

$\delta^{13}\text{C}_{\text{DIC}}$ tracing of dissolved inorganic carbon sources at Three Gorges Reservoir, China

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ABSTRACT

In order to understand water chemistry after impoundment of the Three Gorges Reservoir (TGR), the authors assessed the hydrogeochemical parameters (water temperature, pH, conductivity, dissolved O_2), major element composition, and the carbon stable isotopic value of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in summer and winter at various depths in the water column at TGR in 2009. In reservoir water, the DO values are lower in winter than in summer, but the pH values and conductivity values are higher. Ca^{2+} and Na^+ are the dominant cations and HCO_3^- and SO_4^{2-} are the dominant anions. In surface waters, the $\delta^{13}\text{C}_{\text{DIC}}$ values are more negative in summer than they are in winter, whereas the dissolved inorganic carbon (DIC) concentrations are relatively lower. In the water column, the DIC and $\delta^{13}\text{C}_{\text{DIC}}$ values do not change significantly with water depth or seasons. The DIC content shows a dilution effect in summer and is not modified by phytoplanktonic activity or photosynthesis. Even after the dam obstructed flow, the chemical profile of water in TGR is similar to that of the natural rivers before impoundment. Therefore, in this study, the water at TGR still had riverine characteristics and was still a heterotrophic system.

Key words | carbon isotope, dissolved inorganic carbon, major ions, Three Gorges Reservoir (TGR)

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INTRODUCTION

In recent years, natural systems have been more and more affected by human activities (Dynesium & Nilsson 1994; Arheimer & Lindström 2014; Jaramillo & Destouni 2015; Hafsi *et al.* 2016; Williams *et al.* 2016). In particular, dams built to modulate rivers have extensive effects on the ecological systems of rivers and their drainage basins (Arheimer & Lindström 2014; Yang & Lu 2014). Damming rivers has a global impact on water resources. Impoundments change the characteristics of a water body, affecting not only the hydrology but also physical, chemical, and biological characteristics (Munger *et al.* 2017). Reservoirs disrupt the natural biogeochemical cycles of carbon, nutrients and metals and possibly affect the entire catchment, including downstream ecosystems such as wetlands, estuaries, deltas and adjacent sea areas (Friedl & Wüest 2002; Zhang *et al.* 2014; Maavara *et al.* 2015). Current studies focus on changes in the hydrological status of rivers caused by dam blocking, silt deposition, fish migration, nutrients retained in reservoirs, the biogeochemical cycle of elements within reservoirs, and greenhouse gas emission

among other topics (Milliman 1997; Xiangbin *et al.* 2013; Domingues *et al.* 2014; Gao *et al.* 2015; Ran *et al.* 2015).

Biogeochemical cycles of nutrients in reservoirs, the transfer of energy, and the dynamics of CO_2 and nutrition status are the key factors affecting the aquatic environment (Gomez-Velez *et al.* 2015; Teodoru *et al.* 2015). The biogeochemical cycle of carbon can help us understand the changes in the aquatic environment, ecological processes in waters, and element cycles (Kiel & Cardenas 2014). Variations in the concentrations of dissolved inorganic carbon (DIC) and its isotopic composition ($\delta^{13}\text{C}$) in the aquatic environment can reflect the geochemical behavior of carbon and its biogeochemical characteristics (Das *et al.* 2005; Myrbo & Shapley 2006; Tamše *et al.* 2015). The Yangtze River, as the longest river in Asia, is the most important river in China. In the past several years, many studies about the effect of the Three Gorges Dam (TGD) on the water quality downstream and others assessing the water quality of the Three Gorges Reservoir (TGR) have been carried out (Zhao *et al.* 2013; Gao *et al.* 2016; Lou & Yin 2016).

However, there are few studies of carbon system of TGR waters after impoundment. In this study, the TGR was taken as an example to investigate the dynamics of DIC and carbon isotope transport. It also examined nutrient sources based on monitoring data and field surveys in July and December 2009. Therefore, the objectives of this study were: (1) to better understand the evolution of TGR and its biogeochemical features; (2) to provide basic data for carbon cycle in the Yangtze River; and (3) to provide valuable data on TGR, which is in the early stage of reservoir ecosystem evolution.

SAMPLING SITE AND ANALYTICAL METHODS

Sampling site description

The TGD, the world's largest, was built on the Yangtze River in southern China, with full operation of hydroelectric facilities expected in 2009 (Wang *et al.* 2010). The TGD is 181 m high and its reservoir stores $>39 \text{ km}^3$ (Nilsson *et al.* 2005). The TGR area is located in China at $29^{\circ}16' - 31^{\circ}25' \text{N}$ and

$106^{\circ}50' - 110^{\circ}50' \text{E}$ (Figure 1), covering an overall area of $55,742 \text{ km}^2$ and including 19 districts and counties/cities (Keqiang *et al.* 2009). The potential benefits of the TGR have always been enormous, including flood control, energy production, increased navigability of the Yangtze River and access to fresh water.

