



Composition and variability in the export of biogenic silica in the Changjiang River and the effect of Three Gorges Reservoir

Xiangbin Ran^{a,b,*}, Sen Liu^{a,c}, Jun Liu^{a,d}, Jiaye Zang^a, Hong Che^{a,d}, Yongxing Ma^a, Yibin Wang^a

^a Research Center for Marine Ecology, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China

^b Department of Earth Sciences–Geochemistry, Faculty of Geosciences, Utrecht University, Utrecht, 3508, TA, The Netherlands

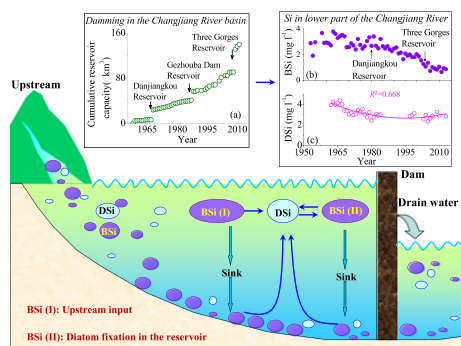
^c Tianjin Marine Environmental Monitoring Central Station, State Oceanic Administration, Tianjin 300450, China

^d Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China

HIGHLIGHTS

- A correlation of BSi and suspended sediments was built for the Changjiang River.
- Middle and lower of the Changjiang basin yielded more BSi than upstream.
- BSi/(BSi + DSi) ratio has decreased from 0.47 before 1980s to 0.19 in 2013–2014.
- BSi dissolution in the TGR contributes to 4–16% of DSi in the Changjiang River.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 April 2016

Received in revised form 17 July 2016

Accepted 17 July 2016

Available online 21 July 2016

Editor: D. Barcelo

Keywords:

Biogenic silica
Changjiang River
Composition
Export
Dissolution

ABSTRACT

Silicon (Si) plays an essential role in biogeochemical processes, but is still poorly characterized in the river system. This study addressed the biogenic silica (BSi) composition, origin and variation in the Changjiang River, and estimated the impacts of natural processes and human activities on the river Si cycling. Our results indicate that phytoliths comprised 14%–64% of BSi, while diatoms accounted for 34%–85% of BSi. The Changjiang River transported 620 Gg yr^{−1} of BSi and 2100 Gg yr^{−1} of dissolved silicate (DSi) loadings, respectively; 55% of the BSi and 51% of the DSi fluxes are transported during the high discharge period from June to September. The Changjiang River carried phytolith BSi mostly comes from the middle and lower reaches area. The ratio of BSi/(BSi + DSi) has decreased from 0.47 before 1980 to 0.19 in 2013–2014 due to the direct retention of BSi. The BSi sedimentation in the Three Gorges Reservoir would cause a decrease of total reactive silica, but contribute to approximately 4%–16% of the DSi loading at the Jiangyin station due to its dissolution. This study demonstrates that phytoliths represent a significant contribution to the biogeochemical cycle of silica in coastal waters, and in-stream process exerts a great influence on the river Si loading and cycling.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Silicon (Si) is an essential element in aquatic ecosystems. Dissolved silicate (DSi) is typically in the form of monosilicic acid (H₄SiO₄) and

* Corresponding author at: Research Center for Marine Ecology, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China.

E-mail address: rxb@fio.org.cn (X. Ran).

required for the growth of diatoms, which represents a major portion of planktonic primary production in the ocean (Nelson et al., 1995; Leblanc et al., 2005). Biogenic silica (BSi) is generated when diatoms, plants and other organisms uptake DSi during photosynthesis; it is an important source of DSi due to its typically amorphous form and thus plays an important role in the Earth's Si cycle (Conley, 2002; Laruelle et al., 2009). Although BSi has been measured in many world rivers (Conley, 1997; Cary et al., 2005; Ran et al., 2015), little is known about its composition, origin and transformation. It is reported that phytoliths are more resistant to dissolution than diatoms based on available data (Saccone et al., 2006; Meunier et al., 2014). The difference in BSi composition (i.e. the relative share of phytoliths and diatoms) is therefore supposed to have differential solubility, which should be included in the Si cycling, especially in the river system with damming. With the increasing Si retention due to dam construction in rivers and consequent Si limitation observed in many coastal aquatic systems (Nelson et al., 1995; Garnier et al., 1999; Conley et al., 2000; Humborg et al., 2000; Beusen et al., 2009; Struyf et al., 2010; Maavara et al., 2014; Meunier et al., 2015), shifts in the quality and structure of phytoplankton populations have been observing simultaneously (Nelson et al., 1995; Humborg et al., 2000; Dai et al., 2011; Jiang et al., 2014). It is therefore important to increase our understanding of Si composition and its transformation processes in the river system.

BSi includes phytoliths (micrometric particles of amorphous silica that form inside cells and cells walls of higher plants) and diatoms and forms a ubiquitous and important component of reactive Si in aquatic ecosystems (Olivé-Lauquet et al., 2000; Sommer et al., 2006; Cornelis et al., 2011). Soils and vegetation are important sources of BSi (Conley, 2002; Cary et al., 2005). Changes in land use may lead to changing runoff from the land carrying suspended particulate matter (SPM), and this may result in changing BSi concentrations in rivers (Conley et al., 2008; Carey and Fulweiler, 2012). BSi in rivers is therefore a key parameter between terrestrial and aquatic ecosystems. Better knowledge of the composition, origin and transformation of BSi will thus yield information on the processes involved in the biogeochemical cycle of silica in rivers.

The Changjiang River (Yangtze River) is the forth largest river in the world in terms of discharge, and supplies huge amounts of DSi (Dai et al., 2011) and BSi (Ran et al., 2013a) to the Yellow Sea and East China Sea. The loaded materials from the Changjiang River exert a great influence on the ecosystem in the estuary and adjacent sea (Dai et al., 2011; Jiang et al., 2014). The construction of dams and the increasing reservoir volume has strongly influenced the sediment and Si retention in the Changjiang River (Li et al., 2007; Dai et al., 2011; Yang et al., 2015), which could produce significant changes of the estuary environment. Here we present a case study for the use of suspended BSi for the identification of the biogeochemical processes controlling Si transformations in the Changjiang River, which was not previously assessed. The purpose of this study was to explore the sources, composition and transformations of Si in the Changjiang River, and to improve our understanding of the impact of human activities on Si cycling in this large turbid river system.

2. Methods

2.1. Investigation area

The catchment area of the Changjiang River is situated between 25° N to 35° N and 90° E to 122° E, about 1/5 of China. The basin area is characterized by a typical subtropical monsoon climate, temperate and humid, except for the headwaters area with cold climate. Temperature is generally higher during the rainy season than in the dry season; the mean value of temperature in July (rainy season) is above 28 °C in the middle and lower river basin, while its average declines to 4–6 °C in January (dry period). The carbonate rocks is the dominant rock type in the Changjiang watershed, followed by silicate rocks and evaporates. The

basin contains 35% of the national population, which is mainly concentrated in the Sichuan basin of upper reaches, the middle-lower Changjiang plain. Natural vegetation is mainly located in the mountainous areas, while cultivated landscapes prevail on the plains. Approximate 24% of national arable land is distributed in the Changjiang River basin. The annual water discharge is clearly a function of precipitation (Yang et al., 2015), and the surface runoff contributes to 70–80% of the total water discharge (Chen et al., 2002). The suspended sediment flux declined by about 70% between 1950 and 2012 (Yang et al., 2015), and mainly affected by dam constructions.

2.2. Sampling

A field sampling was carried out during a one year period (June 2013–May 2014). Water samples were collected on a monthly basis along a transect with 3 sampling points in the Jiangyin reach, Jiangsu Province, downstream of Datong, which is the main channel of Changjiang River shown in Fig. 1.

