

The biogenic silica composition, behavior and budget in the Changjiang Estuary

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Abstract

Three comprehensive surveys were performed in the Changjiang (Yangtze River) Estuary (CJE) to understand the biogenic silica (BSi) composition, behavior and budget. It is indicated that the BSi is composed of phytoliths, phytoplankton and sponges; phytolith BSi has 16 forms and account for 23% to 83% of the bulk BSi in the maximum turbidity zone. The budget shows that the major exogenous BSi source in the water column of the CJE is the riverine input, accounting for 95% of the total BSi input. Dominant processes that maintain BSi levels in the water column are the primary production (55 Gmol/a) and the subsequent BSi sedimentation (46 Gmol/a); and the BSi pool produced by the primary production represents two point three times the BSi loading of the Changjiang River and 63% of the BSi output, respectively. The net export (26 Gmol/a) of BSi from the CJE to the East China Sea and Yellow Sea roughly equals the riverine BSi loading. The observed total accumulation of BSi is one point seven times larger than the loading of total BSi output, with 53% to 88% of phytolith BSi and their assemblage, indicating that there has already been a “filter” of terrestrial BSi. The reverse weathering in sediments is an important process for the reactive silica removal in the CJE due to authigenic alterations. It is indicated that the phytolith fluxes in the suspended load represent a significant BSi source in the estuary, and the CJE would act as a net BSi sink.

Key words: silica cycle, diatoms, phytoliths, budget, Changjiang Estuary

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1 Introduction

Silicon is the second most abundant element in the earth's crust system (Wedepohl, 1995). It occurs as silicate minerals in igneous, metamorphic, and sedimentary rocks. Physical and chemical weathering of these minerals is the major natural source of dissolved silica (dissolved SiO₂, hereafter referred to as DSi) in soils, groundwater and rivers (Berner and Berner, 1996). Terrestrial plants take up a significant portion of the DSi produced during weathering (Bartoli, 1983). Phytoliths are rigid, microscopic structures made of silica, found in some plant tissues and persisting in soils and surface water after the decay of the plant. Biogenic silica (BSi) in phytoliths is an important silicon pool and impacts the silicon transfer from the terrestrial to aquatic systems, due to its high dissolution rates compared to other particulate silica forms in sediment flows.

Rivers transport of both DSi and BSi from land to the ocean is the primary source of “new” silicon in the ocean (Conley, 1997), and plays a key role in coastal marine ecosystems, because diatoms are the essential phytoplankton group that needs silicon as a major nutrient (Conley, 2002). Marine diatoms in particular are often limited by silicon (Kristiansen and Hoell, 2002), especially

under the increasing pressure of nitrogen and phosphorus loadings. Therefore, silicon in the coastal areas has profound impacts on coastal marine ecosystems (Ragueneau et al., 2005).

The silicon for diatoms in coastal waters is delivered by rivers, there is recycling within the water column at the sediment-water interface, and a minor supply from atmospheric deposition (Tréguer and De La Rocha, 2013). Rivers transport 14 Tmol/a of DSi to the world's oceans (Beusen et al., 2009) and assuming BSi amounts to 16% (Conley, 1997), total silicon (DSi plus BSi) transport is 16 Tmol/a. In the ocean, diatoms take up approximately 240 Tmol of DSi produced annually (Tréguer and De La Rocha, 2013). This means that in the oceans there is a large reservoir of BSi and intensive recycling of both DSi and BSi.

Phytoliths may be the most abundant BSi form in estuary systems (Olivé-Lauquet et al., 2000; Street-Perrott and Barker, 2008), while BSi in the ocean consists of diatoms, silicoflagellates, radiolarians and sponge spicules (DeMaster, 1981; Conley and Schelske, 2001). The detailed mechanisms and processes controlling the abundance and composition of the BSi transported by rivers remain, however, poorly understood.

Decreases in DSi and BSi may trigger long-term ecological ef-

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fects in marine systems because of diatom variations and its associated influence (Nelson et al., 1995; Humborg et al., 1997). In the past decades, silicon transport by the Changjiang River has been decreasing (Duan et al., 2007; Dai et al., 2011; Ran et al., 2013) as a result of the construction of dams (e.g., Gezhouba Dam, Three Gorges Dam) and land-use changes (Yang et al., 2007; Dai et al., 2011; Jiang et al., 2013). While the transport of DSi by the Changjiang River has not changed dramatically recently, the transport of BSi has been decreasing due to sediment trapping in reservoirs. This has led to further silica limitation of the East China Sea (Dai et al., 2011). This study focuses on the BSi budget, composition and its biogeochemical behavior in the Changjiang Estuary (CJE), and its contribution to the estuary silicon cycling. The aim is to explore the BSi composition, source roles and quantify the effect of recent riverine sediment and DSi decreasing on estuary silica cycling.

2 Materials and methods

2.1 Study area

Sampling expeditions were performed in the CJE between 121.0°N on the upper section of the CJE and 123.5°N on the East China Sea (ECS). Three comprehensive surveys were made in the CJE in August 2010 (in the rainy season from June to September), November 2010 (in the baseflow season commonly in January to March, and December) and May 2011 (in the interflow periods in April, May, October, and November). Water samples were collected along the salinity gradient, starting from the Xuliujing (a city of Shanghai) Station and moving downwards to the open sea. The sampling locations are shown in Fig. 1.

The water discharge at Datong Station was 1 000 km³ in 2010 (14% higher than the discharge in 1950 minus that in 2010), while in 2011 the discharge was only 670 km³ (26% lower than the mean discharge between 1950 and 2010) (Changjiang Water Resources Commission, 2010, 2011). The sediment discharge was 0.18 Gt and 0.07 Gt in 2010 and 2011, respectively, at Datong Station. The salinity in the study area ranged from 0.1 to 34 (dimensionless, hereinafter), with a mean value of 15 during the rainy season, 21 during the interflow season and 23 during the baseflow season.

2.2 Sample collection

Water samples were taken with 10 L Niskin bottles from the

surface water of the CJE (Fig. 1). Suspended particulate matter (SPM) and DSi were determined for all water samples. The BSi in the water column was analyzed for Stas B1, B2, B3 and E1, which were set up in the maximum turbidity zone of the CJE. A specific volume of the water samples (from 30 to 500 mL, depending on the turbidity) were vacuum-filtered on a pre-weighed 0.45 μm polyethersulfone membrane. The filters were used for SPM analyses, and the filtrates were used to determine DSi (the filtrates were stored in darkness at 4°C before measurement). The water samples (50 to 100 L) taken from Stas B1, B2, B3 and E1 (located in the estuary turbidity maximum) were also filtered to collect the suspended load for BSi concentration and BSi composition analyses.

Sediment core samples were taken with a box core sampler at Stas B3 and C5 in November 2010 to determine their BSi composition and reverse weathering effects. After core retrieval, the sediment core was subdivided in 1 to 2 cm intervals. Pore water was separated by centrifugation for DSi and aluminium analyses. After removing the pore water, the resulting sediment plug was collected in pre-cleaned PE Ziploc-type bags and stored at -20°C for biogenic and reactive silica analyses.

Sampling expeditions were carried out in the Jiangyin (a city in Jiangsu Province, China) reach of the Changjiang River during the same period of 2010 to 2011. Water samples for DSi and BSi measurements were collected once per month at approximately 20 cm below the surface with at least three sampling points across the main channel of the river.

2.3 Sample analysis

The DSi concentration was analyzed using a silicomolybdic blue method by a QuAatro autoanalyzer, with a precision of 5% to 10% at 1 to 10 μmol/dm³, and 1% to 5% at greater than 10 μmol/dm³ (Liu et al., 2003a). The aluminium concentration was determined using a modified aluminum-lumogallion fluorescence measurement (Ren et al., 2001). The SPM concentration was determined by taking the mass difference after drying overnight in an oven at 50°C.

The particulate matter was divided into three parts after drying. One part was for BSi determination, estimated by using an alkaline extraction method (1% Na₂CO₃, 85°C, 8 h) (DeMaster, 1981). The second part was used to measure different silica pools (Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008) by using a modified two-step method that included a mild acid pretreatment (0.1 mol/dm³ HCl, 18 h, 22°C) and subsequent alkaline extraction (DeMaster, 1981).

