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Dissolved inorganic carbon and its isotopic differentiation in cascade reservoirs in the Wujiang drainage basin

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Three cascade reservoirs, built in different periods of time in the Wujiang drainage basin, were investigated in this study. Samples were taken at the surface and also at 20, 40, 60, 80 m depths in front of the dams in April, July, October of 2006 and January of 2007. Chemical parameters were calculated and the concentrations of dissolved inorganic carbon [DIC] and its isotopic composition ($\delta^{13}C_{DIC}$) were determined. In surface waters, the $\delta^{13}C_{DIC}$ values are high in summer and autumn and low in winter and spring, while the DIC concentrations are relatively low in summer and autumn and relatively high in winter and spring. In the water column, the DIC concentrations increase while $\delta^{13}C_{DIC}$ values decrease with water depth. DIC in various reservoirs is significantly different in isotopic composition from that in natural rivers, but is close to that in natural lakes. In addition, in surface waters, the $\delta^{13}C_{DIC}$ values tend to become lower whereas the nutrition level tends to become higher with increasing age of the reservoirs. The conclusion is that after dam blocking, changes took place in the hydrochemical properties of river water, and the impounding rivers developed toward lakes and swamps. In addition, differentiation in DIC isotopic composition may be used to some extent to trace the evolution process of a reservoir.

dissolved inorganic carbon, carbon isotope, reservoir evolution, cascade reservoir

In recent years, the natural properties and processes of rivers have been more and more affected by human activities[1−5], especially, the dams built for modulating rivers have the most important, notable and extensive effect on the ecological systems of rivers and their drainage basins. It was reported that about 20% of global river water which flows into the sea has been dammed according to the statistics data provided by the World Commission on Dams (WCD). By the end of 2005 there had been constructed more than 50000 dams with a height of more than 15 m in the world, of which 22000 are located in China, accounting for 44% of the total (http://www.icold-cigb.org.cn/news/y20070405.pdf).

Dam blocking will obviously change the hydrological status of rivers. Dam construction will make natural river become the impounding rivers. It can be seen from the global rivers as well. Environmental issues aroused from dam construction have attracted much attention of many scientists. The current studies put their focus on changes in the hydrological status of rivers caused by dam blocking[6−8], silt deposition[6,7,9], fish migration[7,10], nutrients blocked by dams[7,10−15], biogeochemical cycle of elements within reservoirs[11,14−16], greenhouse gas release[11,17−20] and so on. However, most of the studies were carried out only in an independent reservoir or several independent dams in different river drainage basins. So, to which extent the dam construction would affect the aquatic environment of cascade reservoirs of a river could not be understood clearly until now.

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Carbon is an indispensable element for life, which is closely related to the biogeochemical cycle of other important elements. Feedback between aquatic biological activities and the change of an aquatic environment and the relationship between the aquatic system and nutrient loads, as well as the process of mutual influence would provide the basic information about the change of on aquatic environment[21]. Biogeochemical cycle of nutrients in reservoirs, transfer of energy, dynamics of CO_2 and nutrition status are the key factors affecting the aquatic environment. The biogeochemical cycle of carbon will help us to understand the change of an aquatic environment, ecological processes in waters, element cycle and their mutual effects[[11]. Variations in the concentrations of dissolved inorganic carbon (DIC) and its isotopic composition ($\delta^{13}C_{DIC}$) in the aquatic environment can reflect the geochemical behavior of carbon and its biogeochemical characteristics[11,22 – 31]. Then, the concentrations of DIC and its isotopic composition could be an important indicator for the evolution of cascade reservoirs and their biogeochemical features.

1 Study area

The Wujiang River originates from the Wumeng Mountain which is located in the west of Guizhou Province and ends at Fuling City where it joins the Changjiang (Yangtze) River, with a total length of 1037 km and a drainage area of 88 267 km^2. The Wujiang River is the largest tributary on the right bank of the Changjiang River in its upper reaches. It winds its way through the central and northeastern parts of Guizhou Province, and it is the largest river passing through Guizhou Province. The study area belongs to the subtropical monsoon humic climate zone, and its average annual temperature is 12.3℃, with the extreme temperatures of 35.4℃ in summer and −10.1℃ in winter. The average temperatures in January (the coldest month) and July (the hottest month) are 3.5℃ and 26℃, respectively. The annual precipitation ranges from 1100 to 1300 mm, and the precipitation from May to October accounts for about 75% of the total annual precipitation.

