Long-term variations in dissolved silicate, nitrogen, and phosphorus flux from the Yangtze River into the East China Sea and impacts on estuarine ecosystem

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Abstract

Variations of dissolved silicate (DSi) flux in the Yangtze River have caused great concern among scientists. Analysis of spatial and temporal variations of DSi indicates that the distribution of DSi concentration (DSiC) is closely related to the occurrence of bedrocks in the river catchment. On average, the upper Yangtze River and Dongting and Poyang Lake of the middle Yangtze basin serve as the major DSi sinks, retaining $3.39 \times 10^4$ t y$^{-1}$, $5.59 \times 10^4$ t and $2.51 \times 10^4$ t y$^{-1}$, respectively. The middle and low Yangtze River remains DSi sources, emitting $2.85 \times 10^4$ t and $2.48 \times 10^4$ t y$^{-1}$, respectively. Geochemical data at Datong hydrological station recorded the flux of nutrients entering into the sea during the flood season, i.e. 74% for DSi, 73% for DIN (Dissolved Inorganic Nitrate) and 68% DIP (Dissolved Inorganic Phosphate). The yearly DSiC and flux show a sharp decrease since 1950s. The mean DSiC was 109.47, 91.09, and 77.56 $\mu$mol l$^{-1}$ in the 1960s, 1970s and 1980s, respectively. The mean DSi fluxes for the same time period were 2.72, 2.23, and $2.13 \times 10^6$ t. A PP (primary productivity) model estimates $3.14 \times 10^5$ t of DSi (13.08% of the annual mean flux entering into the sea) was fixated within the 162 reservoirs in 2002. On the other hand, DIN and DIP concentration and flux have increased greatly since the 1950s. Fertilizer application peaked after the 1980s can interpret these high DIN and DIP. A sharply decreasing DSi flux and quickly increasing DIN and DIP fluxes into the sea have enhanced eutrophication and caused frequent harmful algal blooms in coastal waters. On average, red-tide frequency was from 0.04 during 1933–1979 to 7.0 during 2000–2002. The Skeletonema costatum (siliceous alga), the red-tide-predominant species that is in positive proportion to DSi flux, decreased from 33% during the 1980s to 24% during 2000–2002, which tends to be dominant species of the red tides off the Yangtze estuary. The number of big dams in the Yangtze River basin will double in the next 30–50 years. This will significantly influence the variations of nutrient fluxes in the river basin and estuary, in relation to health management of river-coast ecosystem.

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1. Introduction

It is well known that silicon plays an important role in the primary productivity of the aquatic ecosystem. Diatoms, accounting for 60% of all species of phytoplankton, take up silicon to form cell walls (frustules) (Hamm et al., 2003). The C:Si:N:P molar composition of diatoms is proposed to be 106:16:16:1 (Redfield et al., 1963; Brzezinski, 1985; Rahm et al., 1996). These values also represent the ratios in which the nutrients containing these elements are incorporated during the growth of phytoplankton and are released during their decomposition. So, changes of silicon concentration of the aquatic environment can alter the distribution and abundance of diatom species, in turn altering the trophic and
subtropic composition and ecosystem structure. Furthermore, the marine silicon cycle is linked strongly to the carbon cycle through the activities of diatoms, the ‘workhorses of primary productivity’ (Berner et al., 1983; Smetacek, 1998). The global rates of silicate weathering and deposition of biogenic silica in marine sediments significantly affect the global greenhouse effect (Smetacek, 1999; Van Cappellen, 2003; Raven and Waite, 2004).