The TGR region lies between the Tibetan Plateau in the west and the rolling hills and plains of China's eastern subtropical region. Its annual mean temperature is $16.5 - 19^{\circ} \text{C}$, ranging from $3.4 - 7.2^{\circ} \text{C}$ in January to $28 - 30^{\circ} \text{C}$ in July. Annual mean precipitation is approximately 1,100 mm, with 80% falling between April and October. With the TGD fully functioning in 2009, the water level in the reservoir fluctuates from 145 m in summer to 175 m in winter. In order to investigate nutrient dynamics and transport within the reservoir, the study site was located in the front of TGD.

Analytical methods

Water samples were collected in July and December 2009, which represent the lowest (145 m) and highest (172 m)

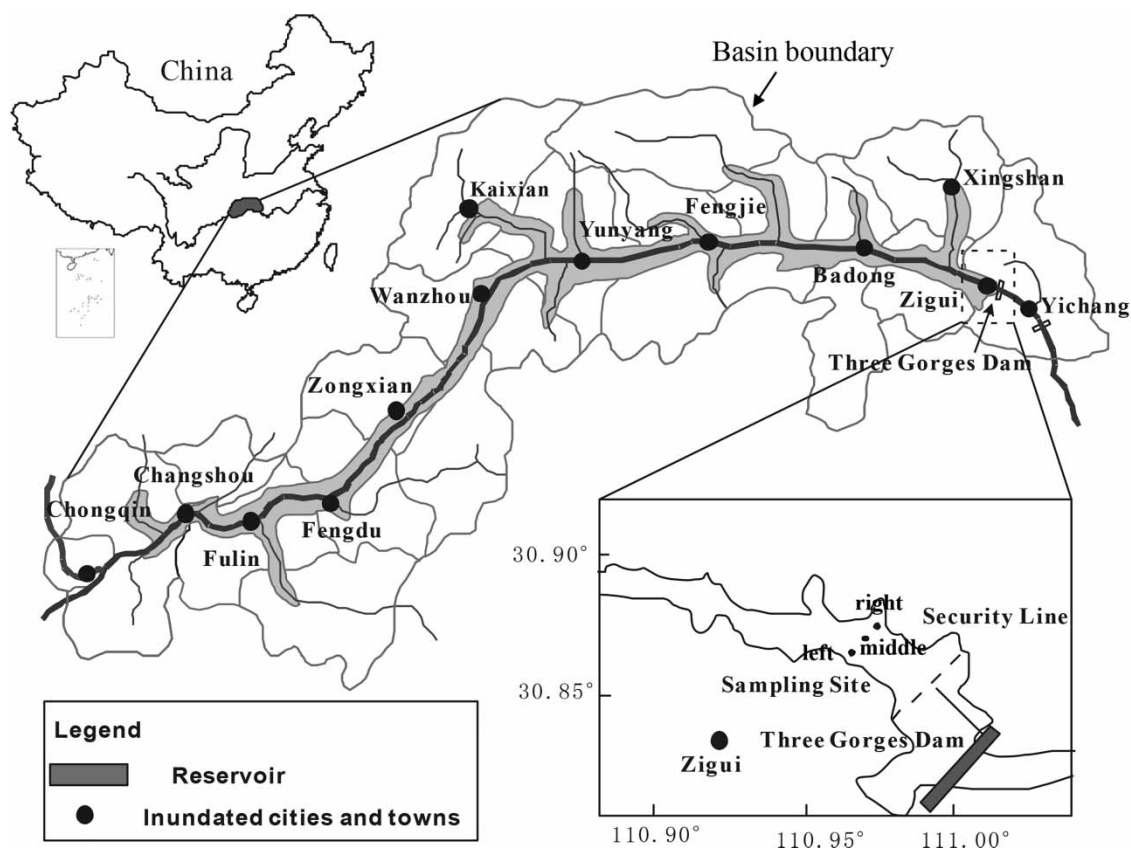


Figure 1 | TGR area, dam location in China and sampling site.

water levels and also the seasonal extremes of summer and winter. The samples were collected at three sites at TGR, where were about 5 km from the dam. The three sites were 500 m from the left bank, in the middle (650 m from right bank) and 300 m from the right bank of Yangtze River (Figure 1). The flow rate were 0.18, 0.23 and 0.20 meters per seconds in left, middle and right, respectively. A security line has been set in front of the TGD for safety reasons, and no vessel can cross the security line. Our sampling sites are very close to the security line.

The pH, temperature, dissolved O₂, electrical conductivity (EC) and turbidity were measured at the sampling sites with a portable YSI 6600V2 (YSI Inc., USA). The samples were collected at different water depths (at increments of 5 m up to 100 m). The depths at the left and right bank are approximately 40 m and the depth in the middle of the river is approximately 100 m. 3,000 mL water were collected for each sample.

HCO₃⁻ was determined using the HCl titration method within hours of sample collection. Immediately after collection, water samples were filtered through 0.45 μm Whatman cellulose acetate membrane filters, and a small portion of these filtered samples was stored for measuring anions, while another portion was acidified with ultra-purified hydrochloric acid to pH < 2 to measure cations. All samples were stored in darkness. The cations (K⁺, Na⁺, Ca²⁺ and Mg²⁺) were determined by atomic absorption spectrometry (AAS, PE-5100-PC), while the anions (F⁻, Cl⁻, NO₃⁻ and SO₄²⁻) were determined by ion chromatography (Donex, ICS-90).

