Silica retention in the Three Gorges Reservoir

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Abstract A mass balance of dissolved silica (DSi) based on daily measurements at the inflow and outflow of the Three Gorges Reservoir (TGR) in 2007 and a more precise budget, with inflow, outflow, primary production, biogenic silica (BSi) settlement, dissolution of BSi in the water column and flux of DSi at the sediment–water interface in the dry season (April) of 2007 were developed. We address the following question: How much does the Three Gorges Dam (TGD) affect silica transport in the TGR of the Changjiang River (Yangtze River)? The DSi varied from 71.1 to 141 μmol/l with an average of 108 μmol/l, and it ranged between 68.1 and 136 μmol/l, with an average of 107 μmol/l in inflow and outflow, respectively, in the TGR in 2007. The linear relationship of DSi between inflow and outflow water is significant ($r = 0.87, n = 362, p < 0.01$). Along the main stream of the TGR, the DSi concentration decreases with an average concentration of 84.0 μmol/l in the dry season. However, the stratification of DSi was not obvious in the main channel of the TGR in the dry season. The BSi is within the range of 0.04–5.00 μmol/l, with an average concentration of 2.1 μmol/l in the main channel of the TGR, while it is much higher in Xiangxi Bay (1.30–47.7 μmol/l, 13.1 μmol/l) than in the main stream of the TGR and the other bays. After the third filling of the TGR, approximately 3.8% of the DSi was retained by the TGR based on a 12-month monitoring scheme in 2007, which would slightly reduce nutrient fluxes of the Changjiang River to the East China Sea (2%). DSi was lost during January to June and November, whereas the additions of DSi were found during the other months in 2007. The budget results also indicate that there is a slight retention of DSi. The retention of DSi in the reservoir is approximately 2.9%, while BSi is approximately 44%. Compared with the total silica load, the retention of DSi and BSi in the reservoir is only 5.0% in the dry season. With its present storage capacity, the reservoir does not play an important role as a silica sink in the channel of the TGR. The DSi load is significantly related to discharge both in inflow and outflow waters ($p < 0.01$). DSi retention, to some extent, is the runoff change due to impoundment.

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Introduction

Rivers are the primary source of silicon to oceans (Tréguer et al. 1995; Conley 1997). The composition of particulate and dissolved silicon in river systems is complex and depends on physical, chemical and biological processes that occur in drainage basins and rivers (Billen et al. 1991; Degens et al. 1991; Humborg et al. 1997; Milliman 1997; Zhang et al. 1999; Nilsson et al. 2005). Therefore, there is a great deal of spatial heterogeneity in riverine dissolved silica (DSi)-fluxes (Dürr et al. 2011). However, the level of silica in rivers is mainly controlled by the combination of lithology, runoff, erosion, temperature, water residence time, land cover, and other factors (Dürr et al. 2011; Hartmann et al. 2010). Human impacts on large river watersheds have affected global cycles of other nutrients (Caraco 1993; Vörösmarty 1997; Syvitskl et al. 2005), which to some extent, alter the global silica cycle. Eutrophication (Caraco 1993; Conley et al. 1993, 2000; Turner and Rabalais 1994), large dams (Friedl et al. 2004; Humborg et al. 2002, 2006), and landscape alterations have created an unnatural abundance of riverine diatoms and a rapid rate of diatom sequestration in reservoir sediments, which could lead to a decrease of DSi in the river system itself. Riverine loads of nitrogen (N) have increased during the past decades (Bouwman et al. 2005), and similar changes have occurred for phosphorus (P) (Smith et al. 2003), but DSi loads have remained constant or have even decreased in many rivers primarily as a result of Si retention in reservoirs and lakes (Conley 2002; Ittekot 2006), which would result in a decrease of the ratios of Si:N and Si:P in the river system. The excess delivery by rivers of N and P relative to Si to the coastal zone has dramatic effects on the development of diatoms in the adjacent seas (Humborg et al. 1997; Humborg et al. 2000). This phenomenon also happened in the Changjiang River and its estuary due to anthropogenic input (e.g. fertilizer application) (Li et al. 2007). Over the last several decades, China has experienced rapid increases in chemical fertilizer use and human population, and this trend will presumably experience a further strengthen because of construction of new dams and increase of population.

River dam construction greatly influences N, P, and DSi flux in river systems (Milliman et al. 1984; Halim 1991; Humborg et al. 1997). In fact, the retention of N and P in lakes and reservoirs can be compensated for by anthropogenic inputs and recycling in the drainage basins, while no such compensation occurs for DSi. The biogeochemical fluxes of silica, therefore, deserve better quantification to understand its role in aquatic environments. Low flow velocity, high transparency and high nutrient levels stimulate planktonic growth within reservoirs. Increased in situ diatom production and subsequent algal sedimentation are the key processes that are thought to explain the downstream DSi decline observed in several dammed rivers. High sedimentation rates (Dean and Gorham 1998) and relatively little dissolution of biogenic silica (BSi) (Humborg et al. 2006) would reduce the flux of DSi to the ocean by rivers, such as the Seine River (Garnier et al. 1999) and the Nile River (Whaby and Bishara 1980). According to a recent study, DSi retention in reservoirs in global river basins may amount to 18–19% (Beusen et al. 2009). This argument has been raised to explain the DSi decrease (approximately 70%) measured in the Danube Delta and the Black Sea shelf (Humborg et al. 1997). However, the most recent study on the Iron Gate I Reservoir indicated a present-day DSi elimination within a range of only 4–5% of the total incoming load (Friedl et al. 2004; McGinnis et al. 2006). Damming of the river headwaters and tributaries exerts a stronger cumulative impact on downstream ecology and nutrient transport than the construction of a single large impoundment (Teodoru and Wehrli 2005; Teodoru et al. 2006). Most importantly, the Changjiang River is a heavily dammed river with thousands of dams built in its basin over the last several decades. The construction of the Gezhouba Dam and the TGD on the main stream of the Changjiang River in recent years has caused drastic reductions in sediment fluxes (Yang et al. 2005, 2007; Dai et al. 2011). Understanding issues regarding the material transport of large dams is therefore of considerable interest. An important question is whether a large dam has an impact on a river system under a low sediment condition, such as the heavily dammed Changjiang River.

Reductions in forest cover in recent decades have resulted in increased soil erosion and weathering rates in the Changjiang River basin (Shi 1999), which may increase DSi concentrations in water systems. However, the concentration of DSi has decreased continuously at the Datong Hydrologic Station over a ten-year period (Li and Chen 2001). Dai et al. (2011) recently showed that the Changjiang River is a heavily disturbed system in which the DSi concentration at the river mouth decreased from 130 to 80 μmol/l from 1955 to 2008. In fact, this trend of DSi decrease has occurred at most stations over the whole Changjiang drainage basin (Li et al. 2007). One reason for this trend is that DSi has been retained by the dams scattered throughout the watershed. DSi decreased in the TGR after impoundment at the TGD began, which may be a reasonable explanation for part of the DSi reduction in the upper sections of the Changjiang River. However, compared with the Datong station, DSi decreased slowly at the Yichang station (slope for Datong: −0.1908 compared with −0.0454 for Yichang) (Li et al. 2007). Clear water release coupled eutrophication may enhance DSi uptake by diatoms due to improvement of the light regime downstream. The most recent study on the Three Gorges Reservoir (TGR) indicated that nearly 2/3 of the suspended sediment from upstream was trapped in the TGR, which would decrease by 31% the sediment flux into the estuary (Yang et al. 2005, 2007) and may significantly affect particle silica transport. The sharp decrease in sediment concentration implies that the turbidity of regulated rivers substantially decreases downstream of the dams, probably increasing diatom production and silica sequestration. Eutrophication effects in rivers also play an important role in silica retention, which may contribute to the decreasing of DSi in the drainage basin. Therefore, regulation of the Changjiang River by damming and eutrophication in river basins has substantially reduced the dissolved silicon concentration in the Changjiang Estuary and its loads to the East China Sea. Internal processes within the reservoir's side bays (e.g., Xiangxi and Daninghe) may be a major factor affecting the dissolved and particle silica trapped in the TGR (Ran et al. 2010, Submitted). There are more than 30 tributaries in this enormous reservoir, which may impact silica retention in the TGR significantly. The effect of these reservoir processes may be as important to the flux of the outflow as the quality of the inflow. In this study, we provide an analysis of the effect of TGR on the transport of silica within the reservoir-dominated basin, which is fundamental to one of these biogeochemical cycling effects, namely, damming-induced DSi in the Changjiang (Yangtze) River. This paper will also help our understanding of how dissolved and biogenic silica is influenced by large dam construction in a heavily regulated river.

Sample collection and methods

Study site

The Changjiang River is the largest river on the Euro–Asia continent and is one of the largest rivers globally in terms of its length (6,300 km), drainage area (1.8×10^6 km^2), runoff (900×10^9 m^3/year) and sediment load (0.5×10^9 t/year). In the Changjiang River basin, 162 large dams (water storage capacity >0.1 km^3) had been emplaced by 2002. Reservoirs can hold nearly 155 km^3, or 95% of the total reservoir volume in the river basin, accounting for 16% of the annual Changjiang runoff discharge into the sea (Committee of Statistical Almanac of the Yangtze River, 1992–2004).