The Wujiangdu reservoir, Dongfeng reservoir and Hongjiadu reservoir are all situated on the middle and upper reaches of the Wujiang River, and were impounded in 1979, 1994 and 2004, respectively. By the year 2006, the reservoirs had been operated for 28 years, 13 years and 3 years, respectively. The main features of these three reservoirs are described in Table 1[32−34].

2 Sampling and analysis

Water samples were collected in April, July and October 2006 and January 2007, which stand for seasons of spring, summer, autumn and winter, respectively. These samples were collected at different water depths (0 m, 20 m, 40 m, 60 m and 80 m). The sample sites are shown in Figure 1.

The pH, temperature, and electrical conductivity (EC) were measured in the field. HCO_3^- was titrated with HCl on the spot. Samples for $\delta^{13}C_{DIC}$ measurement were collected by filtering 100 mL of water through 0.45 mm filters with a syringe into polyethylene vials and then a saturated $HgCl_2$ solution was injected into the vials to poison the samples. The vials were immediately closed without headspace with caps and sealed with seal film (Parafilm). In the laboratory, the samples were kept frozen until analysis.

$\delta^{13}C_{DIC}$ measurements were made following the method described by Atekwana et a1.[28]. 15 mL of each water sample was injected into the closed evacuated glass vessels containing approximately 2 mL of concentrated phosphoric acid and then heated at 50℃ for CO_2 extraction. The extracted CO_2 was quantitatively frozen into an evacuated vial cooled with liquid nitrogen, and the resulting gas was analyzed on an MAT252 mass

Table 1 The main characteristics of the three reservoirs in the study area

Item	Hongjiadu reservoir	Dongfeng reservoir	Wujiangdu reservoir
Reservoir age (Till 2006) (a)	3	13	28
Normal water level (m)	1140	970	760
Working water head (m)	115	116	113
Reservoir capacity (10^8 m^3)	30.98	8.64	24.40
Backwater length (km)	86.00	43.65	82.94
River slope gradient (‰)	1.338	3.168	1.893