The Yangtze River is the third longest in the world and is the largest river in China, with a drainage area of $1.8 \times 10^6$ km$^2$. Wandering 6300 km eastward to the East China Sea, it contributes annually $9 \times 10^{11}$ m$^3$ of freshwater and $4.7 \times 10^8$ t of sediment carrying significant nutrients into its estuary and the sea. It is regarded as an important source of materials in the North Pacific coastal seas, and the materials carried by the river have a significant influence on coastal environmental health, sustaining the productive fisheries in the adjacent seas (Edmond et al., 1985; Tian et al., 1993; Chen et al., 2001). With the development of the economy and the increased demands for preventing floods and saving water resources in China, thousands of water conservation projects have been constructed in the Yangtze River drainage basin (YRDB) during recent decades. Anthropogenic perturbations have caused considerable changes in riverine nutrient concentrations and fluxes to the sea (Zhang et al., 1999). However, little comprehensive data are available on the variations in nutrient concentrations and fluxes and the effects on the coastal ecosystem, in particular, in riverine silicon variation. Variations in DSi distribution and flux in the YRDB have prompted many research projects with common concerns. Hu et al. (1982) pioneered the study of DSi distribution in the Yangtze River basin, followed by Qu et al. (1993), Chen et al. (2002), and Liu et al. (2003). Liu and Shen (2001) estimated the DSi flux ($2.23 \times 10^6$ t y$^{-1}$) into the East China Sea. Despite the considerable efforts have been devoted to the study of the Yangtze River, our understanding of the DSi flux of tributaries in relation to sources and sinks is still limited. The DSi chemistry of the Yangtze River has not been well studied, representing a significant gap in our better understanding of river chemistry, physical and chemical weathering, and elemental cycles on a local and global scale. To improve the situation, the objective of the present study aims at a profound examination on various nutrients distribution in the river basin throughout time, and tends to reveal this distribution in relation to both fluvial variables and anthropogenic factors, leading to a health river-coastal environmental management in the near future.

2. Data and methodology

2.1. Data collection

Long-term mean DSi, DIN, and DIP concentrations at 176 hydrological gauging stations located on the Yangtze River bank were collected from the internal Hydrological Yearbooks of the People’s Republic of China (Yangtze River Water Resource Committee, 1955–1999). Eight stations of the present study are sited along the mainstream river channel, at, from upstream downwards, Benzilin, Shigu, Dukou, Cuntan, Yichang, Chenglingji, Wuhan, and Datong (Fig. 1). Long-term mean runoff of 18 tributaries was collected from the Yangtze River General Thesaurus (Yangtze River General Thesaurus...
compilation committee, 1999). Long-term monthly DSi, DIN, and DIP concentrations and runoff at Datong station of the lower Yangtze River were collected from Hydrographic Data Collection in the Lower Reaches of the Yangtze River (Yangtze River Water Resource Committee, 1955–1985). The sampling frequency ranged from one to three times a month; the temporal series of nutrient data span 1955 to 1985, and the data of runoff and sediment span 1950 to 2000. Volume and runoff at 162 big reservoirs (>0.1 km$^3$ storage capacity) were collected from the Statistical Almanac of the Yangtze River (Committee of Statistical Almanac of the Yangtze River, 1992–2004) and the Yangtze River General Thesaurus (Yangtze River General Thesaurus compilation committee, 1999). Long-term red tide data spanning 1933 to 2002 came from the internal yearbook of the East China Sea Environment Monitoring Center of the People’s Republic of China (East China Sea Environment Monitoring Center, 2002). Dissolved inorganic nutrients measured at Datong station were DSi, dissolved inorganic carbon (DIC), DIN, and DIP. DSi is mainly silicate ($\text{SiO}_3^{2-}$); DIC is chiefly bicarbonate ($\text{HCO}_3^-$); DIN is the sum of ammonium (NH$^+$), nitrite (NO$^2$), and nitrate (NO$^3$); and DIP is phosphate ($\text{PO}_4^{3-}$). Some data from 1970 are unavailable.

In addition, distribution of parent rocks of the Yangtze River drainage basin was systematically examined, chiefly characterized by 4 types of rock nature of the study area: sedimentary rocks, Quaternary alluvium, metamorphic rocks, and igneous rocks mapped in the China geological map (Changjiang Water Conservancy Committee, 1999).

