Chemical and Isotopic Compositions of the Minjiang River, A Headwater Tributary of the Yangtze River

Xiao-Dong Li* Chinese Academy of Sciences
Harue Masuda Osaka City University
Cong-Qiang Liu Chinese Academy of Sciences

We describe the anthropogenic impacts on the major dissolved elements (Cl^-, NO_3^-–N, SO_4^{2-}, and Na^+) in the water from the Minjiang River (a headwater tributary of the Yangtze River) and upper Yangtze River in relation to increasing human activity. The major element chemistry and hydrogen, oxygen, and sulfur isotopic compositions were investigated. When the Minjiang River flows through the populated Sichuan Basin, the concentrations of Cl^-, NO_3^-–N, SO_4^{2-}, and Na^+ gradually increase. The increasing SO_4^{2-} in the highly polluted Minjiang River had high $\delta^{34}S$ values (+6.3 to approximately +13.6‰), implicating the anthropogenic sources of sulfur from air pollutants, domestic wastewater, industrial effluents, and agricultural fertilizers. The water quality of the upper Yangtze River does not worsen after receiving the Minjiang River because the water from the lightly polluted Jinshajiang River contributes most of the total flux in the Yangtze River. However, these rivers deserve attention and further research because the Yangtze River is the most important river in China in terms of water quality.

The Yangtze River, originating from the Tibetan Plateau at an elevation higher than 5000 m, is the longest river (6300 km long) in Asia and the third longest in the world after the Amazon in South America and the Nile in Africa ("Changjiang" means "long river" in Chinese). According to Changjiang River Water Resources Commission in China (CWRC, 2000), the section above Yichang station (where the Three Gorges Dam is located) is called the Upper Reach, which is 4500 km long, with a catchment area of 1.04×10^6 km^2. The Upper Reach accounts for 70.4% of Yangtze River's total area (Fig. 1).

The interest in the Yangtze River lies not only in its enormous size, complex geomorphology, and beautiful scenery but also in the way the river operates as an essential lifeline in China. The Yangtze River is the most important river among the seven national-size water systems in China in terms of the water quality (SEPA China, 2006). The river has influenced the lives of people who live nearby. In return, the people there have attempted to control the river. As an example, the world's largest dam (the Three Gorges Project) is being constructed. This project was formally approved by China's National Peoples' Congress in 1992. Since then, the dam has been under construction. With increasing concern about its effect on the environment, many research works on the upper Yangtze River have been done in the past years (Chen et al., 2000, 2001, 2002; Higgitt and Lu, 2001; Lu and Higgitt, 2001; Varis and Vakkilainen, 2001; Yin and Li, 2001; Tan and Wang, 2004; Zhang and Wen, 2004; Liu et al., 2006; Qin et al., 2006).

The upper reaches of the Yangtze River are of significant strategic importance to the Yangtze River basin and to the sustainable development of the nation. The environment in the upper reaches has deteriorated due to anthropogenic pollution and erosion caused by deforestation and loss of vegetation cover. At the end of 1970s, China opened its country and embarked on economic reform that has been associated with rapid urbanization (Qin and Chen, 2001). The consequences are considerable changes in land use: A large proportion of the peri-urban landscape has changed from agriculture or residential uses to predominantly industrial, whereas other areas have shifted from predominantly paddy rice to intensive vegetable production. The excessive growth of the population and the continually increasing population densities have

Published in J. Environ. Qual. 37:409–416 (2008).
doi:10.2134/jeq2006.0554
Received 20 Dec. 2006.
*Corresponding author (xdlee2002@163.com).

677 S. Segoe Rd., Madison, WI 53711 USA

X.-D. Li and C.-Q. Liu, State Key Lab. of Environmental Geochemistry, Inst. of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou 550002, PR China. H. Masuda, Dep. of Geosciences, Osaka City Univ., Sumiyoshi-ku, Osaka 558-8585, Japan.