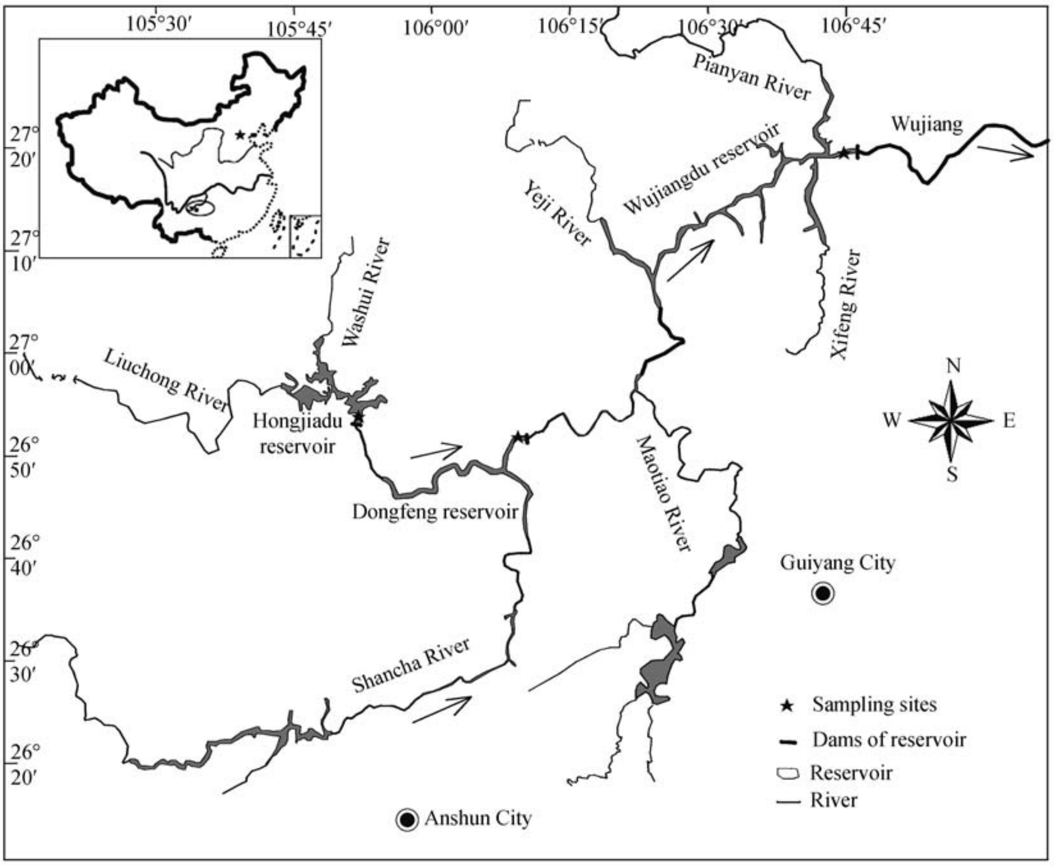

Figure 1 Sketch map showing the sampling sites.

spectrometer at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The $\delta^{13}C_{DIC}$ measurements were normalized to the Pee Dee Belemnite standard (PDB) (see Formula (1)) and the analytical precision is ±0.1‰.

$$\delta^{13}C_{DIC}\ (‰) = [(R_{Sample}-R_{PDB})/R_{PDB}]\times 1\,000. \qquad (1)$$

3 Results

Widespread in the study area are carbonate rocks. The pH values of reservoir water range from 7.1 to 8.95, with an average value of 8.06. Under this condition, the dissolved inorganic carbon in the water body is dominated by HCO_3^-, which accounts for about 90% of the total DIC. So HCO_3^- can be used to represent the DIC in the aquatic system in the study area[23,25].

3.1 Water temperature

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. In winter, the water in the hypolimnion and epilimnion is well blended and there is a small difference in water temperature. The average epilimnion water temperatures in the reservoirs are 17.4℃, 27.6℃, 21.37℃, 13.3℃ and the hypolimnion water temperatures are 11.8℃, 15℃, 14.3℃, 11.9℃ in spring, summer, autumn, and winter, respectively. It is obviously seen that there are seasonal variations in water temperature.

3.2 DIC concentrations

The average concentrations of DIC in spring, summer, autumn and winter are 2.56 mmol/L, 2.21 mmol/L, 2.17 mmol/L and 2.39 mmol/L, respectively, and they are higher in spring and winter than in summer and autumn. Obvious seasonal variations can be observed in all surface water samples (Figure 2).

As can be seen from Figure 2, the DIC concentrations of surface water tend to become higher from the Hongjiadu Reservoir to the Wujiangdu Reservoir, implicating that the reservoirs which were impounded for long and located in the lower reaches would have high DIC concentrations.

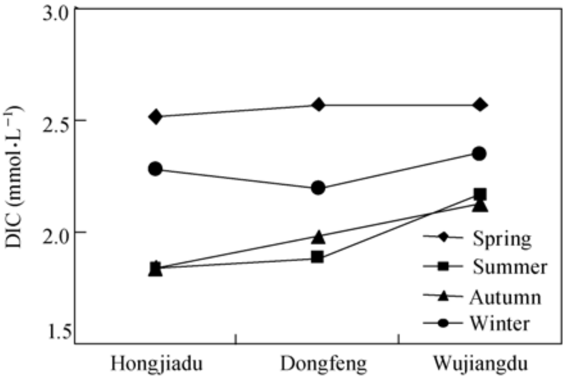

Figure 2 Seasonal variation of DIC in the surface water of each reservoir.

The average DIC concentrations of the surface and bottom water samples collected from the water column are 2.19 mmol/L and 2.48 mmol/L, respectively. The DIC concentrations show significant differences in the whole water column and lager differences between surface and bottom water samples collected in summer and autumn than in winter and spring (Figure 3).

3.3 Isotopic composition of DIC ($\delta^{13}C_{DIC}$)

The average $\delta^{13}C_{DIC}$ values of water samples collected in spring, summer, autumn and winter are –8.68‰, –8.10‰, –8.69‰ and –9.08‰, respectively. The values are more positive in summer than in winter, but there is no obvious variation in spring and autumn. Obvious seasonal variations are noticed in $\delta^{13}C_{DIC}$ values of surface water (Figure 4).