The discharge during the sampling period is shown in Fig. S1. Samples for DSi, BSi, particulate organic carbon (POC), Chla and SPM measurements were collected at ~20 cm below the surface. Two identical filtrations were carried out immediately after sample collection with pre-cleaned and pre-weighed 0.45 µm polyethersulfone membranes in a clean plastic petri dish with cover (60 mm × 15 mm); the first filter was used for SPM and BSi analyses, while the second filter was used for Chla analyses. The filtrates were used to determine the DSi, and stored in the dark at 4 °C before measurement. Another filtration for POC determination was carried out immediately after collection with pre-cleaned and pre-weighed Whatman GF/F membranes in a clean aluminum bag. All the filters were stored in the dark at –20 °C before measurement.

Water samples of 50–100 l were taken in the main channel to collect particles for BSi composition analysis at the middle sampling point. The suspended load was collected by the method of repeated sedimentation and centrifugation before the BSi particle separation was done within 72 h after the water sample collected.

2.3. Analysis

The DSi concentration was analyzed with a QUTRAO Autoanalyzer, using the silicomolybdic blue method, with a precision of 5–10% at concentrations of <0–0.28 mg l^{–1}, and 1–5% at above 0.28 mg l^{–1}. The SPM content was determined by weighing particles trapped on the filters. The BSi content in the suspended particulate matter was measured by extraction with 1% Na₂CO₃ (DeMaster, 1981) with correction of the simultaneous dissolution of mineral silicates, which is often used to analyze BSi in water as well as in sediments (Conley, 1998; Saccone et al., 2006). POC samples were measured using freeze-dried filters, which were decalcified with 6 M HCl in silver boats (Verardo et al., 1990) and dried on a hot plate at 80 °C prior to CHN Elemental Analyzer (EURO EA 3000). Chla was determined by fluorometry (Turner Designs 10-AU) after extraction from filters using 90% acetone, with a detection limit of 0.05 mg m^{–3}.

Dried sediment samples of 2–5 g were sieved with a 2 mm sieve. The extraction of BSi particles followed a wet extraction procedure (Wang and Lv, 1993) consisting of the following steps: (1) dissolution of carbonates using HCl (1 M); (2) oxidation of organic matter using H₂O₂ (30%) at 90 °C; (3) removal of the clay fraction (<2 µm) by decantation; and (4) separation of opal particles by density in a heavy liquid of ZnBr₂ (density of 2.35 g cm^{–3}). Particles were dried and weighed after extraction.

Phytoliths were classified according to the classification of International Code for Phytolith Nomenclature (ICPN). A statistically representative part of slides was investigated, and the phytoliths, diatoms and siliceous sponge spicules were counted. Approximate biovolumes of the observed items were calculated using the measured dimensions

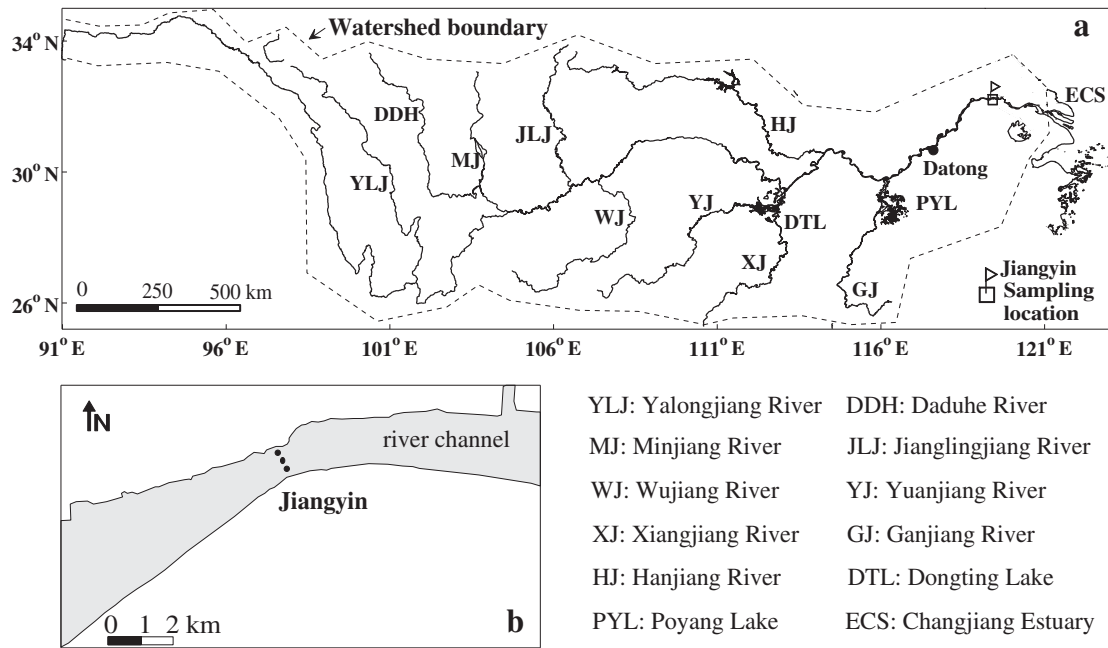


Fig. 1. Sampling station at Jiangyin station in the main channel of the Changjiang River.

by microscopic image analysis with the assumption of the same density and constant degree of silicification for each phytolith form. Biovolume calculations were then employed to assess the relative share of phytoliths, diatoms, silicoflagellates and siliceous sponge spicules within total BSi measured by the extraction method for BSi particles based on the method of Hillebrand et al. (1999). To normalize data, volume measurements of phytoliths and algae detritus fragments were transformed to approximate geometric shapes prior to analysis (See Supporting information SI for detail).

2.4. Flux calculation

The long-term sediment and discharge data were obtained from the Ministry of Water Resources, the People's Republic of China (Changjiang Hydrological Committee, 2015; Ministry of Water Resources of the People's Republic of China, 2015).

SPM, DSi, BSi and POC fluxes are calculated as follows:

$$F = \sum_{i=1}^{12} C_i \times Q_i \quad (1)$$

where F is the flux (Gg yr^{-1}) of SPM, DSi, BSi or POC, C is the concentration of SPM, DSi, BSi or POC (g m^{-3}), and Q is the monthly discharge ($\text{m}^3 \text{month}^{-1}$), i is the month number. Monthly discharge was estimated from daily discharge data obtained from the National water and rainfall information (Ministry of Water Resources of the People's Republic of China, 2015).

Relative errors (δ) for fluxes are calculated as follows on the basis of Fourier series (Fu and Lei, 2003):

$$\delta = \left(\sum_{i=1}^n \frac{Q_i C_i}{n Q_a C_a} - 1 \right) \times 100\% \quad (2)$$

where n is the number of samples in one year, Q_i is daily discharge, Q_a is annual average discharge, C_i is SPM, DSi, BSi or POC concentration, and C_a is the SPM, DSi, BSi or POC annual average value.

2.5. Reconstruction of historical BSi

On the basis of a limited number of months with data for both BSi and SPM, we found that the fraction of BSi in the suspended solids increases with increasing SPM concentration (Fig. S2) according to:

$$[BSi]_c = 0.173 [SPM]_c + 5.07 \quad (R^2 = 0.942, n = 12, p < 0.01) \quad (3)$$

where $[BSi]_c$ is the BSi concentration as mg l^{-1} , and $[SPM]_c$ is the SPM concentration in mg l^{-1} . We employed Eq. (1) in combination with our observed SPM content to estimate the river BSi flux and its alteration due to human activities. Long term data of SPM were collected from several sources (Changjiang Hydrological Committee, 2015; Ministry of Water Resources of the People's Republic of China, 2015). Although there is a significant decline in the sediment loading of the Changjiang River (Yang et al., 2015), the detrital phosphorus (a stable and terrestrially-derived form) and median grain size keep fairly constant in the Changjiang Estuary based on long-term data (Meng et al., 2015), indicating the terrestrial sources and compositions of sediment are stable over time. We therefore conclude that there is no great change in the BSi/SPM ratios pre- and post-dam cases.

