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Long-term changes in nutrient concentrations of the Changjiang River and principal tributaries

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Abstract We present long-term nutrient data on the Changjiang River (Yangtze River) at six hydrological stations and eight principal tributaries during the period 1958–1985. Three patterns of temporal changes were observed in nitrate(NO_3^-) and nitrite (NO_2^-): minimal variations in the upper catchment area, rapid increases in the middle watershed towards the end of the 1970s, and a gradual increase in the lower drainage basin. Prior to the 1970s, the level of NO_3^- throughout the Changjiang River system remained fairly constant. In the 1980s, however, this changed, with the lowest values in the upper Changjiang changing rapidly to the highest in the middle reaches and then declining slowly but steadily in the lower courses. Compared to NO_3^- and NO_2^-, ammonium (NH_4^+) and soluble reactive phosphorus (SRP) showed smaller increases or no long-term variations, while dissolved silica (DSi) concentration generally decreased at most stations. These three patterns of NO_3^- and NO_2^- changes in the Changjiang River system were reflective of the difference in chemical fertilizer use and landscape features (e.g., slope, soil type and water body area) of the drainage basins of the primary tributaries. The decreases in DSi were most likely attributed to a reduction in suspended sediment loading due to dam constructions and increasing diatom consumption. The increase in NO_3^- and NO_2^- with a reduction in DSi concentrations in the Changjiang River could have significant effects on the stoichiometric balance of nutrients delivered to the East China Sea and the ecosystem in this dynamic region.

Keywords Changjiang River · Nitrogen · Phosphorus · Silicon · Si:N

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Introduction

Disproportional changes in nutrient concentrations in rivers as a result of human disturbance (e.g., fertilizer and detergent use, and dam construction) have caused hypoxia, frequent harmful algal blooms, and losses in fishery production in their receiving water bodies (Justic et al. 1995; Rabalais et al. 1996; Hungborg et al. 1997; Turner et al. 2003). Over the last several decades, China has experienced rapid increases in chemical fertilizer use and human population (Xing and Zhu 2002; Yan et al. 2003). During this same period, thousands of dams have been constructed for the triple functions of energy production (hydrological plants), agricultural irrigation, and flood control (Yang et al. 2004; Xu et al. 2006). The constructions of the Gezhouba Dam and Three-Gorges Dam on the mainstream of the Changjiang River (Yangtze River) in recent years have caused drastic reductions in sediment fluxes (Xu et al. 2006) and a shift in the phytoplankton species in East China Sea (Gong et al. 2006). This development emphasizes how imperative it is to know how human activities can affect nutrient concentration and composition in order to predict future nutrient changes in the rivers of China, the largest country in the world in terms of chemical fertilizer use and human population.

A major focus of research on river biogeochemistry in China in recent years is change in the levels of nutrients in the Changjiang River, the largest river in China, and their effects on the environment (Zhang et al. 1994, 1999; Duan et al. 2000a, b; Liu et al. 2003; Shen et al. 2003; Yan et al. 2003; Li et al. 2007). An elevated nitrate (NO_3^-) level was found in the river mouth in the mid-1980s, which was comparable to the levels found in some polluted rivers in Europe and North America (Zhang et al. 1994). Duan et al. (2000a, b) and Yan et al. (2003) reported a several-fold increase in the concentration and flux of dissolved inorganic nitrogen (DIN) between 1962 and 1997 at the Datong hydrological station. They also found a good correlation between the concentration of NO_3^- in the Changjiang River and chemical fertilizer use or manure production in the drainage basin. However, these researchers based their conclusions on just a single station, and other nutrients, especially dissolved silica (DSi), were largely ignored. A one-time investigation on spatial variability of nutrients in the Changjiang River mainstream and primary tributaries was subsequently carried out in May 1997, and the highest NO_3^- and soluble reactive phosphorus (SRP) concentrations were found in the mainstream and tributaries of the middle Changjiang River (Zhang et al. 1999; Liu et al. 2003). However, the question of why NO_3^- and SRP concentration were/are the highest in the middle reachers of the Changjiang River remains unanswered, and little is known on spatial variations in nutrients of the Changjiang River in other seasons.