The silicon pools that can be distinguished on the basis of these treatments are: Si-HCl (mild acid-leachable), Si-Alk (mild alkaline-leachable after acid pre-treatment) and BSi (mild alkaline-leachable without acid pre-treatment) based on the definition of Michalopoulos and Aller (2004) and DeMaster (1981). Σc(Si) is the sum of Si-HCl and Si-Alk concentrations, representing the total reactive silica concentration in the sediment and SPM. Total bioavailable reactive silica (*b*_{TSi}) is the sum of DSi and BSi.

The third part of the suspended matter was used to determine BSi composition after a wet extraction procedure (Wang and Lü, 1993; Ran et al., 2015). Part of the separated particles (more than 200) was then observed under an optical microscope (Nikon Eclipse E100). A statistically representative part of slides was investigated, and the bio-volumes of phytoliths, diatoms and siliceous sponge spicules were calculated. General morphological observations of the other extracted particles were performed with a scanning electron microscope (SEM, FEI Quanta 200)

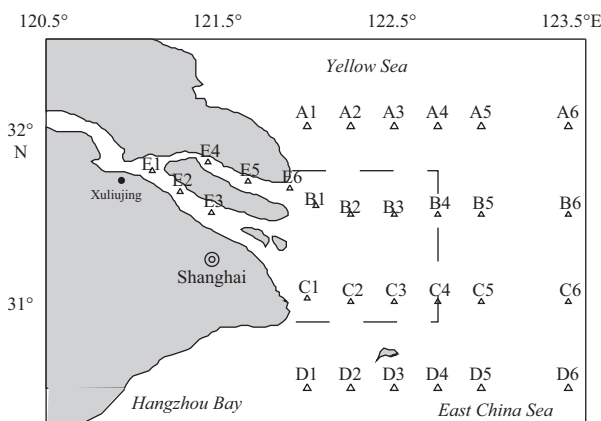


Fig. 1. Sampling stations along the Changjiang Estuary. The area enclosed by the dotted line is the study site for BSi and DSi budget calculation.

equipped with an energy dispersive spectrometer (EDS) system and used for detailed morphological and chemical studies.

2.4 Silica alteration determination

The ratio of the difference between the sum of Si-Alk concentration and Si-HCl one and BSi one to the sum of Si-Alk concentration and Si-HCl ($[\sum c(\text{Si}) - c(\text{BSi})] / \sum c(\text{Si})$) is a proxy commonly related to the “intensity” of the reactive silica regeneration and reverse weathering, and the ratio of the difference between the sum of Si-Alk concentration and Si-HCl one and BSi one to the Si-Alk concentration ($[c(\text{Si-Alk}) - c(\text{BSi})] / c(\text{Si-Alk})$) is a more conservatively proxy generally related to the “extent” of the reactive silica diagenetic alteration (Michalopoulos and Aller, 2004).

2.5 Budget

2.5.1 Water budget

The hydrography of the CJE is largely controlled by the Changjiang River water and exchanges between the CJE and the open sea (including the East China Sea and Yellow Sea). Riverine input, precipitation, groundwater, exchanges between the CJE and the open sea and evaporation are taken into account in the water budget calculation for the shelf in LOICZ budget (Swaney et al., 2011) as follows:

$$(V_r + V_p + V_x + V_g + V_o) + (V_c + V_{rf} - V_x) = 0, \quad (1)$$

$$(S_r V_r + S_p V_p + S_{sea} V_x + S_g V_g + S_o V_o) + (S_c V_c + S_{rf} V_{rf} - S_{sys} V_x) = 0, \quad (2)$$

where V is the water volume (km^3/d), S is salinity, subscripts r , p , x , g , o , rf and e represent for riverine input (r), atmospheric deposition (p), exchanges between study area and open sea (x), groundwater input (g), other flow volume (o), residual flow volume (rf) and evaporation (e), respectively. It should be noted that the net water volume into or out of the box system associated with the exchanges V_x is 0 and thus not a part of the water budget, but the exchanges V_x can be an important flux of DSi and BSi due to the obvious concentration difference between the box and outer sea. S_{sys} and S_{sea} are the salinities in the study area and outer seas close to the study area, respectively. Details on the calculation of water and salt budget (Tables A1 and A2) are shown in the appendix.

2.5.2 Silica mass balance

A mass-balance model was employed for the estuary system to explore the estuary processes in silicon on the basis of the water budget calculation. The exogenous inputs of silicon into the CJE water mass include riverine inputs (F_r), groundwater (F_g), atmospheric deposition (F_a), the East China Sea inflow (F_{ECS}), the Yellow Sea inflow (F_{YS}), BSi regeneration ($F_{rc, \text{DSi}}$) in the water column and benthic flux ($F_{b, \text{DSi}}$), while the silicon outputs are residual outflow to the East China Sea ($F_{rf, \text{ECS}}$), residual outflow to the Yellow Sea ($F_{rf, \text{YS}}$), exchange outflow to the East China Sea ($F_{x, \text{ECS}}$), exchange outflow to the Yellow Sea ($F_{x, \text{YS}}$) and sedimentation ($F_{s, \text{BSi}}$). F_{ECS} , $F_{b, \text{DSi}}$, F_{YS} , $F_{rf, \text{ECS}}$, $F_{rf, \text{YS}}$, $F_{x, \text{ECS}}$, $F_{rc, \text{DSi}}$, $F_{x, \text{YS}}$ and $F_{s, \text{BSi}}$ are calculated by measurements described in this paper, as well as the major contributions of Changjiang River to F_r , while other fluxes are based on literature values. All the loadings are shown in the unit of Gmol/a . Budget terms are discussed in detail below.

River silicon fluxes were calculated based on data measured in the Changjiang River:

$$F_r = k \times c \times Q, \quad (3)$$

where F_r represents for the flux of DSi or BSi (Gmol/a), k is the conversion coefficient of unit, c is the concentration of DSi or BSi ($\mu\text{mol}/\text{dm}^3$, Tables A3); and Q is the river discharge in 2010–2011 (km^3/s). The loads were calculated for each season on the basis of Eq. (1) and then accumulated to annual fluxes.

Atmospheric inputs (F_a) to the CJE were calculated by the DSi concentration in both rainfall and dry deposition at the base station in Qianliyan Island in the Yellow Sea (Zhang et al., 2005, 2007; Han et al., 2013), rainfall (Martin et al., 1993; Zhang et al., 2007), dry deposition rates (Zhang et al., 2007) and areas ($9\,300\text{ km}^2$) of the study CJE (Table A3). BSi in both the rainwater and dry deposition are neglected due to their minor sources (Tréguer and De La Rocha, 2013).

The loadings of the residual outflows and exchanges outflows to the East China Sea and Yellow Sea were calculated by the silicon concentrations and their corresponding water discharges (Tables A2 and A3).

Benthic flux ($F_{b, \text{DSi}}$) of DSi on the water-sediment interface was calculated on the basis of Fick's first law (Berner, 1980):

$$J_f = -\varphi D_s (\partial c / \partial z), \quad (4)$$

$$D_s = D_0 \varphi^{(m-1)}, \quad (5)$$

where J_f represents for the DSi diffusion rate ($\text{mmol}/(\text{m}^2 \cdot \text{d})$); φ is the porosity of sediment (dimensionless, 0.55 to 0.83, from Li (2010)); D_s is the diffusion coefficient ($1/(\text{m}^2 \cdot \text{d})$) in the sediment; $\partial c / \partial z$ is the DSi concentration gradient at the water-sediment interface, c is DSi concentration (mmol/dm^3), z is depth (m) in core; D_0 represents for the solute molecular diffusion coefficient ($1/(\text{m}^2 \cdot \text{d})$) in infinitely diluted solutions (Li and Gregory, 1974); m is an empirical coefficient (dimensionless, for $\varphi \leq 0.7$, $m=2$; for $\varphi > 0.7$, $m=2.5-3.0$ (Ullman and Aller, 1982)).

Sedimentation of BSi ($F_{s, \text{BSi}}$) in the CJE was based on the accumulation rate and the surface area in the study system. The accumulation rate was calculated as follows:

$$r_{\text{BSi}} = 10\,000 \times c_{\text{BSi}} D_r r_w / 28, \quad (6)$$

$$F_{s, \text{BSi}} = r_{\text{BSi}} A, \quad (7)$$

where r_{BSi} is the BSi accumulation rate ($\text{mol}/(\text{m}^2 \cdot \text{a})$); 10 000 is the unit conversion factor (cm^2/m^2); c_{BSi} is the concentration of BSi in surface sediments (%); D_r is the sediment accumulation rate (cm/a); r_w represents for the dry bulk density (g/cm^3), 28 is the silicon molar mass (g/mol); and A is the area (m^2). Pang et al. (2011) reported that the net accumulation rate in the CJE is approximately 4.58 cm/a in close proximity to the river mouth based on lead-210 data. We assume a dry bulk density to be approximately 0.9 to 1.0 g/cm^3 , and a constant accumulation rate.