2.6. Si uptake by diatoms

We used the empirical model developed by Cadée and Hegeman (1974) to estimate the conversion of organic carbon by diatom uptake:

$$P_C = P_s \times Z \times t/2 \quad (4)$$

where, P_C is the carbon (C) fixation by diatom utilization in the euphotic zone ($\text{mg C m}^{-2} \text{d}^{-1}$); P_s is the potential primary production ($\text{mg C m}^{-3} \text{h}^{-1}$); Z is the euphotic depth (m); t is daily exposure time (h d^{-1}), $t = 4-5 \text{ h d}^{-1}$ (Rong and Liu, 2014). Primary production P_s is calculated as follows:

$$P_s = Chla \times q \quad (5)$$

where, $Chla$ is chlorophyll a concentration (mg m^{-3}); q is the assimilation factor ($\text{mg C mg Chla}^{-1} \text{h}^{-1}$), $q = 1.13 \text{ mg C mg Chla}^{-1} \text{h}^{-1}$ (Behrenfeld and Falkowski, 1997). The euphotic depth (Z) is calculated

by the following equation (Zhang et al., 2006):

$$Z = 4.605/k_d \quad (6)$$

where, k_d is the diffuse attenuation coefficient (m^{-1}); k_d is 1.74–2.45 m^{-1} in lakes of the Changjiang River (Zhang et al., 2006). For Changjiang River, the average water depth is about 10 m in the main channel of the sampling station, and the euphotic depth is between 1.88 and 2.65 m.

The Si uptake is calculated from the primary production P_C and the stoichiometric ratio (Brzezinski, 1985) as follows:

$$P_{\text{Si}} = 28 \times (\text{Si/C}) \times P_C/12 \quad (7)$$

where, P_{Si} is the silica fixation by diatom utilization in the euphotic layer ($\text{mg C m}^{-2} \text{d}^{-1}$); 12 and 28 are molecular weights of C and Si, respectively; Si/C is the stoichiometric ratio of freshwater diatoms with ranges from 15/106 (Brzezinski, 1985) to 83/106 (Conley et al., 1989).

2.7. Biogenic silica dissolution

The specific BSi dissolution rate V_{dis} (d^{-1}) is calculated according to Fujii and Chai (2005):

$$V_{\text{dis}} = V_{\text{dis0}} \times \exp.(k_{\text{BSi}} \times T) \quad (8)$$

where V_{dis0} is the specific BSi dissolution rate (d^{-1}) at 0 °C and T is the annual mean water temperature (°C), $T = 15$ °C (Huang et al., 2006) based on the measured water temperatures in the Three Gorges Reservoir (TGR). We set V_{dis0} to 0.05, 0.1 and 0.2 (d^{-1}) to reflect the range of dissolution on the basis of BSi solubility, and k_{BSi} is 0.097 ($^{\circ}\text{C}^{-1}$), representing the dependency of BSi dissolution on water temperature (Fujii and Chai, 2005). In addition to temperature, the dissolution rate of BSi is dependent on the pH (Frayse et al., 2006, 2009; Loucaide et al., 2008). However, pH in the river water of TGR is minor variation and fairly close to 8 (Huang et al., 2006). It therefore can be neglected due to its constant influence.

2.8. Statistical analysis and mapping

Statistics were done using the SPSS 18.0 program. Surfer 11.0 and Origin 8.5 were used for mapping the concentration patterns.

3. Results

3.1. Suspended particulate matter

The average SPM concentration in the Jiangyin reach was 120 mg l^{-1} in 2013–2014, with a strong variation between 41 and 230 mg l^{-1} . The flux of SPM was 105,000 Gg yr^{-1} (Table 1), which is a yield of 58,000 $\text{kg km}^{-2} \text{yr}^{-1}$ in 2013–2014 in the Changjiang River basin. SPM values were higher in the rainy season than in the dry season in the Jiangyin stream ($p < 0.01$). The dominant transport of SPM occurred during the high discharge period from June to September, accounting for 73% of the annual SPM load. A significant increase in SPM was observed from June to August, then decreased significantly after September to the lowest value in February and then increased from February to May 2014 (Fig. 2a).

Table 1
Annual fluxes and errors of SPM, DSI, BSI and POC in the Changjiang River.

Data	Flux (Gg yr^{-1})	Yield ($\text{kg km}^{-2} \text{yr}^{-1}$)	Error (%)
SPM	105,000	58,000	20
DSi	2100	1200	−0.4
BSi	620	340	16
POC	1900	1060	−2.3

3.2. Dissolved silicate

The concentration of DSI in the Jiangyin reach was on average 2.8 mg l^{-1} and varied much less than SPM (between 2.5 and 3.4 mg l^{-1}) in 2013–2014. The Changjiang River flux of DSI across the Jiangyin transect is 2100 Gg yr^{-1} (Table 1), which is a yield of 1200 $\text{kg km}^{-2} \text{yr}^{-1}$ in 2013–2014. DSI values were higher in the rainy season than in the dry season in the Jiangyin reach. The total loads from June to September accounted for 51% of the annual DSI flux. A significant increase in the DSI concentration was observed from June reaching the highest value in October; the DSI concentration decreased significantly after October, and remained relatively stable from November 2013 to May 2014 (Fig. 2b).

3.3. Biogenic silica

The average BSi concentration at Jiangyin station was 0.7 mg l^{-1} with a strong variability (between 0.28 and 1.3 mg l^{-1}) in 2013–2014. This is equivalent to a BSi load of 620 Gg yr^{-1} with a yield of 340 $\text{kg km}^{-2} \text{yr}^{-1}$ (Table 1). The ratios of BSi to SPM varied from 0.0045 to 0.0078, with an average value of 0.0062. The concentrations of BSi and SPM had similar seasonal trends. While the peak flux from June to September accounted for 55% of the annual BSi flux in the Jiangyin reach. BSi values were generally higher in the rainy season than in the dry season. A steep increase in BSi was observed from June with a peak in July. Concentrations of BSi decreased significantly after October, and remained relative stable from November 2013 to May 2014 (Fig. 2c).

Three types of BSi were identified: phytoliths, diatoms and sponges (Table 2 and SII in SUPPORTING INFORMATION). Approximately 43% of the BSi was composed of phytoliths (monthly values range considerably between 14% and 64%). The elongate type of phytolith was the most abundant in the river, accounting for on average of 19% of the phytoliths (6–34%). About 55% (34–85%) of BSi was composed of diatom fragments, and sponges make up 1.9% of total BSi. Some of the most typical geometric BSi forms are presented in Fig. S3 and Fig. S4.

3.4. Particulate organic carbon

The POC concentration in the Jiangyin reach varied between 1.5 and 3.8 mg l^{-1} with an average of 2.6 mg l^{-1} in 2013–2014, or equivalent to a flux of 1900 Gg POC yr^{-1} (Table 1). The ratio of POC to SPM was 5.9% (2.4%–9.6%) and the ratio C to Si in SPM was 14 (4.0–30).

POC values were generally higher in the rainy season than in the dry season. A significant increase in POC was observed from June, and peaking in October, decreasing rapidly after October to relatively stable values from November 2013 to May 2014 (Fig. 2d).

In 2013–2014, the Changjiang River transported 2200 Gg C yr^{-1} with a minimum value of 43 Gg POC in February and maximum value of 320 Gg POC in August. For POC, the high fluxes also occurred during the period from June to October, which accounted for 46% of the annual POC flux carried by the river.

3.5. Chla and primary productivity

The concentration of Chla at Jiangyin station was on average 0.22 mg m^{-3} in 2013–2014, with a variation between 0.06 and 0.33 mg m^{-3} . The Chla is low in May, July and August, and fairly high in the other months (Fig. 3). Carbon sequestration related primary productivity of the euphotic zone was 1.8 $\text{mg C m}^{-2} \text{d}^{-1}$ (monthly values ranging between 0.4 and 2.8 $\text{mg C m}^{-2} \text{d}^{-1}$). The diatom primary productivity was 0.1–5.0 $\text{mg Si m}^{-2} \text{d}^{-1}$, with a median value of 2.6 $\text{mg Si m}^{-2} \text{d}^{-1}$.