This study examines long-term historical datasets (1958–1985) on nutrient levels (NO_3^- and NO_2^-, NH_4^+, SRP, and DSi) of the Changjiang River system from 14 hydrological stations. These datasets provide an overview of the temporal and spatial variations in nutrient concentrations of this river. Our data reveal three different patterns of long-term changes in NO_3^- and NO_2^- in the upper, middle and lower drainage basins as well as decreases in DSi and Si:N ratio in the mainstream and some of the tributaries of the Changjiang River. To explain temporal and spatial variations in nutrients of the Changjiang River, the effects of human disturbance (e.g. chemical fertilizer application and dam construction) and watershed characteristics (e.g. land use, topography, soil types) are also discussed.

Methods

Study area

The Changjiang River is the largest river on the Euro-Asia continent and ones of the largest rivers globally in terms of its length (6300 km), drainage area (1.8×10^6 km^2), fresh water (900×10^9 m^3 year^{-1}), and sediment discharge (0.5×10^9 tonnes year^{-1}) (Milliman 1991). The drainage basin of the Changjiang River covers 20% of the total area of China, 24% of the nation's arable land, 32% of chemical nitrogen (N) fertilizer use, and 35% of the nation's crop production and population in 1992 (Xing and Zhu 2002; Liu et al. 2003). The Changjiang River is divided into three courses (the upper, the middle and the lower) in this study (Fig. 1), based on landscape features and nutrient chemistry. The upper Changjiang River, also called the Jinshajiang River, drains most of the plateau and high mountains. The middle Changjiang River (called the upper Changjiang in some publications) drains a combination of hills, mountains and highlands; the Minjiang, Tuojiang, Jialingjiang, and Wujiang rivers are the principal tributaries in this region. The large tributaries in the lower reaches (below Yichang, but the course from Yichang to Hukou is called the middle Changjiang in some publications) include the Lake Dongting system, the Hanjiang River, and the Lake Poyong system, draining mostly lowland plains and hills. Approximately 20–25% of the water discharge of the Changjiang River below Yichang flows to Lake Dongting during the summer high-discharge period through four channels and comes back to the

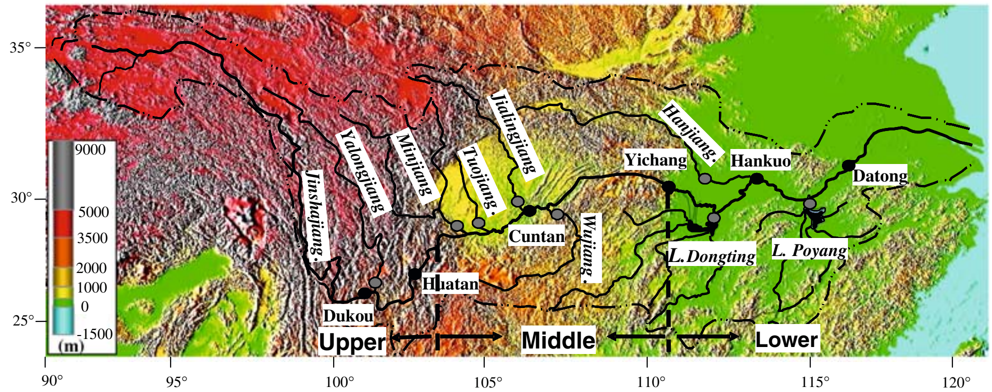


Fig. 1 Map of the Changjiang River drainage basin showing three courses of the mainstream and principle tributaries. The location of six hydrological stations on the mainstream and eight on the primary tributaries (including Lake Dongting, and Lake Poyang) are also shown as *solid circles*. Topographic map are adapted from http://www.ngdc.noaa.gov/mgg/image/2minrelief.html

Changjiang River at Chenglingji above Hankou (Annual Hydrologic Reports of China 1958–1985, Beijing, PCR; Zhao et al. 2005).