For the determination of δ¹³C_{DIC}, water samples were filtered by pressure filtration through a 0.45 μm polycarbonate filter membrane. Samples were then collected in polyethylene bottles with airtight caps and preserved with HgCl₂ to prevent biological activity. Using a modification of the method of Atekwana & Krishnamurthy (1998), a 10-mL water sample was injected by syringe into glass bottles that were prefilled with 1 mL 85% phosphoric acid and that had magnetic stir bars. No detectable gases were produced by unwanted reactions between glass and acid when the glass bottles with 1 mL 85% phosphoric acid and allowed to stand for 24 h (Atekwana & Krishnamurthy 1998). The acid-water reaction began immediately upon injection. CO₂ was extracted into a vacuum line in the laboratory at 50 °C, while stirring for 10 min. It was then cryogenically separated from H₂O by being passed sequentially through an N₂-cooled ethanol trap and then frozen into a manometer cold finger by a liquid N₂ trap. Finally, the CO₂ was transferred cryogenically into a tube for isotope

measurement. Carbon isotope ratios of the DIC were determined on a Finnigan MAT 252 mass spectrometer. The carbon isotope values are reported using the δ notation relative to Pee Dee Belemnite (PDB) in per mil, where

$$\delta^{13}\text{C}(\text{‰}) = \left[\left(\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{PDB}}} \right) - 1 \right] \times 1,000 \quad (1)$$

Routine δ¹³C_{DIC} measurements have an overall precision of ±0.1‰. The isotopic standards of carbonate and IAEA-C3 (cellulose) were measured as a check on reproducibility. A number of duplicate samples were measured, and the results show that the differences were less than the range of measurement accuracy.

For pCO₂ calculation, Henry's constant (K_H) and the first dissociation constants for CO₂ gas in water (K₁) were corrected by temperature and ionic strength (Raymond *et al.* 1997; Barth & Veizer 1999). Then, pCO₂ was calculated from HCO₃⁻ and pH with the corrections for temperature and ionic strength. Calcite saturation index (SI_c) was calculated as follows:

$$\text{SI}_c = \log \left(\frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_c} \right) \quad (2)$$

K_c is the temperature-dependent equilibrium constant for calcite dissociation. If SI_c > 0, water is super saturated with respect to calcite, calcium carbonate could precipitate; if SI_c < 0, water is aggressive to calcite, calcium carbonate could dissolve; and if SI_c = 0, the system reaches equilibrium (Liu *et al.* 2008).

RESULTS

Hydrogeochemical parameters

The field data, major ion compositions and calculations are given in Table 1.

In summer, the surface water is continuously heated by sunlight. Hence, differences in density between the epilimnion and the hypolimnion will lead to a stratification of the water column. The epilimnion water temperatures in the right bank, middle, left bank of the reservoir were 25.3 °C, 24.3 °C, and 26.9 °C in summer. However, all the hypolimnion water temperatures are 23.7 °C in summer. In winter, the water in the epilimnion and hypolimnion is well blended, and there is almost no difference in water temperature. From Table 1, it can be seen that there is no

Table 1 | Major ions ($\mu\text{mol/L}$) and inorganic carbon isotopic data at the TGR