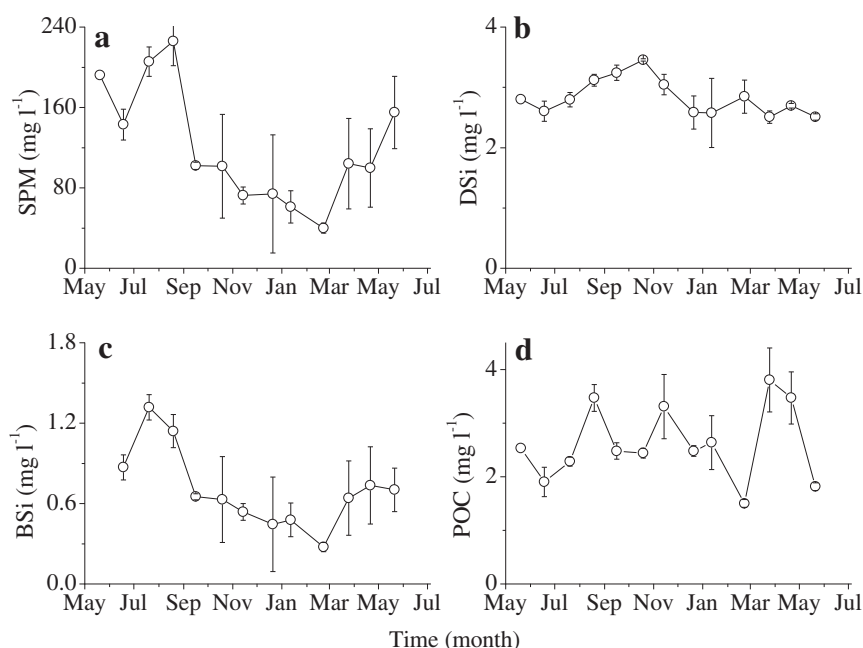


Fig. 2. Suspended particulate matter (a), dissolved silica (b), biogenic silica (c) and particulate organic carbon (d) in the main channel of the Changjiang River. BSi was measured by the alkaline extraction. Error bars show the standard deviation in measurements at 95% confidence level.

3.6. Long-term variability of BSi

The concentrations of BSi showed a fairly constant level from 1950 to 1980 and decreasing trend from 1980 to 2010s at Jiangyin stations of the main channel of the Changjiang River. The average BSi concentration decreased from 2.8 mg l⁻¹ during the 1970s to 1.2 mg l⁻¹ in the 2000s (Fig. 4). This is equivalent to an 18% decrease of BSi per decade. Similarly, BSi fluxes decreased from 2400 Gg yr⁻¹ in the 1970s to 1100 Gg yr⁻¹ in the 2000s in the Jiangyin river channel, but remained an almost constant value of 790 Gg yr⁻¹ during the recent decade.

3.7. Biogenic silica dissolution

The specific BSi dissolution is 0.21 (d⁻¹) in $V_{\text{dis0}} = 0.05$, 0.43 in $V_{\text{dis0}} = 0.10$, and 0.86 in $V_{\text{dis0}} = 0.20$, respectively (Eq. (8)).

4. Discussion

4.1. Silica transport in the Changjiang River

The DSi concentration was relatively high from June to December, but substantially decreased from January to May; this monthly variation showed higher DSi concentrations in the flood season and lower DSi levels in the non-flood season like the observations of previous studies (Duan et al., 2007; Li et al., 2007).

The diatom utilizations are unlikely responsible for the non-flood season DSi decline. There is no clear relationship between Chla and DSi concentrations; and the primary production indicates that in-stream biological uptake may not be driving the DSi level in this river system. Monthly DSi concentrations in the Changjiang River and mean monthly discharges showed only a weak inverse correlation ($R^2 = 0.08$). Counterclockwise trend of DSi versus discharge suggests that a

Table 2
Composition of the particulate biogenic silica in Changjiang River (%^a).

Data	Elongate ^b	Orbicular ^b	Rondel ^b	Cuneiform bulliform cell ^b	Elongate echinate ^b	Lanceolate ^b	Saddle ^b	Ovate ^b	Bilobate short cell ^b	Cylindrical polylobate ^b	Pennatae ^c	Centricae ^c	Spicules ^d
May 2013	12.2	0.70	3.07	1.82	0.98	0.84	1.96	1.12	2.93	n.d. ^e	9.22(0.45)	64.4(0.56)	1.40
June 2013	30.9	0.57	5.44	3.44	2.01	2.29	8.60	2.01	5.44	0.29	24.4(5.73)	12.0(0.29)	2.58
July 2013	13.7	4.64	2.73	2.19	1.64	2.46	4.10	1.37	4.64	0.27	21.3(6.83)	39.6(1.64)	1.37
Aug. 2013	17.2	1.33	4.77	2.12	1.33	2.12	4.24	1.33	2.92	n.d.	24.1(6.63)	37.4(1.06)	1.06
Sep. 2013	18.7	1.56	7.17	0.62	0.93	1.56	2.80	2.49	4.67	0.31	26.5(9.97)	32.1(1.56)	0.62
Oct. 2013	33.8	0.96	6.11	1.93	2.89	2.89	4.50	1.93	8.04	0.64	21.5(9.97)	12.2(0.96)	2.57
Dec. 2013	22.6	3.28	7.66	2.19	2.55	2.92	5.47	2.92	5.11	0.73	28.5(13.9)	12.8(1.09)	3.28
Nov. 2013	6.16	0.74	1.29	0.64	0.55	0.46	2.02	0.74	1.29	0.09	4.87(2.11)	80.4(0.18)	0.74
Jan. 2014	27.0	3.41	8.19	1.71	3.07	2.39	5.46	2.05	6.48	0.34	27.0(11.6)	11.3(1.37)	1.71
Feb. 2014	19.0	3.38	3.90	2.86	4.16	1.82	6.23	1.82	6.23	n.d.	30.9(13.5)	18.2(1.04)	1.56
Mar. 2014	11.8	0.66	1.83	1.00	1.33	1.00	2.82	0.66	2.66	n.d.	10.5(3.65)	64.6(0.66)	1.16
April 2014	18.5	2.43	4.26	1.52	1.82	1.52	8.51	1.82	8.51	n.d.	35.6(15.5)	10.6	4.86

^a Percentages were calculated by the bio-volume of BSi particle; >200 BSi particles were counted.

^b Phytolith.

^c Diatom; data in the brackets represent the contribution of diatom debris to the total BSi in the SPM.

^d Sponge spicules.

^e n.d. means no determination.

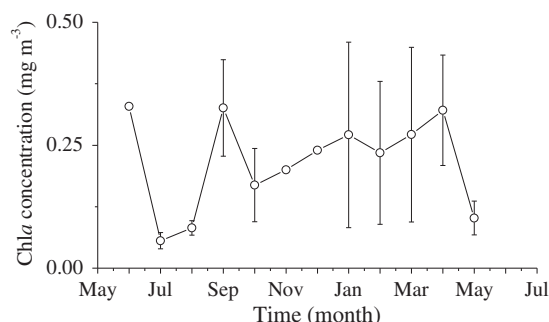


Fig. 3. Chla in the main channel of the Changjiang River. Error bars show the standard deviation in measurements at 95% confidence level.

dilution by less DSi water is occurred like the report in the Pawcatuck River (Fulweiler and Nixon, 2005). Moreover, the non-flood decline in DSi concentrations may be due to the weak silicate weathering due to low temperature, which significantly modifies the river DSi level (White and Blum, 1995; Gaillardet et al., 1999; White et al., 2005; Hartmann and Moosdorf, 2011). DSi concentrations are lower during non-flood season than that in flood period at equivalent water flows (Fig. S5), which could indicate the seasonal variation of silicate weathering.

The variance in DSi export can be explained by river discharges. The total flux of DSi in flood season represents 51% of annual DSi loading, indicating hydrology influence DSi transport in the river system. However, the DSi load into the Changjiang River did not strictly follow river discharges, e.g. the maximum value was observed in October (Fig. 2 and Fig. S1, S5). The high DSi level in October may be delivered from tributaries or upstream contributing areas of the catchment that are further from the Jiangyin reach compared to the major water source areas in the flood season, which can cause a delay in the DSi transport compared to the flood discharge.