The $\delta^{13}C_{DIC}$ becomes more negative with water depth in the water column in front of the dams and the surface water has more positive $\delta^{13}C_{DIC}$ values of 0.81‰, 3.46‰, 1.89‰, and 1.12‰ than the bottom water in spring, summer, autumn and winter, respectively. The largest variations in $\delta^{13}C_{DIC}$ between surface and bottom waters appear in summer (Figure 5).

As can be seen from Figures 4 and 5, the $\delta^{13}C_{DIC}$ values become more negative with increasing age of the reservoirs, as the reservoirs become lower in position in the river basin, especially for the surface water. In other words, the $\delta^{13}C_{DIC}$ values become more negative from the reservoirs in the upper reaches (e.g. the Hongjiadu reservoir which has been impounded for 3 years) to those in the lower reaches (e.g. the Wujiangdu reservoir which has been impounded for 28 years).

4 Discussion

The isotopic composition of DIC ($^{13}C_{DIC}$) is affected mainly by the following three important factors[11,22,26,29,36,37]: (1) the isotopic composition of DIC in the inflow of water body; (2) CO_2 exchange at the interface between water and atmosphere; and (3) photosynthesis and respiration. Among them, the isotopic composition of DIC ($\delta^{13}C_{DIC}$) in the inflow of water body was determined by river water and underground water input into the reservoirs. DIC was derived mainly from CO_2 released from decomposition of organic matter in soil and chemical weathering of rocks in the drainage basin.

According to previous studies, the $\delta^{13}C_{DIC}$ values of DIC derived from decomposition of organic matter in soil in the Wujiang River drainage basin are −19‰ in winter, and −16‰ in summer[11]; those of DIC derived from chemical weathering of carbonate rocks are within the range of 0‰ to 2.0‰[11,25]. In regard to CO_2 exchange at the interface between water and atmosphere, the $\delta^{13}C_{DIC}$ values of HCO_3^- derived from dissolved atmospheric CO_2 vary between 0‰ and −2.5‰[20,22,25,31,38].

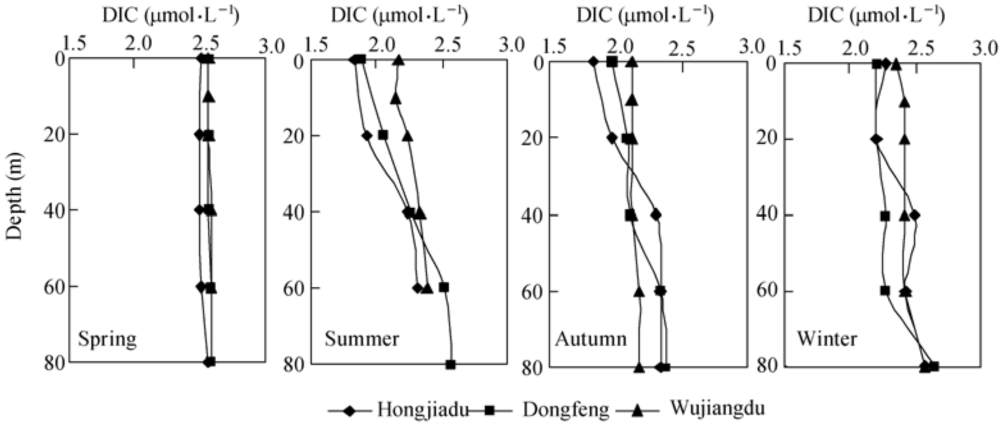

Figure 3 Variations in the DIC concentrations in the water column in front of the dam of each reservoir.