	Depth (m)	T ($^{\circ}\text{C}$)	DO (mg/L)	pH	EC (mS/cm)	Turbidity (NTU)	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	NH ₄ ⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	SiO ₂	HCO ₃ ⁻ (DIC)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	SI _C	pCO ₂ (μatm)	
Summer																					
Right bank	0	25.3	6.02	7.27	372	27.1	528	374	50	1,070	3	8	406	139	500	44	1,952	-11.98	-0.57	6,352	
	10	23.7	5.59	7.22	365	27.4	544	381	52	1,079	8	9	404	135	486	44	1,952	-11.62	-0.63	6,978	
	20	23.7	5.67	7.23	365	27.8	545	381	52	1,080	5	11	409	121	485	45	1,996	-12.12	-0.61	6,974	
	30	23.7	5.70	7.25	365	27.9	541	379	52	1,086	3	10	411	130	492	44	1,979	-11.28	-0.59	6,602	
	35	23.8	5.72	7.30	366	28.5	538	381	52	1,090	4	9	406	140	498	44	1,940	-11.64	-0.55	5,770	
Middle	0	24.3	7.25	7.20	368	28.3	525	370	52	1,070	2	5	373	112	437	46	2,011	-11.13	-0.63	7,599	
	26	23.7	6.67	7.31	363	31.0	561	398	56	1,147	3	7	383	112	441	46	1,996	-11.51	-0.50	5,794	
	50	23.7	7.34	7.28	363	33.8	558	387	53	1,122	5	10	409	111	474	46	2,145	-12.17	-0.51	6,670	
	75	23.7	5.92	7.22	364	35.4	572	397	54	1,153	2	10	401	144	490	27	1,916	-12.00	-0.61	6,839	
	100	23.7	5.76	7.17	364	34.3	532	383	52	1,122	3	8	401	132	480	46	1,913	-10.98	-0.67	7,669	
Left bank	0	26.9	7.73	8.16	369	15.6	564	404	52	1,121	3	8	386	70	458	44	2,018	-11.20	0.37	865	
	5	23.9	5.60	7.04	360	19.0	546	401	51	1,126	2	9	396	104	463	46	1,942	-11.18	-0.79	10,531	
	10	23.9	5.52	7.26	371	20.9	563	413	52	1,161	2	9	409	108	478	47	2,003	-11.38	-0.55	6,531	
	15	23.8	5.50	7.28	370	23.1	553	386	51	1,114	2	7	389	99	450	48	1,968	-11.39	-0.55	6,136	
	23	23.8	5.68	7.33	369	25.7	578	406	54	1,159	2	8	402	70	476	48	1,958	-10.15	-0.49	5,432	
Winter																					
Right bank	0	18.89	5.11	8.03	394	11.50	753	430	54	1,058	7	7	641	97	468	60	2,308	-6.96	0.19	1,211	
	5	18.89	5.11	8.02	394	10.97	754	429	55	1,038	7	7	664	98	485	59	2,214	-6.90	0.16	1,175	
	10	18.89	5.11	8.02	394	17.05	754	424	55	1,044	4	7	646	96	473	61	2,254	-6.93	0.17	1,203	
	15	18.88	5.10	8.01	394	8.10	792	436	55	1,064	7	7	647	65	472	61	2,205	-6.99	0.16	1,197	
	20	18.88	5.05	8.01	394	5.37	754	428	55	1,049	15	8	640	102	469	61	2,200	-6.95	0.15	1,204	
	25	18.87	4.96	7.99	394	6.38	767	431	54	1,033	15	6	643	96	472	59	2,200	-7.01	0.13	1,251	
	30	18.83	5.05	7.85	395	9.28	773	434	55	1,062	42	6	642	85	468	61	2,205	-7.04	-0.01	1,743	
Middle	0	18.82	5.08	8.01	395	2.22	758	431	55	1,048	8	8	641	96	465	58	2,223	-7.09	0.15	1,209	
	10	18.91	4.89	8.06	394	2.28	817	447	57	1,101	21	7	644	97	469	58	2,200	-6.96	0.22	1,064	
	20	18.91	5.01	8.05	394	2.43	784	440	56	1,059	17	5	649	101	475	56	2,214	-7.00	0.20	1,088	
	30	18.92	5.00	8.04	392	2.33	776	445	55	1,079	36	6	641	100	475	59	2,178	-6.99	0.19	1,104	
	40	18.92	5.00	8.03	392	2.18	733	426	55	1,053	42	7	646	98	466	59	2,303	-7.03	0.19	1,195	
	50	18.92	4.93	8.03	391	2.59	769	436	55	1,072	8	7	632	82	453	59	2,205	-6.99	0.18	1,144	
	60	18.92	4.98	8.02	390	3.40	789	441	55	1,073	16	7	636	94	457	57	2,254	-6.96	0.18	1,197	
	70	18.92	4.82	8.02	393	3.18	765	441	54	1,062	15	6	628	94	454	61	2,214	-7.00	0.17	1,176	
	80	18.92	4.83	8.02	392	2.87	806	443	56	1,088	10	6	590	91	430	60	2,200	-6.98	0.18	1,168	
	90	18.93	4.80	8.02	389	3.20	742	415	53	1,045	8	6	644	99	464	61	2,200	-6.99	0.16	1,169	
	100	18.93	4.75	8.02	391	3.25	739	415	53	1,017	12	6	627	98	452	59	2,303	-6.98	0.17	1,224	
Left bank	0.0	18.92	5.00	8.00	393	0.42	784	438	55	1,081	9	4	646	96	457	61	2,200	-7.05	0.16	1,210	
	5	18.95	4.98	8.03	393	0.60	776	442	55	1,080	27	6	644	99	459	61	2,272	-7.04	0.20	1,179	
	10	18.95	4.90	8.04	393	0.50	762	438	55	1,080	6	7	663	98	466	60	2,200	-7.17	0.19	1,116	
	15	18.95	4.83	8.04	393	1.06	741	423	54	1,060	6	7	657	99	462	61	2,273	-7.15	0.20	1,153	
	20	18.95	4.80	8.04	392	1.06	786	447	55	1,085	12	5	645	97	462	61	2,200	-6.99	0.20	1,116	
	25	18.95	4.84	8.04	392	1.15	757	432	54	1,057	7	6	645	92	462	61	2,400	-6.97	0.22	1,231	
	30	18.95	4.87	8.04	391	0.73	771	438	55	1,058	6	6	647	101	460	60	2,200	-7.03	0.19	1,116	
	35	18.96	4.94	8.03	392	1.32	748	421	54	1,029	12	6	648	96	462	60	2,348	-7.00	0.19	1,214	
	40	18.96	4.89	8.03	392	1.34	802	445	56	1,079	12	6	672	97	476	61	2,254	-7.00	0.20	1,162	

variation in the vertical water temperature in winter, and the temperature declines from the surface to lower areas of the water column, with no changes below the 3 m of surface in summer. The epilimnion and hypolimnion water temperature were 18.9 °C in winter.