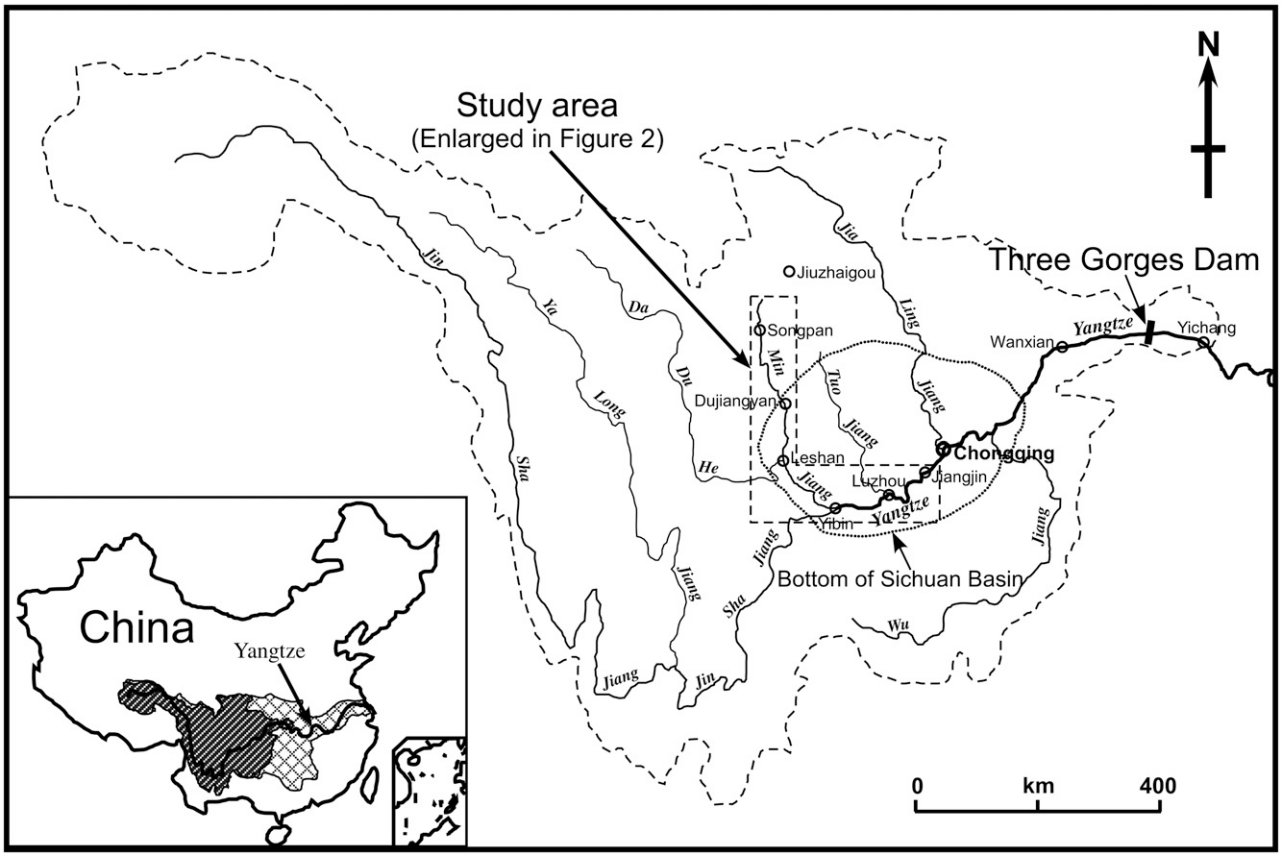

Fig. 1. Location map of the study area. The dotted line denotes the bottom of Sichuan Basin (200–450 m).

resulted in over-cultivation, overgrazing, and haphazard logging and have led to agrochemical pollution, reduction in vegetation, and exacerbated desertification. Human activities, such as the development of mining; the construction of dams, reservoirs, roads, and factories; and the development of fossil fuel–consuming industrial sectors (e.g., metallurgy, chemical industry, coal mine, textile industry, cement plants, and paper mills) often ignore the contaminations on the surroundings. Adequate attention has not been paid by government and officials to the treatment and management of the "three wastes" (waste water, solid, and gas) resulting from the above-mentioned agricultural, industrial, and domestic activities.

As a result, growing concern has arisen about potential surface water contamination in the rapidly developing areas of the upper Yangtze River, particularly after the construction of the Three Gorges Dam because of the changes in flow velocity and the self-purification and dilution–diffusion capacities of the river water (Fig. 1). To reveal the significant impacts on the river water quality in relation to the increasing human activities, we analyzed the major element chemistry and stable isotopic ratios of H, O, and S for river waters from the Minjiang (a headwater tributary of the Yangtze) and upper Yangtze rivers.

Previous Work

Chen et al. (2000) investigated the nitrogen contamination in the Yangtze River system, and the results indicated that the Minjiang and Tuojiang Rivers (the major tributaries of the upper Yangtze River) were the most heavily polluted. The research by Higgitt and Lu (2001) examined sediment yield and its response to catchments disturbance and environmental variables in the upper Yangtze River basin, where the attention of environmentalists has been drawn to the Three Gorges Project. Chen et al. (2002) studied the chemistry of major elements in the river water of the upper Yangtze River and observed a persistent increase in the concentrations of SO_4, a signature of considerable anthropogenic impacts (e.g., acid deposition). Liu et al. (2006) evaluated the effect of human activities on the amount of nitrogen (N) transported to the Three Gorges Dam and suggested that the increased use of synthetic fertilizers and the decrease in the fertilizer N-use efficiency were implicated as major causal factors of increased riverine N transport. Qin et al. (2006) studied the chemical and physical weathering in the Minjiang River, a headwater tributary of the Yangtze River. Using data from the upper Minjiang River and its tributaries as the baseline, they discussed qualitatively the anthropogenic impact on the SO_4 and Cl in the lower Minjiang River. These studies focus on the water quality, sediment yields, and water resources management. Further investigation of water contamination and pollutant sources is needed.

Study Area

The Minjiang, Jinshajiang, Jialingjiang, and Wujiang Rivers are the major tributaries of the upper Yangtze River (Fig. 1). The Minjiang River originates from the undeveloped eastern Tibetan Plateau, is relatively unaffected by human activities, and flows through

the Sichuan Basin to form the Yangtze River main channel, where it joints the Jinshajiang River at Yibin City. The Daduhe River flows through the northwest of the basin to join the Minjiang River at Leshan City. The Tuojiang River flows from north to south within the basin and joins the Yangtze River at Luzhou City. The basic data, such as length, drainage area, long-term water discharge, and population density of the studied rivers, are shown in Table 1.

The Minjiang and Tuojiang Rivers flow through and within the Sichuan Basin, which is one of the most heavily populated and intensely industrialized areas in China and faces serious environmental pollution problems (Streets and Waldhoff, 2000). The basin represents about 2% of the total area of China and contains >10% of the national population. Since the mid-1970s, the Sichuan Basin area has undergone rapid development. Locally, industry, agriculture, and domestic activities have posed great pressure on the ecological environment, especially the aquatic environment. The lack of the treatment plants for the produced wastes and inefficient management results in direct contamination of local surface water systems in this overpopulated region.

Climate and Soil

Average annual temperatures within the study area are in the range of 16.0 to 18.0°C, and the mean annual precipitation is 1200 to 1500 mm in the Sichuan Basin and 500 to 800 mm in the source area of Minjiang River. Precipitation is highly seasonal, with the rainy period (June to September) accounting for about 70% of the total annual precipitation (Bureau of Geology and Mineral Resources of Sichuan Province, 1991). Likewise, water discharge is highly seasonal in the rivers. The soil color changes progressively from dark brown on the Tibetan Plateau to yellow near the Sichuan Basin and to red in the center of the Sichuan Basin (National Soil Survey Office, 1998). Fertile soils and abundant rainfall provide good agricultural characteristics for growing rice and wheat.

Methods

Sampling Sites

For the present study, sampling sites were chosen at the source area of Minjiang River; at Dujiangyan City, where the Minjiang River emerges at the bottom plain of the Sichuan Basin; and around the cities of Leshan, Yibin, Luzhou, and Jiangjin (near Chongqing), for a total of 15 sampling sites for river water from the Minjiang, Daduhe, Jinshajiang, Tuojiang, and Yangtze rivers. Sampling sites are shown in Fig. 2.

