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Stable carbon isotope as a proxy for the change of phytoplankton community structure in cascade reservoirs from Wujiang River, China

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Abstract

Phytoplankton community structure and δ^{13}C of dissolved inorganic carbon (DIC), particulate organic carbon (POC), and phytoplanktonic carbon (PPC), and the related hydro-chemical parameters have been seasonally investigated in the cascade reservoirs from the Wujiang River Basin. Average values of $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$ and $\delta^{13}C_{PPC}$ were −8.1±1.3‰, −29.6±2.8‰, and −30.9±4.5‰, respectively. Seasonal fluctuation of $\delta^{13}C_{PPC}$ was comparable to that of $\delta^{13}C_{POC}$ and larger than that of $\delta^{13}C_{DIC}$. The $\delta^{13}C_{PPC}$ values showed a significant linear correlation with $\delta^{13}C_{POC}$, indicating that endogenetic phytoplankton is the main source of POC in these cascade reservoirs. Compared to environmental factors such as temperature, taxonomic differences are the main factor influencing $\delta^{13}C_{PPC}$ in this study. As a result, the contribution of *Bacillariophyta* to the total phytoplankton showed a significant negative correlation with $\delta^{13}C_{PPC}$ and $\Delta\delta^{13}$C ($\delta^{13}C_{PPC}-\delta^{13}C_{DIC}$), respectively, suggesting that $\delta^{13}C_{PPC}$ can be used to discern the change of phytoplankton community structure although only two kinds of dominant algae (i.e. *Bacillariophyta* and *Chlorophyta*) facilitate achieving this relationship. This relationship will have an important significance in understanding evolvement of phytoplankton community structure with time using geochemical technique once it is confirmed at a larger scale in field study.

1 Introduction

Natural carbon from different sources and experiencing different biogeochemical processes has different stable isotopic compositions. As for phytoplankton, stable carbon isotopic compositions are also dependent on fractionations that occur during photosynthesis and biosynthesis (O'Leary, 1981). Algal carbon fractionation is species-specific. The isotopic signal is significantly affected by biological factors such as cell size and geometry, the mechanism of inorganic carbon acquisition, the type of carboxylating enzyme (i.e. Rubisco form I or II, beta-carboxylases) (Descolas-Gros and Fontugne, 1985; Paneth and O'Leary, 1985; Popp et al., 1998; Keller and Morel, 1999; Riebesell et al., 2000). This species-specific characteristic provides the base on the potential possibility for carbon isotopic signal to discern the change of phytoplankton community structure.

However, environmental factors also significantly influence the algal carbon isotopic fractionation (ε_p). Aqueous CO_2 concentration exhibits a positive correlation to ε_p in marine phytoplankton (Degens et al., 1968). Light climate strongly influences active transport of inorganic carbon into the cell and, in consequence, isotopic fractionation by the cell (Rost et al., 2002). Water velocity can also affect carbon isotopic signal of the attached algae, possibly through effects on boundary layer thickness (Trudeau and Rasmussen, 2003). These studies complicate the interpretation of carbon isotopic data in geochemical and paleoceanographic applications (e.g., Rau et al., 1989; Freeman and Hayes, 1992) in the natural environment.

Although factors influencing algal ε_p are variable and complex, carbon isotopic signal can be used as a powerful tool to understand biologically driven carbon cycle (e.g., Lehmann et al., 2004), especially when only a few factors are important and predictable. Here, we try to use carbon isotopic signal to discern the change of phytoplankton community. This approach is based on fundamental assumptions that influences on algal ε_p by environment factors are predictable and/or the extent of these influences are far less than that by biological factors in a given field, that is, algal ε_p is mainly controlled by algal gene.

Damming river alters its hydrological condition, material cycle and then transforms aquatic ecosystem from riverine type to limnological type (Wetzel, 2001). Reservoirs created by dams show different trophic state due to different running time and geographical location along the impounded river. In natural situation, the upriver reservoir and the aged reservoir present higher trophic state owing to more nutrient load impounded than the downriver reservoir and younger reservoir (e.g., Humborg et al., 1997). However, because anthropogenic nutrient input might overcompensate the impounded effect of damming on the nutrient loads, downriver reservoir, sometimes, exhibits high trophic state (e.g., Wang et al., 2008). Accordingly, this will finally result in presence of different phytoplankton communities in the cascade reservoirs along the impounded river due to their different trophic state.

Wujiang River is a major hydropower source for China's massive west-to-east power transmission project. A series of reservoirs were constructed along the Wujiang River and now it becomes a typical impounded river. We have seasonally investigated the phytoplankton community structure and determined the δ^{13}C values of dissolved inorganic carbon (DIC), particulate organic carbon (POC), and phytoplanktonic carbon (PPC), and related hydro-chemical parameters in the cascade reservoirs from the Wujiang River Basin. The major aim of this study is to demonstrate if the δ^{13}C values of PPC can be a proxy of the change of phytoplankton community structure and to better understand the carbon biogeochemical cycle in the cascade reservoirs. This study provides a linkage between phytoplankton ecology and stable carbon isotope geochemistry, and helps us develop prospective application for stable carbon isotope in the studies such as palaeoecological reconstruction in the aquatic environment.

2 Material and methods

2.1 Study area and sampling

The Wujiang River is a southern tributary of the Changjiang River, with a total length of 1037 km and a drainage area of 88 267 km^2. It has a runoff of 53.4 billion m^3 with a fall of 2124 m and is the largest river in Guizhou Province. Investigations were carried out at eleven reservoirs and a total of 19 stations were selected (Fig. 1).

