure of the extent of REE fractionation was given by Goldstein and Jacobsen (1988):

$$K_{La/Yb}^{diss-susp} = (La/Yb)_{diss} / (La/Yb)_{susp} \quad (1)$$

The values of the dissolved La/Yb ratio normalized to those in SPM ($K_{La/Yb}^{diss-susp}$) are 0.7, 0.7, and 1.5 for the Wujiang River, the Wuyanghe River, and the Qingshuijiang River, respectively. It can be seen that the rivers of lower pH tend to have the highest $K_{La/Yb}^{diss-susp}$ value, and the $K_{La/Yb}^{diss-susp}$ value decreases with increasing pH (Fig. 5), indicating a strong pH control on REE fractionation in the river system. At a global scale, a trend of increasing depletion of dissolved HREE relative to suspended sediments (of decreasing $K_{La/Yb}^{diss-susp}$ value) with increasing pH is apparent in rivers (Goldstein and Jacobsen 1988; Dupre et al. 1996; Gaillardet et al. 1997). At least two mechanisms can be proposed to explain such a control: adsorption processes, whose importance increases with pH (Schindler and Stumm 1987), and the existence of organo-mineral colloids that are present in a dispersed form at low pH and tend to agglomerate and coagulate with increasing pH (Gaillardet et al. 1997). In the future, we hope to carry out ultrafiltration experiments using

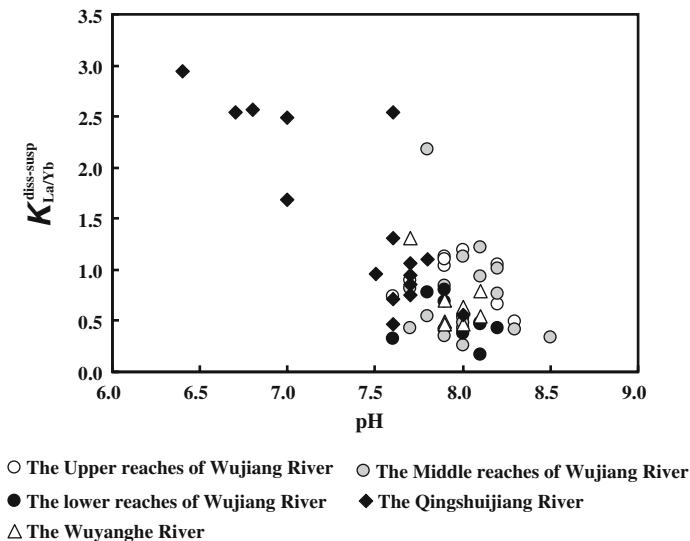


Fig. 5 Variations of $K_{La/Yb}^{diss-susp}$ vs pH of river water samples

different pore size filter, to confirm these proportions and to understand the way by which REE are transported in these rivers.

5.4 Non-Chondritic Y/Ho Ratios During Water/Particle Interaction

As viewed from its position among the lanthanides and based on ionic ratios, the chemistry of Y(III) solution chemistry is closely associated with the behavior of Ho(III) (Liu and Byrne 1995). In contrast, Y and Ho show substantial differences in their potential for covalent binding, potentially attributable to the absence or presence of electrons in the 4f orbitals (Borkowski and Sierkierski 1992). In the process of weathering, the complex ability of Ho to coordinate with organic material or HCO_3^- is greater than that of Y, and Y shows a stronger tendency to adsorb onto solid particles in the process of water/rock interaction (Kawabe et al. 1991). Fractionation between Ho and Y during water/rock interaction has attracted ever-increasing attention of researchers in recent years (Kawabe et al. 1991; Bau et al. 1996; Nozaki et al. 1997; Takahashi et al. 2002; Möller et al. 2003). There is strong evidence that these two elements are significantly fractionated in aqueous systems (Zhang et al. 1994). Lee and Byrne (1993) showed the complexation behavior of Y, which is easy to adsorb on the soft organic surface of particulate matter, is similar to that of LREE, so Y distinctly deviates from Ho and other REE due to the competitive reactions between river water and particulate matter (Nozaki et al. 1997).

The non-chondritic Y/Ho molar ratios in dissolved load range from 43 to 124, with an average value of 78. All of them are higher than the values of the source rock (Y/Ho = 39; Li et al. 1998), and most of them are higher than the value of the continental rocks (Y/Ho = 52; Nozaki et al. 1997). The relative enrichment of Y over Ho in the dissolved load seems to be the result of REE fractionation during the processes of weathering and transport. Y/Ho molar ratios in acid-soluble load and SPM range from 47 to 78 and from 45 to 63, respectively, which are similar to or slightly less than the continental rocks (Y/Ho = 52; Nozaki et al. 1997). Y/Ho molar ratios in dissolved load are also higher than those of acid-soluble loads and SPM. This may suggest that the fractionation between these two elements is due to the water/particle interaction. Figure 6 shows that Y/Ho ratios of most samples are higher than those of the source rocks and continental rocks, suggesting that either Y is preferentially released from the particles or Ho is more rapidly removed from the water relative to Y. With our data set, it is difficult to ensure which mechanism causes the fractionation of Y and Ho in rivers now. However, Byrne and Lee (1993) pointed out the complexation behavior of Y with the organic surface of particulate matter is similar to that of light REE. Therefore, it is likely that Y distinctly deviates from Ho due to the competitive reactions during scavenging by particulate matter.