Groundwater DSi flux (F_g) into the CJE was obtained from radium-228 and radium-226 mass-balance models (Gu et al., 2012) and concentration (c_g) was estimated from the station next to CJE from Kim et al. (2005).

$$F_g = Q_g c_g, \quad (8)$$

where Q_g represents for the discharge (m^3/a); c_g represents for the DSi concentration ($\mu\text{mol}/\text{dm}^3$) in the groundwater (Table A3), $c_g=39\ \mu\text{mol}/\text{dm}^3$ (Kim et al., 2005).

Primary production (p_p) was estimated by carbon-14 method from the *in situ* measured rate of primary production ($\text{mg}/(\text{m}^2 \cdot \text{d})$), calculated by carbon) in the CJE from Zhao et al. (2006). The rates of DSi uptake by phytoplankton and the regeneration rate of BSi were calculated with the ratio of carbon atom number to silicon (108:15) (Brzezinski, 1985). And then BSi fluxes were calculated with the area of CJE. Primary production is calculated as follows:

$$p_p = PAZt, \quad (9)$$

where P is the carbon fixation rate ($\text{mg}/(\text{m}^2 \cdot \text{d})$), ranged from 600 to 1 800 $\text{mg}/(\text{m}^2 \cdot \text{d})$ with a mean value of 1 200 $\text{mg}/(\text{m}^2 \cdot \text{d})$ (Zhao et al., 2006); A is the area of study site, 9 300 km^2 ; Z is the euphotic depth (m), the value is 1.5 (Pu et al., 2001); and t is the time period (d^{-1}), $t=0.19 \text{ d}^{-1}$ in August, 0.09 d^{-1} in November and 0.25 d^{-1} in May, respectively. BSi fixation ($F_{p1, \text{BSi}}$) is then calculated as follows:

$$F_{p1, \text{BSi}} = \frac{15p_p}{12 \times 108}. \quad (10)$$

BSi regeneration ($F_{rc, \text{DSi}}$) within the water column is estimated by the difference of primary production ($F_{p1, \text{BSi}}$), the difference of BSi input ($F_{p2, \text{BSi}}$) and output ($F_{p3, \text{BSi}}$), and sedimentation ($F_{s, \text{BSi}}$). Actually, it is a result of the BSi budget calculation.

$$F_{rc, \text{DSi}} = F_{p1, \text{BSi}} - (F_{p2, \text{BSi}} - F_{p3, \text{BSi}}) - F_{s, \text{BSi}}, \quad (11)$$

where $F_{p1, \text{BSi}}$ is the sum of exogenous BSi (Gmol/a) into the box system, and $F_{p2, \text{BSi}}$ is the total BSi outflow (Gmol/a) out the system.

3 Results

3.1 Suspended particulate matters in water column

The SPM concentration varied between 1.3 and 830 mg/dm^3 with an average of 150 mg/dm^3 during the rainy season of 2010, 140 mg/dm^3 during the interflow season of 2011 and 120 mg/dm^3 during the baseflow time period, respectively. The highest SPM concentrations were observed in August 2010, corresponding to maximum salinity values of approximately 8 to 10. In general, the SPM declined seaward between salinity values of 10–34.

3.2 Biogenic silica concentrations in suspended particulate matters

The BSi concentration varied between 2.4 and 45 $\mu\text{mol}/\text{g}$ with an average of 14 $\mu\text{mol}/\text{dm}^3$ in the CJE (Table 1). The mean Si-Alk concentration was 15 $\mu\text{mol}/\text{dm}^3$ in the CJE, with a range of 2.4–51 $\mu\text{mol}/\text{g}$. The BSi concentration was similar to that of Si-Alk. By contrast, the Si-HCl concentrations exceeded BSi and Si-Alk, with an average value of 24 $\mu\text{mol}/\text{dm}^3$. The BSi concentrations in the water column show a strong seasonality, with higher values during rainy season (20 $\mu\text{mol}/\text{dm}^3$) and lower ones during baseflow (8.3 $\mu\text{mol}/\text{dm}^3$) or interflow (10 $\mu\text{mol}/\text{dm}^3$) periods. The ratio of BSi concentration to b_{TSi} one was in the range of 7% to 52% with an average of 24% in the upper part of CJE, and decreased seaward.

3.3 Dissolved silicate in the water column

The DSi concentration in the CJE varied between 6 and 56 $\mu\text{mol}/\text{dm}^3$, with an average of 33 $\mu\text{mol}/\text{dm}^3$ during the rainy season, 27 $\mu\text{mol}/\text{dm}^3$ during the baseflow period and 23 $\mu\text{mol}/\text{dm}^3$

Table 1. BSi, Si-HCl and Si-Alk concentrations in the water column at Stas B1, B3 and E1 in the Changjiang Estuary ($\mu\text{mol}/\text{dm}^3$)

Date	Station	BSi ¹⁾	Si-HCl ²⁾	Si-Alk ³⁾	$\Sigma c(\text{Si})$ ⁴⁾
Aug. 2010	B1	45.0	72.0	51.0	1.2×10^{-2}
	B3	4.3	4.8	4.0	8.8
	E1	12.0	25.0	14.0	39.0
Nov. 2010	B1	9.6	17.0	9.8	27.0
	E1	7.1	11.0	6.8	18.0
May 2011	B1	23.0	42.0	22.0	64.0
	B2	2.4	5.2	2.4	7.6
	E1	7.9	15.0	8.8	24.0

Note: ¹⁾ BSi was analyzed by the method of alkaline extraction; ²⁾ Si-HCl was extracted using a mild acid pretreatment; ³⁾ Si-Alk was measured by the alkaline extraction after acid pretreatment; ⁴⁾ $\Sigma c(\text{Si})$ is the sum of Si-HCl and Si-Alk.

during the interflow period, respectively. The DSi values were higher during the rainy season than during the dry and normal seasons in the CJE, and they were two times higher in the inner part (42 $\mu\text{mol}/\text{dm}^3$) than in the seaward part of the CJE (21 $\mu\text{mol}/\text{dm}^3$). The DSi concentrations decreased with increasing salinity, i.e. in the seaward direction (Fig. 2). The ratios of BSi concentration to b_{TSi} one in the CJE were respectively 25% for the rainy season, 13% for baseflow, and 25% for interflow conditions, with a mean value of 20% for the whole year (2010).

3.4 Composition of particulate biogenic silica

The particulate BSi is made up of phytoliths (50%), phytoplankton (47%) and sponges (3%). Phytoliths range from 23% to 83%. Elongate phytoliths were generally the most abundant type in the estuary (accounting for 7.6% to 49% of the phytoliths), followed by rondel, cuneiform, lanceolate, orbicular and elongate echinate (Table 2). The proportions of cross, cylindrical polylobate, unciform, trapeziform polylobate, ovate, saddle and bilobate types were low. Phytoplankton BSi contributes 12% to 76% of BSi. Bacillariophyceae were the dominant species to the phytoplankton BSi with an average value of 99%, with less than 1% for *Silicoflagellates* from the Chrysophyta. Centricae was the most abundant one within the Bacillariophyceae, with an average of 62%; *Coscinodiscus*, *Actinopterychus*, *Cyclotella* and *Paralia sulcata* were the common species in Centricae. The Pennatae make up 37% of the Bacillariophyceae on average, consisting of Naviculaceae, *Closterium lunula*, *Pleurosigma* and *Diploneis*. Microscopic observations of phytoliths particles are shown in Fig. A1. Most phytolith sizes ranged from 15 to 150 μm , and the phytoplankton BSi (Figs A2 and A3) was in the range of 20 to 100 μm .