### 2.2. Chemical data treatment

DSi and other nutrients in water samples were analyzed by various laboratories under the authority of the Yangtze River Water Resource Commission, following the methods described in Alekin et al. (1973) and APHA (1985). Dissolved water samples were decanted or filtered (through a 0.45-µm membrane) from the raw water samples and analyzed for $\text{SiO}_2$ (by the molybdenum blue method), NO$_3$ (by EDTA titration), and P$\text{O}_5$ (by difference using an ionic balance or by flame spectrometry). The original data in the Hydrological Yearbooks given in mg l$^{-1}$ were converted into mol l$^{-1}$ to allow direct chemical stoichiometric calculations by authors. Also, the authors calculated the atomic ratios of $\text{SiO}_2^{2-}$ and other elements of 176 stations of the Yangtze River basin.

### 2.3. Data analysis

DSi stations (176) were registered in a Geographic Information System. The spatial distribution of DSi was analyzed with ARCgis software, following the Kriging Gridding Interpolation Method. To calculate the DSi flux of the main river channel section and main tributaries, the long-term annual mean DSi flux is expressed as in Eq. (1):

$$F_r = C_r \cdot Q_r$$

(1)

Where $F_r$ is the long-term annual mean DSi flux of $r$ tributaries, $Q_r$ is the long-term annual mean runoff discharge at the confluence with the main channel of $r$ tributaries, and $C_r$ is the long-term mean DSiC in $r$ tributaries. The DSi flux of the Datong section is calculated by Eq. (2):

$$F_0 = C_0 \cdot Q_0$$

(2)

Where $F_0$ is the DSi flux, $Q_0$ is the mean river flow of the Datong section in the $j$th month of the $i$th year, and $C_0$ is the simultaneous mean nutrient concentration of the section. Then the monthly mean flux of Datong is calculated by the above equations, and then yearly flux can be obtained by summing 12 months. Using the same method gains the monthly and yearly DIN and DIP fluxes. Multiyearly DSi flux of main tributaries, lakes and stem stream of the Yangtze River is also computed, separately.

Silicon fixation in reservoirs is estimated on the basis of upstream nutrient levels and flushing time for primary productivity (pp-model, g C m$^{-2}$ y$^{-1}$) within the 162 big reservoirs from a simple empirical model calculation (Vollenweider and Kerekes, 1980; Canfield and Bachmann, 1981):

$$\sum C = 7 \left[ \frac{([TP]/1 + \sqrt{Tw})^{0.76}}{0.3 + 0.011([TP]/1 + \sqrt{Tw})^{0.76}} \right]$$

(3)

Where $\sum C$ is annual primary productivity fixed by reservoirs, $[TP]$ is the phosphorus load of input streams above reservoirs, and $Tw$ is residence time of impoundment water in reservoirs. $Tw$ can be defined as the quotient of reservoir effective volume ($V_e$) over annual discharge ($Q$), i.e. $Tw = V_e/Q$. Using the ratio of diatom primary productivity to total primary productivity, usually 1:2 in freshwater ecosystems, can calculate the diatom primary productivity (Chinese Encyclopedia Compilation Committee, 1987). We here propose a way of estimating fixed silicon flux using the typical $\text{C}:\text{Si}:\text{N}:\text{P}$ ratio of 106:16:16:1 for diatom assimilation (Redfield et al., 1963; Brzezinski, 1985; Rahm et al., 1996).

$$\sum \text{Si} = 0.5 \times (16/106) \times \sum C$$

(4)

The pp-model was chosen because biological activity is strongly phosphorus-limited in the Yangtze River and its tributaries, as the ratio of N to P is always $>30$ throughout the basin (Hu et al., 1990; Liu et al., 2003). This result was derived from 31 lakes and 8 big reservoirs in China, and the model output and field measurements were generally matchable while estimating the potential carbon content and fixation by reservoirs.

Long-term distribution trends of DSi, DIN, DIP, water discharge, and sediment load were analyzed by statistical test performed with the Social Package of Statistic Software 11.0.