The average conductivities of water samples were 366 $\mu\text{S}/\text{cm}$ in summer and 392 $\mu\text{S}/\text{cm}$ in winter. The average dissolved oxygen (DO) values were 6.1 mg/L in summer and 4.9 mg/L in winter. The pH values were 7.3 in summer and 8.0 in winter. The pH values and conductivity values were higher in winter. However, the DO values were lower in winter than in summer.

Major ion compositions

Variations in major ion compositions are shown in the cation and anion ternary diagrams (Figure 2), and they are compared with previous studies (Chen *et al.* 2002; Chetelat *et al.* 2008; Jian *et al.* 2010). In reservoir water, Ca^{2+} and Na^+ are the dominant cations and HCO_3^- and SO_4^{2-} are the dominant anions (Table 1). Ca is the major cation, with average concentrations 1,113 $\mu\text{mol}/\text{L}$ in summer and 1,061 $\mu\text{mol}/\text{L}$ in winter. HCO_3^- is the most important anion, with an average value of 1,979 $\mu\text{mol}/\text{L}$ in summer and 2,238 $\mu\text{mol}/\text{L}$ in winter. It accounts for approximately 60% of the total anions. SO_4^{2-} and Cl^- are the second most important anions with average values of 473 $\mu\text{mol}/\text{L}$ and 399 $\mu\text{mol}/\text{L}$ in summer and 464 $\mu\text{mol}/\text{L}$ and 643 $\mu\text{mol}/\text{L}$ in winter. The chemical composition of reservoir water is characterized by an anion concentration sequences of $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ in most cases, and for cations, the average concentration of Ca^{2+} are higher than those of Na^+ , Mg^{2+} and K^+ .

Our data showed that the reservoir water has a chemical composition similar to that of nearby sampling sites in the Yangtze River before the impoundment of TGR (Figure 2, Chen *et al.* 2002; Chetelat *et al.* 2008; Jian *et al.* 2010). The dominance of Ca^{2+} and Na^+ , together with HCO_3^- and SO_4^{2-} , and the lesser roles of Si and K^+ in major ion compositions should be come from upstream in the TGR. The outcrops in the upper reaches of TGR are mainly carbonate rocks and evaporate (Chetelat *et al.* 2008; Jian *et al.* 2010). Therefore, the chemical characteristics of the water reflect carbonate weathering and of the dissolution of evaporated strata into the solutes of river water.

DIC concentrations and isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$)

Carbonate rocks and evaporate are widespread in the Yangtze basin (Ming-hui *et al.* 1982; Chetelat *et al.* 2008). The average pH value of reservoir water was 7.3 in summer and 8.0 in winter. Under these conditions, the DIC in the water body is dominated by HCO_3^- , which accounts for more than 95% of the total DIC. Therefore, HCO_3^- can be used to represent the DIC in aquatic systems of the TGR.

The DIC data are presented in Table 1 and depicted as depth profiles in Figure 3. In summer, the concentrations of DIC range from 1.9 mmol/L to 2.1 mmol/L, with an average value of 2.0 mmol/L. In winter, the concentrations of DIC vary from 2.1 mmol/L to 2.4 mmol/L, with an average value of 2.2 mmol/L. Obvious seasonal variations can be observed in all water samples (Figure 3).

The partial pressure of CO_2 ($p\text{CO}_2$) in the surface water ranged from 865 to 10,531 μatm and demonstrated a

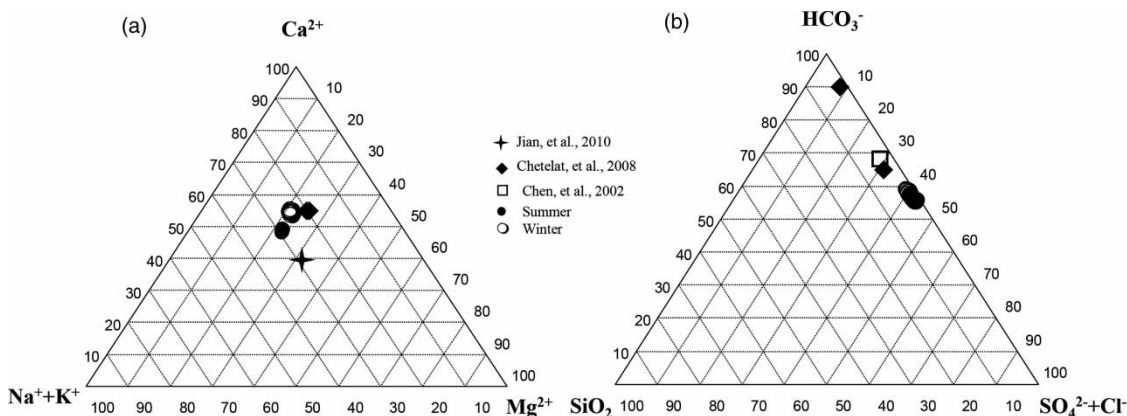


Figure 2 | Triangular diagrams for cation (a) and anion (b) compositions in the waters at TGR (Jian *et al.* 2010, sampled near the Three Georges Dam at May 2003; Chen *et al.* 2002, sampled at Yichang hydrochemical station from 1958–1990; Chetelat *et al.* 2008, sampled at TGD at August 2006).