Obviously, phytoliths dominated the BSi forms here during the summer/rainy season, which contributed a mean value of 63%, 50% during the fall/baseflow season and 39% during the spring/interflow season. Phytoplankton BSi makes up 61% of BSi during spring, the dominant BSi form during the low river sediment load. Phytoliths represent a larger share of BSi in the inner estuary (<121.8°E) than in the seaward part of the estuary, while phytoplankton BSi shows the reverse pattern (lower in the inner estuary than in the outer part of the estuary). We found a positive correlation between the ratio of phytolith mass to BSi one (hereinafter) and SPM ($r=0.780$, $n=8$, $P=0.023$)

3.5 Concentrations of dissolved silicate and aluminum in sediment pore water

The average DSi concentrations in Cores B3 and C5 were 140

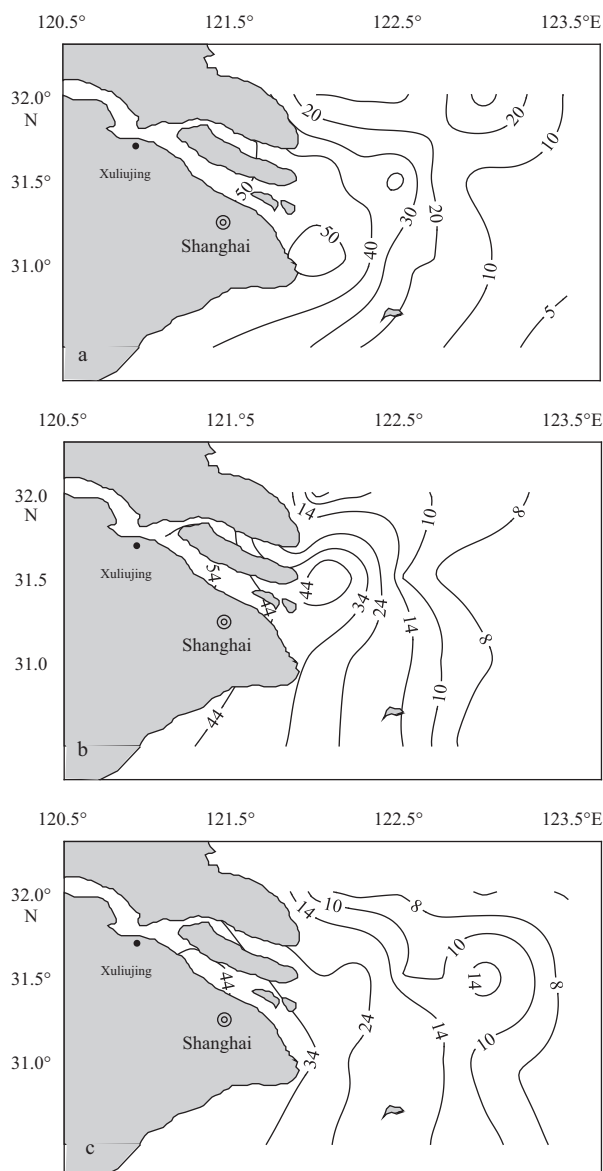


Fig. 2. DSi distributions ($\mu\text{mol}/\text{dm}^3$) in the Changjiang Estuary in August 2010 (a), December 2010 (b) and May 2011 (c).

$\mu\text{mol}/\text{dm}^3$ and $230 \mu\text{mol}/\text{dm}^3$, respectively. The average aluminium concentrations were $52 \mu\text{mol}/\text{dm}^3$ and $66 \mu\text{mol}/\text{dm}^3$ in Cores B3 and C5, respectively. The gradient of the DSi concentration vs. a depth was generally steep in the top and more gradual at larger depths, and it was relatively constant in Core B3. However, the DSi gradient shows an increasing down-core trend in Core C5. The aluminium concentration in Core C5 is relatively constant, while the aluminium concentration increases with depth in Core B3. The ratios of silicon concentration to aluminium one range from 1.5 to 4.8 at B3, decreasing with depth, and 1.9 to 7.8 at C5, showing an increase with depth (Fig. 3).

3.6 Concentrations of sedimentary biogenic/reactive silica

The BSi concentration in Core B3 varied between 81 and 120 $\mu\text{mol}/\text{g}$, and averaged $97 \mu\text{mol}/\text{g}$ in the CJE sediments (Fig. 4). The mean sediment Si-Alk concentration was $140 \mu\text{mol}/\text{g}$, with a range of 120 to 210 $\mu\text{mol}/\text{g}$ in Core B3. The mean Si-HCl concentration was $100 \mu\text{mol}/\text{g}$, with a range between 93 and 120 $\mu\text{mol}/\text{g}$

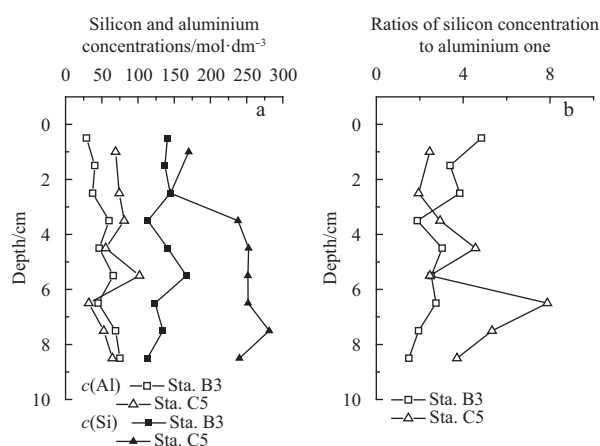


Fig. 3. Distribution of DSi (a) and aluminium (b) in the pore water of sediment at different stations.

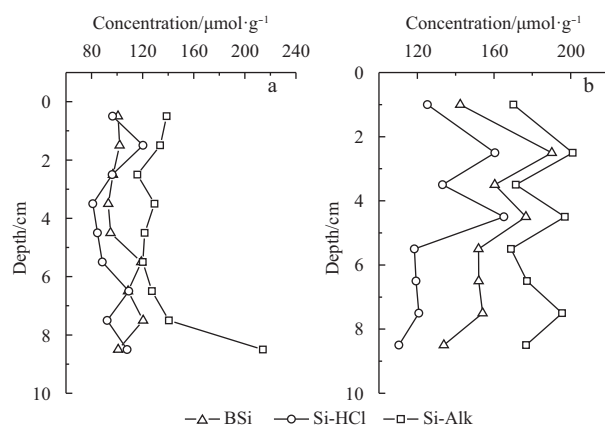


Fig. 4. Distributions of BSi, Si-HCl and Si-Alk concentrations in the sediment at Stas B3 (a) and C5 (b) in November 2010.

in Core C3. The total silica ($\sum c(\text{Si})$) concentration varied between 210 and 320 $\mu\text{mol}/\text{g}$. BSi represents a substantial portion of the total silica concentration in the core sediments. The BSi concentration was similar to the Si-Alk concentration, and the ratios of Si-Alk concentration minus BSi one to Si-Alk one ranged between 0.1 and 0.5. The average reactive pool ratios at Core B3 were 0.42 of ratio of Si-HCl concentration to the sum of Si-Alk concentration and Si-HCl one, 0.41 of ratio of BSi concentration to the sum of Si-Alk concentration and Si-HCl one, and 0.58 of ratio of Si-Alk concentration to the sum of Si-Alk concentration and Si-HCl one, and 0.72 of ratio of BSi concentration to Si-Alk one, respectively.

The BSi concentration varied between 110 and 160 $\mu\text{mol}/\text{g}$ with an average of $130 \mu\text{mol}/\text{g}$ in Core C5 for the CJE sediment. The mean Si-Alk concentration was $180 \mu\text{mol}/\text{g}$, with a range of 170–200 $\mu\text{mol}/\text{g}$ in Core C5 for the sediment. The BSi concentration was less than Si-Alk at all depths (Fig. 4), and the ratios of Si-Alk concentration minus BSi one to Si-Alk one ranged between 0.04 and 0.44. The mean Si-HCl concentration was $160 \mu\text{mol}/\text{g}$, with a range from 130 to 190 $\mu\text{mol}/\text{g}$ in Core C5. There was little regular variation with depth for the different reactive silica in both Cores B3 and C5. Generally, the BSi concentration was lower than that of Si-Alk, and it was higher than that of Si-HCl (Fig. 4). The biogenic silica composition in sediment was similar