Samples and Pretreatment in the Field

The locations of river water samples are shown in Fig. 2. To investigate the seasonal variability, pairs of samples were taken at the end of the dry (March) and rainy (September) seasons. Water samples from the source area of the Minjiang River and Dujiangyan City were collected in September 2003, and water samples from the Leshan, Yibin, Luzhou, and Jiangjin areas were collected in March and September 2004.

Water samples were collected from the mainstream of each river from a ship and taken from a fixed depth (0.5 m below the water surface). After initial filtration through a 0.45-μm membrane filter (A045A047A; Advantec, Dublin, CA) on the spot for removing suspended particles including microorganisms, water samples were stored in two bottles: One bottle was acidified with 1:1 HCl (for the analysis of cations), and the other was untreated (for the analysis of anions, hydrogen, and oxygen isotopes). An additional aliquot of 1 to approximately 2 L of water was sampled, and 10 to approximately 20 mL of 1:1 HCl were added to this sample for preparation for S isotope analysis. The sample was filtrated later in the laboratory.

Table 1. Basic data for the studied rivers.†

River name	Length	Drainage area	Water discharge	Population density
	km	km^2	$\times 10^8\ m^3\ yr^{-1}$	persons km^{-2}
Minjiang	735	136,000	861	72
Daduhe	1062	82,700	473	42
Jinshajiang	2308	485,100	1529	45
Tuojiang	623	27,000	158	469

† Data are from National Compilation Committee of Hydrology Almanac, 2005.

Analytical Methods

Immediately after sampling, we measured water pH in the field using Horiba electrodes (6066–10C; Horiba, Kyoto, Japan). Concentrations of Ca^{2+} and Mg^{2+} were determined in the laboratory by EDTA titration (Japan Society for Analytical Chemistry, 2000). Sodium and K^+ were analyzed by atomic absorption spectrophotometry (SAS7500; Seiko Instruments, Chiba, Japan), and anions (F^-, Cl^-, Br^-, NO_3^-–N, PO_4^{3-}, and SO_4^{2-}) were analyzed using an ion chromatograph (DX-120; Dionex, Sunnyvale, CA). Dissolved silica (as SiO_2) was analyzed by ammonium heptamolybdate photometry, and ammonium (as NH_4^+–N) was analyzed by indophenol photometry (Japan Society for Analytical Chemistry, 2000). The analytical precision for cations and anions was better than 5% relative standard deviation.

The oxygen isotope composition of water was measured using the automated CO_2/H_2O equilibration method originally developed by Epstein and Mayeda (1953); analytical precision for this method is <0.1‰ for $\delta^{18}O$. Hydrogen isotope analysis was performed using the Cr-reduction method (Itai and Kusakabe, 2004), which has an analytical precision for duplicated samples of <0.5‰.

Sulfate-sulfur isotopes were measured for SO_4^{2-} ion fixed as $BaSO_4$. After adding 10% $BaCl_2$ solution, dissolved SO_4^{2-} was recovered by $BaSO_4$ precipitation collected on a 0.45-μm Millipore membrane filter and dried in an oven at 60°C for 2 h. The $BaSO_4$ was thermally decomposed to SO_2 according to the method described by Yanagisawa and Sakai (1983); analytical precision for $\delta^{34}S$ was <0.2‰.

A VG SIRA10 mass spectrometer (V-G Isogas Ltd., Middlewich, UK) was used to measure δD and $\delta^{34}S$ isotopic ratios, and $\delta^{18}O$ was measured using a VG PRISM mass spectrometer. All the isotope analyses were performed at the Institute for Study of the Earth's Interior, Okayama University, Japan. Results are expressed using the standard delta notation with