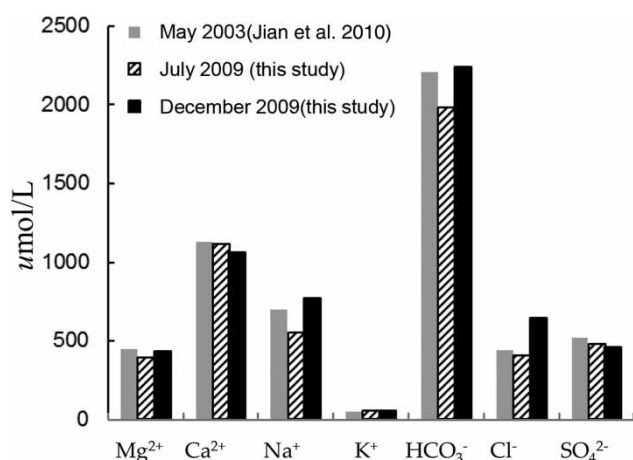


Figure 3 | Variations of the concentration of $\delta^{13}\text{C}_{\text{DIC}}$ and DIC in the water at TGR.

significant seasonal variation. In most samples, $p\text{CO}_2$ was above the atmospheric level (i.e. approximately 390 ppm). However, the $p\text{CO}_2$ was significantly different between the surface and bottom of the TGR (Table 1). Even when controlled by the $p\text{CO}_2$, the saturation index of calcite (SI_c) also demonstrated an obvious seasonal variation (Table 1). The SI_c results of the samples collected in winter were above zero, indicating that the water was oversaturated with CaCO_3 . Precipitation of calcite was thermodynamically favored at the TGR in winter. However, in summer, the SI_c results fell below zero.

The $\delta^{13}\text{C}_{\text{DIC}}$ values of water samples collected in summer ranged from -10.2‰ to -12.2‰ , with an average value of -11.4‰ . The $\delta^{13}\text{C}_{\text{DIC}}$ values of water samples collected in winter ranged from -6.9‰ to -7.2‰ , with an average value of -7.0‰ . The $\delta^{13}\text{C}_{\text{DIC}}$ values changed little through the water column at the TGR. The values were more positive in winter than summer, and there was obvious seasonal variation (Figure 3).

DISCUSSION

Seasonal variation of chemical composition

In general, the average concentrations of Ca^{2+} , Na^+ , Mg^{2+} , HCO_3^- and SO_4^{2-} are lower in summer than winter (Figure 4). This can be attributed to dilution by rain. The summer's huge influx of water into the reservoirs can dilute the solute concentrations of the reservoir water body, decreasing the ion and DIC concentrations. With respect to the previous studies, the concentrations of Na^+ , Mg^{2+} , K^+ , Ca^{2+} , SO_4^{2-} , HCO_3^- are similar to the results

from Jian *et al.* (2010), which is newest data (sampled at May, 2003) before the closure of TGD. The concentrations of NO_3^- in the reservoir are higher than previously recorded (Chen *et al.* 2002; Chetelat *et al.* 2008; Li *et al.* 2010), indicating changes in human activities, for the main sources of nitrate in Changjiang catchment are agriculture/urban (Chetelat *et al.* 2008).

Controlling factors of $\delta^{13}\text{C}$

The $\delta^{13}\text{C}_{\text{DIC}}$ is affected mainly by the following factors: the isotopic composition of DIC in the inflow of water body, CO_2 exchange at the interface between water and atmosphere, photosynthesis and respiration (Dubois *et al.* 2009; Karim *et al.* 2011). Among them, the $\delta^{13}\text{C}_{\text{DIC}}$ in the inflow of water body was determined by river water and the underground water input into the reservoirs. In this study, all of the samples had $p\text{CO}_2$ higher than atmospheric levels. Accordingly, DIC was derived mainly from the CO_2 released from decomposition of organic matter in soil and chemical weathering of rocks in the drainage basin (Wachniew & Rózański 1997; Myrbo & Shapley 2006; Yu *et al.* 2008). According to previous studies (Wu *et al.* 2007), the $\delta^{13}\text{C}_{\text{DIC}}$ values derived from decomposition of organic matter in soil in the Yangtze River drainage range from -31.2‰ to -23.8‰ . There is almost no C isotopic fractionation when CO_2 is produced by the oxidation of soil organic matter (Palmer *et al.* 2001), and the $\delta^{13}\text{C}_{\text{DIC}}$ value may decline 7.9‰ when gaseous CO_2 is changed into DIC (Das *et al.* 2005). If the DIC mainly originates from soil and organic matter oxidation, $\delta^{13}\text{C}_{\text{DIC}}$ value will be -23.3‰ to -15.9‰ . Usually, marine limestone typically has an average $\delta^{13}\text{C}$ of 0‰ (Dubois *et al.* 2009), and its dissolution in soil water generally produces DIC with $\delta^{13}\text{C}$ around -8.5‰ (Karim *et al.* 2011).