Water samples were collected at surface water (upper 0.5 m) in July and October 2007 and in January and April 2008, which stand for summer, autumn, winter and spring, respectively. Water temperature, dissolved oxygen, and pH were measured in situ using a calibrated water quality probe (model YSI 6600). Samples for major cations and anions were filtered through 0.45 µm filters. Samples for cation analysis were acidified to pH 2 with ultrapurified HNO_3^-. Major cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were analyzed by atomic absorption spectrometry (AAS, PE51002, America) and the anions (SO_4^{2-}, NO_3^-, and Cl^-) by high performance liquid chromatography (HP1100, SHIMADZU, Japan). HCO_3^- was titrated with HCl on the spot. Samples for $\delta^{13}C$ of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) measurement were collected by filtering 100 mL of water through 0.45 µm 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). Samples for $\delta^{13}C$ of particulate organic carbon ($\delta^{13}C_{POC}$) measurement were stored in high-density polyethylene bottles with screw closure (1500 mL, leak-poof). Bottles were rinsed three times prior to formal storage of water samples. Then they were filtered within 12 h with preburned (500 °C, 5 h) 47 mm Whatman GF/F glass fibre filter (0.65 µm). In the laboratory, the samples were stored at –20 °C and freeze-dried before analysis. Samples for $\delta^{13}C$ of phytoplankton ($\delta^{13}C_{PPC}$) measurement were collected using a 64 µm nylon mesh and immediately filtered with the same mesh on the spot, and then phytoplankton obtained were transported into vials and kept cool (0–4 °C) in the field and were dried at 45 °C in the laboratory within 24 h.

2.2 Quantitative and qualitative analysis of phytoplankton

1.5 L of surface water sample was preserved with Lugol's Solution for quantitative analysis of phytoplankton. Phytoplankton for qualitative analysis was collected by a 64 µm nylon mesh and preserved with formaldehyde solution (2% final concentration). The precipitation method was used for taxon identification and counting (Zhang and Huang, 1991). Phytoplankton was quantitatively and qualitatively determined by a standard light microscope. The wet weight of phytoplankton was calculated according to its volume and density (Zhang and Huang, 1991).

2.3 Analysis of stable carbon isotope

Water sample for $\delta^{13}C_{DIC}$ measurement was injected into the closed evacuated glass vessels containing the concentrated phosphoric acid and then heated at 50 °C for CO_2 extraction (Atekwana et al., 1998). Samples for $\delta^{13}C_{POC}$ and $\delta^{13}C_{PPC}$ measurements were acidified with dilute hydrochloric acid and oven-dried overnight at 60 °C just prior to carbon isotope determination. PPC and POC were transformed into CO_2 using the high-temperature (850 °C, 5 h) sealed-quartz tube combustion method with copper oxide as oxidant (Buchanan and Corcoran, 1959) since the low-temperature (550 °C, 1 h) combustion method could lead to large analytical uncertainty (Tao et al., 2001). CO_2 was cryogenically separated and its pressure and temperature were measured in a sensor (Edwards Barocel® 600). The $^{13}C/^{12}C$ ratio of CO_2 was determined on a dual-inlet isotope ratio mass spectrometer (MAT 252). Carbon isotope data were reported and normalized following the "δ" denotation of Craig (1953) relative to the Vienna Pee Dee Belemnite (VPDB). The total precisions for concentration and $\delta^{13}C$ analysis were better than 3% (1σ), and 0.1‰ (1σ), respectively.

Statistical analysis of the data was done with the software SPSS (version 11.5; SPSS Inc.). Pearson's correlation coefficient analysis was carried out.

3 Results

3.1 Hydrogeochemical characteristics

The study area has a subtropical monsoon humid climate. The average water temperature was 18.5 °C. The average dissolved oxygen (DO) and pH value were 8.6 mg L^{-1} and 8.2, respectively (Table 1). The high pH value and DO are due to CO_2 uptake and O_2 release during algal photosynthesis. The Wujiang River Basin is underlain mainly by Permian and Triassic carbonate rocks. The river water chemistry is dominated by Ca^{2+}, HCO^{3-}, Mg^{2+} and SO_4^{2-} (Table 1) and controlled by carbonate dissolution by both carbonic and sulfuric acid (Liu, 2007). There are no significant differences in main hydro-chemical parameters of the investigated reservoirs among the main Wujiang River, the Sancha River, and the Maotiao River (Table 1).

3.2 Phytoplankton community structure

The seasonal variations of phytoplankton community and biomass were investigated (Table 2). Average biomass of phytoplankton (wet weight) was 13.90 mg L^{-1} in July 2007, 5.16 mg L^{-1} in October 2007, 4.42 mg L^{-1} in January 2008 and 7.05 mg L^{-1} in April 2008, respectively. In eutrophic reservoirs Hongfeng and Baihua, the dominant algae were *Cyanophyta* and *Chlorophyta*. And in other reservoirs, they were *Bacillariophyta* and *Chlorophyta*. *Dinophyta* was only largely observed in July 2007. Different reservoir showed different phytoplankton community structure, for example, the dominant algae in Hongfeng Reservoir were *Chlorophyta* and that in Wujiangdu Reservoir were *Bacillariophyta* in April 2008. Generally, phytoplankton in release water showed similar community structure to phytoplankton in surface water before dam from the same reservoir; however, the former had less biomass than the later, probably because release water came from the deep water of the reservoir and had lower temperature than surface water before dam (Wang et al., 2008).

3.3 Carbon isotopic compositions

Average values of $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$ and $\delta^{13}C_{PPC}$ were −8.1±1.3‰ (n=75), −29.6±2.8‰ (n=74), and −30.9±4.5‰ (n=63), respectively (Table 3). $\delta^{13}C$ values spanned a range from −3.3 to −10.0‰ for DIC, from −19.6 to −34.5‰ for POC, and from −15.1 to −39.2‰ for PPC, respectively. Seasonal fluctuation of $\delta^{13}C_{PPC}$ was comparable to that of $\delta^{13}C_{POC}$ and larger than that of $\delta^{13}C_{DIC}$. For example, the average $\delta^{13}C_{PPC}$ values were −25.7±3.3‰ in July 2007 and −33.1±3.1‰ in January 2008; however, the average $\delta^{13}C_{DIC}$ values were −7.8±1.5‰ in July 2007 and −8.6±0.7‰ in January 2008. During thermal stratification in water column (i.e. July 2007 and April

2008), $\delta^{13}C_{DIC}$ of release water showed more negative values than that of surface water before dam from the same reservoir (Table 3). The $\delta^{13}C_{PPC}$ values showed significant differences in the different reservoirs. For example, it was −15.1‰ in the Hongfeng Reservoir and −31.7‰ in the Wujiangdu Reservoir in April 2008, respectively.