The relatively recent TGD, located in Sandouping, Hubei Provence, is the largest hydropower scheme in the world. Construction of the dam began in 1994 and was completed by 2009. The TGD is made up of a 2-km stretch of concrete that creates a 650-km long reservoir with a total volume of nearly 390×10^8 m^3 and a water area of 1,100 km^2 (Wu et al. 2003). When the TGD comes into operation at a stage of 175 m, the upstream water level will be raised by 180 m. The projected power generation capacity of the TGD is 18,200 MW.

There are more than 30 tributaries in this enormous reservoir (e.g., Xiangxi and Daninghe Rivers), and many bays have formed downstream from these tributaries since the TGR has been filled. The stream flow in these tributaries was considerably lower than in the main channel. The mean daily flows for most of these tributaries were generally less than 100 m^3/s, whereas they were high in the main stream (mean daily flow 6300 m^3/s). In general, these tributaries may contribute to 5% of the water discharge in the TGR. It was estimated that with the completion of the TGR in 2009, the average flow velocity in the main stream would decrease to 0.17 m/s (Li et al. 2002) and the average flow velocity in the Xiangxi would decrease to 0.0012–0.0037 m/s (Luo and Tan 2000).

Sampling and analytical methods

Reservoir monitoring in April 2007

The TGR marks the border between Cuntan and the TGD with a length of 550 km, including the backwater areas of tributaries between them in this study. During 20 April to 5 May 2007, 4 years after the first filling stage of the TGR (135 M) and 1 year after the third filling stage of the TGR (156 M) was completed, a survey was carried out in the main channel of the Changjiang River between the city of Chongqing (reservoir inflow), on the upper section of the Changjiang River, and Zigui (reservoir outflow), on the lower section of the TGR. Water samples were collected for 550 km along the main channel, starting from Zigui (the city of Wuhan) and moving upstream. The water samples were taken using 10 l Niskin bottles at various depths in the main channel of the TGR and its tributaries, i.e., the Xiangxi, Daninghe, Xiaojiang and Wujiang rivers (Fig. 1), for DSi, chlorophyll-*a* (Chl-*a*), and BSi analyses. Four transections were set along the TGR: the transection before the dam, the Wanzhou transection, the Qingxichang transection, and the Mutong transection. At each transection, three monitoring points were evenly set up across the river. Six sediment samples were obtained during a cruise in April 2007 using a gravity corer (left bank before dam, right bank before dam, centerline before dam, Xiangxi station, and Wanzhou station; locations documented in Fig. 1). Short-term monitoring shows that riverine discharge in the period mostly approaches the annual average value (i.e., 25,000 m^3/s) without a significant change of flow conditions.

In April 2007, the water samples were immediately filtered through 0.45 μm membrane filters. Separate filter membranes were used to collect particulate samples for the measurement of Chl-*a* and BSi (Chl-*a*: 0.45 μm cellulose acetate membrane; BSi: 0.45 μm polyethersulfone membrane), and the filtrates were used for the determination of DSi. DSi (stored in darkness at 4°C before measurement) was analyzed by a Bran–Luebbe AAIII autoanalyzer, using the silicomolybdic blue method, with a precision of 5–10% at <1–10 μmol/l and 1–5% at 10–100 μmol/l. BSi in the suspended particulate matter was measured by a modified method of Ragueneau (Ragueneaua et al. 2005; Ragueneau and Treguer 1994; Chen et al., 2007). The BSi measurement process consisted of a double wet-alkaline digestion where the filter sample was submitted to a first digestion (NaOH, 0.2 M, 4 ml; pH: 13.3) at 100°C for 40 min. At the end of this first leach, all the BSi and part of the lithogenic silica were converted into $Si(OH)_4$. The Si and Al concentrations ($[Si]_1$ and $[Al]_1$) in the supernatant were analyzed. After rinsing and drying (freeze drying at −60°C), the filter was submitted to digestion again, exactly identical to the first one, leading to the determination of the $(Si:Al)_2$ ratio that is characteristic of the silicate minerals present in the sample. The corrected biogenic silica concentration is thus given by $[BSi] = [Si]_1 - [Al]_1(Si:Al)_2$. Al was determined by a modification of the aluminum–lumogallion fluorescence measurement (Ren et al. 2001). Duplicate BSi samples are typically obtained in 10% of the total number of samples in order to evaluate sample variance. The precision of BSi analysis, measured as a relative standard deviation, is below 5% (Chen et al. 2007). Chl-*a* was determined by fluorometry (Turner Designs 10-AU) after extraction from filters using 90% acetone with a detection limit of 0.05 μg/l (State environmental protection administration of China, 2002).

BSi in the sediments was measured by the method of Ye (2002), which begins with extraction with a wet-alkaline digestion process (40 ml, 2 mol/l Na_2CO_3) at 85°C for 8 h. Each hour, a 0.5 ml supernatant sample was taken from each bottle with a pipette for DSi measurement (Mortlock and Froelich 1989). Then, the corrected biogenic silica concentration was obtained by the method of DeMaster (1981) with a slope correction.

Time series monitoring at the Fuling and Guizhou stations in 2007

Two monitoring stations included the inflow of the TGR: Fuling, a station located 10 km downstream the confluence with the Wujiang River; and the outflow of the TGR at Guizhou (the city of Yichang in Hubei) at a distance of 30 km in front of the TGD (Fig. 1). Daily samples were collected at each station at the surface water from 01 January to 31 December, 2007, for DSi sampling. The water samples were immediately filtered through a 0.45 μm membrane filter (syringe filter, 13 mm 0.45 μm, PTFE). The filtrates (stored in darkness at 4°C before measurement) were used to determine the DSi level, which was analyzed by a Bran–Luebbe AAIII Autoanalyzer, exactly identical

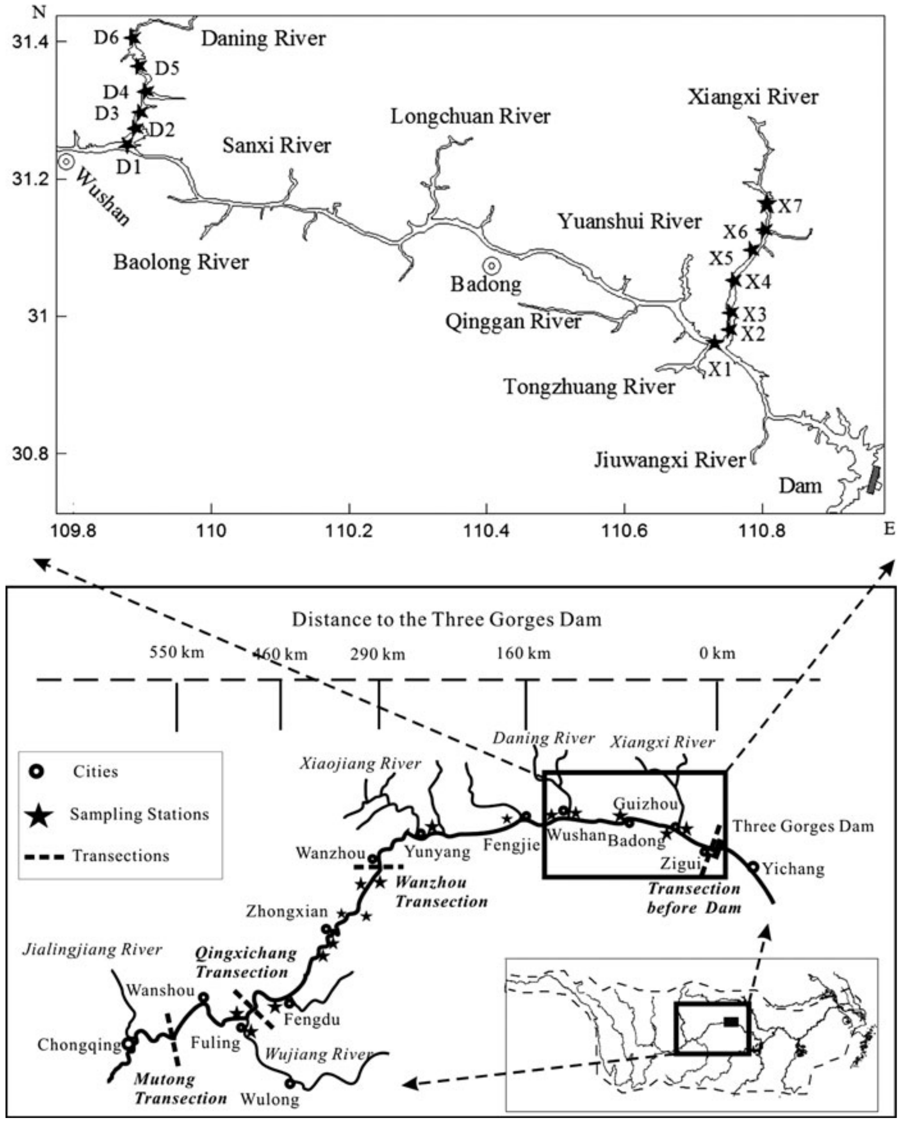

Fig. 1 Sampling locations in the TGR ("Distance to the Three Gorge Reservoir" means the channel length)

to that of April 2007. The daily discharge data were collected from the Ministry of Water Resources of the People's Republic of China.