5.5 Implication for the REE Fractionation During Water/Particle Interaction

Speaking in general, in studying, water/particle interaction, the variation of dissolved load REE concentrations may not easily be reflected by the corresponding variation of acid-soluble load fraction, since the concentrations of acid-soluble load REE are much higher than those of the dissolved fraction. But the relative proportion of REE in dissolved load and acid-soluble load can reflect the REE reactivity associated with suspended particles. Therefore, the distribution coefficients (K_D), which can reflect the migration capacity of REE in surface waters, are usually used for understanding geochemical processes and contaminant fluxes in river water (Ingri et al. 2000).

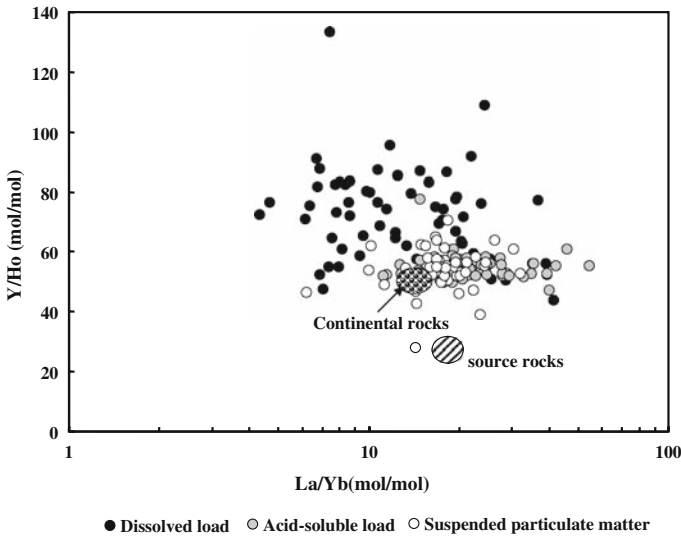


Fig. 6 Variations of La/Yb vs Y/Ho molar ratios of river waters, the source rocks (data from Li et al. 1998), as well as the continental rock (data from Nozaki et al. 1997)

The data for the SPM, acid-soluble load, and dissolved load from each of the river mentioned above can be used to calculate “partition coefficients” between the soluble and suspended phases. This concept has been adopted in river chemistry, for example, by Whitfield and Turner (1979). Distribution coefficients of 1,000–1,000,000 (or even larger) for REE partitioning between aqueous solution and particle surfaces (carbonates, Fe–Mn oxides) have been reported by many authors on the basis of experimental and observational studies as well as modeling approaches (Koeppenastrop and De Carlo 1992, 1993; Zhong and Mucci 1995; De Carlo et al. 1998; Tang and Johannesson 2005; Quinn et al. 2006). In our study, the distribution coefficients for REE are defined as $K = C_A/C_W$, $K = C_A/C_S$ and $K = C_S/C_W$, where C_W , C_A , and C_S are the REE concentrations in dissolved load, acid-soluble load, and SPM, respectively (Fig. 7). As it is seen from Fig. 7, the REE fractionation was caused by the water/particle interactions. One can see that in mildly acid solution, LREE and Ce would be preferentially released from river particles (Fig. 7a), showing that the REE fractionation is associated with the release of absorbed and mildly dissolvable REE in river particles (Fig. 7b).

6 Conclusions

This study shows that the dissolved load, acid-soluble load, and SPM are significantly different REE compositions.

1. The concentrations of dissolved load REE in karst rivers are very low relative to many large rivers in other parts of the world. The high pH values of the rivers in the karst region of Guizhou are the main factors leading to the lower REE concentrations of dissolved load in the rivers. The PAAS-normalized REE patterns of dissolved load from the three rivers, like those of many rivers in other parts of the world, are characterized by HREE enrichment. The fractionation between HREE and LREE can