The seasonal dynamics of BSi in the Changjiang River were clearly controlled by the SPM because the significant linear BSi and SPM relationship ($p < 0.05$). Chla measurements and diatom production show clearly that biological processes can be minor contribution to the BSi loading. Counterclockwise trend of BSi versus discharge suggests that BSi is mainly originated from the river basin (Fig. S5). Both high concentrations of DSi and ratio of BSi/(BSi + DSi) in the flood season (0.25) can indicate soil erosion become significant in governing the BSi transport.

The ratio of BSi/(BSi + DSi) was 0.19 at Jiangyin, indicating approximately 19% of the total Si is delivered to the Yellow Sea and East China Sea as BSi. Levels of BSi in the Changjiang River are lower than the world average of 0.79 mg l^{-1} for some large river systems (Conley, 1997). The annual flux of BSi (620 Gg yr^{-1}) transported by the Changjiang River is 3 and 5 times higher than that of the Mississippi and Lena Rivers, respectively. However, the BSi flux of the Changjiang River is much smaller than those of rivers draining tropical rainforest areas (e.g. BSi from Changjiang is 4% of that the Amazon River and 39% of that of the Congo River (Conley, 1997)).

4.2. Biological impacts on silica loads

The phytoliths/BSi ratio is 0.43 on average (0.14 and 0.64) from June 2013 to May 2014, and the diatom/BSi ratios varied from 0.34 to 0.85 at Jiangyin station. Phytoliths therefore add a significant contribution to the BSi pool carried by the Changjiang River. The seasonal variations of the phytolith/BSi ratios recorded in the Jiangyin channel are similar to those in the Huanghe River (Ran et al., 2015), but with a higher diatom/BSi ratio. Diatoms are the dominant BSi form in the Jiangyin reach of Changjiang River, which is different from the previous reports (Cary et al., 2005; Ran et al., 2015).

The identified phytolith assemblages indicate that BSi in the Jiangyin reach of Changjiang River was produced mainly by herbaceous plants. Different types of phytoliths reflect different geographical origins at the watershed scale. Bilobate mainly comes from *Panicoidae*, reflecting the climate of origin place is warm and humid, which is significant correlation with Elongate ($R^2 = 0.411$, $p = 0.034$; Table S1), the dominant phytolith type; the short saddle type is common in *Eragrostoidae Pilger*, reflecting the climate of origin place is hot and dry, which show a weak linear relationship with Elongate ($R^2 = 0.264$, $p = 0.106$; Table S1). Therefore, phytoliths in the Changjiang River mostly come from an area with warm and humid climate, which is consistent with the climatic characteristics of the middle and lower Changjiang River basin (mean temperature $16\text{--}18^\circ\text{C}$). Recent studies indicated that terrestrial plants are the major POC source in the lower channel of the Changjiang River (Yu et al., 2011; Wang et al., 2012; Zhang et al., 2014). This observation is confirmed by our BSi composition data.

There appears to be a positive relationship between DSi concentrations and the shares of Elongate, debris of Pennatae, debris of Centricae, and other phytoliths (Table S1), suggesting the soil erosion directly influences the DSi level and BSi composition. In contrast, a negative but not significant correlation exists between DSi concentrations and the share of well-preserved Pennatae, which may reflect the utilization of DSi by diatoms in the basin. The correlation of Pennatae and Centricae diatoms (Table S1) may show some kind of competitive growth due to their negative relationship.

Although diatom is the dominant algal type in the Changjiang River (Zeng et al., 2006), Chla and productivity are very low in the water, especially in the rainy season, indicating that authigenic production in the river water at Jiangyin contributes to a minor share of POC and BSi. Most of the POC and BSi should come from the upstream before the Jiangyin and deliver with water flow. However, we can see a trend for a higher Chla production between January and April, which could match the depletion of DSi and indicate that the influence of diatom productivity cannot be completely ruled out in the dry season.

There are three groups of POC and BSi according to the atomic ratios between POC and BSi in the Changjiang River. One group matched by the high level of BSi during the period from June to August when the ratio of POC/BSi (mol ratio) is between 4/1 and 8/1. The second group is characterized by the moderate BSi level in May and September to November, respectively, when the ratio of POC/BSi is between 8/1 and 16/1. The third group typically has a low BSi content during the months from January to April, when the ratio of POC/BSi varies from 16/1 to

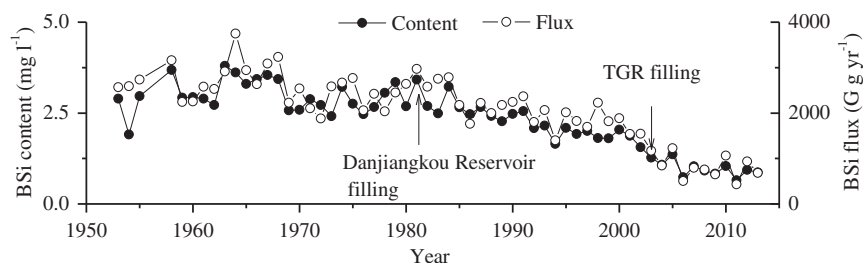


Fig. 4. Long-term variability of BSi content and flux in lower part of the Changjiang River. Data of BSi were calculated the Eq. (3).

32/1 (Fig. S6). The POC/BSi ratios in the water column were generally lower than those reported for plants and algae (Redfield, 1958; Brzezinski, 1985; Wang and Lv, 1993), which suggests that POC is easy to degrade during the transport in the river system. A High BSi and low POC concentration are generally found in the rainy season, when soil erosion prevails in the river system with soil particles characterized by low C contents. In contrast, a low BSi concentration and high POC level are generally found in the dry season, when algae growth is the dominant POC source due to lower turbidity than in the rainy seasons. Therefore, POC/BSi ratios vary along with the terrestrial inputs and in-stream growth.

4.3. Human activities impacts on silica loads

The minor contribution of primary production to BSi in the Changjiang River and the counterclockwise (Fig. S5) relationship between BSi concentrations and discharge suggests that BSi mainly come from the basin soils. Also, the general increase trend of BSi/(BSi + DSi) with the increasing sediment flux (Fig. 5) indicates that the river sediment and soils erosion are important factors in contribution BSi fluxes to the river.

The sharpest decrease in the concentration of BSi occurred in the Changjiang River after the Danjiangkou Dam and Three Gorges Dam (TGD) operation (Fig. 4). Mean values of BSi at Jiangyin station remained at almost constant at $\sim 3.1 \text{ mg l}^{-1}$ (1953–1980) prior to the Danjiangkou Dam and TGD construction with a ratio of BSi/(BSi + DSi) 0.47 (DSi data are from Dai et al. (2011)). However, the BSi concentration had decreased after these two dams impoundment in 1980 and 2003, respectively. Therefore, damming in the Changjiang basin has had a much greater effect on the BSi concentration than the impact on the DSi level.

Approximately 75% of total decrease in sediment flux can be attributed to the dams in the Changjiang River basin over the post-TGD period (Yang et al., 2015). As a rough verification of BSi retention, dams would reduce the BSi fluxes in the Jiangyin reach of the Changjiang River into the East China Seas significantly on the basis of sediment retention by reservoirs (Yang et al., 2007; Yang et al., 2015). Based on the field measurements, about 44% of BSi inflow loading is trapped in the TGR (Ran et al., 2013b), indicating that the amount of BSi retention accounts for a large part of reactive Si trapping in the reservoir. Approximately 50% of the sedimented BSi can be dissolved in the TGR (Ran et al., 2013b). The BSi dissolution in the reservoir may thus be a part and new source of the river DSi due to the increased hydrological retention time, hence keeping DSi level downstream of the TGD. In the latter instance, although there are an increase damming and eutrophication in the Changjiang River basin, DSi concentrations increased slightly since

1980s and remained fairly stable after 2000s (Dai et al., 2011). The dissolution of sediment BSi should be incorporated into Si pools.

The land use/cover change and associated soil erosion can influence DSi transfer from terrestrial system to the river (Carey and Fulweiler, 2012). In the Changjiang River basin, human activities have been affecting the DSi transport (Li et al., 2007; Dai et al., 2011), in which construction of dams may have exhibited a significant role in DSi export. Unfortunately, no study has reported silicate weathering data in the Changjiang River. It is, however, unlikely that the variation of silicate weathering due to the land use and climate change in the Changjiang River is significant because the discharge varies minor on the basis of long-term data (Yang et al., 2015), which is considered as the driving factor of DSi production and export in the river basins (Hartmann and Moosdorf, 2011; Hartmann et al., 2014).