Budget method

A silica budget was established for the TGR. The model is shown in Fig. 2, which consists of inflow, outflow, primary production, BSi settlement, dissolution of BSi in the water column and the flux of DSi at the sediment–water interface. The net atmospheric inputs of water are much smaller than the input from tributaries and the main stream. An annual input of 7.25–11.6 $\times$ 10^8 m^3/year was estimated by Guo (2008), which accounts for 0.01% of the total discharge input to the reservoir and is therefore not included in the budget.

Flux analysis

Silica fluxes were studied for the inflow and outflow of the TGR.

$$F_{load} = C \times Q \quad (1)$$

where, F_{load} is the flux of DSi or BSi, C is the concentration of DSi or BSi, and Q is the flow rate. For the inflow and outflow of the reservoir, the loads were calculated for each day on the basis of Eq. 1.

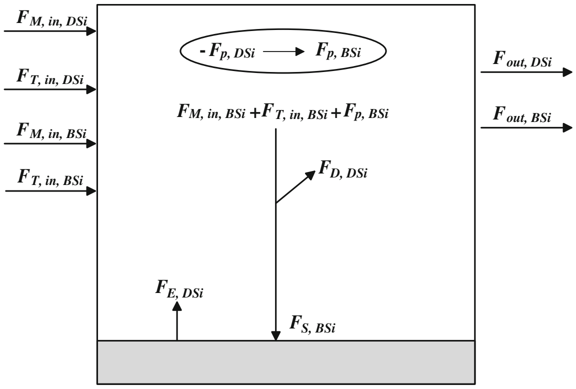

Fig. 2 Biogeochemical cycle of silica on the Three Gorges Reservoir. $F_{M,\mathrm{in,DSi}}$ DSi flux at the inflow of the TGR, $F_{M,\mathrm{in,BSi}}$ BSi flux at the inflow of the TGR, $F_{T,\mathrm{in,DSi}}$ DSi flux of the tributaries in the TGR, $F_{T,\mathrm{in,BSi}}$ BSi flux of the tributaries in the TGR, $F_{\mathrm{out,DSi}}$ DSi flux at the outflow of the TGR, $F_{\mathrm{out,BSi}}$ BSi flux at the outflow of the TGR, $F_{S,\mathrm{BSi}}$ BSi net deposit, $F_{E,\mathrm{DSi}}$ silicate flux at the sediment–water interface $F_{P,\mathrm{BSi}}$ BSi gross production; $F_{P,\mathrm{DSi}}$ DSi assumption by primary production, $F_{D,\mathrm{DSi}}$ silicate flux recycled in the TGR

Flux of BSi to sediment

The silica flux to the sediment was calculated on the basis of Eq. 2.

$$F_{S,\mathrm{BSi}} = C_{\mathrm{BSi}} \times R_{\mathrm{SPM}} \tag{2}$$

where C_{BSi} is the average concentration of the top cores, and R_{SPM} is the amount of SPM trapped in the TGR.

Silicate flux at the sediment–water interface

With laboratory incubation experiments, the benthic exchange rate of DSi at the sediment–water interface was measured. The incubation water came from the TGR. The average DSi exchange rate was calculated with a method that makes use of a continuous function, taking into consideration the culturing time, sampling time and time interval of sampling (Jiang et al. 2002). For each sampling site within the TGR, the DSi exchange amount at a given time (M_i) was calculated as

$$M_i = V \times (C_i - C_0) + \Delta M_{iD} \tag{3}$$

$$\Delta M_{iD} = V_D \times \sum_{i=1}^{n} C_{i-1} \tag{4}$$

where M_i is the exchange amount at t_i (μmol), C_i is the DSi concentration of incubation water at t_i (μmol/l), V is the volume of the incubation water (l), ΔM_{iD} is the amount of DSi that was drawn at t_i (μmol), and V_D is the sample volume at one time (l).

Because the exchange amount versus time in the incubation experiments is nonlinear, the benthic exchange rate of DSi at the sediment–water interface in the TGR was calculated as

$$v_i = \frac{\Delta M_i}{A \times \Delta t_i} \tag{5}$$

$$\Delta M_i = M_{i+1} - M_i \tag{6}$$

$$\bar{v} = \frac{1}{n-1} \sum_{i=2}^{n} v_i \tag{7}$$

where v_i represents the exchange rate at t_i (μmol/m^2/h), ΔM_i represents the exchange amount between t_i and t_{i+1} (μmol), A represents sediment–water areas (m^2), $\Delta t_i = t_{i+1} - t_i$, $\bar{v}$ represents the mean value of exchange rate for the period of t (μmol/m^2/h), and n represents the sampling number. The total incubation time in the series is approximately 50 h.

BSi production and cycling

A first estimate of the BSi production can be obtained by using a method for fixed parameter assignment.

$$(F_{M,\mathrm{in,BSi}} + F_{T,\mathrm{in,BSi}} + F_{P,\mathrm{BSi}})\,\beta = F_{S,\mathrm{BSi}} + F_{\mathrm{out,BSi}} \tag{8}$$

where β is the conservation coefficient of BSi in the reservoir, which was estimated from α, $\beta = (1 - \alpha)$, α is the dissolution rate of BSi, $F_{P,\ \mathrm{BSi}}$ is the BSi production, $F_{M,\mathrm{in,BSi}}$ is the BSi flux upstream of the main channel, $F_{T,\mathrm{in,BSi}}$ is the upstream loads of tributaries, $F_{S,\mathrm{BSi}}$ is the BSi flux to sediment, and $F_{\mathrm{out,BSi}}$ is the outflow load of BSi for the TGR. $F_{M,\mathrm{in,BSi}}$, $F_{T,\mathrm{in,BSi}}$, $F_{S,\mathrm{BSi}}$, and $F_{\mathrm{out,BSi}}$ can be individually calculated. If we can set a reasonable value of β, we can obtain the value of $F_{P,\mathrm{BSi}}$.

A second method of obtaining the BSi production is by using a simple empirical model. On the basis of the nutrient levels of input streams (e.g., $[TP]_i$: phosphorus load of input waters [Survey data in July, 2007, "unpublished data"]) and flushing time (Tw), an estimate was made for the silicon fixation ((PP) g C/m^2/year) within the TGR from a simple empirical model calculation (Vollenweider and Kerekes 1980; Canfield and Bachmann 1981).

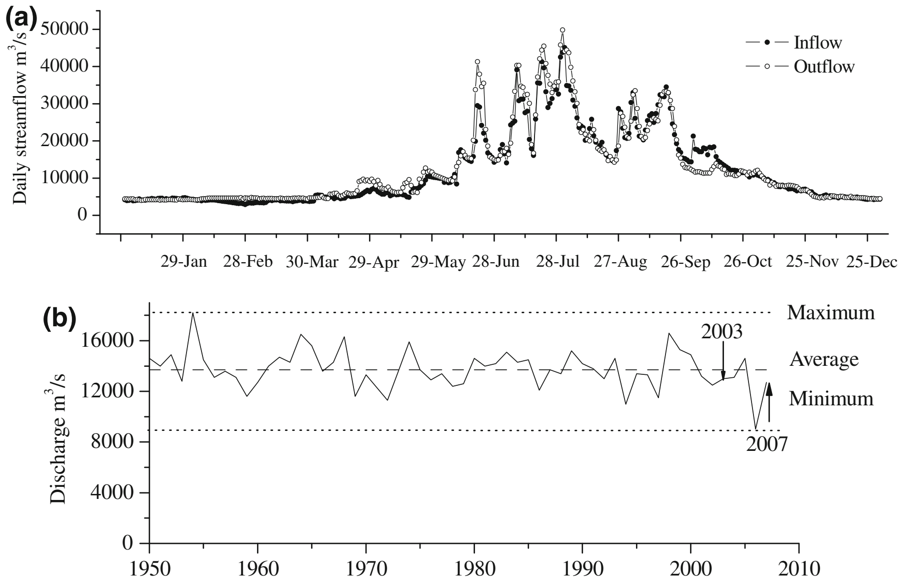

Fig. 3 **a** The inflow rate at Qingxichang (at the Changjiang River, approximately 18 km downstream of the confluence with the Wujiang River) and the outflow rate at Yichang (37 km downstream of the TGR) measured for the Three Gorges Reservoir during 2007. **b** Time series flow rate at Yichang station from 1950 to 2007 according to the Changjiang River Discharge Database

$$\sum C\left(\mathrm{g\,m^{-2}year^{-1}}\right) = 7\frac{\left([TP]_i/\left(1+\sqrt{Tw}\right)\right)^{0.76}}{0.3+0.011\left([TP]_i/\left(1+\sqrt{Tw}\right)\right)^{0.76}} \quad (9)$$

where $\sum C$ is the annual primary productivity fixed by reservoirs, $[TP_i]$ is the phosphorus load of input streams, and Tw is the water flushing time of the reservoir. Tw can be defined as the quotient of reservoir effective volume (Ve) over annual discharge (Q), i.e., $Tw = Ve/Q$. The model outputs were examined by the data of field measurements from 31 nationwide lakes and 8 large reservoirs in China, including 7 of the 10 largest lakes (Zhang et al. 1999). The model output and field measurements generally agree within a factor of 2, which suggests that the model is a feasible approach to estimating the potential carbon fixation of the TGR.