In CO_2 exchange at the interface between water and atmosphere, the $\delta^{13}\text{C}_{\text{DIC}}$ values derived from dissolved atmospheric CO_2 vary between 0‰ and -2.5‰ (Louis *et al.* 2000; Wang & Veizer 2000; Hélie *et al.* 2002; Myrbo & Shapley 2006). Usually, aquatic photosynthesis makes use of dissolved CO_2 , with an isotope fractionation of approximately 20‰ – 23‰ (Louis *et al.* 2000; Hélie *et al.* 2002), thus enriching the isotopic composition of DIC in the remaining water in ^{13}C (Herczeg 1987; Barth & Veizer 1999; Hélie *et al.* 2002; Myrbo & Shapley 2006). Respiration can induce the decomposition of organic matter, and the DIC derived from this process has a similar $\delta^{13}\text{C}_{\text{DIC}}$ to that of the organic source (van Breugel *et al.* 2005).

DIC and $\delta^{13}\text{C}_{\text{DIC}}$ values in the reservoir waters are shown in Figure 5(a). Most samples showed that $\delta^{13}\text{C}_{\text{DIC}}$ values increased little with DIC content. These distributions

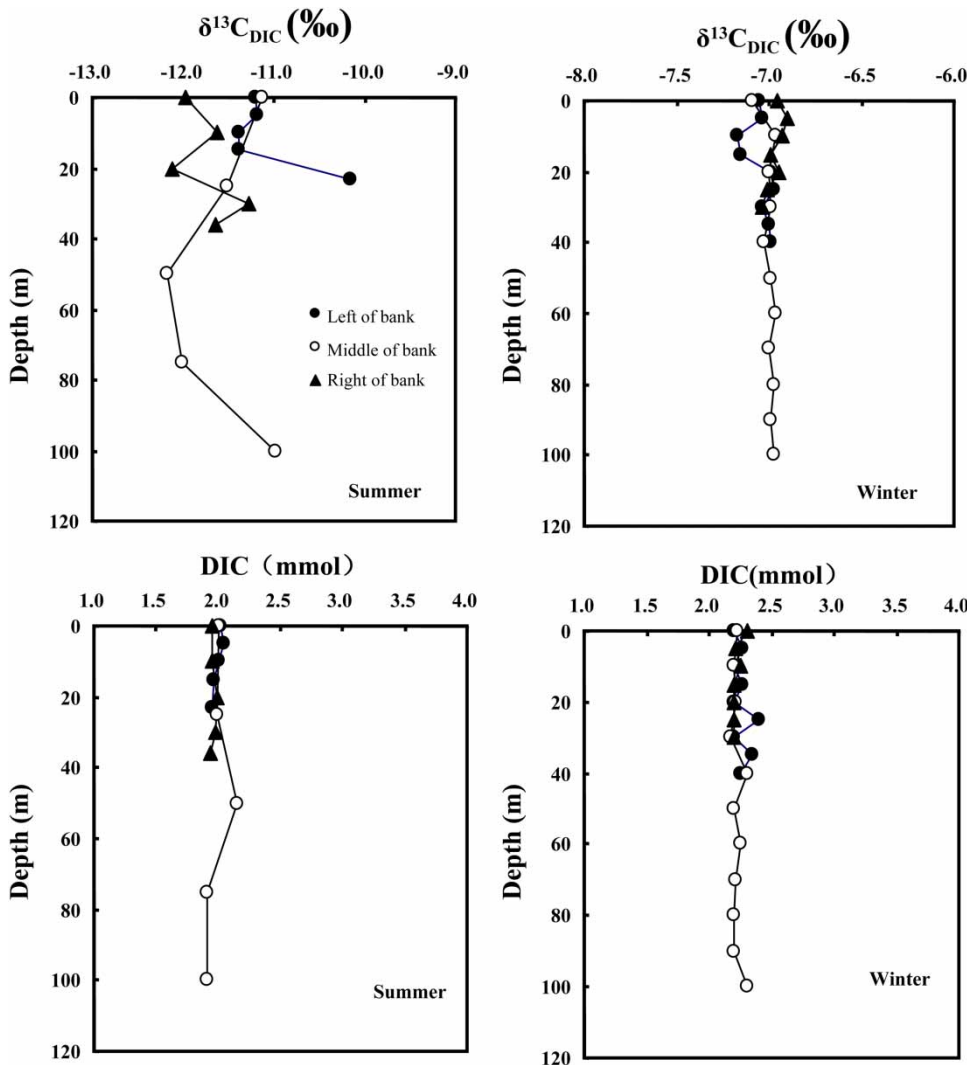


Figure 4 | Comparison of major ions before and after the construction of the TGD (data of 2003 from Jian et al. (2010)).