Few studies have reported detailed BSi data and its alteration for reservoirs. BSi retention are an important feature in reservoirs associated with the SPM removal due to the river damming (Ran et al., 2013b; Maavara et al., 2014). Recently study indicates that 65% of the SPM decline since 2003 can be attributed to the TGD, while other factors (i.e. precipitation change and soil conservation) play a minor role in the sediment decline (Yang et al., 2015). Over the study, BSi ranged from 0.28 to 1.3 mg l^{-1} and appears to come mainly from a soil erosion (Fig. S5). The ratio BSi to BSi + DSi varies around 0.2 in the Changjiang River, indicating that in-stream BSi dissolution may not be neglected in this system. Therefore, the SPM retention by damming and sequential BSi transformation may alter the Si cycling in the river water because the reservoir is a slow water system with a long residence time. We assume that the sediment BSi may change the pattern of Si cycling and contribute to a part of DSi loadings due to its regeneration in the river water and sediment. In 2013, the TGR trapped $94,000 \text{ Gg yr}^{-1}$ of suspended sediment (Changjiang Hydrological Committee, 2015), which would reduce 83 mg l^{-1} of SPM and 0.53 mg l^{-1} of BSi on average each year (Eq. (2)), respectively; the dissolution process of sediment BSi may contribute 0.11 to 0.45 mg l^{-1} of DSi to the water column on the basis of Eq. (8), representing approximately 4%–16% of the DSi loading at the Jiangyin station, which almost equals to the DSi retention by damming in the Changjiang River (Li et al., 2007). Our estimation of BSi dissolution is confirmed by the measured data in the TGR (Ran et al., 2013b), which observed 50% of BSi is dissolved in this huge reservoir.

Other factors include hydrological alterations with river damming, urbanization and soil conservation in the basin, which in China have greatly increased in the most recent decade. These processes may decrease local sediment yields and DSi loadings from land into the river. However, the DSi concentration in the Changjiang River keeps instant recently, and shows an inverse relationship with the degree of damming (Fig. 6). Hence, in view of the basin scale of the Changjiang River, these factors are limited to small regional scales, and their comprehensive impacts on DSi and sediment discharges are probably very minor compared with the impacts of the aforementioned factors.

Dams may provide favorable preconditions for algal growth, which would alter BSi contents and compositions due to the potential enhancing productivity in the reservoir. However, the Chl_a in the main channel TGR (Ran et al., 2013b) revealed low concentrations ($0.06\text{--}1.49 \text{ mg m}^{-3}$), not supporting a significant influence of diatoms on BSi in the Changjiang River system. Additional, change in particle size of SPM by damming may alter BSi compositions and contents, but it cannot reflect in the Eq. (3). Simplifications and assumptions must be employed in short-term Si cycling because the luckiness of measurement data and hydrodynamic processes, which is helpful in exploring the relative importance of the driving factors in this study. Uncertainties of fluxes largely depend on the uncertainties in estimates of discharge and Si and SPM concentrations. The uncertainty expressed by the relative error is 20% or less for the SPM and Si fluxes (Table 1) based on the Eq. (2). With this small uncertainty in flux estimates, the uncertainty in our estimated BSi dissolution is also small.

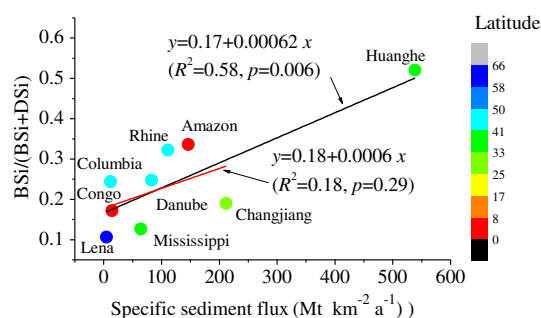


Fig. 5. Relationship between BSi/(BSi + DSi) and specific sediment flux. The color represents their average latitude for each river basin. BSi/(BSi + DSi) of Changjiang River from this study, Huanghe River is from Ran et al. (2015), Danube from Garnier et al. (1999) and other data from Conley (1997); sediment yield and basin areas from Milliman and Meade (1983). The black line is fitted by all the data, while the red one is obtained by the data without Huanghe River.

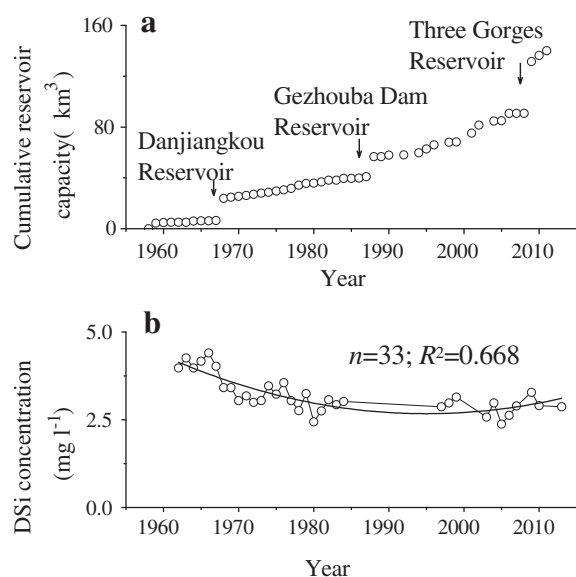


Fig. 6. Time series variations of cumulative reservoir capacity in the Changjiang River basin (a) and DSi in lower part of the Changjiang River (b). (a) Data are from World River Database, <http://www.cws.net.cn/riverdata/>; (b) Data of DSi are from Liu et al. (2003), Dai et al. (2011), and this study.

4.4. Implications

Many rivers are being dammed in China at increasing rates (Dai et al., 2011). The TGD of the Changjiang River is the world's largest hydro-power project, which may trigger possible ecological effect due to significant reductions in particulate matter (Dai et al., 2011; Yang et al., 2015). Our results show that about 6.25% of river SPM transported by the Changjiang River is actually BSi. Their fluxes have dramatically decreased over the past few decades because of the riverine damming. Although the reservoir capabilities keep increasing recently (Fig. 6) and would trap more DSi than the past decades, the DSi concentration in the Changjiang River slightly increased or keep constant in recent decade (Fig. 6), which implies an increasing DSi loading than in the past a few decades. The change in the BSi dissolution due to damming may be partly responsible for the recent increase in the DSi concentration of the Changjiang River. As a latter instance, the minor retention of DSi by TGR (Ran et al., 2013b) may indicate that the BSi recycling seems to counterbalance the DSi decline in this huge pool. Long-term observations of SPM and BSi contents at Datong indicate that slightly increasing DSi loading originated by the dissolved BSi may continue in the future if no large-scale changes in the sediment and BSi retentions by dams are implemented.

In the earlier stage of TGR operation, Li et al. (2007) concluded that approximately 10% of DSi was removed in the TGR. However, these researchers only accounted for the uptake by primary production based on empirical models and ignored other transformation processes. Therefore, the DSi retention estimated by Li et al. (2007) is 2 times higher than the result of detailed investigations (Ran et al., 2013b). Undoubtedly, the dissolved BSi in reservoirs would counteract the increased DSi retention due to the damming in the Changjiang River basin. However, the permanent BSi sedimentation by damming would affect the Si cycling in the adjacent area of the Changjiang Estuary, and thereby limit the primary production in the Yellow and East China Seas close to the Changjiang River Estuary. Therefore, more knowledge should be known about how the dam in the river basin affects the BSi transfer and dissolution within a river from land to sea. Supplementary monitoring would be required to address these questions and should ideally be specifically targeted to determine the influence of the damming on the Si cycling of the large river.

5. Conclusions

The concentration of BSi is 0.7 mg l^{-1} ; and the BSi level is slightly lower in the Changjiang River than in other major rivers in the world. Phytoliths comprise 14%–64% of the total BSi, with the elongate type being the dominant form.