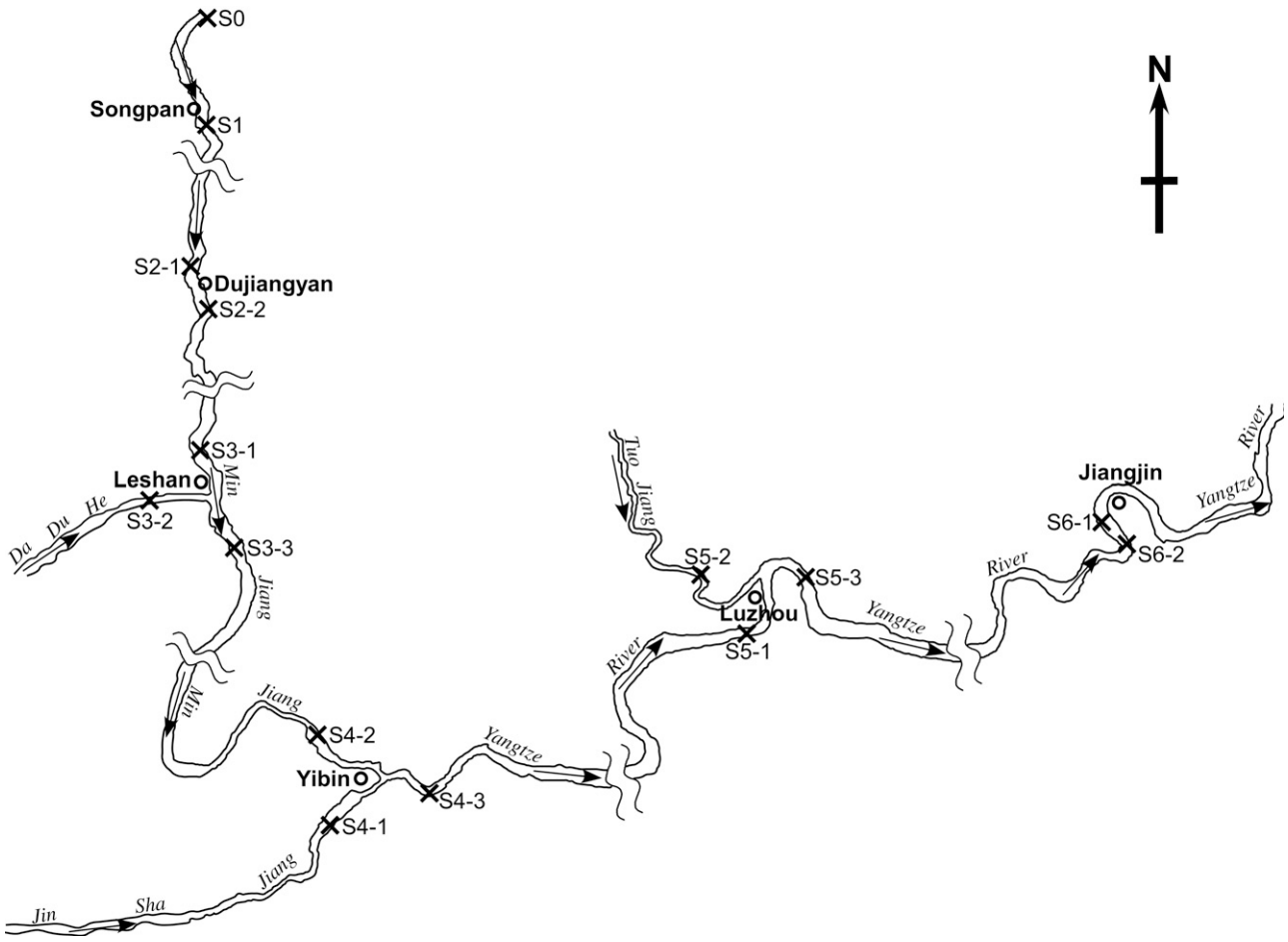

Fig. 2. Sketch map of sampling sites. The arrow indicates the direction of river flow. The pair of wiggly lines indicates the length of the river in the sketch map is not real.

reference to the V-SMOW (Vienna-Standard Mean Ocean Water) scale for δD and $\delta^{18}O$ values of water and the CDT (Canyon Diablo Troilite) scale for $\delta^{34}S$ values of SO_4^{2-}.

Results

Major Chemical Compositions

The chemistry and stable isotopic ratios of river waters are shown in Table 2. The concentrations of anions and cations in the samples from the same places were generally higher in March than in September (Fig. 3 and 4). In general, the concentrations of ions in surface waters are significantly higher during the dry season than the wet season because of the dilution by large quantities of rainfall in the latter.

The concentrations of Cl^-, NO_3^-–N, SO_4^{2-}, Na^+, and K^+ were the lowest in the water from the source area of the Minjiang River (S0 and S1; Table 2), whereas the concentrations of these ions in Minjiang River waters gradually increased toward Dujiangyan City (S2–1 and S2–2; Table 2). Downstream at the Leshan sampling site, the Minjiang River water (S3–1) had high concentrations of Cl^-, NO_3^-–N, SO_4^{2-}, Na^+, and K^+; after mixing with the Daduhe River water (S3–2), which contains low concentrations of these ions, the water quality of the mixture (S3–3) became better (Fig. 3). Toward the end of the Minjiang River at Yibin City (S4–2), the concentrations of these ions were similar to those from Leshan (S3–3), but the concentration of SO_4^{2-} increased remarkably in the March sampling campaign and decreased in the September sampling campaign (Fig. 3). From the Leshan to the Yibin sites, the increasing SO_4^{2-} in March suggested the additional input of sulfur source; the decreasing SO_4^{2-} in September implied the dilution by rainfall in the rainy season during the flow. The water quality of the Yangtze River at Yibin City (S4–3) did not worsen after it joined the polluted Minjiang River because the less-polluted Jinshajiang River water (S4–1) flows into the Yangtze River (Table 2).

Downstream at the Luzhou site, the concentrations of Cl^-, NO_3^-–N, SO_4^{2-}, Na^+, and K^+ of the Yangtze River water (S5–1) became slightly higher than those of the river water (S4–3) at the Yibin site (Fig. 4). The high concentrations of these ions in the Tuojiang River water (S5–2) did not significantly affect the water quality of the Yangtze River (S5–3) at the Luzhou site after the rivers converged (Table 2; Fig. 4). The concentrations of these ions in the Yangtze River water (S6–1 and S6–2) at the Jiangjin site did not change greatly from those of the river water (S5–3) at the Luzhou site (Fig. 4).

In contrast, Ca^{2+}, Mg^{2+}, and SiO_2 concentrations of all sampled river waters remained within a similar range downstream. Relatively high concentrations of NH_4^+–N were recorded in the waters from the Minjiang and Tuojiang rivers in March (Table 2).

Table 2. Chemistry and stable isotopic data of sampled river waters.