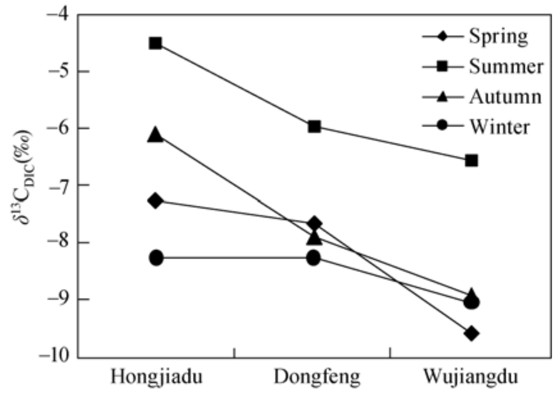

Figure 4 Seasonal variations in DIC carbon isotopic composition of the surface water of each reservoir.

Both photosynthesis and respiration are a pair of opposite processes. In fresh water, aquatic photosynthesis mainly makes use of dissolved CO_2, with an isotope fractionation of about 20‰—23‰[20,25], thus making the isotopic composition of DIC in the remaining water body ^{13}C-enriched[11,22,25,29,30,36]. The respiration can induce the decomposition of organic matter; DIC derived from this process is also referred to as respiration- derived DIC[39], which has a similar $\delta^{13}C$ to that of the organic source. Although this process is not associated with obvious isotope fractionation, a lot of ^{12}C would be released from decomposition of organic matter, which may make $\delta^{13}C_{DIC}$ more negative[11,22,25,29,36,39], at the same time, may make it increase the DIC concentrations in the water body.

4.1 Spatiotemporal distribution characteristics of DIC concentrations and $\delta^{13}C_{DIC}$ values

A negative correlation can be found between DIC concentrations and $\delta^{13}C_{DIC}$ in surface water of the reservoirs (Figure 6).

This can be explained by the following possible reasons. On the one hand, a huge water input into the reservoirs during the high flow period can dilute the solute concentrations of the reservoir water body, leading to a decrease in DIC concentrations. On the other hand, due to stronger sunlight in summer, aquatic photosynthesis will be more intense in the epilimnion during the high flow period, leading to an increase in $\delta^{13}C_{DIC}$ and a decrease in DIC concentrations. In addition, with the disappearance of thermal stratification during the low flow period, the epilimnion will mix with the hypolimnion, leading to the upward diffusion of respiration-derived DIC at the bottom to the epilimnion, which will result in a decrease in $\delta^{13}C_{DIC}$ and an increase in DIC concentrations. In the three reservoirs studied, dissolved CO_2 is the main inorganic carbon source for aquatic photosynthesis. The synthesis of new organic matter will preferentially make use of the light isotopes, with an isotope fractionation of 20‰—23‰[22,25], so this process will make the isotopic composition of DIC in the remaining water body more positive and, at the same time, will give rise to the reduction of DIC concentrations. In the three reservoirs investigated, dissolved CO_2 is the main inorganic carbon source for aquatic photosynthesis.

In the vertical profile, the $\delta^{13}C_{DIC}$ values decrease with depth, while the DIC concentrations gradually increase with depth. This kind of variation tendency is more remarkable in summer (Figure 5). Aquatic photosynthesis is very strong in summer, which is controlled by permeability depth, thermal stratiphication and so on. The mixed epilimnion is the main part in the reservoir, where the highest primary productivity is expected. Photosynthesis in the epilimnion can reduce the DIC concentrations to some extent and simultaneously can

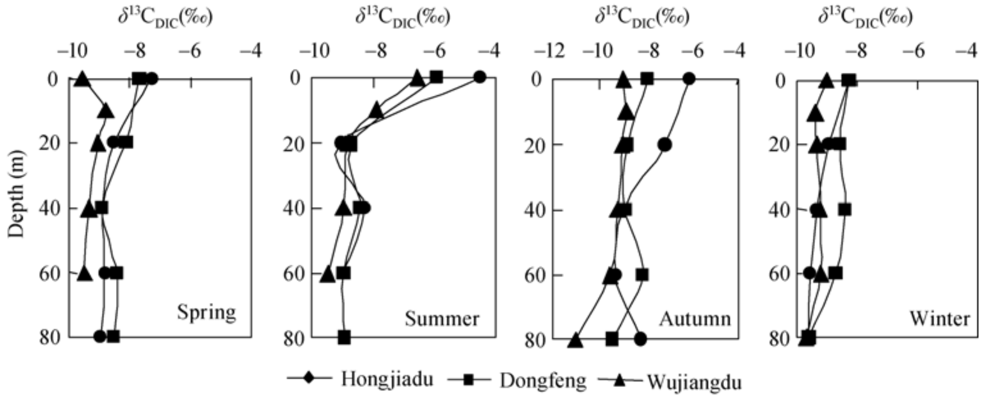

Figure 5 The carbon isotopic composition of DIC in the water column in front of each dam.