The Changjiang River transports 620 Gg yr^{-1} of BSi and 2100 Gg yr^{-1} of DSi loadings, respectively; 55% for the BSi and 51% for the DSi loadings transported by the Changjiang River occurs during the high discharge period from June to September.

The BSi carried in suspension by the Changjiang River is an important component of the rivers silica load, with ratios of BSi/(BSi + DSi) and BSi/SPM 0.19 and 0.0062, respectively. The river loading of phytolith BSi mostly originates from the middle and lower Changjiang River basin areas, and the discharge and runoff exert greatly influence on the BSi composition.

The ratios of BSi/(BSi + DSi) has decreased from 0.47 before 1980 to 0.19 in 2013–2014. However, the dissolution of sediment BSi in the TGR would contribute to approximately 4%–16% of DSi pool in the Jiangyin reach of the Changjiang River, which would counteract the DSi retention by damming.

The TGR impacts the transport of BSi and DSi in the Changjiang River. The direct BSi sedimentation and subsequent dissolution would represent a significant contribution to the DSi in the river water. However, the net sinking of BSi by damming would result in a net decreasing of reactive silica in the river basin.

Acknowledgements

This study was supported in part by Natural Science Foundation of China (Project No. 41106072 and 41376093) and Basic Scientific Fund for National Public Research Institutes of China (2016). We would like to thank Xu Houjian, Xu Houqin, Sun. Tao, and Chen Jibing for their assistance in the field sampling. We greatly appreciate Prof. Bouwman for his insightful comments on earlier version. We thank four anonymous reviewers for their constructive reviews.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.07.125>.

References

- Behrenfeld, M.J., Falkowski, P.G., 1997. Photosynthetic rates derived from satellite-based chlorophyll concentration. *Limnol. Oceanogr.* 42, 1–20.
- Beusen, A.H.W., Bouwman, A.F., Dürr, H.H., Dekkers, A.L.M., Hartmann, J., 2009. Global patterns of dissolved silica export to the coastal zone: Results from a spatially explicit global model. *Glob. Biogeochem. Cycles* 23, GB0A02. <http://dx.doi.org/10.1029/2008GB003281>.
- Brzezinski, M.A., 1985. The Si:C:N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. *J. Phycol.* 21, 347–357.
- Cadée, G.C., Hegeman, J., 1974. Primary production of phytoplankton in the Dutch Wadden Sea. *Neth. J. Sea Res.* 8, 240–259.
- Carey, J.C., Fulweiler, R.W., 2012. Human activities directly alter watershed dissolved silica fluxes. *Biogeochemistry* 111, 125–138.
- Cary, L., Alexandre, A., Meunier, J.D., Boeglin, J.L., Braun, J.J., 2005. Contribution of phytoliths to the suspended load of biogenic silica in the Nyong basin rivers (Cameroon). *Biogeochemistry* 74, 101–114.
- Changjiang Hydrological Committee, 2015. *Changjiang Sediment Bulletin (2000–2015)*. Changjiang Press, Wuhan (in Chinese).
- Chen, J.S., Wang, F.Y., Xia, X.H., Zhang, L.T., 2002. Major element chemistry of the Changjiang (Yangtze River). *Chem. Geol.* 187, 231–255.
- Conley, D., 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. *Glob. Biogeochem. Cycles* 16, 68–168–8.
- Conley, D.J., 1997. Riverine contribution of biogenic silica to the oceanic silica budget. *Limnol. Oceanogr.* 42, 774–777.
- Conley, D.J., 1998. An interlaboratory comparison for the measurement of biogenic silica in sediments. *Mar. Chem.* 63, 39–48.
- Conley, D.J., Humborg, C., Smedberg, E., Rahm, L., Papush, L., Danielsson, Å., Clarke, A., Pastuszek, M., Aigars, J., Ciuffa, D., Möhr, C.M., 2008. Past, present and future state of the biogeochemical Si cycle in the Baltic Sea. *J. Mar. Syst.* 73, 338–346.