No.	Location	River name	Sampling date	F^-	Cl^-	NO_3^-–N	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+–N	SiO_2	pH	δD	$\delta^{18}O$	$\delta^{34}S$
				mg L^{-1}											‰		
S0	Source part	Minjiang	2003–09	0.09	0.99	1.31	6.97	42.1	4.91	1.70	0.63	0.05	3.97	8.1	−89.3	−12.9	−5.0
S1	Source area	Minjiang	2003–09	0.12	1.38	1.56	7.21	52.2	12.4	3.44	0.84	0.07	4.86	8.4	−89.5	−12.9	−†
S2–1	Dujiangyan	Minjiang	2003–09	0.12	1.96	4.21	18.8	38.9	8.84	2.76	1.92	0.05	5.45	8.0	−87.7	−12.8	1.7
S2–2	Dujiangyan	Minjiang	2003–09	0.12	1.91	4.26	19.7	35.6	8.84	3.00	1.81	0.06	5.99	8.2	−89.2	−13.1	1.3
S3–1	Leshan	Minjiang‡	2004–03	0.63	29.8	6.01	106	74.4	10.6	48.7	7.34	2.57	6.66	7.7	−63.8	−9.9	12.2
S3–2	Leshan	Daduhe	2004–03	0.27	4.96	0.91	29.0	42.3	8.85	4.61	1.44	0.10	5.45	9.0	−85.0	−13.3	9.7
S3–3	Leshan	Minjiang§	2004–03	0.32	18.6	2.93	58.7	48.1	9.51	29.9	3.15	1.33	5.06	8.2	−72.0	−11.2	12.0
S4–1	Yibin	Jinshajiang	2004–03	0.18	6.67	0.47	26.5	40.9	11.5	6.89	1.28	0.07	6.51	8.4	−91.1	−13.8	7.8
S4–2	Yibin	Minjiang	2004–03	0.17	16.7	1.43	188	96.3	36.3	17.7	7.87	0.21	3.46	8.3	−61.2	−8.4	13.6
S4–3	Yibin	Yangtze	2004–03	0.22	8.38	0.94	36.8	46.9	17.5	10.0	1.69	0.20	6.36	8.4	−86.2	−12.8	9.6
S5–1	Luzhou	Yangtze¶	2004–03	0.24	9.13	1.26	34.7	42.3	11.2	10.0	1.74	0.24	5.98	8.1	−89.5	−12.8	8.4
S5–2	Luzhou	Tuojiang	2004–03	1.05	82.7	5.36	100	89.0	14.5	49.7	7.74	3.65	7.20	7.7	−56.9	−8.3	9.0
S5–3	Luzhou	Yangtze#	2004–03	0.27	11.0	1.63	38.1	43.8	12.0	11.0	1.90	0.33	6.44	8.0	−86.1	−12.7	8.5
S6–1	Jiangjin	Yangtze††	2004–03	0.27	11.2	1.68	39.6	46.1	9.20	12.0	1.94	0.23	6.46	8.3	−87.4	−12.4	8.4
S6–2	Jiangjin	Yangtze††	2004–03	0.26	10.4	1.62	38.6	43.8	13.3	11.6	1.86	0.25	6.85	8.3	−87.2	−12.5	8.4
S3–1	Leshan	Minjiang‡	2004–09	0.22	11.5	2.45	46.2	53.2	10.8	11.1	3.11	0.06	7.63	7.4	−75.3	−11.0	8.4
S3–2	Leshan	Daduhe	2004–09	0.12	2.96	0.77	13.7	29.0	7.82	1.54	1.10	0.05	5.43	7.7	−101	−14.1	5.9
S3–3	Leshan	Minjiang§	2004–09	0.13	10.2	1.25	43.6	51.4	8.86	9.00	2.31	0.05	6.77	7.5	−82.5	−12.0	6.9
S4–1	Yibin	Jinshajiang	2004–09	0.16	16.7	0.73	19.1	32.2	8.80	11.8	0.88	0.05	7.67	8.0	−106	−14.5	6.6
S4–2	Yibin	Minjiang	2004–09	0.13	4.05	1.06	21.3	33.8	7.82	3.86	0.83	0.07	6.20	8.2	−89.7	−12.8	8.1
S4–3	Yibin	Yangtze	2004–09	0.14	10.8	0.83	20.4	32.7	8.28	8.23	0.85	0.06	7.34	8.1	−101	−14.0	6.7
S5–1	Luzhou	Yangtze¶	2004–09	0.13	10.4	1.03	22.6	32.2	7.82	6.79	1.30	0.06	6.10	7.6	−96.1	−13.3	5.4
S5–2	Luzhou	Tuojiang	2004–09	0.36	19.2	2.58	67.8	64.5	8.80	11.5	3.54	0.08	9.50	8.1	−57.7	−8.4	6.3
S5–3	Luzhou	Yangtze#	2004–09	0.14	11.5	1.04	23.4	33.8	7.82	7.51	1.29	0.07	6.57	8.0	−94.2	−13.2	5.8
S6–1	Jiangjin	Yangtze††	2004–09	0.14	10.3	1.04	21.6	33.8	7.82	8.46	1.08	0.07	7.27	7.9	−92.6	−13.0	5.9
S6–2	Jiangjin	Yangtze††	2004–09	0.14	9.50	0.93	21.0	33.8	7.82	8.13	1.04	0.09	7.53	8.0	−93.8	−13.1	5.8

† Not measured.

‡ Before mixing with the Daduhe River.

§ After mixing with the Daduhe River.

¶ Before mixing with the Tuojiang River.

After mixing with the Tuojiang River;

†† Two riversides of Yangtze River.

Hydrogen and Oxygen Isotopes

The δD and $\delta^{18}O$ values of river waters at the source area and Dujiangyan City fall within narrow ranges (−89.5 to −87.2‰ and −13.1 to −12.8‰, respectively) (Table 2). Similar low δD and $\delta^{18}O$ values were recorded from Daduhe and Jinshajiang rivers (−106 to −85.0‰ and −14.5 to −13.3‰, respectively), which flow from high mountainous areas. In comparison, relatively high δD and $\delta^{18}O$ values were recorded in the lower part of the Minjiang and Tuojiang rivers (−89.7 to −56.9‰ and −12.8 to −8.3‰, respectively), which flow through the center of the Sichuan Basin. The $\delta^{18}O$ values of river water samples taken in March were higher than those of samples taken in September.

Sulfur Isotopes

The $\delta^{34}S$ values of river water were −5.0 ‰ at the source area of Minjiang River and +1.3 and +1.7‰ at the Dujiangyan site. Downstream from the Dujiangyan site, the $\delta^{34}S$ of river water ranged from +7.8 to +13.6‰ for samples collected in March and from +5.4 to +8.4‰ for samples collected in September (Table 2). The highest values of $\delta^{34}S$ were found in the waters from the Minjiang River (+12.0 to +13.6‰ in March and +6.9 to +8.4‰ in September). Values of $\delta^{34}S$ were higher in the waters from the Tuojiang River (+9.0‰ in March and +6.3‰ in September). The $\delta^{34}S$ values of river water were consistently about 2‰ lower in September than in March. Most river waters had higher $\delta^{34}S$ values than rainwater collected from the same site (+1.5 to +6.0‰) (Li et al., 2006a).