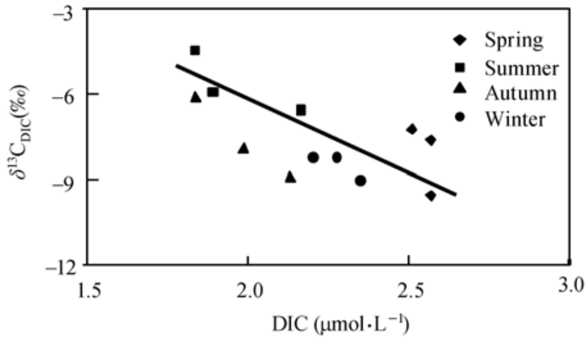

Figure 6 Relationship between DIC concentrations and $\delta^{13}C_{DIC}$.

also be responsible for the increase of $\delta^{13}C_{DIC}$ values for the remaining DIC. The newly formed organic particles may be degraded during the subsidence process in the water column, and in the surface sediments as well, and the decomposition of organic matter will be accompanied with the extensive release of $^{12}CO_2$ into the water column, thus making DIC with more negative $\delta^{13}C_{DIC}$ values accumulate at the lower levels of the water body. For this reason, the DIC concentrations are increased at the deep levels of the water body (Figures 3, 5 and 6).

In the water column, the thermal stratification structure may be maintained in the reservoir water body during the entire summer[14], which has effectively constrained not only the mixing of water at upper level with that at lower level, but also the exchange among different stratified water bodies. At the same time, summer is the main season for the growth of aquatic species, which induces significant differences both in DIC concentrations and in $\delta^{13}C_{DIC}$ between the epilimnion and the hypolimnion (Figure 7).

In the autumn-winter seasons, the water body tends to be mixed with the disappearance of thermal stratification structure. The exchange between surface water DIC and bottom water DIC with negative $\delta^{13}C_{DIC}$ values will occur, which can reduce the differences in DIC concentrations and $\delta^{13}C_{DIC}$ values, thus making DIC evenly distributed in the water body from the surface to the bottom (Figures 4 and 5).

Similar results have been acquired from other lakes, such as the Hongfeng Lake in Guizhou Province of China, the Meech Lake of Canada, the Biwa Lake of Japan, etc.[11,40,41]. The $\delta^{13}C_{DIC}$ values of surface water are more positive in summer but more negative in winter, while the DIC concentrations are low in summer but high in winter. As indicated by the studies of natural rivers, the $\delta^{13}C_{DIC}$ values of the water body are more negative in summer than in winter[11,31,40]. This demonstrates that great changes have taken place in hydrochemical characteristics of the rivers after dam blocking and the rivers have gradually evolved toward the limnological type[38].

4.2 Reservoir blocking, DIC concentrations and isotopic composition of DIC ($\delta^{13}C_{DIC}$)

The Hongjiadu reservoir, Dongfeng reservoir and Wujiadu reservoir belong to cascade reservoirs situated on the Wujiang River Watershed, which display almost the same geological background and climatic conditions. The three reservoirs have been impounded for 3, 13 and 28 years, respectively.

The highest concentrations of DIC in surface water body are produced in the Wujiangdu reservoir, followed by the Dongfeng and Hongjiadu reservoirs (Figure 2), while the $\delta^{13}C_{DIC}$ values show an opposite variation trend (Figure 4). Due to similar geological background