4 Discussion

4.1 Carbon biogeochemical cycle in the reservoirs

Understanding carbon biogeochemical cycle driven by phytoplankton is helpful to discover what are main factors controlling $\delta^{13}C$ of phytoplankton. DIC and POC are the main carbon species in the reservoirs. pH values in these reservoir waters were generally larger than 8, indicating a predominance of bicarbonate in DIC. River HCO_3^- is mainly derived from the carbonate weathering and CO_2 originated from soil organic matter, and it theoretically has $\delta^{13}C$ value of −11.5‰ (Liu et al., 2008) since CO_2 originated from the decomposition of soil organic matter is generally characterized by $\delta^{13}C$ value of −23‰ (Cerling et al., 1991). Contribution of HCO_3^- from precipitation is ignorable because pH values of rain are generally lower than 5.6 in Guizhou province. The annual average partial pressure of CO_2 in the reservoirs is higher than that of air (Lu et al., 2007; Yu et al., 2008a), suggesting the CO_2 from atmosphere could also be ignored. Soil organic matter and aquatic phytoplankton are the possible contributors of riverine POC. $\delta^{13}C_{PPC}$ showed a perfect linear relationship with $\delta^{13}C_{POC}$ (Fig. 2), suggesting that POC was mainly derived from phytoplankton. With the development of reservoir after damming, riverine heterotrophic ecosystem is transformed to autotrophic one, and phytoplankton becomes the dominant contributor of POC.

Previous study indicated $\delta^{13}C_{DIC}$ in various reservoirs is significantly different from that in natural rivers, but is close to that in natural lakes (Yu et al., 2008b). The average $\delta^{13}C_{DIC}$ value was ca. −8‰ and larger than −11.5‰ mentioned above because algal cells discriminate ^{13}C during photosynthetic CO_2 fixation, which leaves the residual DIC pool enriched in ^{13}C. HCO_3^- concentrations decreased while the $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ increased in the surface water of the reservoirs (Fig. 3). With the increase of phytoplanktonic biomass, algae assimilate more inorganic carbon and thereby exhibit more positive δ^{13}C value (Fig. 3). So, photosynthesis is one of the main processes that affect $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ in the surface water. Compared to the surface water before dam, DIC in release water showed the deficit in ^{13}C when thermal stratification developed in July 2007 and April 2008. Release water is from deep water of reservoir (Wang et al., 2008), and $\delta^{13}C_{DIC}$ values decrease with water depth (Yu et al., 2008b) as photosynthesis declines and respiration increase. Thus, respiration, which makes the DIC pool enriched in ^{12}C, is the other main process affecting $\delta^{13}C_{DIC}$ in these reservoirs. Compared to DIC, POC (and PPC) showed larger fluctuations in δ^{13}C values (Table 3; Fig. 3) because phytoplankton had more influences on $\delta^{13}C_{POC}$ (and $\delta^{13}C_{PPC}$) than that on $\delta^{13}C_{DIC}$ during the transformation of inorganic carbon into organic carbon.

4.2 Constraints on variations of the δ^{13}C of phytoplankton

The δ^{13}C of assimilating inorganic carbon and carbon isotopic fractionation during photosynthetic carbon fixation control the δ^{13}C of phytoplankton. Bicarbonate dominates DIC (Table 1). An equilibrium isotope effect in the hydration/dehydration reactions between bicarbonate and CO_2 concentrates isotopically light carbon in the CO_2 in a temperature sensitive manner, with CO_2 values 12‰ lower than those of bicarbonate at 0 °C and 8.4‰ lower at 30 °C (Mook et al., 1974). The maximum carbon fractionation by all cellular carboxylation reactions has been suggested to lie in the range of 25.4–28.3‰ (Goericke et al., 1994). In order to interpret our results, we adopted a value of −10‰ and −27‰, respectively, which represent the mid-point of the range in two scenarios mentioned above. Thus, the δ^{13}C value of ca. −18‰ is to be expected for CO_2 involved photosynthetic carbon fixation if these CO_2 are totally derived from the bicarbonate with δ^{13}C average value of ca. −8‰ (Table 3). And the most negative $\delta^{13}C_{PPC}$

value of ca. −45‰ is to be expected when diffusive CO_2 uptake dominates inorganic carbon flux into cell with carboxylation fractionation of ca. −27‰. However, it is hard to obtain the maximum fractionation in cellular carboxylation reactions in field study (e.g., Raven et al., 2002). In this study, the average value of $\delta^{13}C_{PPC}$ was −30.9‰, about 68% of the most negative $\delta^{13}C_{PPC}$.

There are several factors influencing the $\delta^{13}C_{PPC}$. First is the inorganic carbon source. In this study, a significant negative correlation between the HCO_3^- concentration and $\delta^{13}C_{PPC}$ was found (R=−0.558, P<0.01). Obviously, HCO_3^- as inorganic carbon source of phytoplankton can cause higher $\delta^{13}C_{PPC}$ values than CO_2 does. Compared to CO_2 uptake, the transport of HCO_3^- through the plasmalemma alters the isotopic composition of the inorganic carbon pool inside the cell, which translates into a change in ε_p. Second is temperature. Temperature can directly influence carboxylase activity and cellular metabolism (Li et al., 1984) and thereby result in a change in ε_p. Increasing temperature can stimulate algal growth and thereby increase phytoplankonic biomass (e.g., Wang et al., 2008) and decrease the concentration of HCO_3^-, and thus causes more positive $\delta^{13}C_{PPC}$ values. Third are biological factors such as taxonomic differences. Different algal taxa possess different carbon metabolism and growth rate, and will have much more influence on carbon isotopic fractionation in phytoplankton (e.g., Burkhardt et al., 1999). We will thoroughly discuss the effect of taxonomic differences in the below.