Results

Discharge

The hydrological time series of the inflow at Qingxichang (QXC) was compared with the reservoir outflow at the dam (Fig. 3a). For a period of 12 months in 2007, the inflow and outflow showed the same trend. The highest flow rate over 49,800 m^3/s was recorded on 31 July, while the lowest value of ~4,000 m^3/s was reached during the first week of January. To test whether 2007 was an exceptional year concerning the hydrologic regime, its average flow was compared with the time series of the annual flow measured 37 km below the Three Gorges Dam at the Yichang station (Fig. 3b). The plot indicates that an average discharge of 12,700 m^3/s for 2007 is comparable to the average discharge of the time series 1950–2007 of 13,800 m^3/s. Therefore, 2007 was a normal year regarding the flow regime.

DSi, BSi, and Chl-*a* in the Three Gorges Reservoir

DSi, BSi, and Chl-a in the main channel of the TGR

The DSi concentrations in the main channel of the TGR varied from 76.6 to 99.8 μmol/l, with an average concentration of 84.0 μmol/l in July 2007. The BSi concentration ranged from 0.04 to 5.00 μmol/l, with a mean value of 2.10 μmol/l. The average concentration of Chl-*a* was found to be 0.62 μg/l, and its concentration varied from 0.06 to 1.49 μg/l.

Figure 4 shows the spatial distribution of DSi, BSi, and Chl-*a* in the main channel of the TGR in April, 2007. DSi and BSi show decreasing trends, with high concentrations upstream of the mail channel of the TGR that decreased gradually with the flow direction, resulting in low concentrations of DSi and BSi in the middle and lower areas of the reservoir. The distribution of Chl-*a* did not present a wedge-shaped form like silica and had no detectable trend, but higher Chl-*a* concentrations were observed in the middle part of the main stream of the TGR. The stratification of DSi, BSi, and Chl-*a* was not obvious in the TGR.

DSi, BSi, and Chl-a in the Xiangxi and Daninghe bays of the TGR

The DSi concentrations in Xiangxi Bay varied from 11.6 to 83.6 μmol/l, with an average concentration of 63.4 μmol/l in July 2007. The BSi concentration ranged from 1.30 to 47.7 μmol/l, with a mean value of 13.1 μmol/l. The average concentration of Chl-*a* was found to be 14.2 μg/l, and its concentration varied between 0.06 and 67.3 μg/l. In Daninghe Bay, the DSi concentrations varied from 54.8 to 80.9 μmol/l, with an average concentration of 71.6 μmol/l in July 2007. The BSi concentration ranged from 0.37 to 3.82 μmol/l, with a mean value of 1.61 μmol/l. The average concentration of Chl-*a* was found to be 2.06 μg/l, and its concentration varied between 0.31 and 7.24 μg/l. In general, the DSi, BSi, and Chl-*a* in Xiangxi Bay were commonly higher than in Daninghe Bay.

Figures 5 and 6 represent the spatial distribution of DSi, BSi, and Chl-*a* in the Xiangxi and Daninghe bays, respectively. These two bays have a similar distribution trend. The DSi concentrations were rather low in the bays. Although only a minimal longitudinal distribution pattern was discernible, the stratification of DSi was obvious, with a rapid increase from the upper layer (<20 m deep) downward to the bottom. In general, BSi and Chl-*a* were significantly higher in the surface waters than the bottom waters ($p < 0.05$), especially in the upper bay; the highest BSi and Chl-*a* concentration was observed in Xiangxi Bay.

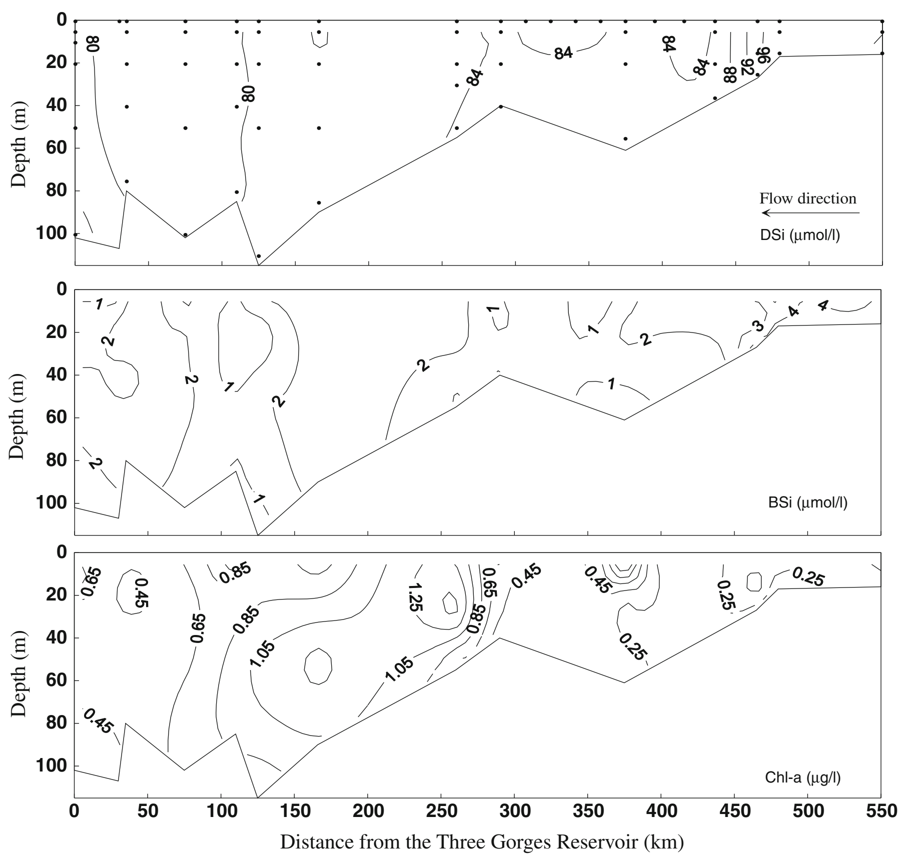

Fig. 4 Distribution of DSi, BSi and Chl-*a* in the TGR

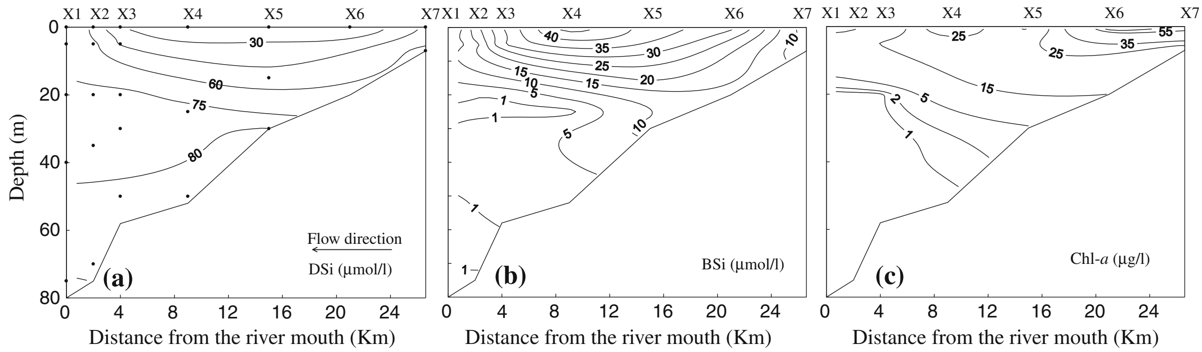

Fig. 5 Distribution of DSi, BSi and Chl-*a* in Xiangxi Bay

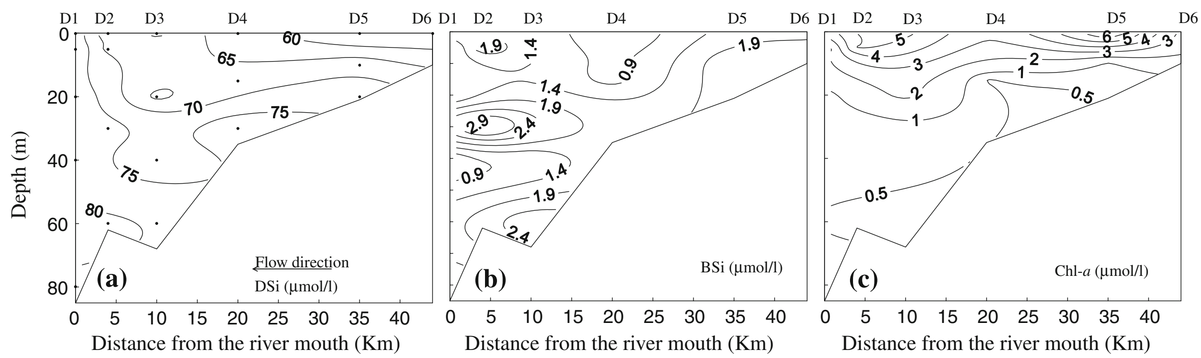

Fig. 6 Distribution of DSi, BSi and Chl-*a* in Daninghe Bay

DSi in several transections along the TGR

The DSi concentrations in the Qingxichang transection varied from 89.8 to 97.0 μmol/l, with a mean value of 94.0 μmol/l. In the Wanzhou transection, the DSi concentrations ranged from 81.8 to 86.9 μmol/l, with an average of 84.1 μmol/l. The average concentration of DSi was found to be 83.2 μmol/l, and its concentration varied between 80.4 and 88.4 μg/l in the transection before the dam.