Table 2. Composition (%) of the particulate BSi in the Changjiang Estuary¹⁾

		Water column									Sediment	
		Aug. 2010/rainy season			Nov. 2010/dry season		May 2011/interflow season			B3	C5	
		B1	B3	E1	B1	E1	B1	B2	E1			
Phytolith	elongate	29.0	17.0	26.0	22.0	11.0	31.0	7.6	8.2	49.0	27.0	
	cuneiform	9.5	0.7	4.5	10.0	5.4	7.6	1.9	3.1	14.0	2.0	
	lanceolate	6.0	1.8	3.7	4.4	3.7	4.0	2.2	2.7	—	—	
	cross	—	—	—	—	—	0.3	—	0.2	7.2	5.6	
	orbicular	6.4	1.5	5.7	4.7	2.7	2.4	1.9	2.5	1.9	2.6	
	trapeziform polylobate	0.8	1.8	1.6	1.4	3.4	1.2	0.6	1.3	0.9	0.9	
	rondel	12.0	11.0	13.0	3.3	5.7	3.4	3.8	5.4	4.7	6.7	
	saddle	7.5	1.5	1.2	1.4	2.7	1.8	0.9	2.1	3.1	2.0	
	bilobate	2.0	3.3	4.1	2.2	3.0	1.8	2.5	2.9	1.2	2.4	
	elongate echinate	7.1	1.1	3.7	6.6	0.7	2.8	1.3	1.0	3.4	3.2	
	unciform	0.4	—	2.9	0.6	0.7	—	—	0.8	—	—	
	ovate	2.8	—	—	3.0	—	—	—	0.4	1.2	—	
	cylindrical polylobate	—	0.4	—	—	—	0.6	—	—	0.3	0.9	
Sum of phytolith	83.0	39.0	66.0	60.0	39.0	57.0	23.0	30.0	88.0	53.0		
Bacillario-phyceae	centricae	8.3	34.0	7.8	26.0	19.0	36.0	58.0	41.0	6.3	27.0	
	pennatae	3.6	25.0	23.0	4.9	40.0	2.4	17.0	27.0	0.9	3.5	
Chrysophyta	<i>silicoflagellates</i>	—	—	—	—	—	—	0.9	0.6	—	1.5	
Sum of phytoplankton		12.0	59.0	31.0	31.0	59.0	38.0	76.0	68.0	7.2	32.0	
Spicules		5.2	1.5	2.9	9.1	1.7	5.2	1.6	1.0	5.3	14.0	

Note: ¹⁾ The BSi particles were separated by heavy liquid.

to that of the water column.

3.7 Scanning electron microscope observations of phytolith

SEM observations indicated that the phytolith surface had been corroded (Fig. A4), and part of the phytolith was covered by mineral coatings, which may protect from dissolution by a remnant of surface coatings. Phytolith elements primarily composed of silicon and oxygen, while carbon and aluminium contributed minor to their mass. EDS measurements indicated that the material consists of cation-rich aluminosilicate phases, such as aluminium, potassium, magnesium and iron.

3.8 Budget of dissolved silicate and biogenic silica

The concentration of DSi at Jianguyin station of the Changjiang River varied between 90 and 110 $\mu\text{mol}/\text{dm}^3$ with an average of 97 $\mu\text{mol}/\text{dm}^3$. An estimate for the Changjiang River indicates that the flux of DSi is 91 Gmol/a. The concentration of BSi at Jianguyin Station varied between 4.9 to 47 $\mu\text{mol}/\text{dm}^3$, and averaged 21 $\mu\text{mol}/\text{dm}^3$. An estimate for the Changjiang River indicates that the flux of BSi is 24 Gmol/a.

Atmospheric input to the CJE is about 0.004 Gmol/a in 2010–2011. The estimated groundwater DSi flux is 3.0 Gmol/a. And the diffusion rate of DSi ranges from 0.08 to 0.13 $\text{mmol}/(\text{m}^2 \text{d})$, with a yield of 0.3 to 0.5 Gmol/a. The average of the sum of Si-Alk concentration and Si-HCl one in the CJE is 97 to 130 $\mu\text{mol}/\text{g}$; total accumulation of reactive silica is 37 to 55 Gmol/a with an average of 46 Gmol/a (Fig. 5).

Observed b_{TSi} outflows of the Yellow Sea ($F_{x, \text{YS}} + F_{\text{rf, YS}}$, 17 Gmol/a) and the East China Sea ($F_{x, \text{ECS}} + F_{\text{rf, ECS}}$, 71 Gmol/a) roughly equal amounts of river loading of DSi. DSi exports to the East China Sea and the Yellow Sea through the study area account for 46%, and 12% of the total DSi input (110 Gmol/a), respectively. The net exchange of BSi between the CJE and the outer sea (the Yellow Sea and East China Sea) is 26 Gmol/a, is close to results of riverine BSi inputs.

On the basis of the mean rate of primary production, phyto-

plankton composition, euphotic depth and total area, calculated silicon fixation ($F_{\text{p1, BSi}}$) is 55 Gmol/a. The estimated sedimentation loading ($F_{\text{s, BSi}}$) in the CJE is 58% of the total BSi (80 Gmol/a) that is discharged by rivers and produced by diatom each year. While, the BSi regeneration (7 Gmol/a) in the CJE amounts to only 8% of the total BSi pool, and the remain part (34%) is discharged to the open seas.

The groundwater discharge (F_{g}) and net diffusion between the sediment and the water column are much less than the riverine silica flux, indicating that groundwater and benthic flux are minor sources of exogenous silicon in this fairly small area. Also, the BSi regeneration within the water column is not an important process of DSi in comparison with other processes. Considering all input fluxes of DSi into the CJE, river loading is the major source of DSi in the CJE, contributes 85% of total DSi input. While, groundwater discharge, benthic flux and atmospheric deposition adds only 2.5%, less than 0.4%, and less than 0.004% of DSi, respectively.

Our results indicate that the major exogenous BSi source in the CJE is the riverine input, representing 95% of total BSi input ($F_{\text{p2, BSi}}$, 25 Gmol/a, Fig. 5). Dominant processes that maintain BSi in the CJE are primary production and subsequent BSi sedimentation; and the BSi pool yielded ($F_{\text{p3, BSi}}$, 27 Gmol/a) by diatom production accounts for 63% of the BSi output (Fig. 5). The significance of the sedimentary of BSi is in agreement with our observed higher BSi concentration in the sediment.

4 Discussion

4.1 Biogenic silica composition of the Changjiang Estuary water

The BSi concentration in suspended matter accounts for 21% of the sum of BSi and DSi in the CJE, which is lower than the average ratio in the Huanghe River (52%; Ran et al., 2015), but consistent with that in Changjiang River, but higher than that in the East China Sea (11%) (Liu et al., 2005) and the average ratio in the world's rivers (16%) (Conley, 1997), indicating that BSi is an im-

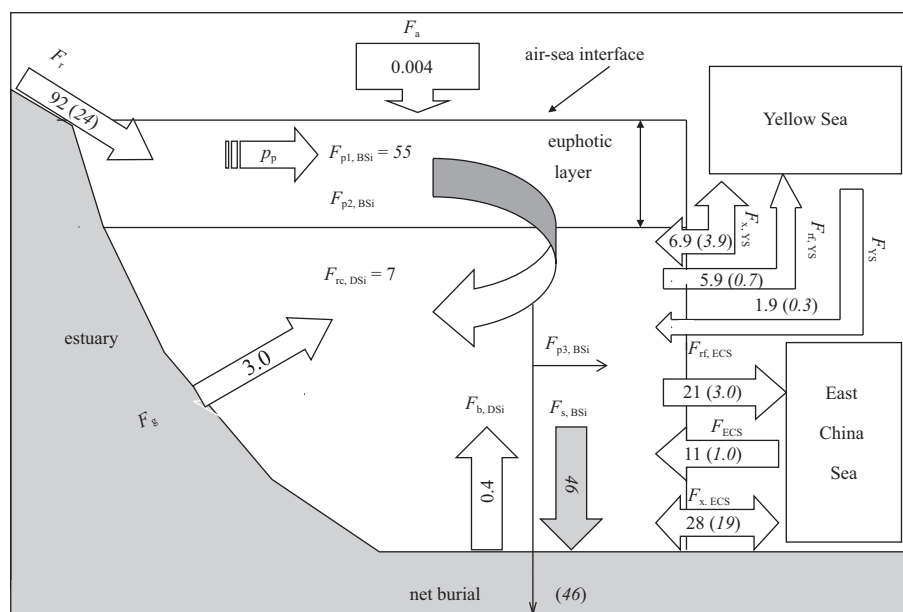


Fig. 5. Flux (Gmol/a) and budget (Gmol/a) of BSi and DSi in the CJE. Italic numbers represent the flux and budget of BSi. Budget terms into or out the CJE water mass were calculated. F_r represents river input, F_a atmospheric deposition, $F_{p1, BSi}$ BSi from primary production, $F_{rc, DSi}$ DSi from internal recycle, $F_{s, BSi}$ BSi sedimentation, $F_{b, DSi}$ benthic diffusion flux of DSi, F_{VS} input from the Yellow Sea, F_{ECS} input from to the East China Sea, F_g groundwater discharge, $F_{HF, ECS}$ and residual outflow to the East China Sea, $F_{HF, VS}$ residual outflow to the Yellow Sea, $F_{X, ECS}$ tide exchange outflow to the East China Sea (Positive values mean export from the box, hereinafter), $F_{X, VS}$ tide exchange outflow to the Yellow Sea, p_p primary production by diatom, $F_{p2, BSi}$ total loading of BSi from exogenous input on the basis of the budget calculation (25 Gmol/a, not a part of the budget), and $F_{p3, BSi}$ total fluxes of BSi export to the East China Sea and Yellow Sea (27 Gmol/a, not a term of the budget).

portant contributor for the reactive silica in the CJE.