4.3 Effect of taxonomic differences on carbon isotopic fractionation

The dominant phyla were *Bacillariophyta* and *Chlorophyta* in the investigated reservoirs (Fig. 4), thus the variation on the contribution of *Bacillariophyta* to the total phytoplankton (CBTP) was used to indicate the change of phytoplankton community structure. The ratio of *Chlorophyta* to *Bacillariophyta* (CTB) was also calculated. The CBTP showed a significant correlation to the $\delta^{13}C_{PPC}$ and $\Delta\delta^{13}C$ ($\delta^{13}C_{PPC}$–$\delta^{13}C_{DIC}$), respectively (Fig. 5), so did CTB (R=0.613 and 0.496, P<0.01, respectively), indicating different phytoplankton community with different $\delta^{13}C_{PPC}$ and ε_p. This phenomenon is caused by reason that the mechanism of inorganic carbon acquisition and subsequent carbon isotopic fractionation during photosynthetic CO_2-fixation are species-specific.

Phytoplankton obtains inorganic carbon either by passive diffusion of CO_2 or active uptake of CO_2 and/or HCO_3^-. Active HCO_3^- entry is relative to algal CO_2 concentrating mechanism (CCM), which is different among the phytoplankton taxa (Moroney and Ynalvez, 2007; Raven et al., 2008). Phytoplankton can use HCO_3^- either by direct uptake or by extracellular conversion to CO_2 by carbonic anhydrase (CA). Although the isotope fractionation associated with the conversion by CA would eliminate the isotopic difference between HCO_3^- and CO_2 and make the two carbon sources isotopically indistinguishable (Riebesell and Wolf-Gladrow, 1995), the change in activity of CA has an obvious influence on the net CO_2 assimilation rate and thereby affects carbon isotope discrimination (Cousins et al., 2006).

Diatoms possess C_4-like pathway whereby C_4 compound such as malate and oxaloacetate (OAA) is decarboxylated to deliver CO_2 to Rubisco (Reinfelder et al., 2004). After delivery of HCO_3^- by specific transporter into cell, HCO_3^- is either fixed into C4 compound by beta-carboxylase activity or conversion to CO_2 through CA activity (Kroth et al., 2008). Beta-carboxylase activity appears related to strictly anaplerotic processes and reduces ε_p associated with carbon fixation by no more than 2‰ (Hayes, 2001; Cassar and Laws, 2007). This CCM provides sufficient CO_2 for Rubisco in diatom. Extensive diatom blooms that occur in high nutrient low chlorophyll regions of the oceans (Gervais et al., 2002) suggest that diatoms are not CO_2 limited under natural oceanic conditions. Obviously, larger ε_p in CO_2 fixation by Rubisco will be obtained under enough supply of CO_2 (Fry, 1996), thus results lower $\delta^{13}C$ of diatoms.

Compared with diatoms, green algae had higher $\delta^{13}C$ in this study. CA plays an important role in CCM of green algae (Moroney and Ynalvez, 2007). External CA may significantly accelerate the rate of CO_2 supply to the cell surface, and its activity can be induced by low-CO_2 condition (Dionisio-Sese et al., 1990). Previous study demonstrated that external CA activity had a significant positive correlation with the density of *Chlorophyta* in reservoirs Hongfeng and Baihua, and this phenomenon was not found for *Bacillariophyta* because of little proportion of *Bacillariophyta* with external CA (Wu et al., 2008). This means that, compared to diatoms, CO_2 supply of green algae is not enough for photosynthetic carbon fixation by Rubisco, and smaller ε_p under this circumstance will be obtained for *Chlorophyta*. Cyanobacteria have a sophisticated CCM that, to some degree, is similar to green algae (Moroney and Ynalvez, 2007). It was also found that the activity of external CA showed close relation to the density of *Cyanophyta* in Aha reservoir (Wu et al., 2008). *Cyanophyta* possess Rubisco II for which the maximum carbon isotopic fractionation is 22‰, lower 8‰ than ε_p via Rubisco I that belongs to green algae and diatoms (Hayes, 2001). So, *Chlorophyta* and *Cyanophyta* should exhibit higher $\delta^{13}C$ than *Bacillariophyta*.

4.4 $\delta^{13}C_{PPC}$ versus the change of phytoplankton community structure

Whether or not $\delta^{13}C_{PPC}$ can be used as a proxy of the change of phytoplankton community depends on what extent it is caused to change by algal species differences. In the Fig. 5, we can find the fluctuations of $\delta^{13}C$ values along the both sides of regression line, indicating that, besides taxonomic differences, other factors such as temperature and bicarbonate also have some influences on $\delta^{13}C_{PPC}$ and $\Delta\delta^{13}C$. We chose the data in April 2008, which had relative smaller temperature variations compared to the whole year, calculated and found a significant correlation between $\delta^{13}C_{PPC}$ and CBTP ($R=-0.61$; $P<0.01$), indicating the more effect of taxonomic differences than that of temperature on $\delta^{13}C_{PPC}$. We also calculated the data when phytoplankton were predominated by *Chlorophyta* (CBTP<10%) and by *Bacillariophyta* (CBTP>90%), respectively. These results demonstrated only biomass variation may be the other main factor affecting $\delta^{13}C_{PPC}$ when *Chlorophyta* predominate phytoplankton, and variations of bicarbonate and temperature had no significant influences on $\delta^{13}C_{PPC}$ (Fig. 6). Thus, taxonomic differences were the main factor influencing $\delta^{13}C_{PPC}$ in this study and both showed synchronous variations. $\Delta\delta^{13}C$ exhibited similar variation to $\delta^{13}C_{PPC}$ because

$\delta^{13}C_{PPC}$ had much larger fluctuation than $\delta^{13}C_{DIC}$ did here. It is expected that $\Delta\delta^{13}C$ should show better relationship with algal species difference than $\delta^{13}C_{PPC}$ does in other field study at larger scale.