Figure 7 represents the vertical distributions of DSi in the three transections of the main channel of the TGR. The concentration of DSi within a given transection decreased along the water direction. No obvious variation trend with depth and width was observed in these transections.

Concentration and load of DSi in the inflow and outflow of the TGR

DSi concentration

The concentration of DSi varied from 71.1 to 141 μmol/l, with an average of 108 μmol/l, while it ranged between 68.1 and 136 μmol/l with an average of 107 μmol/l in inflow and outflow, respectively, in the TGR in 2007. The linear relationship of DSi between inflow and outflow water is significant ($r = 0.87$, $n = 362$, $p < 0.01$).

The DSi inflow at Fuling is compared to the outflow concentrations at Guizhou in the TGR (Fig. 8). The outflow DSi followed the pattern of the inflow concentrations. Slightly lower outflow concentrations were observed for almost the entire year of 2007, except the period during February to March and December. Also, the concentration of DSi was slightly lower during 1 January to 15 June than the other periods in 2007.

DSi loads

The DSi variations in different transections are not obvious; therefore, it is representative for Guizhou and Fuling stations to calculate the loads of DSi. The loads were calculated first by multiplying the concentrations by the discharge of the sampling days. Then, the loads

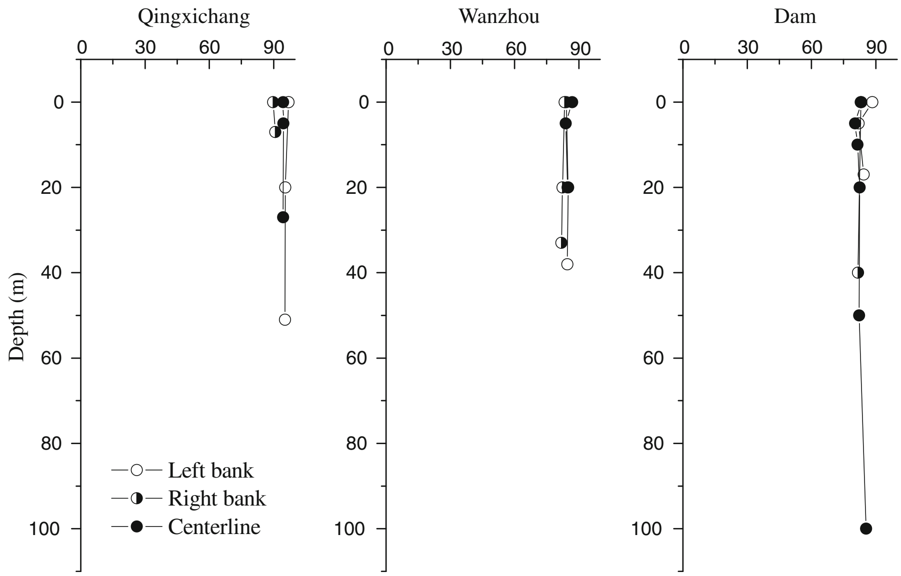

Fig. 7 *Vertical* distributions of DSi in three transections of the main channel of the TGR

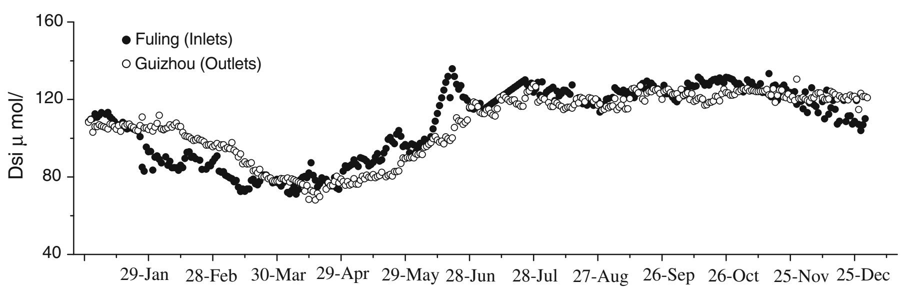

Fig. 8 Daily variation of DSi concentrations at the Fuling and Guizhou stations of the TGR

(mol/s) were numerically integrated to determine the mass over the month period (*t*/month). The total load for the studied period was 44.4×10^9 mol/year at the inflow (upstream of the TGR) and 44.7×10^9 mol/year at the outflow. The maximum load of approximately 9.62×10^9 mol/month at the inflow and 10.1×10^9 mol/month at the outflow were recorded in July, while the minimum load of approximately 0.79×10^9 mol/month at the inflow and 1.07×10^9 mol/month at outflow were recorded in March. The DSi outflow was always higher than the inflow, except from September to October.

Figure 9 presents the monthly variation of DSi fluxes at the Fuling and Guizhou stations of the TGR. The DSi load follows the discharge pattern, with relatively high values during the flood period, especially from July to September.

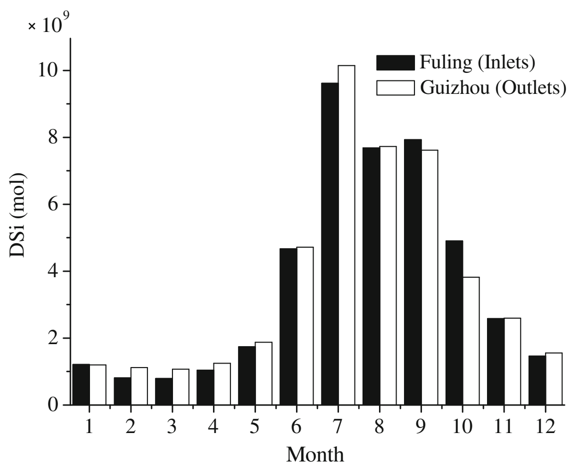

Fig. 9 Monthly variation of DSi fluxes at the Fuling and Guizhou stations of the TGR. *Numbers* on the *graph* represent the serial number of the month in 1 year

Discussion

Influence of reservoirs on material distribution

Distributions of DSi, BSi, and Chl-a in the Xiangxi and Daninghe bays in April 2007

Compared with the results at the same time in 1997 (Liu et al. 2003), the concentrations of DSi in 2007 are low, especially for the reach near the dam. The reduction of DSi in the upper sections of the river occurred after the creation of the TGR. Water that had passed through the TGR exhibited reduced DSi concentrations in April 2007 (Fig. 4).

The concentrations of BSi in the Changjiang River are lower than the global average of 28 μmol/l for large river systems (Conley 1997). However, the BSi and Chl-*a* concentrations in the Xiangxi and Daninghe bays were significantly higher than in the main channel. The concentration of BSi generally decreased from the upper to lower sections of the TGR and its tributaries, which corresponds with a drop in DSi upstream of the TGR and its tributaries (Figs. 4 and 5).

We hypothesize that the decrease of DSi resulted from several factors, including the biological uptake of silicate (e.g., DSi conversion to BSi by diatoms) and fluctuation upstream. High concentrations of BSi and Chl-*a* in Xiangxi Bay and their decrease along the water direction in the tributary may be a reasonable explanation for part of the DSi reduction in the side bays of the TGR. However, the pattern becomes more complex under changing flow and concentration. During base flow, when the inflow concentrations and flow rates are low, the concentrations immediately below the headwaters decline sharply and reach relatively low levels in the downstream portions of the reservoir. At the time of the survey, the water outflow remained constant, while the water inflow increased slightly post-survey (Fig. 3a). Therefore, DSi fluctuation in the upstream, to some extent, may slightly expand the variations between the inflow and outflow of the TGR. In contrast to the main stream, the survey of the tributaries was completed within one day; thus, the fluctuation effect in the tributaries could be neglected.

In general, the side bay influence (i.e., DSi uptake) tends to be weak in the reservoir as water approaches the dam, particularly when associated with relatively long retention times. For example, Xiangxi Bay is closer to the TGD than Daning Bay (the former distance is 32 km, while the latter is 123 km). Therefore, the side bay effect of Xiangxi Bay is more strongly influenced by the TGD compared with Daning Bay. The DSi, BSi, and Chl-*a* in Xiangxi Bay were commonly higher than in Daninghe Bay, which may be clear proof of a side bay effect.

Concentration and load of DSi in the inflow and outflow of the TGR in 2007

At the Yichang station, the average concentration of DSi was approximately 116 μmol/l in 1958–1973, and 108 μmol/l in 1980–1985 (Duan et al. 2007). Therefore, the concentrations of DSi decreased slightly at Yichang in the main stream of the Changjiang River. Compared with historical data in 1980–1985, the DSi in 2007 ($\sim$110 μmol/l) displayed smaller variations but was slightly lower than that in the period 1958–1973. The seasonal variations of the DSi distribution recorded at Fuling station are similar to Guizhou station, with lower values in January to May and higher values in June to December. In general, the TGR was in the filling stage during October to April of the following year, and its water level rose to nearly 156 m (from 145 to 156 m). Compared with the period of January to March, the DSi concentration is high at the beginning of the filling stage in these waters (October to December), which may mix with other inflow waters, enhancing the DSi concentration at the outflow in the subsequent few months (Fig. 8). Dam operation may have caused the DSi concentration to be higher in Guizhou than Fuling in January to May (Fig. 8). Of course, the BSi dissolution in the TGR may be a small source of DSi, causing a rise in the DSi level. High water level and low flow may increase the rate of diatom dissolution in the TGR during the period of January to March. However, the BSi level is low in the TGR, and its role in the silica budget may be limited.