Data collection

The data of nutrients (NO_3^- and NO_2^-, NH_4^+, SRP, and DSi) and water discharge of the Changjiang River mainstream and tributaries are collected from the open files of Annual Hydrologic Reports of China (1958–1985). Since 1956, the Ministry of Water of China has set up more than 500 hydrological monitoring stations in succession in the Changjiang River system, and samples were collected and analyzed for water quality in some stations as early as 1958. In this study, six hydrological stations in the mainstream of Changjiang River were selected: Dukou and Huatan in the upper course, Cuntan and Yichang in the middle course, and Hankou and Datong in the lower course (Fig. 1). Eight hydrological stations nearest to the confluences with the Changjiang River were chosen as sampling sites for the eight primary tributaries (including two lake systems). The drainage area above these eight stations accounts for 82% of total area of the Changjiang River. The amount of data on the nutrients in these datasets differs among these stations. Hankou has the longest dataset, extending back to 1958, while nutrient data on Lake Dongting and the Yalongjiang are generally available only after mid-1970. Most datasets were began in the 1960s and are generally not continuous during the whole period. Nutrient data after 1985 are not open to the public, although DIN data during the 1985–1997 period at Datong Hydrological Station have been reported (Duan et al. 2000a; Yan et al. 2003). In order to compare consistent data from all the stations, in this study we report only nutrient data for the period between 1958 and 1985.

Water samples were collected by the staff of the Changjiang hydrological stations, and the nutrients were analyzed in five laboratories under the authority of the Yangtze River Water Resource Commission, following the methods described by Duan et al. (2000a), Yan et al. (2003), and Li et al. (2007). In general, mixed water samples (surface and bottom layers) were collected at each station at a frequency of once per several months during low-flow period to several times per month during the flooding season. Duplicate water samples were collected from the composite and filtered through filter papers prior to analysis. The filtrates were analyzed for NO_3^- (by the phenol disulfonic acid method), NO_2^- (by the Griess reagent method), NH_4^+ (by Nessler reagent method), SRP (by differences in ionic balance or by flame spectrometry), and DSi (by the molybdenum blue method). The original precision of the data for DRP and DSi were particularly rough. The initial units of micrograms per liter given in the Hydrological Yearbooks for NO_3^-, NO_2^-, NH_4^+, P_2O_5 or SiO_2 were converted to micromole per liter (or μM), which enabled atomic nutrient ratios to be calculated.

Nutrient fluxes were estimated by multiplying monthly average nutrient concentrations with the total water discharge of the same month, under the assumption that nutrient concentrations were constant throughout this period. Nutrient fluxes of the Lake Dongting system were calculated by subtracting 23% of the Changjiang River's fluxes at Yichang from the measured fluxes at the mouth of the lake because 20–25% of the middle Changjiang discharge flowed to this lake. Nutrient budgets were made for three sections of the Changjiang River and for Lakes Poyang and Dongting. Nutrient inputs were taken as the summary of annual nutrient fluxes of all tributaries, and they were extrapolated from the nutrient inputs of the primary tributary by multiplying the ratio of output discharge to the discharge of the primary tributaries (called calibrated inputs). Nutrient outputs of the upper Changjiang and Lakes Poyang and Dongting were annual fluxes of the Changjiang River at Huatan, of Lake Poyang at Hukou and of Lake Dongting at Chenglingji, respectively. Nutrient outputs of the middle and lower Changjaing River were calculated as the difference in nutrient fluxes between Yichang and Huatan, and between Datong and Yichang, respectively. Because the nutrient concentration of the primary tributaries of Lake Dongting were not measured at hydrological stations close to the river mouth, we multiplied the total water discharge of five primary tributaries (Xiangjiang, Yuanjiang, Zishui, Lishui, and Miluojiang) by the average nutrient concentrations at ten locations far above the confluences; consequently, the nutrient inputs to Lake Dongting may be largely biased.

Watershed nutrient yields for each tributary were calculated by dividing the annual nutrient fluxes of the river with the drainage area. Data on land use, population density, and chemical fertilizer use in the watersheds of principal tributaries were adapted from 'Compilation of Social and Economical Data of the Changjiang Drainage Basin' (China State Statistical Bureau 1985, Beijing, PRC), and they are only available for 1983. Data on the human population, fertilizer use and cropland area of the Changjiang drainage basin from 1958 to 1985 are based on *Annual Reports of China* (China State Statistical Bureau 1978–1985, Beijing, PRC). For the period of 1979–1985, these were calculated from area-normalized data of each province; the data before 1979 were obtained from values of the whole country, assuming that the percentages of the Changjiang Basin to the whole country before 1979 equaled the average values of the period 1979–1985.