Factors influencing $\delta^{13}C_{PPC}$ are complex. We simplify these factors into two sorts: environmental factors (e.g. temperature, nutrients, and light) and biological factors (e.g. carboxylase activity and CCM). Experimental studies have demonstrated influences on ε_p by environmental factors are comparable to that by biological factors (e.g., Burkhardt et al., 1999; Rost et al., 2002). However, Raven et al. (2002) compiled substantial data about $\delta^{13}C$ of organic matter in marine macroalgae and seagrasses collected from the natural environment and found the $\delta^{13}C$ value correlates primarily with taxonomy and secondarily with ecology. This result was not consistent with the experimental studies, probably because experimental conditions could be controlled and influence of environmental factors on $\delta^{13}C_{PPC}$ therefore might be artificially expanded.

What's more, environmental factors, to a great extent, indirectly affect $\delta^{13}C$ of phytoplankton via working on biological factors such as cellular metabolism and physiochemical function. Biological factors involve inorganic carbon acquisition and fixation and directly influence ε_p. As a result of the evolution of algae best adapted to the environment, existent algae that dominate in the aquatic environment are not fortuitous. From this point of view, $\delta^{13}C$ and/or ε_p of phytoplankton can reflect the change of phytoplankton community structure. In this study, we have demonstrated tight relationship between the $\delta^{13}C_{PPC}$ and phytoplankton community structure although only two kinds of dominant algae (i.e. *Bacillariophyta* and *Chlorophyta*) in the investigated reservoirs facilitate achieving this relationship. Extensive studies in experiment and field are needed to testify this relationship in the future. Once this relationship is confirmed at a larger scale, it will have an important significance in understanding evolvement of phytoplankton community structure with time using geochemical technique.

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Table 1. Basic hydrochemical parameters of the reservoirs.

	Along Maotiao River	Along Sancha River	Along main Wujiang River
Temperature (°C)	19.0±4.6[a] (11.1–26.4)[b]	18.6±5.3 (9.7–28.9)	18.0±5.0 (10.9–30.0)
pH	8.3±0.6 (7.6–9.4)	8.2±0.3 (7.7–8.7)	8.1±0.5 (7.4–9.3)
DO ($mg\,L^{-1}$)	8.0±3.4 (3.4–15.0)	9.0±0.9 (7.4–10.5)	8.8±2.4 (5.0–18.1)
Ca^{2+} ($mg\,L^{-1}$)	54.9±7.1 (35.5–63.9)	61.1±8.8 (45.0–75.9)	57.6±4.9 (43.4–63.2)
Mg^{2+} ($mg\,L^{-1}$)	14.7±0.9 (11.9–16.2)	9.6±1.7 (6.0–12.0)	9.8±1.2 (6.9–12.0)
HCO_3^- ($mg\,L^{-1}$)	139.1±27.5 (82.4–180.9)	152.9±12.3 (135.3–182.9)	141.4±12.2 (105.8–181.3)
SO_4^{2-} ($mg\,L^{-1}$)	102.3±19.3 (56.8–133.9)	105.5±23.8 (72.1–151.6)	80.4±8.2 (59.8–94.0)

[a] Average±SD.

[b] Min–Max. DO, dissolved oxygen.

Table 2. Compositions of phytoplankton community structure from the reservoirs.

Site	*Bacillariophyta*	*Chlorophyta*	*Cyanophyta*	*Dinophyta*	Site	*Bacillariophyta*	*Chlorophyta*	*Cyanophyta*	*Dinophyta*
	mg L^{-1} (wet weight)					mg L^{-1} (wet weight)			
July 2007					January 2008				
M1	0.86	9.68	24.68	0.00	M1	1.58	13.33	0.12	0.00
M2	0.44	3.65	2.54	4.40	M2	1.87	1.69	0.09	0.55
M3	0.26	1.80	0.06	3.30	M3	3.50	0.68	0.00	0.00
M4	0.15	3.67	0.00	0.03	M4	5.46	0.57	0.04	0.00
M5	1.76	23.98	0.27	27.50	M5	–	–	–	–
S1	3.60	7.39	0.01	0.12	S1	14.78	0.35	0.00	0.00
S2	0.59	1.34	0.00	0.03	S2	5.76	0.00	0.02	0.00
S3	1.89	5.15	0.04	2.20	S3	3.17	0.26	0.00	0.00
S4	0.78	2.11	0.00	0.02	S4	1.28	0.44	0.01	0.00
W1	0.87	4.09	0.00	0.00	W1	0.62	0.62	0.00	0.00
W2	0.30	2.64	0.00	0.00	W2	0.70	0.70	0.00	0.00
W3	5.51	2.42	0.00	0.12	W3	0.48	0.88	0.00	0.00
W4	1.49	0.84	0.00	0.05	W4	0.53	0.70	0.00	0.00
W5	0.63	2.71	0.00	1.65	W5	0.44	1.80	0.00	0.00
W6	0.42	2.64	0.00	1.65	W6	0.92	1.67	0.00	0.00
W7	0.30	6.16	0.00	2.75	W7	1.65	1.14	0.01	0.00
W8	1.27	18.79	0.01	15.40	W8	3.12	0.48	0.00	0.00
W9	1.30	34.54	0.16	12.10	W9	0.44	4.14	0.00	0.00
W10	0.68	2.95	0.03	0.55	W10	0.97	1.06	0.00	0.00
October 2007					April 2008				
M1	0.66	6.60	0.74	0.28	M1	0.48	49.72	0.05	0.00
M2	3.28	4.03	7.55	0.22	M2	0.75	2.90	0.11	0.00
M3	2.84	1.47	0.18	0.10	M3	0.97	2.29	0.01	0.00
M4	2.68	2.75	0.03	0.10	M4	0.31	0.84	0.00	0.00
M5	4.53	2.46	0.02	0.30	M5	1.28	1.96	0.01	0.00
S1	1.80	2.79	0.00	0.05	S1	3.54	0.33	0.00	0.00
S2	1.08	1.54	0.00	0.01	S2	3.01	0.40	0.00	0.00
S3	2.22	2.02	0.00	0.02	S3	10.56	0.31	0.00	0.00
S4	1.06	2.02	0.00	0.00	S4	9.11	0.40	0.00	0.00
W1	3.67	7.81	0.24	0.03	W1	1.74	0.90	0.00	0.01
W2	0.13	0.97	0.00	0.00	W2	0.88	0.26	0.00	0.00
W3	3.78	1.65	0.05	0.00	W3	1.30	1.83	0.00	0.02
W4	2.71	0.86	0.03	0.00	W4	1.50	0.88	0.00	0.00
W5	2.51	2.20	0.06	0.00	W5	1.94	0.59	0.00	0.00
W6	1.56	1.47	0.00	0.00	W6	1.72	1.48	0.00	0.00
W7	1.52	2.38	0.01	0.02	W7	2.24	0.84	0.00	0.02
W8	1.74	1.30	0.19	0.55	W8	8.93	0.18	0.00	0.00
W9	0.84	0.81	0.19	0.14	W9	12.91	1.67	0.00	0.00
W10	0.62	0.51	0.08	0.05	W10	2.95	0.09	0.00	0.00