Furthermore, the seasonal variations of DSi in 2007 are slightly different from the historical results of Li et al. (2007). The DSi changes from ca. 79 to 105 μmol/l, with high values (95–105 μmol/l) in the flood season and low values (79–95 μmol/l) in the non-flood season (Li et al. 2007). These results are probably related to the erodibility of the parent rocks and to impoundment (especially in the non-flood season) in the river basin. Additionally, the DSi at

Guizhou station is slightly lower than that at Fuling station during most of the study period, i.e., April–November. However, the monthly fluxes of DSi and discharge show the same trend of variations, i.e., higher values in the flood season and lower values in the non-flood season (Figs. 3a, 9). The load of DSi at the Fuling and Guizhou stations in the flood season to the annual total is 67%, indicating that runoff is the key factor in controlling the DSi fluxes in the Changjiang River.

Transport coefficients, which were determined for the water and chemical fluxes as output/input for each reservoir reach, provide a simple measure of net transport 'efficiency' throughout the reservoir. If the transport coefficient is unity, output equals input, indicating that the net transport is not altered by the reservoir. Where the coefficients are greater than unity, the output exceeds the input, indicating net transport is magnified or increased by passage through the reservoir. Conversely, where the coefficients are less than unity, the output is less than the input, indicating the net reduction of transport associated with the presence of the reservoir. Analysis of the seasonal variability in transport of DSi through the reservoirs is provided by a comparison of transport coefficients for mean monthly fluxes of water and DSi (Fig. 10). Where the transport coefficients fall close to the 1:1 correspondence line, the solute transport was essentially coincident with the water transport, indicating little net change between the inflow and outflow

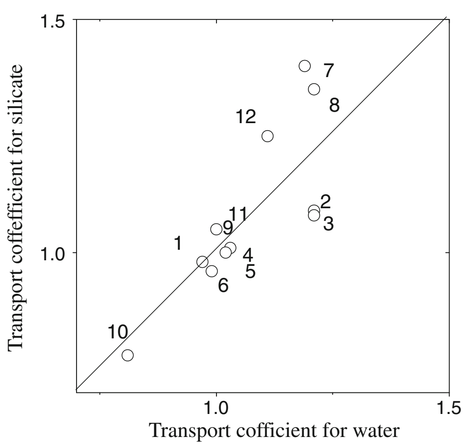

Fig. 10 Comparison of transport coefficients for water and silicate at the Fuling and Guizhou stations of the TGR. Transport coefficients calculated as the ratio between out/input for mean monthly flux. *Numbers* on the *graph* represent the serial number of the month in 1 year

for the reservoir. This pattern occurred in January. If the solute transport coefficients were less than the water transport coefficients, then the water released from the reservoir was diluted relative to the input, indicating the net retention of input loads in the reservoir. This pattern was observed during February to June and October in the TGR. Finally, if the solute transport coefficients were greater than the water transport coefficients, the water released from the reservoir was relatively concentrated compared with the input, indicating a net increase of solute transport from the reservoir. This pattern was observed during July, August, September, November and December.

Silicate (DSi) input–output mass balance for the TGR

To examine the changes in silicon due to dam construction, a set of mass balance models was developed for the system. The total input to the reservoir, including the inflow at Fuling and the lateral input from the tributaries of the Three Gorges Reservoir, must be equal to the losses, including the output at the dam and the reservoir retention. In the steady state, the difference between the total input and output into the system must approach zero. We hypothesize that the TGR is a system that only includes water and suspended and dissolved material in the water column. The equation is as follows:

$$L_{in} + L_T - L_{out} - L_R = 0 \qquad (10)$$

where L_{in} and L_{out} stand for the inflow and outflow loads, L_T represents the input from the catchments and L_R is the net retention of the reservoir. (L_T: the lateral input was calculated from the values of the discharge (5%) from the major tributaries into the TGR based on the assumption that there is no significant difference in concentration between tributaries and the main channel).

As Fig. 11 indicates, the loss of DSi is not the significant process in the flux balance. Compared with the total input, the retention load by dam represents approximately 3.8% DSi in the TGR. This study, to some extent, does not support the hypothesis that the TGR played a major role in silicon elimination. In general, 55% of the water supply for the Datong station originated upstream from Yichang. As a rough verification of DSi retention, TGR would reduce the DSi fluxes of the Changjiang River into the East China Sea by 2%. In contrast to other results worldwide

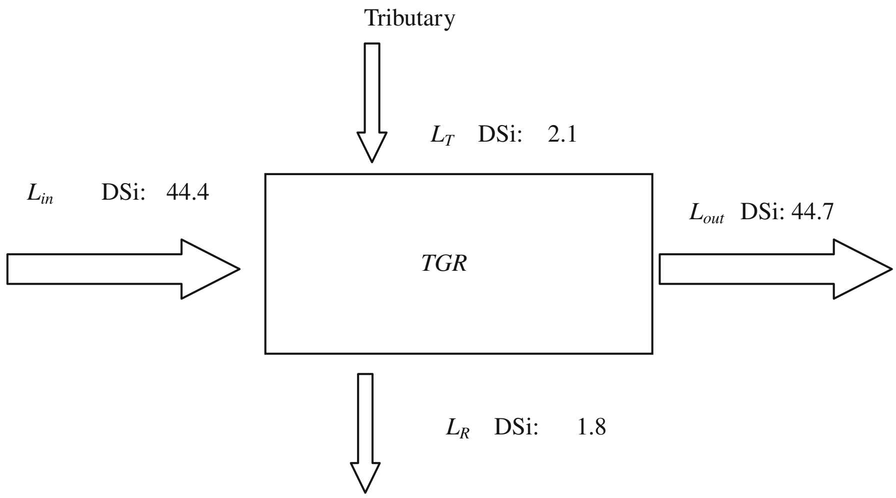

Fig. 11 Mass balances for DSi in the TGR with the *box* representing the reservoir pool from 1 January through 30 November 2007. The loads are in 10^9 mol/year

(Goto et al. 2007; Sferratore et al. 2008; Triplett et al. 2008; Dürr et al. 2009; Perran et al. 2010), the retention efficiency of silica in the TGR is very low. The size of the reservoir may be an important factor impacting silica retention (Conley et al. 2000). In 2007, during the third filling of the TGR, the size of the reservoir was only 50% of the area of the normal water level of 175 m, which might mean that the silica retention is not significant. Furthermore, hydrological and physical changes may have occurred during the maturation stage (175 m) of the reservoir. Compared with the 175-m stage, the high flow and exchange rates and short hydro retention time prevent the development of a stable stratification and limit primary production in the early stage of the TGR (156 m). Therefore, the TGR was not the most important cause for the decrease in the riverine silica load in the early stage of the TGD. Additionally, the present BSi level is very low, so it could not have played a major role in the silica loads in the Changjiang River.

Silica budget and cycling for the TGR

Silica inflow and outflow

The inflow station is located at the QXC transection, while the outflow site is located at the transection before the dam (approximately 1 km distance to the dam). Additionally, the upstream concentrations were applied to the tributaries of the TGR. The concentrations used in the fluxes were mean values in each transection. The concentrations of DSi and BSi upstream of the TGR and each tributary's inflow and outflow were multiplied by the corresponding monthly discharges to obtain the monthly mass fluxes of DSi and BSi into and out of the TGR. The silica fluxes for days without silica measurements were represented by the nearest stream's downstream reservoir that had monitoring stations. The fluxes of DSi and BSi are listed in Table 1.

The TGR discharge over the period of study reached 163.3×10^8 m^3/s in April 2007 after the Yichang Hydrostation dam was established. The mean values of DSi and BSi before the dam are 83.2, and 1.19 µmol/l, respectively. The total outflow loads at the dam were 13.6×10^8 mol for DSi and 0.19×10^8 mol for BSi in April 2007. Input to the reservoir was dominated by the main-stem of Changjiang River, which contributed to more than 90% of the mean annual water flux into the TGR. In contrast, the tributaries in the TGR supplied approximately 5% of all the river water discharged into the reservoir. Therefore, the main silica source input to the TGR comes upstream of the Changjiang River.