### 3. Spatial distribution of dissolved silicate

Data from 176 hydrological gauging stations revealed that higher value of long-term mean DSiC was recorded at the upper
YRDB (including Yalongjiang and Puduhe) and Dongting-Poyang Lake basins (including Yuanjiang, Ganjiang, Xiushui, Wuhe, Xinshui, Raohe, and lower Hanjiang) (I and III in Figs. 2A and 3A). In those areas, DSiC value was often higher than 98.00 μmol l⁻¹ (Fig. 3A), and was as high as 235.53 μmol l⁻¹ at Dahuizhuang station of Jinshajiang tributary. Lower value was recorded in downstream Sichuan basin (i.e. Three-Gorges valley (i.e. Niulanjiang, Hengjiang, Minjiang, Tuojiang, Jialingjiang, WuJiang), and part of the middle Yangtze basin (i.e. Xiangjiang and Lishui), and the lower Yangtze basin (II and IV in Figs. 2A and 3A). In those tributaries, DSiC was generally less than 80.00 μmol l⁻¹ (Fig. 3A), but the lowest was 8.94 μmol l⁻¹ at the Qixingqiao of the Wujiang drainage basin. In addition, the long-term mean DSiC from the 18 major tributaries varied over one order of magnitude throughout the drainage basin, ranging from 43.42 to 159 μmol l⁻¹. The DSiC in some southern tributaries of the YRDB was more than that in the northern tributaries (Fig. 2A).

DSiC value in the main stream measured at 8 major stations follows the spatial distribution of the YRDB, ranging from 87.00 to 115.79 μmol l⁻¹ (Fig. 3B). DSiC was higher than 87.00 μmol l⁻¹ at the upper Yangtze and generally lower than 80.00 μmol l⁻¹ at Three-Gorges valley and part of the middle Yangtze basin (Fig. 3B). Relative higher values (92.00–96.00 μmol l⁻¹) appear below Wuhan.

Weathering of various parent rocks yields different combinations of dissolved cations and anions (Garrels and Mackenzie, 1971; Stumm, 1992). The atomic ratio of each anion and cation to total anions and cations provides a means of probing the different weathering reactions in the YRDB. On average, SiO₃²⁻ accounted for 4.01% of total anions, HCO₃⁻ for 80.3% of total anions, and Ca²⁺ for 59.0% of total cations in the YRDB (Fig. 3C). Seemingly, the weight ratio of SiO₃²⁻ was far less than those of HCO₃⁻ and Ca²⁺. These results indicate that the chemistry of the YRDB is dominated primarily by the weathering of sedimentary rocks, chiefly, siliciclastic and limestone (Changjiang Water Conservancy Committee, 1999), while supplemented by the weathering of silicate. In contrast, Quaternary alluvium, igneous and sedimentary rocks, although widely occurring in the YRDB, yield a lower DSi regarding its hardness for chemical weathering (Figs. 2A, B).

In some of main tributaries, including Niulanjiang, Hengjiang, Minjiang, Tuojiang, Jialingjiang, WuJiang, Xiangjiang and Lishui of the upper and lower YRDB (Fig. 1), the atomic ratios of SiO₃²⁻ to total anions were all less than 4.01%, the average ratio in the YRDB, and the atomic ratios of HCO₃⁻ and Ca²⁺ to total anions were more than 59% and 80.3% (II and VI in Fig. 3C). This is determined by widely distributed sedimentary rocks (primarily limestone), and Quaternary alluvium in these tributaries (Changjiang Water Conservancy Committee, 1999) (Fig. 2B). In other main tributaries of the upper (Puduhe) and middle YRDB, surrounding Poyang Lake, i.e. Yuanjiang, Ganjiang, Xiushui, Wuhe, and Xinshui, the atomic ratios of SiO₃²⁻ to total anions were more than...
the average ratio, and the atomic ratios of HCO$_3^-$ and Ca$^{2+}$ to

total anions were all less than the average ratio (I and III in

Fig. 3C). Igneous rocks occurred broadly in these tributary basins (Fig. 2B) to produce SiO$_3^{2-}$ and DSiC, which is obviously

higher than those of other rivers (Fig. 3C).