Results

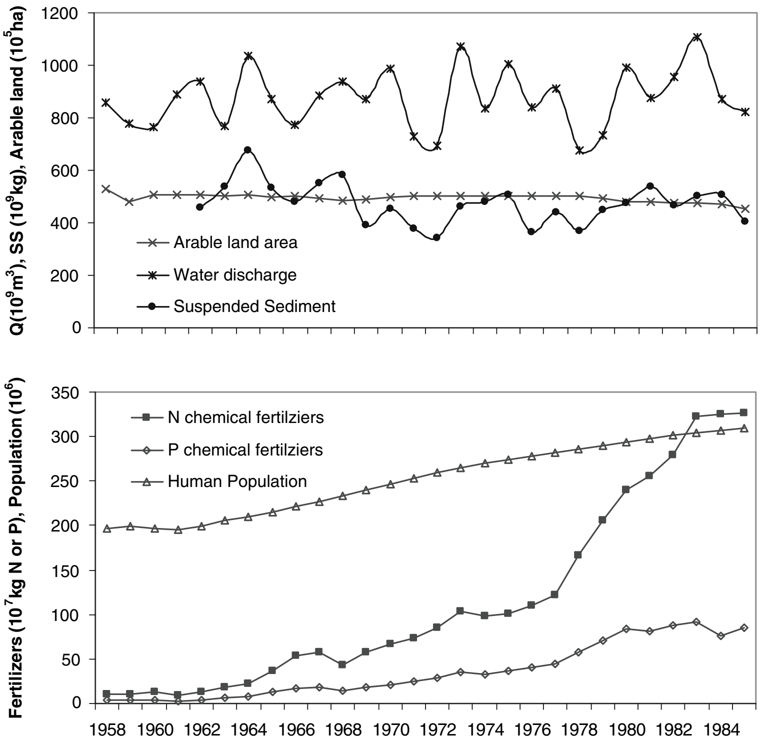
Long-term changes in river water discharge and watershed parameters

The annual water discharge of the Changjiang River varied from 675 to 1106 × 10^9 m^3 [coefficient of variation (CV) = 13%] between 1958 and 1985, and no long-term change in water discharge was observed (Fig. 2). Concurrently, the fluxes in suspended sediment (SS) decreased by 16% from 557 × 10^7 (mean of 1962–1964) to 470 × 10^7 m^3 (mean of 1983–1985). Conversely, N and phosphorus (P) chemical fertilizer usage in the Changjiang River Basin increased by 30-fold (from 12.5 × 10^7 in 1958 to 327 × 10^7 kg in 1985) and 23-fold (from 3.6 × 10^7 in 1958 to 85 × 10^7 kg in 1985), respectively. The most rapid increase in N chemical fertilizer use was observed during the 1978–1980 period, at which time it was an average of 39.3 × 10^7 kg $year^{-1}$, compared to 7.5 × 10^7 kg $year^{-1}$ in the early 1970s and 17.4 × 10^7 kg $year^{-1}$ between 1981 and 1985. During this 28-year period, the human population increased much slower (by 58%), while the area of arable land experienced a 14% decrease.

Long-term variations in nutrient concentrations and Si:N ratio

Three patterns of long-term changes in NO_3^- and NO_2^- concentrations were observed in the Changjiang River mainstream and its primary tributaries during the period 1958–1985 (Figs. 3, 5). In the upper Changjiang mainstream (Dukou and Huatan) and tributary (Yalongjiang River), NO_3^- (Fig. 3 and 5) and NO_2^- concentrations (Fig. 4) were close to the background levels of global rivers (NO_3^-<25 μM, NO_2^-<0.6 μM) and remained largely unchanged during the study period. In the middle reaches (Cuntan and Yichang), the levels of$NO_3^-$and NO_2^- were the same as those in the upper Changjiang before the 1970s, but they increased drastically towards the end of the 1970s from 20 and 0.4 μM (mean values unless otherwise stated) in 1978 to 45