BSi flux to sediment

The BSi concentrations from each sediment top core within the reservoir are presented in Table 2. The sediment cores from the reservoir show similar concentrations of approximately 0.57 to 0.63%, with an average of 0.61%. The net sedimentation in the reservoir was estimated by discharges and the SPM in the water based on the measurements in the TGR. According to Table 3, the load of SPM entering the TGR is 3659.5×10^8 g, while it is only 280.8×10^8 g

Table 1 DSi and BSi flux from the main channel and tributaries into the TGR in April 2007 (downstream by QXC)

Name	Discharge (10^8 m^3)	DSi (μmol/l)	DSi flux ($\times10^8$ mol)	BSi (μmol/l)	BSi flux ($\times10^8$ mol)
Main stream (QXC)	134.6	94.0	12.7	3.39	0.46
Qixihe River	0.38	XJ[a]	0.034	XJ[a]	0.0010
Bixihe River	0.06		0.005		0.0001
Longhe River	1.50		0.132		0.0039
Chixihe River	0.03		0.003		0.0001
Dongxihe River	0.06		0.005		0.0002
Huangjinhe River	0.37		0.033		0.0010
Ruxihe River	0.31		0.027		0.0008
Rangxihe River	0.12		0.011		0.0003
Zhuxihe River	0.11		0.010		0.0003
Xiaojiang River (XJ)	3.01	87.9	0.264	2.60	0.0078
Total (QXC to XJ)	5.96	87.9	0.52	2.60	0.016
Tangxihe River	1.46	DNH[b]	0.107	DNH[b]	0.0036
Modaoxi River	1.56		0.114		0.0039
Changtanghe River	0.72		0.052		0.0018
Meixihe River	0.84		0.061		0.0021
Caotanghe River	0.21		0.015		0.0005
Daxihe River	0.78		0.057		0.0019
Daninghe River (DNH)	2.54	73.1	0.186	2.49	0.0063
Total (XJ to DNH)	8.11	73.1	0.59	2.49	0.02
Guanduhe River	0.16	XX[c]	0.012	XX[c]	0.0010
Baolonghe River	0.17		0.012		0.0011
Shenlongxi River	0.52		0.037		0.0033
Qingganhe River	0.51		0.037		0.0032
Tongzhuanghe River	0.17		0.012		0.0011
Zhaxihe River	0.22		0.016		0.0014
Xiangxihe River	1.23	72.2	0.089	6.40	0.0079
Total (DNH to XX)	2.97	72.2	0.21	6.40	0.02
Jiuwaxi River	0.45	Dam[d]	0.038	Dam[d]	0.0005
Maopingxi River	0.06		0.005		0.0001
Total (XX to Dam)	0.52	83.2	0.04	1.19	0.0006
Sum of tributaries	17.6		1.37		0.06
Sum	152.1		14.0		0.51

[a] Tributary concentration between QXC and XJ represented by XJ

[b] Tributary concentration between XJ and DNH represented by DNH

[c] Tributary concentration between DNH and XX represented by XX

[d] Tributary concentration between XX and dam represented by the section near the dam. The discharge of tributaries comes from Huang and Li (2006)

of the SPM output from the reservoir. The retention of SPM indicates that BSi is trapped behind the TGR. An independent estimate of BSi retention can be made by using the sediment accumulation of 3378.7×10^8 g and the average biogenic silica concentration of 0.61% of the top cores measured in the TGR. This calculation yields a BSi retention of 2.06×10^9 g/month ($F_{S,BSi} = 0.73 \times 10^8$ mol/month).

Table 2 BSi concentrations of the top cores representing the sedimentary silica deposition

Station	Left bank before dam	Centerline before dam	Right bank before dam	Xiangxi	Wanzhou	Average
Concentration (Si)	0.59%	0.54%	0.61%	0.63%	0.57%	0.61%

Table 3 Flux and concentration for transection of QXC, transection before dam, and major tributaries in April 2007

Station	Discharge ($\times 10^8$ m^3)	SPM (mg/l)	SPM Flux ($\times 10^8$ g)
Qingxichang	134.6	27.1	3640.5
Xiaojiang River	3.01	2.14	6.42
Daninghe River	2.54	3.51	8.90
Xiangxi River	1.23	2.98	3.66
Sum of SPM input	/	/	3659.5
Sum of SPM output	163.3	1.72	280.8
Retention	/	/	3378.7

Silicate flux at the sediment–water interface

According to the "silicate flux at the sediment–water interface" method, the calculation shows that the exchange rate ranged from 67.8 to 78.6 μmol/m^2/h, with a mean of 73.3 μmol/m^2/h (Table 4).

By considering the area percentage of different sediment patterns in the total area of the TGR, the exchange flux of DSi from the sediments to the water in the TGR was 0.382 × 10^8 mol/month.

Then, the DSi flux at the sediment–water interface can be calculated as:

$$F_{E,\ \mathrm{Dsi}} = \Phi \times A \times t \tag{11}$$

where $F_{E,\ \mathrm{DSi}}$ is the DSi flux at the sediment–water interface, Φ is the benthic exchange rate, A is the benthic areas of the TGR (m^2), and t is time (h). After the third filling of the TGR, the benthic area of the TGR was approximately 724.7 km^2 in April 2007. Therefore, we can obtain the amount of DSi flux at the sediment–water interface. The total load is 3.82 × 10^7 mol/month ($F_{E,\ \mathrm{DSi}} = 0.382 \times 10^8$ mol/month).

BSi production and cycling

The budget method was used to estimate the production and dissolution of BSi in the reservoir. The upstream loads of the main-stem ($F_{M,\ \mathrm{in},\ \mathrm{BSi}}$) and tributaries ($F_{T,\ \mathrm{in},\ \mathrm{BSi}}$) and the BSi produced ($F_{P,\ \mathrm{BSi}}$) in the reservoir were the major sources of BSi in the TGR, while BSi sedimentation, BSi outflow, and BSi dissolution were the main paths of BSi removal in the reservoir. It was not practical to directly measure in-reservoir BSi production in this large, dynamic riverine reservoir. Therefore, we chose a mass balance approach using the BSi fluxes rather than the DSi fluxes to solve for

$$(F_{M,\mathrm{in,BSi}} + F_{T,\mathrm{in,BSi}} + F_{P,\mathrm{BSi}})\,\beta = F_{S,\mathrm{BSi}}; + F_{\mathrm{out,BSi}}$$

where β is the conservation coefficient of BSi in the reservoir, which was estimated from α. $\beta = (1 - \alpha)$, α is the dissolution rate of BSi. According to the calculations above,

$$F_{M,\mathrm{in,BSi}} = 0.46 \times 10^8 \mathrm{mol/month}$$

$$F_{T,\mathrm{in,BSi}} = 0.06 \times 10^8 \mathrm{mol/month}$$

$$F_{\mathrm{out,BSi}} = 0.19 \times 10^8 \mathrm{mol/month}$$

$$F_{S,\mathrm{BSi}} = 0.73 \times 10^8 \mathrm{mol/month}$$

$$\text{so, } (0.46 + 0.06 + F_{P,\mathrm{BSi}})\,\beta = 0.73 + 0.19$$

$$F_{P,\mathrm{BSi}} = (0.92/\beta) - 0.52$$

the BSi dissolution was relative to the silica budgets. For example, approximately 690 *t*/a silica was dissolved and recycled at the sediment interface in the Marne Reservoir, which accounted for 66% of the primary production of silica (Garnier et al. 1999), while more than 95% BSi was dissolved and recycled in the marine water column (Tréguer et al. 1995). In

Table 4 Benthic exchange rate of DSi at the sediment–water interface in the TGR (μmol/m^2/h)

Station	Left bank before dam	Centerline before dam	Right bank before dam	Xiangxi	Wanzhou	Average
Exchange rate	76.1	71.7	67.8	72.2	78.6	73.3

the East China Sea, approximately 75% ($\beta = 0.25$) of the BSi production dissolved in the deep water column according to the calculation of Liu et al. (2005). However, the hydraulic retention time in the reservoir might be shorter than in the ocean. Therefore, the BSi regeneration efficiency may be lower than that of the East China Sea. In this study, β was chosen to be 1, 0.8, and 0.5, which indicates that 0, 20, and 50% of the BSi was dissolved, respectively. Therefore, the $F_{P,\ \mathrm{BSi}}$ was 0.40 ($\beta = 1$), 0.64 ($\beta = 0.8$) and 1.33 ($\beta = 0.5$), respectively. To determine how much BSi production ($F_{P,\ \mathrm{BSi}}$) and dissolution ($F_{D,\ \mathrm{DSi}}$) contributed to the reservoir, a simple empirical model calculation was used to estimate the production of BSi in the reservoir.

The pp model was used by Zhang et al. (1999) in the TGR. The model output shows that the primary production in the TGR would be 350 gC/m^2/year, with a range of 262.5–437.5 gC/m^2/year. Using the ratio of diatom primary productivity to total primary productivity, which is usually 1:2 in freshwater ecosystems, the diatom primary productivity can be calculated (Chinese Encyclopedia Compilation Committee 1987). Here, we propose a way of estimating fixed silicon flux using the typical C:Si:N:P ratio of 106:16:16:1 for diatom assimilation (Redfield et al. 1963; Brzezinski 1985; Rahm et al. 1996).

$$\sum \mathrm{Si} = 0.5 \times (16/106) \times \left(\sum \mathrm{C}/12\right) \tag{12}$$

The model output shows that the potential primary production in the TGR would be 1.6 $\sim$ 2.7 mol/m^2/year, which corresponds to a total annual silicon fixation of 1.2 $\sim$ 2.0 $\times$ 10^9 mol/year, taking into account the surface area of 724.7 km^2 in the stage of 156 m after the third filling of the TGR. Thus, the silicon fixation in the TGR would be (1.0–1.6) $\times$ 10^8 mol/month as a simplified process. For comparison, empirically derived BSi production is similar to the result of 1.33 $\times$ 10^8 mol/month ($\beta = 0.5$, $\alpha = 0.5$). Therefore, we chose the calculation of 1.33 $\times$ 10^8 mol/month as the result of the BSi production. Thus, the BSi dissolution is: $F_{D,\mathrm{DSi}} = (F_{M,\mathrm{in,BSi}} + F_{T,\mathrm{in,BSi}} + F_{P,\mathrm{BSi}})\ \alpha = 0.92 \times 10^8$ mol/month.