Multiyearly DSi flux in the main Yangtze River channel obviously increases from $0.10 \times 10^6$ t y$^{-1}$ at the uppermost Ben-

zilan station to $2.37 \times 10^6$ t y$^{-1}$ at the lowermost Datong

station (Fig. 3D). This range is primarily due to varied runoff

from 200 km$^3$ y$^{-1}$ at the uppermost Benzilan station to 2.37

$\times 10^6$ t y$^{-1}$ and $2.51 \times 10^6$ t y$^{-1}$ DSi fluxes as sink value in the

upper Yangtze reach (above Yichang), Dong and Poyang lakes

of the middle YRDB (Figs. 1 and 3F). However, DSi flux in the middle and lower Yangtze River channel is $-2.85 \times 10^4$ t y$^{-1}$ and $-2.45 \times 10^4$ t y$^{-1}$, indicating a source emitting for down-

stream coast, and the sea (Fig. 3F).

4. Seasonal variations of dissolved silicate, nitrogen, and phosphorus

Database of the present study indicates that DSiC and DIN recorded at Datong station have the same trend of incremental value from non-flood season to flood season (Table 1). For instance, DSiC changes from ca. 79 to 105 $\mu$mol l$^{-1}$, and DIN is from ca. 40 to 60 $\mu$mol l$^{-1}$. Of note, DSiC reaches the higher value in September, but DIN peaks to its value in June. However, DIP has its higher value in the non-flood sea-

son ($0.33-0.35$ $\mu$mol l$^{-1}$) and lower value ($0.12$ $\mu$mol l$^{-1}$) in the flood season. Using Eq. (2), the contributions of DSi, DIN,
and DIP in the flood season to the annual total are 53.39%, 51.43%, and 47.33%, respectively.

The seasonal variations of DSiC distribution recorded at Datong station resembles a stable to slow increasing trend from the 1950s to the early 1980s (Figs. 4D–G). A decreasing trend of yearly mean DSiC occurs obviously from the 1960s to 1990s (Fig. 4C). This proposes the control of DSiC on decreasing trend of DSi flux over long time period, rather than runoff. The yearly DIN and DIP concentrations and fluxes have doubled the N/Si and P/Si ratios (Figs. 4H,I). This is mostly caused by increasing nitrogen and phosphate in waters, as diatoms will assimilate DSi in the ratio to C, P, and N as 16:106:16:1 (Redfield et al., 1963; Brzezinski, 1985; Rahm et al., 1993; Dubravko et al., 1995; Conley, 1997). This is also show a decreasing trend with time (Fig. 4B). Over the long term, the inter-annual variations in runoff have kept stable as evidenced in the lower YRDB (Fig. 4C). This proposes the control of DSiC on decreasing trend of DSI flux over long time period, rather than runoff. The exceptional case is in the 1998, when historical flood with a 60-year recurrence occurred. More than 80,000 m³ s⁻¹ discharge was recorded at Datong, and this may cause unexpected weathering of bedrocks in relation to DSiC and its flux highs (Xu et al., 2005) (Figs. 4A,B).

The yearly DIN and DIP concentrations and fluxes show a stable to slow increasing trend from the 1950s to the early 1980s (Figs. 4D–G), but, since then, those of nitrate and phosphate increased abruptly. This phenomenon can be interpreted by a large amount of fertilizer and chemical plants came into operation in the Yangtze River basin after the 1980 (Cheng et al., 1992). We noted that Chemical fertilizer applied to the YRDB in 1991 (625 × 10⁶ t) was 48 times more than that in 1962 (Shen et al., 2001).

The decrease of DSi flux and increases of DIN and DIP fluxes have doubled the N/Si and P/Si ratios (Figs. 4H,I). The annual N/Si ratio was 0.23 in the 1970s, 0.63 in the 1980s, and 1.42 in the 1990s. The yearly P/Si ratio was 0.0015 in the 1970s, 0.0044 in the 1980s, and 0.0186 in the 1990s.

Decreasing silicon concentrations in some surface waters such as in Po River and Mississippi estuary have been observed and interpreted as an effect of eutrophication (Conley et al., 1993; Dubravko et al., 1995; Conley, 1997). This is mostly caused by increasing nitrogen and phosphate in waters, as diatoms will assimilate DSi in the ratio to C, P, and N as 16:106:16:1 (Redfield et al., 1963; Brzezinski, 1985; Rahm et al., 1996). Thus increasing DIN and DIP flux, particularly after the 1980s in the Yangtze River basin results in depletion of DSiC, through growing phytoplankton biomass.