Discussion

Mixing Model

The sampling strategy of collecting three samples around major tributary junctions suggests that a mixing model would be appropriate to establish the relative contribution from each branch. This would enable the consistency of the results to be checked by long-term water discharge of each river. Mass balance (stable isotope values $\delta^{18}O$) was calculated to estimate the mixing ratios of the water originating from different rivers into the mixture:

$$f_{river1} + f_{river2} = 1.0$$

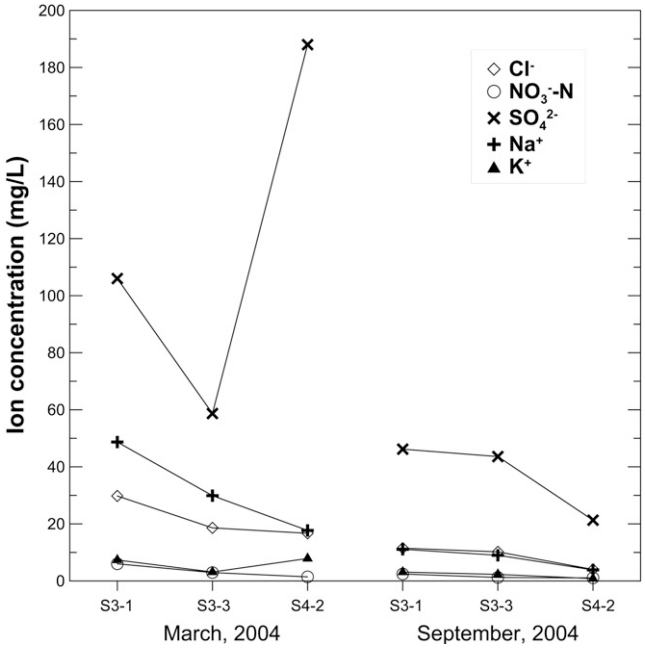

Fig. 3. Ion concentrations in the water along the Minjiang River in different seasons.

$$\delta^{18}O_{river1} \times f_{river1} + \delta^{18}O_{river2} \times f_{river2} = \delta^{18}O_{mixture}$$

where f_{river1} and f_{river2} denote the fractions of water from river1 and river2, respectively.

Downstream from the Dujiangyan site, the confluence of different branches can be described using the $\delta^{18}O$ values of river waters taken in March and September. For example, in March, at the Leshan site, the $\delta^{18}O$ of water samples from Daduhe River (S3–2) and upstream in the Minjiang River before the junction (S3–1) were −13.3 and −9.9‰, respectively. Upon mixing, the $\delta^{18}O$ of the downstream water (S3–3), below the junction of those two rivers, was −11.2‰, suggesting that the flux of water from the Daduhe River represents about 38.2% of total flux in downstream Minjiang River (S3–3) (Fig. 2). At the other site and in a different sampling season, mixing ratios of the water originating from different rivers into the mixture were counted and are shown in Table 3. At the Yibin site, the flux of water from the Jinshajiang River represents about 81.5 and 70.6% of total flux in the Yangtze River in March and September, respectively (Fig. 2); at the Luzhou site, the flux of water from the Tuojiang River represents about 2.2 and 2.0% of total flux in downstream Yangtze River (S5–3) in March and September, respectively (Fig. 2). These results approximated the data calculated from the long-term water discharge (Table 3).

Pollutant Source

The source areas of the Minjiang, Daduhe, and Jinshajiang rivers are mountainous areas with altitudes >3000 m and low population density. Precipitation in these areas is >2000 mm (National Climatic Data Center, 2003), and the surface water is pollution free. In the source area of the Minjiang River, the total ion concentrations of the river water were approximately the same as those of local rainwater (Li et al., 2006b). Before the Daduhe and Jinshajiang rivers enter into the Sichuan Basin, they flow through the mountainous areas, and the waters are not polluted intensively (Table 2; Fig. 1). On the contrary, when the Minjiang River flows through the Sichuan Basin, the concentrations of Cl^-, NO_3^-–N, SO_4^{2-}, and Na^+ gradually increase from the Dujiangyan to Leshan sites and increase further at the Yibin site (Table 2).

Chloride Source

Because chloride (Cl^-) does not participate in weathering reactions and behaves conservatively throughout the hydrological cycle, the increasing Cl^- could be introduced by anthropogenic sources, such as household sewage that contains table salt, animal manure, and chlorine disinfecting treatment of tap water (e.g., Sherwood, 1989). The increasing Na^+ had the same pattern as Cl^- (Fig. 3 and 4), indicating that Na^+ is also sourced from table salt as well as silicate weathering and cation exchange (Négrel and Pauwels, 2004).

Nitrogen (NH_4^+–N and NO_3^-–N) Source

High NH_4^+–N and NO_3^-–N concentrations were recorded in the river waters taken in March (Table 2), especially for the Minjiang River at Leshan and the Tuojiang River at Luzhou. This is in accord with the results reported by Chen et al. (2000), who studied the nitrogen contamination in the Yangtze River system. Nitrogen contamination of surface water was widespread in the areas of intensive land use because NO_3^- is highly mobile in the environment (Négrel and Pauwels, 2004). To fulfill the increased food demands as the population of the Sichuan Basin increases, agricultural activities have become extremely intensive, using enormous amounts of nitrogen-containing chemical fertilizers (Chen et al., 2000; Liu et al., 2005). Therefore, nitrogen leached from the agricultural soils could result in the high NH_4^+–N and NO_3^-–N concentrations in the river waters. In addition, other sources, such as household

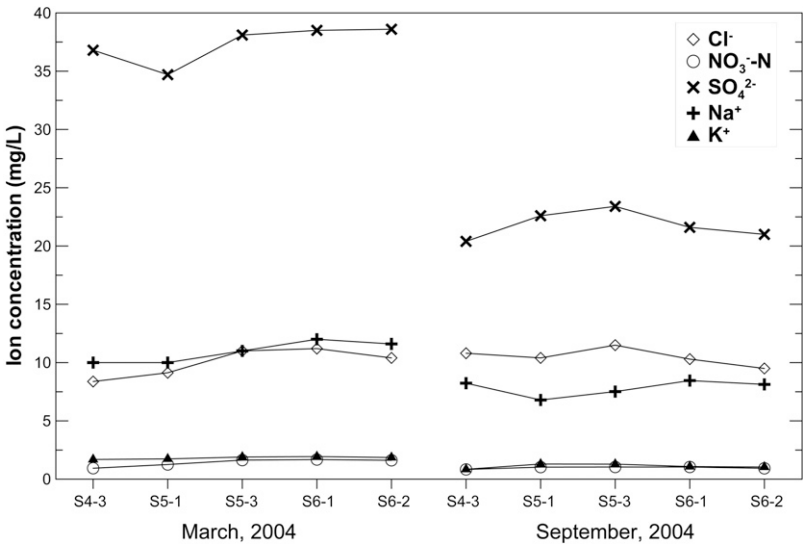

Fig. 4. Ion concentrations in the water along the Yangtze River in different seasons.

sewage and industrial wastewater from chemical fertilizer plants, might be linked to elevated nitrogen concentrations.