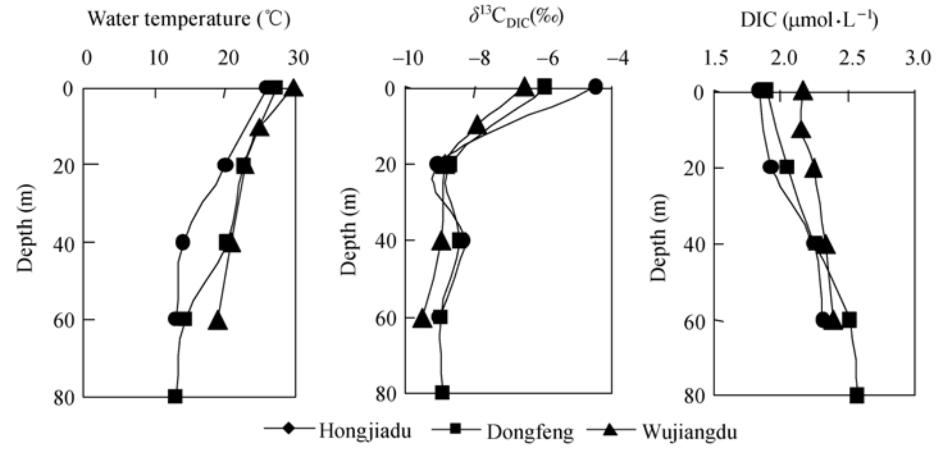

Figure 7 The temperature, DIC and its isotopic composition in the water column in front of the dam in summer.

and climatic conditions, the difference in hydrochemistry should be attributed to the evolution process, operating history and spatial location of the reservoirs with respect to their cascade sequence.

A positive correlation can be found between the reservoir operating time and the DIC concentrations, namely, the longer the reservoir operating time is, the higher its DIC concentrations will be. In the reservoirs, the hydrodynamic conditions have changed and the velocity of water flow has slowed down obviously due to dam construction, which has caused nutrients to be retained in the water body or accumulated in the bottom sediments. According to Zhu et al., the primary productivity is lower in the Dongfeng reservoir than in the Wujiangdu reservoir, where the average chlorophyll concentrations are 2.47 μg/L and 6.33 μg/L, respectively[15], indicating that the longer the operating time of reservoirs is, the higher the nutrition level of the water body will be, and the higher the nutrition level is, the larger the contribution of biogenic DIC will be[41]. Therefore, the $\delta^{13}C_{DIC}$ values of the water body are more negative.

Moreover, in the vertical profile, the DIC concentrations are higher in the hypolimnion than in the epilimnion, while the $\delta^{13}C_{DIC}$ values are more negative in the hypolimnion than in the epilimnion. All the investigated reservoirs are characterized by sluice near the hypolimnion.

Due to the cascade-style development of reservoirs, the hypolimnion of upstream reservoirs has the highest DIC concentrations and most negative $\delta^{13}C_{DIC}$ values, and the outflow water from the reservoirs with more negative $\delta^{13}C_{DIC}$ values will pour into the epilimnion of the downstream reservoirs. This kind of spatial cumulative effect would possibly cause the DIC concentrations to become higher and the $\delta^{13}C_{DIC}$ values to become more negative of the surface water body in the downstream reservoirs than in the upstream reservoirs.

5 Conclusions

During the cascaded development of hydropower resources the natural rivers are blocked to form segmentation-style impounding rivers. Corresponding changes will take place in chemical characteristics of the natural river-reservoir system. The $\delta^{13}C_{DIC}$ values of surface reservoir water are higher in summer than in winter, which is opposite to what was reported in previous studies. In the water column, bottom water samples have more positive $\delta^{13}C_{DIC}$ values than upper water samples (especially in summer), indicating that the photosynthesis and respiration of plants have a great influence on the carbon isotopic composition ($\delta^{13}C_{DIC}$) of reservoir water. Water released from the upper- and middle-stream reservoirs may affect the hydrochemistry of water body of the downstream reservoirs. To sum up, the chemical characteristics of river water have changed after dam blocking, and then the water-storage rivers tend to develop toward swamps.

The reservoir is an evolution system. With the elongation of operation of the reservoirs the nutrition level will be enhanced progressively in case there is no external disturbance. This study indicates that the isotopic composition of DIC coupled with its concentrations can be used to trace the evolution process of reservoirs. It is shown that at a given depth, the $\delta^{13}C_{DIC}$ values will become more negative with operating time of a reservoir increasing. Unfortunately, we have only investigated the seasonal variation trend of DIC in the three cascade reservoirs, so more research work should be done to support our results, and we will pay more attention to this aspect of research in the future time.

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