Other researches said that the major cause for the DSi reduction results from impoundment of reservoirs on rivers for mitigating floods and generating clean electricity (Christoph et al., 1997). In the YRDB, numerous big dams (162, water storage capacity >0.1 km³) were emplaced before 2002 (Committee of Statistical Almanac of the Yangtze River, 1992–2004). The dam construction sharply increased the water storage volume during the 1970s–1990s (Fig. 5A). Reservoirs can hold nearly 155.44 km³ (Table 2), or 95% of the total reservoir volume in the river basin (Committee of Statistical Almanac of the Yangtze River, 1992–2004), accounting

### Table 1
Long-term monthly mean variations in DSiC and flux (FDSi), DIN and flux (FDIN), DIP and flux (FDIP), and discharge (Qm), recorded at Datong station. Letters in BOLD were discussed in text (data source: Changjiang River Water Resource Committee, 1955–1985)

<table>
<thead>
<tr>
<th>Month/Season</th>
<th>Qm km³</th>
<th>DSi μmol l⁻¹</th>
<th>DIN μmol l⁻¹</th>
<th>DIP μmol l⁻¹</th>
<th>FDSi 10⁴ t</th>
<th>FDIN 10⁴ t</th>
<th>FDIP 10² t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan.</td>
<td>26.53</td>
<td>78.80</td>
<td>41.11</td>
<td>0.15</td>
<td>5.85</td>
<td>1.53</td>
<td>1.24</td>
</tr>
<tr>
<td>Feb.</td>
<td>25.73</td>
<td>83.98</td>
<td>45.29</td>
<td>0.13</td>
<td>6.05</td>
<td>1.63</td>
<td>1.06</td>
</tr>
<tr>
<td>Mar.</td>
<td>42.33</td>
<td>88.75</td>
<td>52.22</td>
<td>0.13</td>
<td>10.52</td>
<td>3.09</td>
<td>1.66</td>
</tr>
<tr>
<td>Apr.</td>
<td>67.64</td>
<td>88.53</td>
<td>50.37</td>
<td>0.14</td>
<td>16.77</td>
<td>4.77</td>
<td>2.92</td>
</tr>
<tr>
<td>May</td>
<td>96.11</td>
<td>90.43</td>
<td>57.91</td>
<td>0.16</td>
<td>24.34</td>
<td>7.79</td>
<td>4.70</td>
</tr>
<tr>
<td>Jun.</td>
<td>109.53</td>
<td>95.71</td>
<td>59.48</td>
<td>0.19</td>
<td>29.35</td>
<td>9.12</td>
<td>6.54</td>
</tr>
<tr>
<td>Jul.</td>
<td>136.58</td>
<td>93.83</td>
<td>50.19</td>
<td>0.12</td>
<td>35.88</td>
<td>9.60</td>
<td>5.25</td>
</tr>
<tr>
<td>Aug.</td>
<td>114.75</td>
<td>101.49</td>
<td>46.54</td>
<td>0.17</td>
<td>32.61</td>
<td>7.48</td>
<td>6.09</td>
</tr>
<tr>
<td>Sep.</td>
<td>103.90</td>
<td>105.49</td>
<td>44.34</td>
<td>0.19</td>
<td>30.69</td>
<td>6.45</td>
<td>6.13</td>
</tr>
<tr>
<td>Oct.</td>
<td>89.97</td>
<td>95.83</td>
<td>39.50</td>
<td>0.26</td>
<td>24.14</td>
<td>4.98</td>
<td>7.34</td>
</tr>
<tr>
<td>Nov.</td>
<td>59.11</td>
<td>87.89</td>
<td>42.83</td>
<td>0.33</td>
<td>14.55</td>
<td>3.54</td>
<td>5.98</td>
</tr>
<tr>
<td>Dec.</td>
<td>35.71</td>
<td>80.86</td>
<td>49.51</td>
<td>0.35</td>
<td>8.09</td>
<td>2.48</td>
<td>3.85</td>
</tr>
<tr>
<td>Dry season average</td>
<td>42.84</td>
<td>84.80</td>
<td>46.89</td>
<td>0.20</td>
<td>10.30</td>
<td>2.84</td>
<td>2.78</td>
</tr>
<tr>
<td>Flood season average</td>
<td>99.10</td>
<td>95.37</td>
<td>49.26</td>
<td>0.19</td>
<td>26.76</td>
<td>6.89</td>
<td>5.55</td>
</tr>
<tr>
<td>Flood season sum</td>
<td>650.84</td>
<td>582.79</td>
<td>297.96</td>
<td>1.10</td>
<td>177.01</td>
<td>45.41</td>
<td>36.05</td>
</tr>
<tr>
<td>Annual sum</td>
<td>907.89</td>
<td>1091.60</td>
<td>579.31</td>
<td>2.32</td>
<td>238.83</td>
<td>62.46</td>
<td>52.75</td>
</tr>
<tr>
<td>Flood/year</td>
<td>71.69</td>
<td>53.39</td>
<td>51.43</td>
<td>47.33</td>
<td>74.12</td>
<td>72.71</td>
<td>68.34</td>
</tr>
</tbody>
</table>