Sulfur Source

The trend of increasing of sulfur (SO_4^{2-}) concentrations can be produced by anthropogenic sources. Chen et al. (2002) studied the major element chemistry of the Yangtze River and argued that the increasing SO_4^{2-} concentrations in the upper part of this river correspond very well with coal consumption in the Sichuan Basin. Qin et al. (2006) compared the analytical results of river water in upstream and downstream sites of the Minjiang River. They suggested that the increasing SO_4^{2-} would be produced by anthropogenic activities and that acid rain is a potential pollution source.

Sulfate-sulfur isotopic compositions are often used to discriminate between different potential sources of anthropogenic sulfate in river waters that remain oxygenated (Spence et al., 2001). The $\delta^{34}S$ of SO_4^{2-} in the river water from the source area of the Minjiang River was −5.0‰, and such low values mean that the sulfate-sulfur source of the river water would be natural because anthropogenic pollution is negligible in this area. The $\delta^{34}S$ values of SO_4^{2-} were higher in the Minjiang and Tuojiang rivers than in the Daduhe and Jinshajiang rivers (Table 2). Such different high $\delta^{34}S$ values (+6.3 to approximately +13.6‰) were indicative of the different anthropogenic sources of sulfur in these highly polluted rivers (the concentration of SO_4^{2-} increased in the March sampling campaign in the Minjiang River from Leshan to Yibin site [SO_4^{2-}, 188 mg L^{-1}; $\delta^{34}S$, +13.6‰]). The $\delta^{34}S$ ratios of SO_4^{2-} in household wastewater and industrial effluent have rarely been reported. Li et al. (2006b) demonstrated that $\delta^{34}S$ values of SO_4^{2-} >6.0‰ from dissolved SO_4^{2-} in groundwater in the source area of the Minjiang River probably resulted from the influence of household wastewater. Vitòria et al. (2004) measured $\delta^{34}S$ values of SO_4^{2-} in detergents ranging from +8.5 to +13.6‰ in Spain and reported that SO_4^{2-} in domestic detergent is an anthropogenic sulfur source in river water via domestic wastewater. The $\delta^{34}S$ values of SO_4^{2-} from industrial effluent from leather tanning plants and paper mills ranges from +10.0 to +14.0‰ (Soler et al., 2002), which indicates that SO_4^{2-} in the river water ($\delta^{34}S$ values, +12.2 to approximately +13.6‰) analyzed in this study could also have originated from industrial effluent. Such effluent would be discharged by the factories located on the banks of the Minjiang and Tuojiang Rivers in the intensely industrialized Sichuan Basin (Tan and Wang, 2004). The currently applied superphosphate fertilizers in the Sichuan Basin, which include SO_4^{2-} contamination from the manufacturing process, had $\delta^{34}S$ values of dissolved SO_4^{2-} from +7.6 to +8.9‰ (Li et al., 2006b), suggesting the fertilizers are one of the sulfur sources in the river water.

Li et al. (2006a) reported that $\delta^{34}S$ values of SO_4^{2-} in rain water were +1.5 to +6.0‰ in the Sichuan Basin; therefore, the mixing of SO_4^{2-} from air pollutants and detergents, industrial effluents, and superphosphate fertilizers is a possible explanation of the $\delta^{34}S$ values obtained in some studied river waters. The increasing SO_4^{2-} concentrations in river waters are affected by coal consumption and acid rain, but the sulfur from the domestic, agricultural, and industrial wastewaters is also responsible for the SO_4^{2-} increase.

Table 3. Mixing ratios of the water from different rivers into the mixture.

			Mixing ratio			$\delta^{18}O$	
No.	Place	River name	2004–03	2004–09	Long-term†	2004–03	2004–09
			%			‰	
S3–1	Leshan	Minjiang‡	61.8	67.7	64.5	−9.9	−11.0
S3–2	Leshan	Daduhe	38.2	32.3	35.5	−13.3	−14.1
S3–3	Leshan	Minjiang§	100	100	100	−11.2	−12.0
S4–1	Yibin	Jinshajiang	81.5	70.6	64.0	−13.8	−14.5
S4–2	Yibin	Minjiang	18.5	29.4	36.0	−8.4	−12.8
S4–3	Yibin	Yangtze	100	100	100	−12.8	−14.0
S5–1	Luzhou	Yangtze¶	97.8	98.0	93.8	−12.8	−13.3
S5–2	Luzhou	Tuojiang	2.2	2.0	6.2	−8.3	−8.4
S5–3	Luzhou	Yangtze#	100	100	100	−12.7	−13.2

† Column data calculated from the long-term water discharge (Table 1).

‡ Before mixing with the Daduhe River.

§ After mixing with the Daduhe River.

¶ Before mixing with the Tuojiang River.

After mixing with the Tuojiang River.

Conclusions

In this study, we examined the anthropogenic impacts on the major dissolved elements in the river waters from the Minjiang and upper Yangtze rivers. When the Minjiang River flows through the populated Sichuan Basin, the concentrations of Cl^-, NO_3^-–N, SO_4^{2-}, and Na^+ gradually increase. The increasing of these ions and sulfate-sulfur isotopic values suggest that the bad water quality of the highly polluted Minjiang and Tuojiang Rivers resulted from air pollutants, domestic wastewater, industrial effluents, and agricultural fertilizers. The water quality of Yangtze River is not largely affected because the flux of water from the lightly polluted Jinshajiang River represents most of total flux in the Yangtze River.

Anthropogenic impacts on the aquatic environment in the Sichuan Basin are increasing. Without proper mitigation, this contamination will impose great pressure on the river water quality downstream due to fluvial transport of the contaminants.

Acknowledgments

We thank Ms. Xiong Jingxuan, Yu Jing, and Mr. Zeng Haiao for their help during field work and sample pretreatment. Technical laboratory assistance from Ms. K. Okazaki, T. Nogi, and Mr. T. Itai is also appreciated. We thank the two anonymous reviewers for critical comments and constructive suggestions, which helped to improve the manuscript. This work was supported by the scientific fund of the Nippon Seimei Foundation and by the International Partnership Project of Chinese Academy of Science.