- Conley, D.J., Kilham, S.S., Theriot, E., 1989. Differences in silica content between marine and freshwater diatoms. *Limnol. Oceanogr.* 34, 205–212.
- Conley, D.J., Staltnacke, P., Pitkanen, H., Wilander, A., 2000. The transport and retention of dissolved silicate by rivers in Sweden and Finland. *Limnol. Oceanogr.* 45, 1850–1853.
- Cornelis, J.T., Delvaux, B., Georg, R.B., Lucas, Y., Ranger, J., Opfergelt, S., 2011. Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers: a review. *Biogeosciences* 8, 89–112.
- Dai, Z.J., Du, J.Z., Zhang, X.L., Su, N., Li, J.F., 2011. Variation of riverine material loads and environmental consequences on the Changjiang (Yangtze) estuary in recent decades (1955–2008). *Environ. Sci. Technol.* 45, 223–227.
- DeMaster, D.J., 1981. The supply and accumulation of silica in the marine environment. *Geochim. Cosmochim. Acta* 45, 1715–1732.
- Duan, S.W., Xu, F., Wang, L.J., 2007. Long-term changes in nutrient concentrations of the Changjiang River and principal tributaries. *Biogeochemistry* 85, 215–234.
- Frayse, F., Pokrovsky, O.S., Schott, J., Meunier, J.D., 2006. Surface properties, solubility and dissolution kinetics of bamboo phytoliths. *Geochim. Cosmochim. Acta* 70, 1939–1951.
- Frayse, F., Pokrovsky, O.S., Schott, J., Meunier, J.D., 2009. Surface chemistry and reactivity of plant phytoliths in aqueous solutions. *Chem. Geol.* 258, 197–206.
- Fu, G., Lei, K., 2003. Analysis of the estimation methods for the river pollutant fluxes(II): error judgment of time-averaged or section-averaged dispersion fluxes. *Res. Environ. Sci.* 16, 5–10 (in Chinese).
- Fujii, M., Chai, F., 2005. Effects of biogenic silica dissolution on silicon cycling and export production. *Geophys. Res. Lett.* 32.
- Fulweiler, W.R., Nixon, W.S., 2005. Terrestrial vegetation and the seasonal cycle of dissolved silica in a southern New England coastal river. *Biogeochemistry* 74, 115–130.
- Gaillardet, J., Dupré, B., Louvat, P., Allegre, C.J., 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30.
- Garnier, J., Leporcq, B., Sanchez, N., Philippon, X., 1999. Biogeochemical mass-balances (C, N, P, Si) in three large reservoirs of the Seine basin (France). *Biogeochemistry* 47, 119–146.
- Hartmann, J., Moosdorf, N., 2011. Chemical weathering rates of silicate-dominated lithological classes and associated liberation rates of phosphorus on the Japanese archipelago – implications for global scale analysis. *Chem. Geol.* 287, 125–157.
- Hartmann, J., Moosdorf, N., Lauerwald, R., Hinderer, M., West, A.J., 2014. Global chemical weathering and associated P-release – the role of lithology, temperature and soil properties. *Chem. Geol.* 363, 145–163.
- Hillebrand, H., Dürselen, C.D., Kirschtel, D., Pollinger, U., Zohary, T., 1999. Biovolume calculation for pelagic and benthic microalgae. *J. Phycol.* 35, 403–424.
- Huang, Z.L., Li, Y.S., Chen, Y.C., Li, J.X., Xing, Z.H., 2006. Water Quality Prediction and Water Environmental Carrying Capacity Calculation for Three Gorges Reservoir. China Water Power Press, Beijing (in Chinese).
- Humborg, C., Conley, D.J., Rahm, L., Wulff, F., Cociasu, A., Ittekkot, V., 2000. Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. *Ambio* 29, 45–50.
- Jiang, Z.B., Liu, J.J., Chen, J.F., Chen, Q.Z., Yan, X.J., Xuan, J.L., Zeng, J.N., 2014. Responses of summer phytoplankton community to drastic environmental changes in the Changjiang (Yangtze River) estuary during the past 50 years. *Water Res.* 54, 1–11.
- Laruelle, G.G., Roubeix, V., Sferatore, A., Brodherr, B., Ciuffa, D., Conley, D.J., Dürr, H.H., Garnier, J., Lancelot, C., Le Thi Phuong, Q., Meunier, J.D., Meybeck, M., Michalopoulos, P., Moriceau, B., Ni Longphui, S., Loucaides, S., Papush, L., Presti, M., Ragueneau, O., Regnier, P., Saccone, L., Slomp, C.P., Spiteri, C., Van Cappellen, P., 2009. Anthropogenic perturbations of the silicon cycle at the global scale: key role of the land-ocean transition. *Glob. Biogeochem. Cycles* 23, GB4031. <http://dx.doi.org/10.1029/2008GB003267>.
- Leblanc, K., Quéguiner, B., Raimbault, P., Garcia, N., 2005. Efficiency of the silicate pump at a coastal oligotrophic site in the Mediterranean Sea. *Biogeosciences* 2, 219–229.
- Li, M.T., Xu, K.Q., Watanabe, M., Chen, Z.Y., 2007. Long-term variation of dissolved silicate flux from the Yangtze River into the East China Sea and impact of estuarine ecosystem. *Estuar. Coast. Shelf Sci.* 71, 3–12.
- Liu, S.M., Zhang, J., Chen, H.T., Wu, Y., Xiong, H., Zhang, Z.F., 2003. Nutrients in the Changjiang and its tributaries. *Biogeochemistry* 62, 1–18.
- Loucaides, S., Cappelle, P.V., Behrends, T., 2008. Dissolution of biogenic silica from land to ocean: role of salinity and pH. *Limnol. Oceanogr.* 53, 1614–1621.
- Maavara, T., Dürr, H.H., Van Cappellen, P., 2014. Worldwide retention of nutrient silicon by river damming: from sparse data set to global estimate. *Glob. Biogeochem. Cycles* 28, 842–855.
- Meng, J., Yao, P., Bianchi, T.S., Li, D., Zhao, B., Xu, B.C., Yu, Z.G., 2015. Detrital phosphorus as a proxy of flooding events in the Changjiang River basin. *Sci. Total Environ.* 517, 22–30.
- Meunier, J.D., Keller, C., Guntzer, F., Riotte, J., Braun, J.J., Anupama, K., 2014. Assessment of the 1% Na₂CO₃ technique to quantify the phytolith pool. *Geoderma* 216, 30–35.
- Meunier, J.D., Riotte, J., Braun, J.J., Sekhar, M., Chalié, F., Barboni, D., Saccone, L., 2015. Controls of DS_i in streams and reservoirs along the Kaveri River. South India. *Sci. Total Environ.* 502, 103–113.
- Milliman, J.D., Meade, R.H., 1983. World-wide delivery of river sediment to the oceans. *J. Geol.* 91, 1–21.
- Ministry of Water Resources of the People's Republic of China, 2015i. National Water and Rainfall Information Ministry of Water Resources of the People's Republic of China. (Beijing (<http://www.mwr.gov.cn/>), Data retrieved 15 January 2015 in Chinese).
- Nelson, D.M., Tréguer, P., Brzezinski, M.A., Leynaert, A., Quéguiner, B., 1995. Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation. *Glob. Biogeochem. Cycles* 9, 359–372.
- Olivé-Lauquet, G., Allard, T., Bertaux, J., Muller, J.P., 2000. Crystal chemistry of suspended matter in a tropical hydrosystem, Nyong basin (Cameroon, Africa). *Chem. Geol.* 170, 113–131.
- Ran, X.B., Che, H., Zang, J.Y., Yu, Y.G., Liu, S., Zheng, L.L., 2015. Variability in the composition and export of silica in the Huanghe River basin. *Sci. China Earth Sci.* 58, 2078–2089.
- Ran, X.B., Yu, Z.G., Chen, H.T., Zhang, X.Q., Guo, H.B., 2013a. Silicon and sediment transport of the Changjiang River (Yangtze River): could the Three Gorges Reservoir be a filter? *Environ. Earth Sci.* 70, 1881–1893.
- Ran, X.B., Yu, Z.G., Yao, Q.Z., Chen, H.T., Guo, H.B., 2013b. Silica retention in the Three Gorges Reservoir. *Biogeochemistry* 112, 209–228.
- Redfield, A.C., 1958. The biological control of chemical factors in the environment. *Am. Sci.* 46, 205–221.
- Rong, Y., Liu, X., 2014. The decrease of the flow and its cause at Datong hydrological station of the Yangtze River. *J. Water Resour. Res.* 3, 326–336 (in Chinese).
- Saccone, L., Conley, D.J., Sauer, D., 2006. Methodologies for amorphous silica analysis. *J. Geochem. Explor.* 88, 235–238. <http://dx.doi.org/10.1016/j.jgexplo.2005.1008.1045>.
- Sommer, M., Kaczorek, D., Kuzyakov, Y., Breuer, J., 2006. Silicon pools and fluxes in soils and landscapes – a review. *J. Plant Nutr. Soil Sci.* 169, 310–329.
- Struyf, E., Smis, A., Van Damme, S., Garnier, J., Govers, G., Van Wesemael, B., Conley, D.J., Batelaan, O., Frot, E., Clymans, W., Vandevenne, F., Lancelot, C., Goos, P., Meire, P., 2010. Historical land use change has lowered terrestrial silica mobilization. *Nat. Commun.* 1, 129.
- Verardo, D.J., Froelich, P.N., McIntyre, A., 1990. Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 analyzer. *Deep Sea Res. Part A Oceanogr. Res. Papers* 37, 157–165.
- Wang, X.C., Ma, H.Q., Li, R.H., Song, Z.S., Wu, J.P., 2012. Seasonal fluxes and source variation of organic carbon transported by two major Chinese rivers: the Yellow River and Changjiang (Yangtze) River. *Glob. Biogeochem. Cycles* 26, GB2025. <http://dx.doi.org/10.1029/2011GB004130>.
- Wang, Y., Lv, H., 1993. *Phytolith Research and Application*. China Ocean Press, Beijing (in Chinese).
- White, A.F., Blum, A.E., 1995. Effects of climate on chemical weathering in watersheds. *Geochim. Cosmochim. Acta* 59, 1729–1747.
- White, A.F., Schulz, M.S., Vivit, D.V., Blum, A.E., Stonestrom, D.A., Harden, J.W., 2005. Chemical weathering rates of a soil chronosequence on granitic alluvium: III. Hydrochemical evolution and contemporary solute fluxes and rates. *Geochim. Cosmochim. Acta* 69, 1975–1996.
- Yang, S.L., Xu, K.H., Milliman, J.D., Yang, H.F., Wu, C.S., 2015. Decline of Yangtze River water and sediment discharge: impact from natural and anthropogenic changes. *Sci. Rep.* 5, 12581.
- Yang, S.L., Zhang, J., Dai, S.B., Li, M., Xu, X.J., 2007. Effect of deposition and erosion within the main river channel and large lakes on sediment delivery to the estuary of the Yangtze River. *J. Geophys. Res. Earth Surf.* 112.
- Yu, H., Wu, Y., Zhang, J., Deng, B., Zhu, Z.Y., 2011. Impact of extreme drought and the Three Gorges Dam on transport of particulate terrestrial organic carbon in the Changjiang (Yangtze) River. *J. Geophys. Res. Earth Surf.* 116.
- Zeng, H., Song, L.R., Yu, Z.G., Chen, H.T., 2006. Distribution of phytoplankton in the Three-Gorge Reservoir during rainy and dry seasons. *Sci. Total Environ.* 367, 999–1009.
- Zhang, L.J., Xue, M., Wang, M., Cai, W.J., Wang, L., Yu, Z.G., 2014. The spatiotemporal distribution of dissolved inorganic and organic carbon in the main stem of the Changjiang (Yangtze) River and the effect of the Three Gorges Reservoir. *J. Geophys. Res. Biogeosci.* 119, 741–757.
- Zhang, Y.L., Qin, B.Q., Hu, W.P., Wang, S.M., Chen, Y.W., Chen, W.M., 2006. Temporal-spatial variations of euphotic depth of typical lake regions in Lake Taihu and its ecological environmental significance. *Sci. China Earth Sci.* 49, 431–442.