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Table 3. Values of $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$, and $\delta^{13}C_{PPC}$ (‰) from the reservoirs.

Site	$\delta^{13}C_{DIC}$	$\delta^{13}C_{POC}$	$\delta^{13}C_{PPC}$	Site	$\delta^{13}C_{DIC}$	$\delta^{13}C_{POC}$	$\delta^{13}C_{PPC}$
July 2007				January 2008			
M1	−5.1	−22.1	−24.9	M1	−6.3	−31.0	−33.1
M2	−7.1	−24.2	−22.9	M2	−9.4	−33.8	−39.2
M3	−8.5	−26.3	−24.1	M3	−8.8	−34.5	−38.2
M4	−9.0	−27.2	–	M4	−8.0	−31.6	–
M5	−6.7	−20.8	−18.6	M5	–	–	–
S1	−6.4	−29.5	−28.0	S1	−7.5	−32.8	−38.1
S2	−9.6	−28.3	−31.2	S2	−7.7	−30.3	−33.8
S3	−7.7	−28.9	−28.1	S3	−8.5	−31.3	−38.0
S4	−9.3	−29.2	−30.7	S4	−8.4	−30.4	−28.9
W1	−4.5	−32.3	–	W1	−8.9	−31.1	−33.8
W2	−8.8	−28.4	–	W2	−9.0	−30.9	−31.0
W3	−6.5	−27.4	−26.3	W3	−8.9	−31.6	−31.5
W4	−9.1	−29.3	–	W4	−9.1	−31.6	−30.9
W5	−8.6	−26.0	−26.0	W5	−8.8	−30.6	−29.9
W6	−9.2	−29.2	–	W6	−8.7	−30.2	–
W7	−7.6	−30.9	−25.7	W7	−8.6	−29.7	−33.9
W8	−5.5	−19.6	–	W8	−8.9	−29.5	−33.9
W9	−7.3	−22.3	−24.3	W9	−9.0	−30.9	−32.6
W10	−9.4	−26.0	−24.1	W10	−9.0	−29.5	−31.9
October 2007				April 2008			
M1	−8.0	−29.1	−28.3	M1	−3.3	−24.0	−15.1
M2	−9.3	−31.0	−33.1	M2	−5.4	−26.1	−26.7
M3	−9.6	−30.2	−30.0	M3	−7.4	−29.4	−30.2
M4	−9.4	−29.3	–	M4	−7.6	−29.1	–
M5	−9.2	−32.1	−33.2	M5	−5.7	−32.1	−33.6
S1	−8.0	−31.3	−33.0	S1	−6.2	–	−31.5
S2	−8.9	−30.9	−32.5	S2	−7.2	−29.3	−35.6
S3	−8.5	−32.4	−29.6	S3	−6.8	−30.2	−29.6
S4	−8.7	−30.3	−29.4	S4	−7.5	−31.0	−36.3
W1	−8.1	−32.1	–	W1	−7.8	−30.5	−35.2
W2	−9.5	−29.7	–	W2	−9.5	−30.8	−34.1
W3	−8.5	−30.2	−33.1	W3	−7.4	−32.8	−35.5
W4	−8.9	−29.3	−30.6	W4	−8.6	−30.2	−30.8
W5	−9.2	−30.5	−32.6	W5	−8.2	−31.6	−34.8
W6	−8.9	−30.2	−31.1	W6	−8.6	−30.4	−33.5
W7	−9.0	−30.3	−29.8	W7	−7.9	−32.3	−37.6
W8	−9.5	−27.1	−30.2	W8	−6.6	−31.9	−33.6
W9	−10.0	−31.9	−30.7	W9	−6.9	−30.1	−31.7
W10	−9.7	−31.0	−30.2	W10	−8.6	−30.5	−32.0

– Stands for not detected.