References

Bureau of Geology and Mineral Resources of Sichuan Province. 1991. Regional geology of Sichuan Province. Geological Publishing House, Beijing (in Chinese).

Chen, J.S., F.Y. Wang, X.H. Xia, and L.T. Zhang. 2002. Major element chemistry of the Changjiang (Yangtze River). Chem. Geol.

187:231–255.
Chen, J.S., X.M. Gao, D.W. He, and X.H. Xia. 2000. Nitrogen contamination in the Yangtze River system, China. J. Hazard. Mater. A73:107–113.
Chen, X.Q., Y.Q. Zong, E.F. Zhang, J.G. Xu, and S.J. Li. 2001. Human impacts on the Changjiang (Yangtze) River basin, China, with special reference to the impacts on the dry season water discharges into the sea. Geomorphology 41:111–123.
CWRC. 2000. The General to the Yangtze River Basin. Changjiang River Water Resources Commission in China. Available at http://www.cjw.com.cn/eng/eng-about.asp (verified 27 Nov. 2007).
Epstein, S., and T. Mayeda. 1953. Variations of the $\delta^{18}O$ content of water from natural sources. Geochim. Cosmochim. Acta 4:213–224.
Higgitt, D.L., and X.X. Lu. 2001. Sediment delivery to the three gorges: I. Catchment controls. Geomorphology 41:143–156.
Itai, T., and M. Kusakabe. 2004. Some practical aspects of an on-line chromium reduction method for D/H analysis of natural waters using a conventional IRMS. Geochem. J. 38:435–440.
Japan Society for Analytical Chemistry. 2000. Water quality analyses. p. 253–256. *In* Japan Society for Analytical Chemistry, Hokkaido Branch (ed.) Japan Society for Analytical Chemistry, Tokyo, Japan.
Li, X.D., H. Masuda, M. Kusakabe, F. Yanagisawa, and H.A. Zeng. 2006a. Degradation of groundwater quality due to anthropogenic sulfur and nitrogen contamination in the Sichuan Basin, China. Geochem. J. 40:309–332.
Li, X.D., H. Masuda, M. Ono, M. Kusakabe, F. Yanagisawa, and H.A. Zeng. 2006b. Contribution of atmospheric pollutants into groundwaters in the northern Sichuan Basin, China. Geochem. J. 40:103–119.
Liu, C., Q.X. Wang, and M. Watanabe. 2006. Nitrogen transported to the three Gorges Dam from agro-ecosystems during 1980–2000. Biogeochemistry 81:291–312.
Liu, G.D., W.L. Wu, and J. Zhang. 2005. Regional differentiation of non-point source pollution of agriculture-derived nitrate nitrogen in groundwater in northern China. Agric. Ecosyst. Environ. 107:211–220.
Lu, X.X., and D.L. Higgitt. 2001. Sediment delivery to the three gorges: II. Local response. Geomorphology 41:157–169.
National Climatic Data Center. 2003. World Meteorological Organization Climatic Data Online. Available at http://lwf.ncdc.noaa.gov/cgi-bin/res40.pl?page=climvisgsod.html (verified 27 Nov. 2007).
National Soil Survey Office, 1998. The soil of China. Chinese Agricultural Publishing House, Beijing (in Chinese).
Négrel, P., and H. Pauwels. 2004. Interaction between different groundwaters in Brittany catchments (France): Characterizing multiple sources through strontium- and sulphur isotope tracing. Water Air Soil Pollut. 151:261–285.
Qin, M.Z., and Y.Z. Chen. 2001. Analysis on land use change and its impact on soil quality in fast urbanization region: Guangzhou as a case study. Res. Agric. Modern. 22:119–122 (in Chinese, with English abstract).
Qin, J.H., Y.S. Huh, J.M. Edmond, G. Du, and J. Ran. 2006. Chemical and physical weathering in the Min Jiang, a headwater tributary of the Yangtze River. Chem. Geol. 227:53–69.
SEPA China. 2006. Report on environmental status of China in 2005. State Environmental Protection Administration of China. Available at http://www.zhb.gov.cn/plan/zkgb/05hjgb/200607/t20060727_91443.htm (verified 27 Nov. 2007) (in Chinese).
Sherwood, W.C. 1989. Chloride loading in the South Fork of the Shenandoah River, Virginia, USA. Environ. Geol. Water Sci. 14:99–106.
Soler, A., À. Canals, S.L. Goldstein, N. Otero, N. Antich, and J. Spangenberg. 2002. Sulfur and strontium isotope composition of the Llobregat River (NE Spain): Tracers of natural and anthropogenic chemicals in stream waters. Water Air Soil Pollut. 136:207–224.
Spence, M.J., S.H. Bottrell, S.F. Thornton, and D.N. Lerner. 2001. Isotopic modeling of the significance of sulphate reduction for phenol attenuation in a contaminated aquifer. J. Contam. Hydrol. 53:285–304.
Streets, D.G., and S.T. Waldhoff. 2000. Present and future emissions of air pollutants in China: SO_2, NO_x, and CO. Atmos. Environ. 34:363–374.
Tan, Y., and Y.Q. Wang. 2004. Environmental migration and sustainable development in the upper reaches of the Yangtze River. Popul. Environ. 25:613–636.
Varis, O., and P. Vakkilainen. 2001. China's 8 challenges to water resources management in the first quarter of the 21st Century. Geomorphology 41:93–104.
Vitòria, L., N. Otero, A. Soler, and À. Canals. 2004. Fertilizer characterization: Isotopic data (N, S, O, C, and Sr). Environ. Sci. Technol. 38:3254–3262.
Yanagisawa, F., and H. Sakai. 1983. Preparation of SO_2 for sulfur isotope ratio measurements by thermal decomposition of $BaSO_4$–V_2O_5–SiO_2 mixtures. Anal. Chem. 55:985–987.
Yin, H.F., and C.A. Li. 2001. Human impact on floods and flood disasters on the Yangtze River. Geomorphology 41:105–109.
Zhang, X.B., and A.B. Wen. 2004. Current changes of sediment yields in the upper Yangtze River and its two biggest tributaries, China. Global Planet. Change 41:221–227.