5. Inter-annual variations of dissolved silicate, nitrogen, and phosphorus impacts of dams

Yearly mean DSiC recorded at Datong station ranges from 75.66 to 125.00 μmol l⁻¹, (on average, 93.10 μmol l⁻¹) (Fig. 4A). A decreasing trend of yearly mean DSiC occurs obviously from the 1960s to 1990s. Yearly mean DSi flux ranges from 1.13 × 10⁶ t y⁻¹ to 3.39 × 10⁶ t y⁻¹ (on average, 2.38 × 10⁶ t y⁻¹), and also show a decreasing trend with time (Fig. 4B). Over the long term, the inter-annual variations in runoff have kept stable as evidenced in the lower YRDB (Fig. 4C). This proposes the control of DSiC on decreasing trend of DSi flux over long time period, rather than runoff. The exceptional case is in the 1998, when historical flood with a 60-year recurrence occurred. More than 80,000 m³ s⁻¹ discharge was recorded at Datong, and this may cause
for 16% of the annual Yangtze runoff discharging into the sea. With the increase of reservoirs storage and runoff residence time, the assimilation and fixation of DSi by phytoplankton will greatly increase in the near future.

The pp-model, using Eqs. (3) and (4) shows that fixed DSi has increased annually since 1950, and the total fixed DSi in 162 reservoirs reached $0.31 \times 10^6$ t until 2002 (Fig. 5A; Table 2), accounting for 13.08% ($2.60 \times 10^6$ t) of DSi mean flux at Datong station, entering into the sea (Fig. 3D). Therefore, DSi fixation in reservoirs is inevitable in terms of potential deterioration of river basin environment. Given the example of Three-Gorges reservoir, i.e. the water storage of 30.90 km$^3$, impoundment water will fix $4.57 \times 10^9$ mol DSi annually, or $0.64 \times 10^4$ t DSi (Table 2). The Yangtze River basin water will receive additional 184 new big programming dams to prevent floods and generate electricity, to meet rapid growth of population and economic development over the whole drainage basin (Changjiang River Statistical Almanac Committee, 1992–2004). This plans the volume of programming dams of 222.83 km$^3$ (Table 2), and will induce further decrease in DSi flux into the sea.

The dams have also resulted in a decrease in sediment flux to the sea. The yearly sediment load recorded at Datong station has verified this sharp reduction since the 1950s (Fig. 5B). Consequently, silting in reservoirs greatly lowered DSiC and flux.