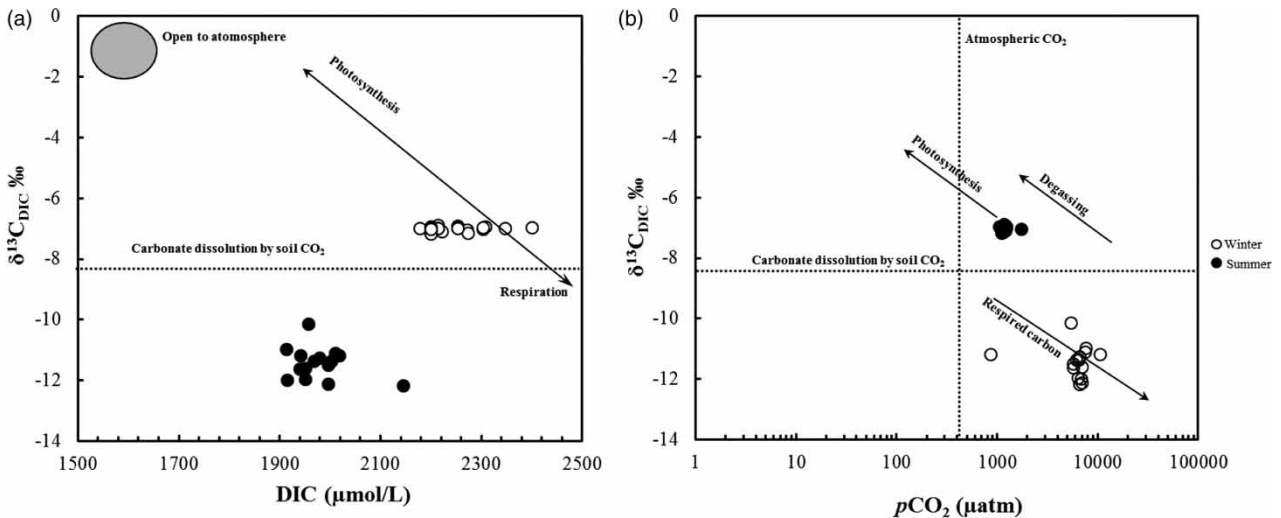


Figure 5 | $\delta^{13}C_{DIC}$ values vs. DIC (a) and pCO_2 (b) in the waters at the TGR.

are different from 'textbook' behavior of lacustrine water-column DIC (Cohen 2003). The photosynthesis of phytoplankton was not the major factor to affect the $\delta^{13}\text{C}_{\text{DIC}}$ values of reservoir water. From Figure 5(a), it can be seen that all samples in winter were above the dissolution line of carbonate, indicating an influence of carbonate weathering and atmospheric input. However, the $\delta^{13}\text{C}_{\text{DIC}}$ value is about -11.0‰ in summer, which is lighter than that in winter. There are two sources: silicate weathering by carbonic acid and the degradation of organic matter. The concentrations of dissolved Si in the samples were very low. So, the DIC in the TGR mainly comes from a mix of carbonate weathering and the degradation of organic matter. Moreover, the turbidity is very high at the TGR in summer (Table 1), which limits the intensity of photosynthesis. According to the concentrations of dissolved ions, the photosynthesis at TGR is very weak, which cannot affect the DIC concentration of water.

$p\text{CO}_2$ is significantly higher in TGR than atmospheric levels. There was significant variation in the seasonal distribution of $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{DIC}}$ (Figure 5(b)). The hypolimnion had high $p\text{CO}_2$ in summer, and there was little variation in winter due to the elimination of thermal stratification. The increase of water $p\text{CO}_2$ decreases the carbonate saturation index, indicating an increase in erosion. After TGR was impounded, algal photosynthesis is enhanced due to both the greater transparency in the reservoir and the decrease in flow speed.

In the TGR, the hydrodynamic conditions have changed, and the velocity of water flow has slowed conspicuously since the dam was built, which has caused nutrients to be retained in the water body or accumulated in the bottom sediments. It can be seen that the $\delta^{13}\text{C}_{\text{DIC}}$ values of surface waters are more negative in summer but more positive in winter, while the DIC concentrations are low in summer but high in winter. Similar results have been acquired from some natural rivers (Wang & Veizer 2000; Karim *et al.* 2011). As indicated by lacustrine research, the $\delta^{13}\text{C}_{\text{DIC}}$ values of the water body are more negative in winter than summer (Myrbo & Shapley 2006; Yu *et al.* 2008). This suggests that no changes have taken place in the hydrogeochemical characteristics of the rivers as a result of TGD blocking.

CONCLUSIONS

$\delta^{13}\text{C}_{\text{DIC}}$ is an important ecological proxy, in spite of the complexity of DIC cycling and the ambiguities inherent in

the interpretation of carbon isotopes in reservoir sediment records. Our data showed that the $\delta^{13}\text{C}_{\text{DIC}}$ values of surface reservoir water are lower in summer than winter, which is consistent with previous reports from the Yangtze River (Li *et al.* 2010). In the water column, lower water samples have more positive $\delta^{13}\text{C}_{\text{DIC}}$ values than upper water samples in summer, indicating that both photosynthesis and respiration of plants have a strong influence on the carbon isotopic composition of reservoir water. Water temperature (T), pH value, DIC and the $\delta^{13}\text{C}_{\text{DIC}}$ value in TGR are similar to those of natural Yangtze River water. Before and after the impoundment of TGR, the concentrations of DIC changed little. At a given depth, the $\delta^{13}\text{C}_{\text{DIC}}$ value will become more negative the longer the reservoir operates. However, the operation time of the TGR is very short as yet, and the hydrogeochemical character of the waters in TGR was more consistent with natural rivers than the waters of established reservoirs.

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