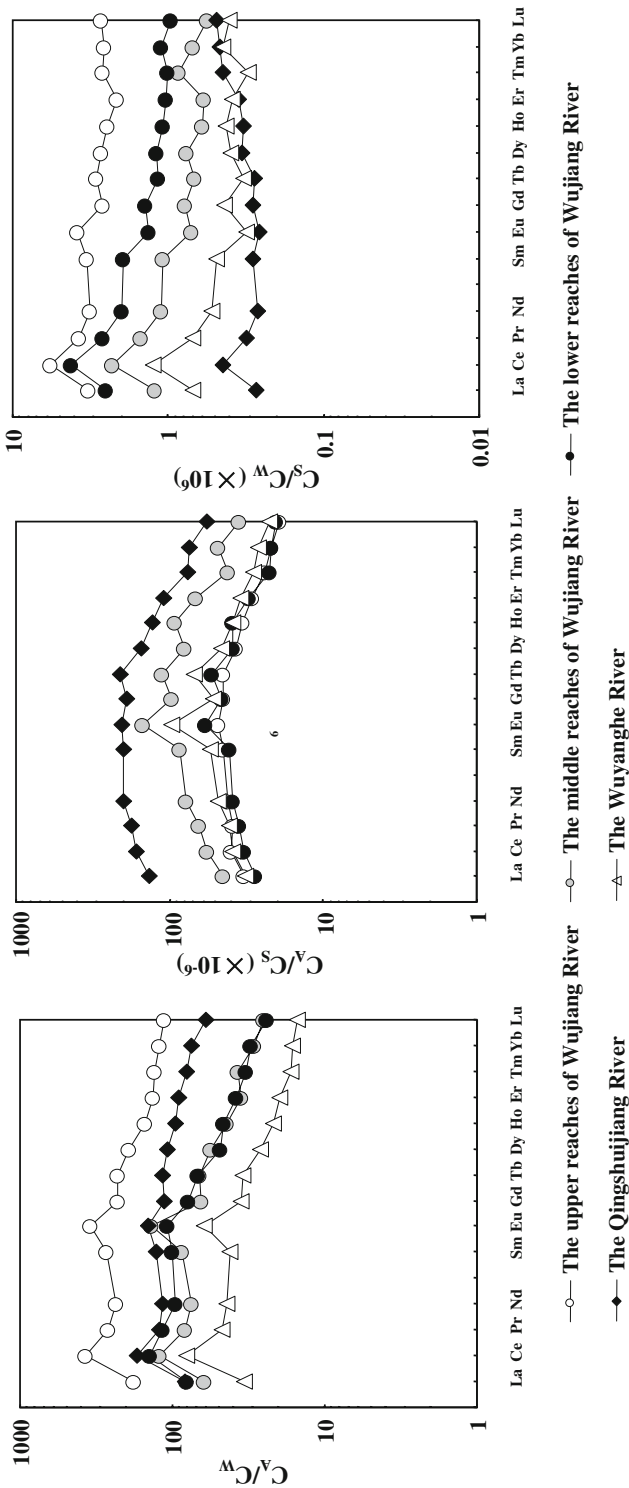


Fig. 7 Average REE abundances in acid-soluble loads normalized to the REE abundance of dissolved loads and SPM for the studied rivers. C_W are the REE concentration in dissolved loads, C_A are the REE concentration in acid-soluble loads, C_S are the REE concentration in the SPM

- be ascribed to high pH values and the formation of carbonate and hydroxide complexes in alkaline solution. In addition, the hydrolysis reactions that are usually enhanced at high pH might also lead to fractionation of REE through enhanced particle reactivity. The dissolved REE from karst river waters are significantly depleted in Ce and Eu relative to the PAAS composition. Negative Ce anomalies are strongly dependent on redox chemistry, while the negative Ce anomaly is strongly pH-dependent in high-pH river. Negative Eu anomalies are dependent on the source rocks. REE fraction, which took place in the processes of weathering and transport, would lead to an obvious HREE enrichment and negative Ce anomalies in dissolved load relative to acid-soluble load and SPM.
2. The REE distribution patterns in acid-soluble load from these river waters are characterized by MREE and slight LREE enrichment. This implies that LREE and MREE are more soluble than HREE, or there exist more LREE and MREE than HREE in the exchangeable phase, because the particle-absorbed phase is often highly enriched in MREE.
 3. The contents of REE in SPM are relatively high. The PAAS-normalized REE patterns of SPM from the three rivers are flat, with no Ce anomalies but remarkable negative Eu anomalies. This indicated that the REE contents and distributed patterns are closely related to the lithological character of the source rocks.
 4. Non-chondritic Y/Ho ratios in dissolved load are higher than those in the source rocks and the average values of continental rocks; non-chondritic Y/Ho ratios in acid-soluble load and SPM are close to those of the host rock, indicating that these two elements were fractionated during weathering and transport processes.

Acknowledgments This work was supported jointly by the Innovation Program of Chinese Academy of Sciences (No. KZCX2-YW-306), and the Foundation of International Partnership Project from Chinese Academy of Sciences, and the Chinese National Natural Science Foundation (Nos. 40673010, 40721002). The authors gratefully acknowledge Profs. E.R. Sholkovitz and E.H. DeCarlo for their constructive comments that significantly improved the presentation of the manuscript.

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