A positive correlation between the ratio of phytolith concentration to BSi one and SPM one indicates that BSi and SPM have the same sources in the estuary. This phenomenon was further supported by the composition of BSi, in which 23% to 83% of BSi forms are composed by phytoliths in the water column (Table 2). In summary, phytoliths dominated the BSi forms in the CJE water column, suggesting that BSi is transported by rivers and that the river flux of phytoliths in the suspended load represents a significant contribution to the estuary biogeochemical cycle of silica. It should be noted, however, that all the four stations for determination of the BSi composition were located in the estuary turbidity maximum area, suggesting the contribution of the Changjiang River to the estuary BSi; thus, the phytoplankton BSi in the CJE is similar to the diatom composition along the main channel of the Changjiang River (Zeng, 2006) with a fairly high share of freshwater and brackish water species. In fact, Marine species, e.g., *Skeletonema costatum*, are not found, which is mainly due to the relatively small and low salinity survey area for BSi in the CJE. As the dominant species in the CJE (Li et al., 2007), *Skeletonema costatum* may have a significant BSi concentration associated in the study area.

4.2 Geochemical behavior of bio-reactive silica

4.2.1 Sediment silica alteration

A reverse weathering process has been proposed as an important silicon trap (Mackenzie and Garrels, 1966; Michalopoulos et al., 2000; Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008). It is the formation of clay minerals by incorporating DSi, BSi, cations and clay in marine sediments. A sig-

nificant correlation between the Si-Alk concentration and Si-HCl one ($r=0.68$, $n=16$, $P<0.01$) in the sediment was found, indicating that a diagenetic effect that was established after deposition. At Sta. B3, the ratio of the difference between the sum of Si-Alk concentration and Si-HCl one and BSi one to the sum of Si-Alk concentration and Si-HCl one was 0.59 in the sediment with a range of 0.49 to 0.66. Similar to Sta. B3, at Sta. C5 station the ratios of the difference between the sum of Si-Alk concentration and Si-HCl one and BSi one to the sum of Si-Alk concentration and Si-HCl one was 0.62 (from 0.49 to 0.68). The ratios of the difference between the sum of Si-Alk concentration and Si-HCl one and BSi one to the sum of Si-Alk concentration and Si-HCl one were similar to the average value of 71% for the Zhujiang Estuary (Qin et al., 2012) and the Mississippi River Delta (Presti and Michalopoulos, 2008). In both Stas B3 and C5, the average ratios of the difference between Si-Alk concentration and BSi one to Si-Alk one are 0.28. Thus, the formation of authigenic clays accounts for 28%–62% of the reactive silica alteration in the CJE sediment.

The formation of authigenic clays may have an important role in reactive silica alteration in the CJE sediment. The aluminosilicate matrix consists predominantly of aluminium, potassium and iron in addition to magnesium (Fig. A4), which is required by reverse weathering (Michalopoulos and Aller, 1995, 2004) and gives additional proof for formation of authigenic clays. We observed a significant positive correlation between the ratios of the difference between the sum of Si-Alk concentration and Si-HCl one and BSi one to the sum of Si-Alk concentration and Si-HCl one and aluminium ($r=0.17$, $n=16$, $P<0.05$), suggesting that the solubility of aluminium in sediments may limit diagenetic processes.

Although there is no direct documentation for the conversion of phytoliths to clays at the CJE sediment and the majority of the

phytolith appear to be unaltered, parts of the frustules are covered by mineral coatings, which is similar to the diatom BSi observations (Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008). We observed characteristic discoid particles that had size ranges and morphological characteristics identical to those of the well-preserved phytolith frustules (Fig. A4).

4.2.2 Water column silica alteration

The formation of authigenic clay could be 18–36 months (Michalopoulos et al., 2000). Similar authigenic phases can occur in as little as 10 months in lab incubation experiments (Loucaides et al., 2010). Given the time required for reverse weathering (e.g., 10 months at minimum), the residence time (11–22 d) of particles in pelagic environments are way too short for this to be occurring in the water column. The ratios between Si-Alk concentration and BSi one to Si-Alk one in the water column were lower than those in the sediment, while the ratio of the difference between the sum of Si-Alk concentration and Si-HCl one and BSi one to the sum of Si-Alk concentration and Si-HCl one is comparable in both the water column and sediment. Reverse weathering is therefore not an important removal process for reactive silica in the water columns, and aluminosilicate materials within SPM are largely due to the sediment transport and resuspension by physical processes.

4.3 Budget of dissolved silicate and biogenic silica

There is a massive sink (46 Gmol/a) of BSi by the sedimentary to balance the silicon budget (Fig. 5). Total BSi accumulation ($F_{s, \text{BSi}}$) represents 50% of the Changjiang River DSi load (91 Gmol/a), indicating a significant share of riverine silicon inputs can be removed by estuary processes. Fifty-three percent to eighty-eight percent of phytoliths in the sediment (Table 2) also suggests most of the riverine BSi loading is trapped in the study area. These results suggest that the preservation rate (58%) of BSi in the CJE is much higher than that in the open sea (3%) (Tréguer and De La Rocha, 2013).

The b_{TSi} outflows from the box to the Yellow Sea and East China Sea represent amounts of river loading of DSi, indicating the silicon pool in the CJE is in steady state. In comparison with the riverine loading, the BSi loading contributes to a relatively higher share of reactive silica in the outflows, implying an important contribution of authigenic diatom BSi to the reactive silica.

Benthic recycling ($F_{b, \text{DSi}}$) of BSi also contributes to the DSi pool in the estuary. Most of DSi in the pore water of the CJE are much higher than those in the water column with a range between 110 to 280 $\mu\text{mol}/\text{dm}^3$ in this site, and would be a part of the additions of DSi. The estimated benthic flux ($F_{b, \text{DSi}}$) in the CJE, however, is less than 1% of the loading of the Changjiang River. In this study, the benthic flux varied from 0.08 to 0.13 $\text{mmol}/(\text{m}^2 \text{d})$, which is lower than the previously reported data (Liu et al., 2003b, 2011) in the Yellow Sea and Bohai Sea and in the East China Sea (Liu et al., 2005). We recognize that the reasonable high (28% to 62%) silica alteration decreases the contribution of DSi from the benthic process. In this region the highest net silicon accumulation and reverse silicate weathering support our argument greatly.

The fairly shallow water depth (about 10 m) and short exchange time (11–22 d) reduce the contribution of BSi regeneration. On the basis of our data, most of riverine BSi were mainly trapped in the CJE, implying that there already has been a sink of terrigenous silicon. Furthermore, the contribution of phytoliths

to the total BSi is fairly higher in the sediment than in the water column, probably suggesting that phytoliths are relatively insensitive to dissolve in comparison with the diatom BSi. The groundwater discharge and the atmospheric deposition also contribute to a minor share of the exogenous silicon, which is much lower than that in the East China Sea (Liu et al., 2005). We think the fairly high riverine silicon loading would decrease the contributions of groundwater and precipitation to the total exogenous silicon.

Similar to DSi, the net exchange of BSi (26 Gmol/a) between the CJE and the outer sea (Yellow Sea and East China Sea) represent major fluxes with roughly equivalent amounts of riverine BSi loading, indicating that the exchange is a huge source of BSi for the adjacent areas of the CJE with significant impact on the regional carbon cycle. Combined with the observed primary production in the outer sea (Zhao et al., 2006; Li et al., 2014), the continuous supply of silicon from the CJE would imply a fairly higher primary production in the adjacent areas of the CJE than other areas without influence of river plume.