![Fig. 4. Inter-annual variations of DSi, DIN, and DIP recorded at downstream-most Datong station of the lower Yangtze, since 1950. (A) Yearly mean DSiC; (B) DSi flux; (C) runoff discharge; (D) DIN concentration; (E) DIP concentration; (F) DIN flux; (G) DIP flux; (H) N/Si; and (I) P/Si (data sources: Changjiang River Water Resource Committee, 1955–1985; Changjiang River Statistical Almanac Committee, 1992–2004).](image)

![Fig. 5. A) accumulative volume of 162 major reservoirs of the YRDB since 1950; and B) sediment load fluctuations recorded at Datong (data sources: Changjiang River Water Resource Committee, 1955–1985; Changjiang River General Thesaurus Compilation Committee, 1999; Changjiang River Statistical Almanac Committee, 1992–2004).](image)
6. Impacts on estuarine ecosystem

Changes in the proportions of dissolved Si, N, and P in riverine nutrient loads will cause shifts of phytoplankton populations in water bodies, and will accelerate algal growth through eutrophication, and consequently degrade water quality through oxygen depletion (Officer and Ryther, 1980). The increasing N:Si ratio (Fig. 4H) could exacerbate eutrophication by reducing the potential for diatom growth in favor of noxious flagellates, and also increase in P:Si ratio (Fig. 4I) is closely associated with significant blooms of non-siliceous algae in coastal waters worldwide (Officer and Ryther, 1980).

Decreasing DSi and increasing DIN and DIP flux into the East China Sea have impacted the predominant algae species, the frequency of red tides and the composition of red tide phytoplankton (Figs. 4B,F,G; Table 3). There were 75 red tides recorded in the coastal seas adjacent to the Yangtze estuary during 1933−2002, i.e. 2 times in 1933−1979, 33 times in the 1990s and 21 times in 2000−2002. On average, red tide frequency changes from 0.04 during 1933−1979 to 7.0 during 2000−2002. The total area of red tide has now reached 34,308 km², which is significantly expanded while comparing with the historical records (Table 3).

In addition, dominant species in red tides appeared 101 times, of them, the ratio of *Skeletonema costatum* (siliceous alga) to the total predominant species lessened continuously, from 33% during the 1980s to 31% during the 1990s, to 24% during 2000−2002 (Table 3). In contrast, the ratio of *Pro- rocentrum dentatum* (non-siliceous alga) to the total predominant species, increased rapidly, from 12.5% in the 1980s to 14.3% in the 1990s, to 36% during 2000−2002. The ratio of *Noctiluca scintillans* (non-siliceous alga) to the total predominant species remained fairly constant, from 54% during the 1980s to 55% during the 1990s, but reduced to 40% in 2000−2002. It is therefore that the changes of siliceous and non-siliceous algae can largely deteriorate the coastal ecosystem, in the views of reducing DSi flux into the sea with time (Fig. 4).

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7. Conclusions

The DSiC in the Yangtze River basin primarily depends on the weathering of igneous rocks, which occurs widely in some major tributaries, including Puduhe, Jialingjiang, Yuanjiang, Ganjiang, Xiushui, Xinshui, and lower Hanjiang. The long-term data indicate that the upper Yangtze reach (above Yichang), and Dongting and Poyang Lakes serve as the DSI flux sink, while the middle and lower Yangtze main river channels act as DSI flux source.

Seasonal variations of DSiC in the river basin has linked to discharge dilution, but DIN and DIP, which seems much likely to be controlled by chemical fertilizer used in the basin, especially after the 1980s. The flux of nutrients entering into the sea during the flood season is 74% for DSi, 73% for DIN and 68% DIP.

Annual DSIc and DSI flux have decreased sharply since the 1950s. Approximately, 0.31 × 10^6 t y^-1 of silicon — 13.08% of the total silicon flux entering into the sea have been fixed by phytoplankton within 162 big reservoirs in the Yangtze River basin. On the other hand, DIN and DIP concentration and flux have a slow increase in the 1950s, but a great increase after the 1980s, due to chemical fertilizer application.

Increasing DIN and DIP flux from the river basin yields more non-siliceous algae (dominated by *Prorocentrum dentatum*) in the red tide off the Yangtze River mouth and the East China Sea recently. Non-siliceous algae are replacing the dominant siliceous algae (represented by *Skeletonema costatum*) in red tide, due to remarkably declining DSI flux in the upstream reservoirs. This change accelerates the frequency of red tide occurrence off the river mouth.

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References