Silica budget and retention

The budgets for BSi and DSi are shown in Fig. 12. As Fig. 12 indicates, the DSi inflow and outflow are the most significant processes in the flux balance.

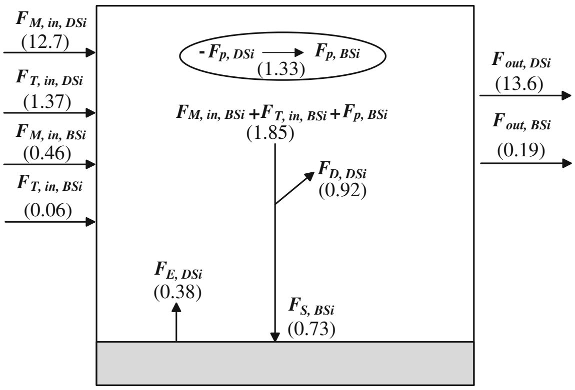

Fig. 12 Biogeochemical cycle of silica at the TGR. All fluxes are in 10^8 mol/month.

The total inflow load of DSi is 14.1 $\times$ 10^8 mol/month from main stem and lateral input. More than 90% of the DSi into the TGR comes from upstream of the Changjiang River. The total outflow load of DSi is 13.6 $\times$ 10^8 mol/month. For DSi, approximately 4.7 $\times$ 10^7 mol/month was retained by the TGR, which accounts for 3.3% of the total inflow load (based on the Eq. 10). While this is a highly uncertain estimate based on a single sampling, this value of DSi retention agrees well with our result (3.8%) measured in the TGR in 2007 based on 12-month data. Additionally, the total inflow and outflow loads of BSi are 5.1 $\times$ 10^7 mol/month and 1.9 $\times$ 10^7 mol/month, respectively. According to the input–output balance (Eq. 10), approximately 3.2 $\times$ 10^7 mol/month of BSi was trapped in the TGR, which accounts for 63% of the total inflow load.

However, considering all input budgets of DSi into the reservoir, the benthic silicate flux ($F_{E,\ \mathrm{DSi}}$) and recycled silicate ($F_{D,\ DSi}$) account for 2.5 and 6.0%, respectively. Overall, the removal of DSi is mainly by BSi production. The BSi production is approximately 1.33 $\times$ 10^8 mol/month, which is 2.6 times higher than the river BSi inputs from the main stream and tributaries. For BSi, more than 7.3 $\times$ 10^7 mol/month was trapped in the TGR, which accounts for 44% of the total inflow load and BSi production. Approximately 0.92 $\times$ 10^8 mol/month of BSi was dissolved in the TGR, which represents more than 50% of the BSi in the TGR. Although 50% of the sedimented BSi was dissolved in the TGR, the in-reservoir BSi dissolution was small relative to the total silica budgets. According to the silica recycling and budget, approximately

0.44×10^7 mol/month of DSi was lost in the TGR, which represents only 2.9% of the total input budget of DSi. The budget results are very close to the results we estimated based on the 12-mouth data, which also indicated that there is a slight retention of DSi. Compared with the total silica inflow load (BSi + DSi), the retention of DSi and BSi in the reservoir is only 5.0% in the dry season. This study shows that it is similar to the result of Iron Gate I (Friedl et al. 2004; McGinnis et al. 2006). As Fig. 12 indicates, the loss of particulate BSi is the most significant process in the flux balance. TSi_b was calculated as the sum of DSi plus BSi. The ratio of BSi/TSi_b was 0.035 (3.5%) at the inflow of the TGR and 0.014 (1.4%) at the outflow of the TGR near the TGD. The species structure has a significant change in the reservoir; the percentage of BSi decreases from 3.5 to 1.4% in the influx to outflow. The BSi sedimentation in the reservoir results in lower BSi/TSi_b and decreases the BSi load in the TGR. However, the ratios of BSi/TSi_b were quite low in the TGR. The results of BSi/TSi_b suggest that the contribution of BSi, carried in the suspension by the Changjiang River, was not an important contributor to the silicon budget in the TGR. Therefore, to some extent, this study, indicates that the TGR itself played a minor role in trapping incoming silicon in the river channel of the Three Gorges directly.

Prior to the operation of the TGD in 2003, there was no significant change of DSi and SPM concentration in the TGR river channel (Liu et al. 2003). Since the operation of the dam, SPM deposition has been observed in the TGR; however, DSi variation in the reservoir is mostly ignored based on the data in 2007. According to the results of the present study, it is clear that the TGR is more similar to a river than a reservoir (e.g., long and narrow, well mixed, and no stratification). And the conversion of the river into a 650 km long reservoir is not expected to significantly change the water quality with respect to algal production and silica retention. However, damming a river decreases the water velocity, which increases sedimentation and results in greater light penetration, stratification and algal growth. This effect is enhanced in the embayments due to even lower water velocities and shelter from high flow events (McGinnis et al. 2006). Large amounts of water entered the bay from the main stream (Ran et al. 2010), and exchange between the main channel and the embayment would result in a nutrient decrease in the TGR. The BSi and Chl-*a* concentrations are much higher in the Xiangxi and Daninghe bays than in the main channel of the TGR. Diatom production would be significant within the embayments, where the nutrient loads are higher and the flow is lower. Therefore, embayment may play an important role in silicon cycling in the TGR. However, with its present storage capacity, the reservoir does not play an important role in tapping incoming silica. Potential uncertainties and additional sources may be contributing to the deviations of retention in the load balance. One possible source contributing to the unaccounted load could be internal loading by silicon released from sediments. The sediment accumulated in front of the dam has a significant BSi content and the highest settling rate, which must be considered in the future.

Silica elimination by the TGR is limited, being $<5\%$ in the third filling stage. Based on these current results, the reservoir only trapped a small amount of incoming silica, which could not result in a significant reduction of DSi in the Changjiang Estuary directly. Retention in the middle and lower reaches of the Changjiang, including lakes connected to the main channel, are also presumed to considerably reduce DSi flux to the sea. Long-term decreases in the DSi concentration in the tributaries, such as in lakes Dongting and Poyang (Duan et al. 2007), may be added proof. The removal capacity of the aquatic continuum downstream is considerably affected by the TGD. It is because that clear water release from the dam may improve the light regime downstream of the dam, resulting in the considerable development of diatoms. Therefore, DSi retention downstream may be enhanced by clear water release, following TGD construction, both because the total streambed area increases with respect to the watershed area and because the considerable development of diatoms is favored in downstream Changjiang with lower slopes and more light compared with the headwater streams. In the latter instance, the Chl-*a* level is high in the middle Changjiang River (Ran et al. Submitted), showing that silica retention occurs in the downstream water of the TGR. The river sediment discharge is reduced largely due to the TGD (Yang et al. 2005, 2007), which may stimulate diatom growth downstream of the TGD. The siltation rate of Dongting lake may be reduced after the completion of the TGD due to the decreasing sediment (Yin et al. 2007), which will favor the retention of silica in Dongting lake to some extent. However, very little is known about how the TGD affects downstream DSi transfer from land to sea. Supplementary monitoring would be required downstream of the reservoirs to address these questions and should ideally be specifically targeted to determine the influence of the TGR on the Changjiang River. Additionally, the water level of the TGR was raised from 156 to 175 m above sea level in 2009. After the full operation of the TGD, even more BSi from upstream will be trapped in the TGR, which will impact the silica fluxes for centuries.

Conclusions

Based on the results of this study, the following general conclusions can be drawn:

(1) The DSi varied from 71.1 to 141 μmol/l, with an average of 108 μmol/l, while it ranged between 68.1 and 136 μmol/l, with an average of 107 μmol/l in the inflow and outflow, respectively, in the TGR in 2007. The linear relationship of the DSi between the inflow and outflow water is significant ($r = 0.87$, $n = 362$, $p < 0.01$).

(2) The DSi concentration is falling along the main stream of the TGR, with an average concentration of 84.0 μmol/l in the dry season. Stratification of the DSi was not obvious in the main channel of the TGR. The BSi is within the range of 0.04–5.00 μmol/l, with an average concentration of 2.10 μmol/l in the main channel of the TGR, while it is much higher in Xiangxi Bay (1.3–47.7 μmol/l, average concentration 13.1 μmol/l) than in the main stream of the TGR and other bays.

(3) After the third filling of the TGR, approximately 3.8% of incoming dissolved silica was retained by the TGR based on a 12-month monitoring scheme in 2007, which would reduce its fluxes from the Changjiang River to the East China Sea by 2% directly, without consideration of the downstream effect. The DSi was lost during January to June and November, whereas additions of DSi were found in other months in 2007. The DSi load is significant related to the discharge both in the inflow and outflow waters ($p < 0.01$). The DSi retention, to some extent, is the runoff change due to impoundment.

(4) The budget results indicate that there is a slight retention of DSi. The retention of DSi in the reservoir is approximately 2.9%, while the BSi is approximately 44%. Compared with the total silica load, the retention of DSi and BSi in the reservoir is only 5.0% in the dry season. With its present storage capacity, the reservoir itself does not play an important role in trapping incoming silica directly within the reservoir-dominated channel. However, very little is known about how the TGD affects the downstream DSi transfer, which should be considered in the future.

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