4.4 Implication of changing biogenic silica in the Changjiang Estuary

The controlling factor of BSi is the sedimentation and export to the system other than regeneration; this agrees with the results presented in Table 2 that shows a fairly high share of phytolith BSi in the sediment. Changes in riverine BSi and SPM fluxes may influence the functioning of marine ecosystems. Although the riverine input of DSi to the CJE changed little in the Changjiang River in recent 10 a (Dai et al., 2011), more than 70% of sediment (Yang et al., 2007) was trapped in the Changjiang River relative to the pre-Three Gorges Dam values. The ongoing damming of the Changjiang River basin may lead to further decreasing BSi loads to the CJE due to the retention of SPM, which would alter the BSi composition and the diatom growth in the estuary area, with important consequences for the silicon cycle. The so-called “clear water” by damming may stimulate the primary production due to the improvement of transparency, which would trap more silicon in the study area. Recent study (Li et al., 2014) saw an increase of chlorophyll concentrations in the CJE after the impoundment of the Three Gorges Reservoir. A long-term dataset also reveals that the maximum biomass of phytoplankton has expanded to a lower salinity region with the operation of Three Gorges Dam (Wang et al., 2016), which supports our argument greatly. The BSi composition, the diatom production and the BSi sedimentation have thus probably altered as a result of decreasing riverine SPM and BSi inputs in the Changjiang effluent plume. As a result, the “clear water” can reduce export of DSi to the open sea due to enhancing the primary production, which may decrease silicon availability in the Yellow Sea and East China Seas, which should be concerned in the future.

5 Conclusions

We report the compositions, behaviors and budget of silica in the CJE, which is highly impacted by terrestrial processes. BSi is mainly composed by phytoliths and phytoplankton BSi in the CJE. Phytoplankton BSi is composed of Bacillariophyceae and Chrysophyta (*Silicoflagellates*), accounting for 97% to 100% of the phytoplankton BSi in the CJE. Approximately 23% to 83% of the BSi was composed of phytoliths, with a mean value of 56% in water column. Authigenic clays account for 28% to 62% of the reactive silica accumulation in the CJE sediment.

The major exogenous BSi source in the water column of CJE is the riverine input, accounting for 95% of total BSi input. The net

export (26 Gmol/a) of BSi from the CJE to the East China Sea and Yellow Sea roughly equals the riverine BSi loading. Dominant processes that maintain BSi in the water column of CJE are the primary production (55 Gmol/a) and subsequent BSi sedimentation (46 Gmol Si/a). The total accumulation of BSi is one point seven times larger than the riverine input in this area, in which about 53% to 88% of BSi is phytoliths and their assemblage.

Riverine input contributes 85% of total DSi input in the estuary area, while the groundwater discharge, the benthic flux and the atmospheric deposition adds only 2.5%, less than 0.4%, and less than 0.004% respectively. The exports of DSi to East China Sea and Yellow Sea account for 46%, and 12% of DSi output, respectively.

This study suggests that the flux of phytoliths in the suspended load may represent a significant source of the estuary biogeochemical cycle of silica, and the ongoing damming in the Changjiang River may result in an increasing DSi and BSi removal in the CJE. The CJE therefore acts as a net sink for BSi.

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Appendix:

Water and salinity budget

The study area is approximate 9 300 km², with a depth of 12 m and a volume of 110 km³. The Changjiang Estuary (CJE) was defined as being in a steady-state during the three seasons of sampling.

Estimated terrestrial water inputs from are listed in Table A1. Taking all the discharges into account, and assuming no internal source or sinks of water, residual flow volume (V_r) can be solved based on LOICZ frame. The calculation is as follow:

$$V_{rf} = V_{rc} + V_{rh} + V_g + V_o + V_p - V_e. \quad (A1)$$

Residual flow volume (V_{rf}) export to the Yellow Sea ($V_{rf,YS}$)

and East China Sea ($V_{rf,ECS}$) were estimated by the ratios from Liu et al. (2003). V is water volume (km³/d), subscripts rc, rh, g, o, p and e denote Changjiang River input, Huangpujiang River input, groundwater input, other flow volume, atmospheric deposition, and evaporation, respectively.

And then, water exchange with the Box and outer seas are calculated from the formulas:

$$V_x = S_{rf} \times V_{rf} / (S_{sea} - S_{sys}), \quad (A2)$$

where S_{sys} and S_{sea} are the salinity in the box and outer seas, respectively; S_{rf} is the mean value of S_{sys} and S_{sea} . The water exchange with the Yellow Sea (V_{xy}) and East China Sea (V_{xe}) are followed the same proportions as the V_{rf} terms. S_{sys} and S_{sea} are respective 11.16 and 26.23 in August 2010, 18.98 and 33.00 in November 2010, and 23.97 and 29.71 in May 2011.

Table A1. Main discharges of terrestrial input, atmospheric export and evaporation in the Changjiang Estuary

	Aug. 2010	Nov. 2010	May 2011
V_{rc} (Changjiang) ¹⁾	4.4	1.6	1.4
V_{rh} (Huangpujiang) ²⁾	0.028	0.028	0.028
V_g ³⁾	0.37 ^a	0.22 ^b	0.08 ^c
V_o ⁴⁾	0.002	0.002	0.002
V_p ⁴⁾	0.004	0.004	0.0009
V_e ⁴⁾	0.010	0.010	0.014

Note: The unit is km³/d. ¹⁾ Ministry of Water Resources of the People's Republic of China (2011; 2012); ²⁾ Ministry of Water Resources of the People's Republic of China (2014); ³⁾ Gu et al. (2012), ^{a, b} and ^c 0.04, 0.024 and 0.008 m³/(m²·d) of groundwater discharge rate were employed with the thought of seasonal effect (Kelly and Moran, 2002); ⁴⁾ Li et al. (2011), water discharges in rivers were collected between June 2010 and May 2011.

Table A2. Residual outflow and water exchanges

	Aug. 2010 ^a	Nov. 2010 ^b	May 2011 ^c
V_{rf}	4.8	1.9	1.5
$V_{rf,YS}$ ¹⁾	1.2	0.2	0.1
$V_{rf,ECS}$	3.6	1.7	1.4
V_x	5.4	3.0	6.5
$V_{x,YS}$ ¹⁾	1.4	0.4	0.3
$V_{x,ECS}$	4.0	2.6	6.2

Note: The unit is km³/d. ¹⁾ Liu et al. (2003); ^{a, b} and ^c 26%, 10% and 5% of the Changjiang River discharges are exported into the Yellow Sea.

Table A3. Concentrations of DSi and BSi in each loading of the Changjiang Estuary

Concentration	Aug. 2010		Nov. 2010		May 2011	
	DSi	BSi	DSi	BSi	DSi	BSi
c_t (Changjiang) ¹⁾	110	35	92	19	90	12
c_t (Huangpujiang) ²⁾	130	—	110	—	50	—
c_g ³⁾	39	—	39	—	39	—
c_o	—	—	—	—	—	—
c_p ⁴⁾	3.1	—	3.1	—	3.1	—
c_e	—	—	—	—	—	—
F_{ECS}	13.3 ¹⁾	1.3 ⁵⁾	12.8 ¹⁾	1.3 ⁵⁾	16.0 ¹⁾	1.3 ⁵⁾
F_{YS}	10.8 ¹⁾	1.5 ⁵⁾	9.2 ¹⁾	1.5 ⁵⁾	7.5 ¹⁾	1.5 ⁵⁾
$F_{rf,ECS}$ ¹⁾	31.6	4.3	17.4	3.4	20.7	2.4
$F_{rf,YS}$ ¹⁾	34.6	4.3	28.4	3.4	17.7	2.4
$F_{x,ECS}$ ¹⁾	27.2	19.1	19.7	7.1	11.0	9.8
$F_{x,YS}$ ¹⁾	29.7	18.9	23.3	6.9	19.5	9.6

Note: The unit is $\mu\text{mol}/\text{dm}^3$. ¹⁾ From this study; ²⁾ Cui et al.(2011); ³⁾ the data of station 1# from Kim et al. (2005); ⁴⁾ Zhang et al. (2007); ⁵⁾ Liu et al. (2003, 2005). — means under determination.