Fig. 2 Annual water discharge (Q) and suspended sediment load (SS) of the Changjiang River at Datong hydrological station, and human population, annual chemical fertilizer (N and P) use and arable land area in the Changjiang drainage basin above Datong from 1958 to 1985



and 1.0 μM in 1980 (Figs. 3, 4). The change in NO_3^- levels in the primary tributaries of middle Changjiang (Minjiang River, Tuojiang River, Jialingjiang River and Wujiang River) followed the same pattern as the Changjiang mainstream (Fig. 5). NO_3^- and NO_2^- concentrations in the lower course of Changjiang (Hankou and Datong) were also as low as the those in upper reaches before the 1970s, but they increased gradually and slowly (slope for NO_3^- : 0.07–0.11 compared to 0.14–0.17 for the middle Changjiang; slope for NO_2^- : 0.0015 compared to 0.0031 for the middle Changjiang), from 20 and 0.6 μM in 1978 to 25 and 0.7 μM in 1980, respectively. Similar to the lower Changjiang mainstream, the primary tributary (Hanjiang River) or lakes (Lake Dongting) also experienced a gradual but slow increase in NO_3^- levels (slope: 0.08–0.09 compared to 0.09–0.65 for the tributaries of the middle Changjiang) (Fig. 5). Thus, average NO_3^- concentrations throughout the whole Changjiang River system were fairly consistent (8–13 μM) before the 1970s. This pattern changed during the 1980s (Fig. 6), with low concentrations (<20 μM) remaining in the upper Changjiang (Dukou and Huatan), rapidly increasing levels occurring in the middle reach – with the highest concentration (49.4 μM) found at Cuntan following input from three NO_3^--enriched tributaries (the Minjiang, Tuojiang, and Jialingjiang Rivers), and slowly decreasing levels occurring after Cuntan following mixing with the outflow from Lake Dongting, the Hanjiang River, and Lake Poyang, which were relatively low in NO_3^-.

Compared to NO_3^- and NO_2^-, NH_4^+ concentrations in many stations of the Changjiang River system did not change significantly between 1958 and 1985 (Figs. 3 and 5). One exception was the Tuojiang River, which experienced a drastic increase in NH_4^+ in late 1970s, increasing to the maximum concentration (average = 34.5 μM) in the Changjiang River system. Smaller increases in NH_4^+ were also observed in the Changjiang mainstream at Dukou and Cutan, the Wujiang River, and Lake Dongting. Spatially, NH_4^+ concentrations were generally higher in the lower Changjiang mainstream and tributaries than tn the upper and middle reaches of the Changjiang River system ($p < 0.05$, t-test, two-tailed) if the Tuojiang River was excluded from the dataset (Fig. 6).

Long-term changes in SRP concentration were not consistent in the Changjiang River mainstream (Fig. 7). SRP did not change significantly at Huatan,