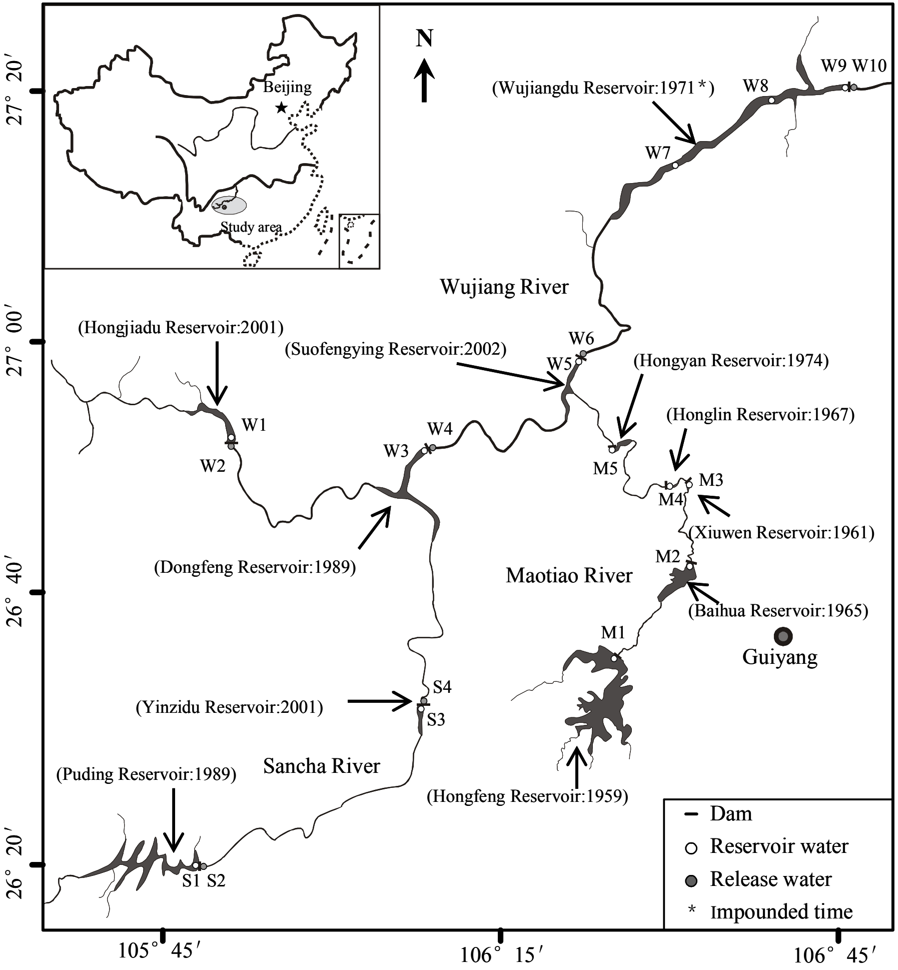

Fig. 1. Map showing sampling locations and sample numbers.

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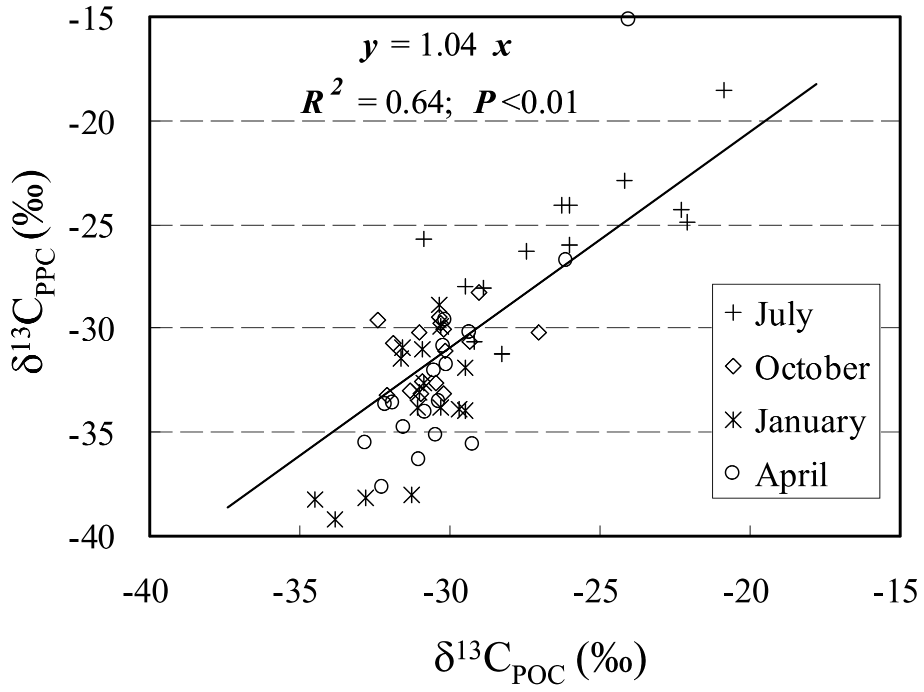

Fig. 2. $\delta^{13}C_{POC}$ vs. $\delta^{13}C_{PPC}$.

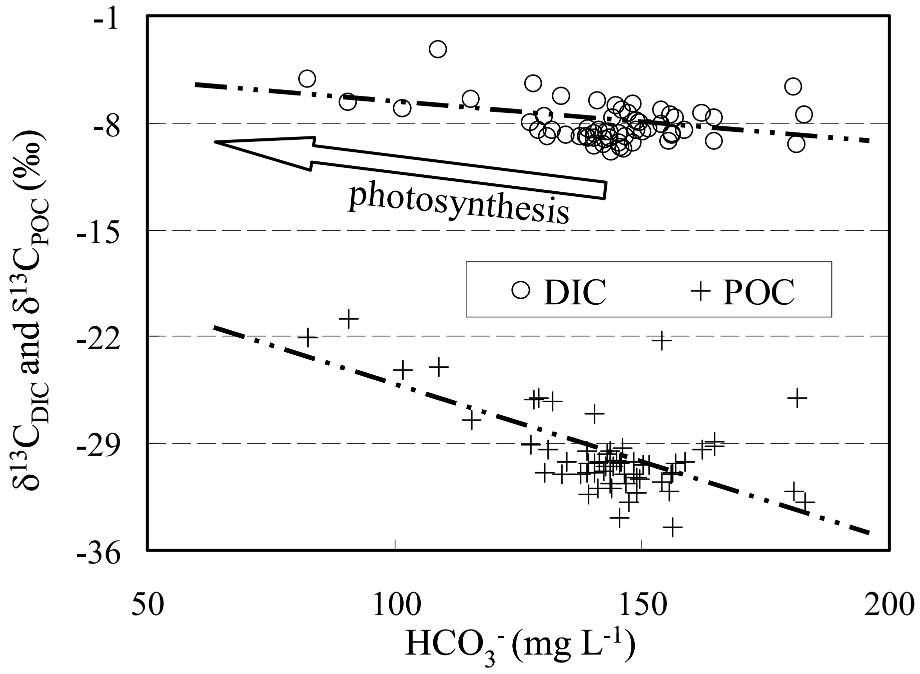

Fig. 3. Concentration of HCO_3^- vs. $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$, respectively.