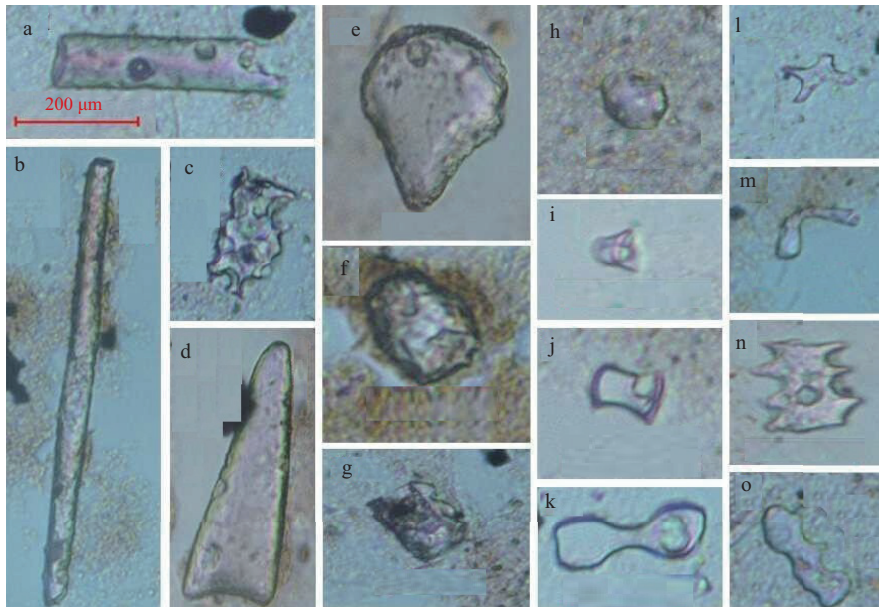


Fig. A1. Microscopic observation of phytolith BSi particles in the Changjiang Estuary. a, b and c. Elongate, and c shows weathering feature; d. Lanceolate; e. Cuneiform; f. Ovate; g. Trapeziform polylobate; h. Orbicular; i. Rondel; j. Saddle; k. Bilobate; l. Cross; m. Unciform; n. Elongate echinate; and o. Cylindrical polylobate.

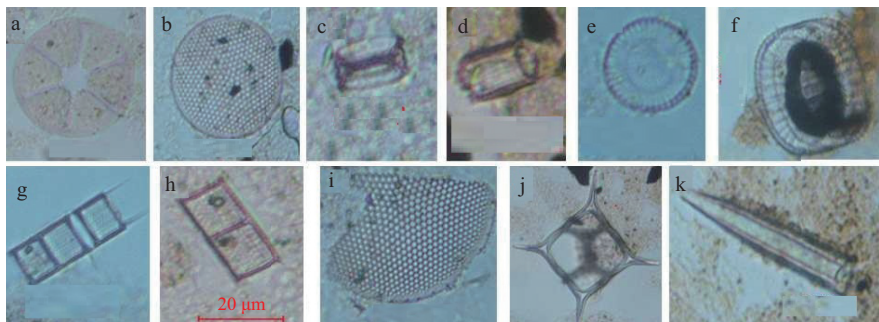


Fig. A2. Microscopic observation of diatom BSi of centricae particles in the Changjiang Estuary. a. Actinoptychus; b. Coscinodiscus; c, e, and f. Cyclotella; d, g, and h. Melosira; i. fragments of the Coscinodiscus; j. Dictyocha fibula; and k. sponge spicule.

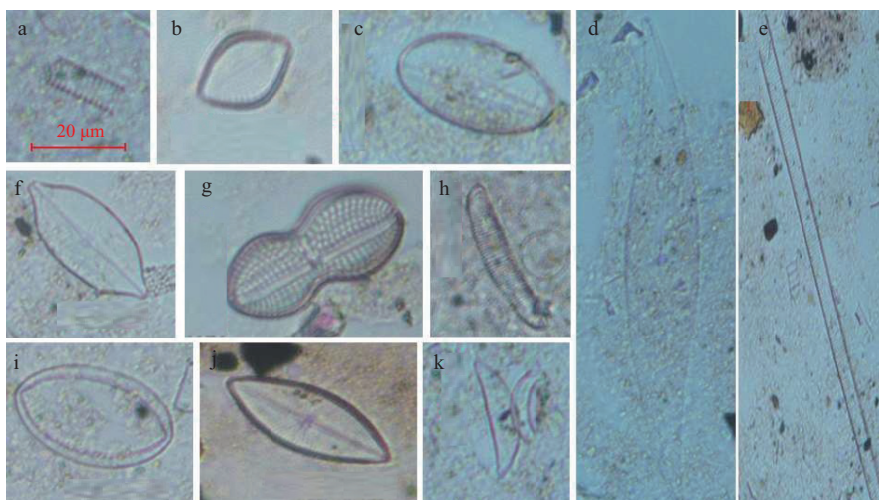


Fig. A3. Microscopic observation of diatom BSi of pennatae particles in the Changjiang Estuary. a. Detritus fragments of diatom in pennatae; b. *Mastogloia*; c. *Diploneis*; d. *Gyrosigma*; e. fraction of *Synedra*; f. *Navicula*; g. *Diploneis*; h. *Cymbella*; i. *Neidium*; j. *Navicula*; and k. *Cymbella*.

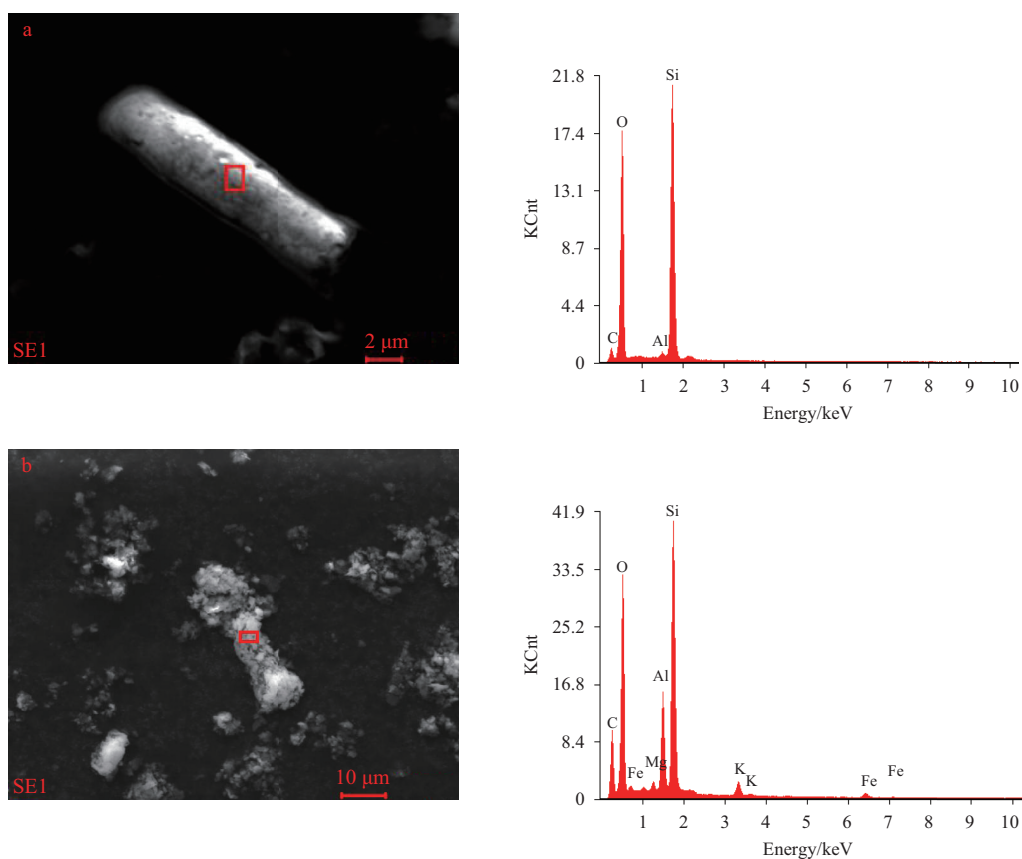


Fig. A4. Scanning electron microscope image and energy dispersive spectrometer spectral analysis of phytolith (a and b) in the Changjiang Estuary. a. The scanning electron microscope photo from well-preserved phytolith in the CJE; and b. the scanning electron microscope photo of altered phytolith.

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