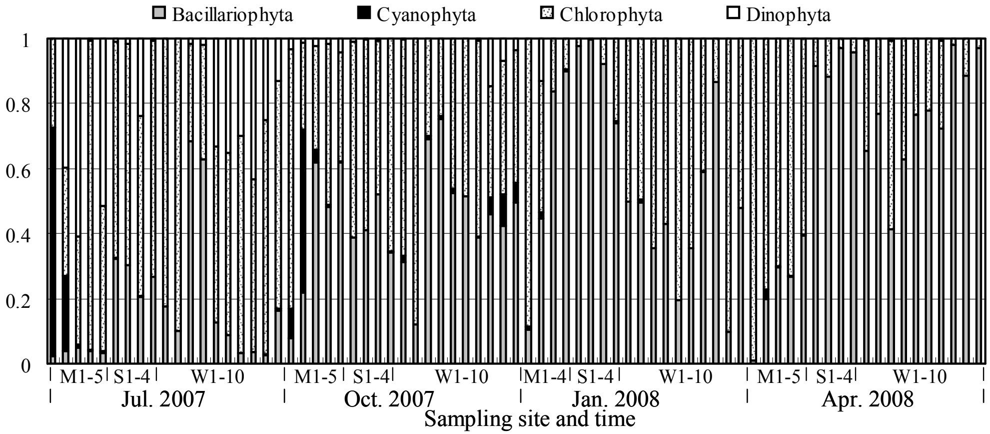

Fig. 4. Phytoplankton community structure in these reservoirs.

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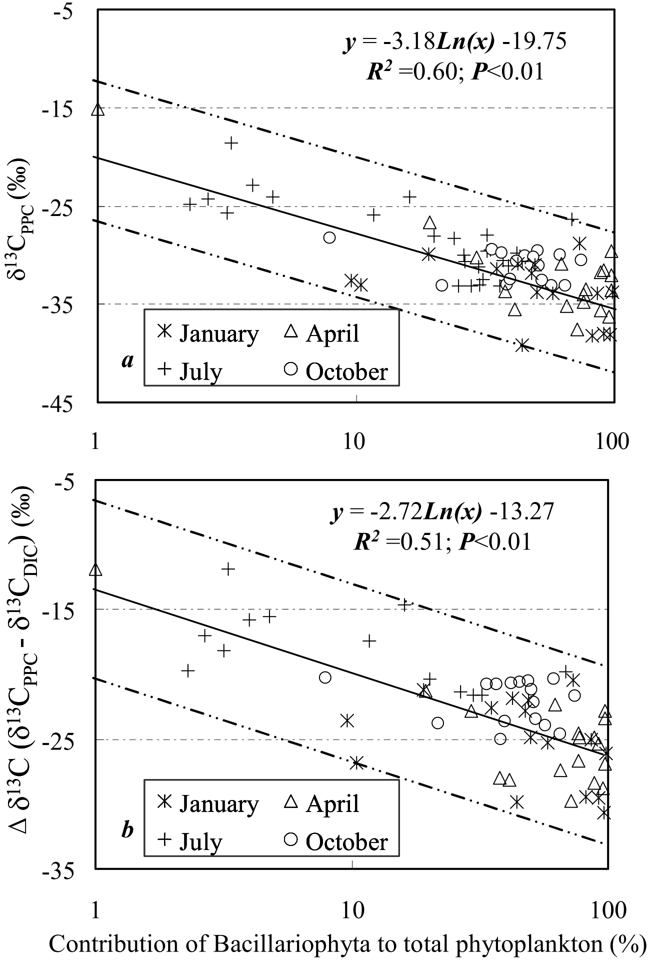

Fig. 5. Contribution of *Bacillariophyta* to the total phytoplankton vs. $\delta^{13}C_{PPC}$ and $\Delta\delta^{13}C$ ($\delta^{13}C_{PPC}-\delta^{13}C_{DIC}$), respectively.

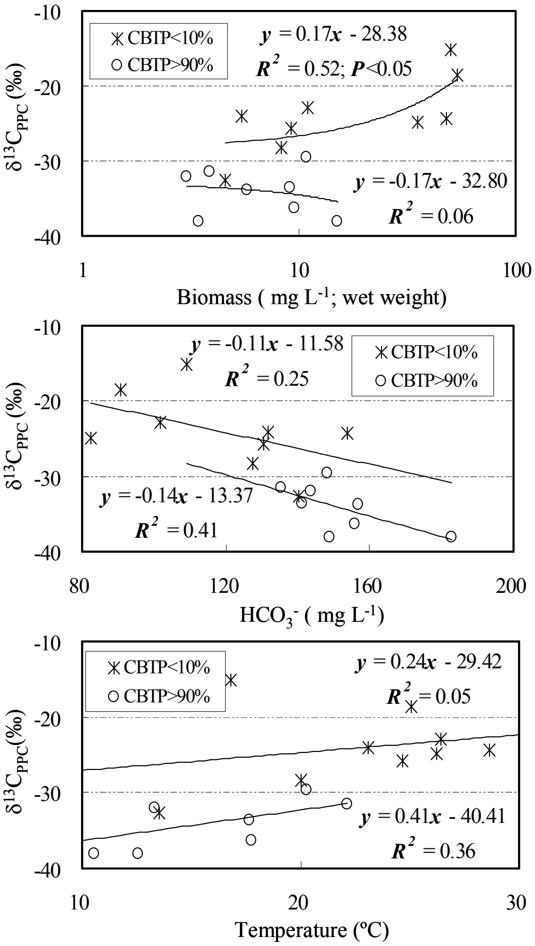

Fig. 6. $\delta^{13}C_{PPC}$ vs. biomass of phytoplankton, HCO_3^-, and temperature, respectively, at CBTP>90% and <10% conditions.