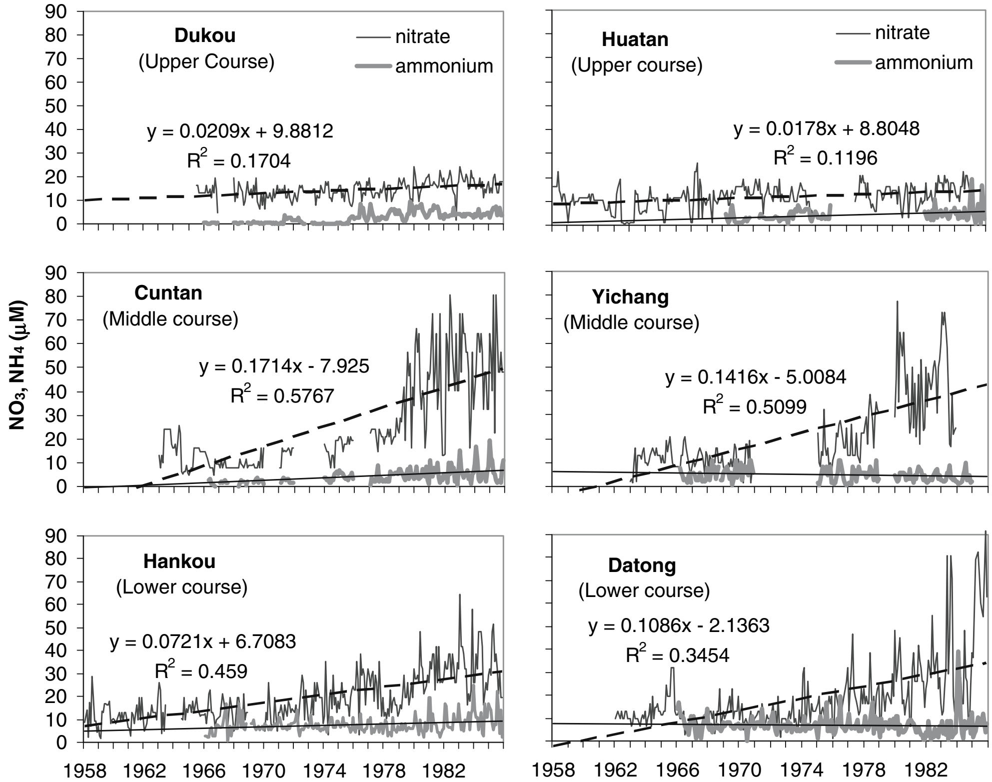


Fig. 3 Concentrations of nitrate and ammonium in the six mainstream hydrological stations of the Changjiang River from 1958 to 1985. Trend of long-term changes in nitrate and ammonium are also indicated with *straight lines* and *equations* (for nitrate)

Yichang, and Hankou ($R^2 < 0.01$, slope < 0.0001), but it did increase at the other stations – Dukou, Cutan, and Datong ($R^2 > 0.11$, slope > 0.0005). SRP concentrations in most of the primary tributaries did not change significantly during the study period ($R^2 < 0.02$, slope < 0.0002) except in the Tuojiang River ($R^2 = 0.36$, slope = 0.003), where SRP rose rapidly from 0.2 μM in 1978 to 0.7 μM in 1980, thereby becoming the highest in the Changjiang River system. Spatially, SRP concentrations were generally lower in the tributaries than in the Changjiang River mainstream ($p < 0.05$, *t*-test, two-tailed) if the Tuojiang River was excluded from the dataset (Fig. 6).

In contrast to NO_3^-, the concentrations of DSi decreased slightly in the Changjiang River mainstream at the middle and lower reaches during the study period (Fig. 8). The largest decrease (by 25%) occurred in Datong (slope = −0.19, $R^2 = 0.19$), followed in descending order by Cuntan (slope = −0.13, $R^2 = 0.08$), Hankou (slope = −0.10, $R^2 = 0.05$), and Yichang (slope = −0.05, $R^2 = 0.02$). Apparent long-term decreases in DSi concentration were also found in the tributaries, such as in the Wujiang (slope = −0.16, $R^2 = 0.07$) and Jialingjiang rivers (slope = −0.15, $R^2 = 0.08$), and Lakes Dongting (slope = −0.11, $R^2 = 0.04$) and Poyang (slope = −0.12, $R^2 = 0.03$) (Fig. 9). Compared to other nutrients, DSi displayed smaller spatial variations (96–149 μM in 1958–1973; 81–172 μM in 1980–1985), but significantly higher values ($p < 0.05$, *t*-test, two-tailed) were observed in the upper Changjiang River (Fig. 6).

The Si:N ratio showed no apparent long-term change at the stations of the upper Changjiang River (Dukou and Huatan) (slope > −0.002, $R^2 < 0.003$; Fig. 10); however, it did decrease substantially at the other four mainstream stations (slope < −0.025, $R^2 > 0.47$) and most primary tributaries (slope < −0.024, $R^2 > 0.20$; Fig. 11). The general trend was a decrease from 10–15 in the early 1960s to 5 in the 1970s, and then to 2–3 in the early 1980s. Before the 1970s, the Si:N ratio was in general consistently

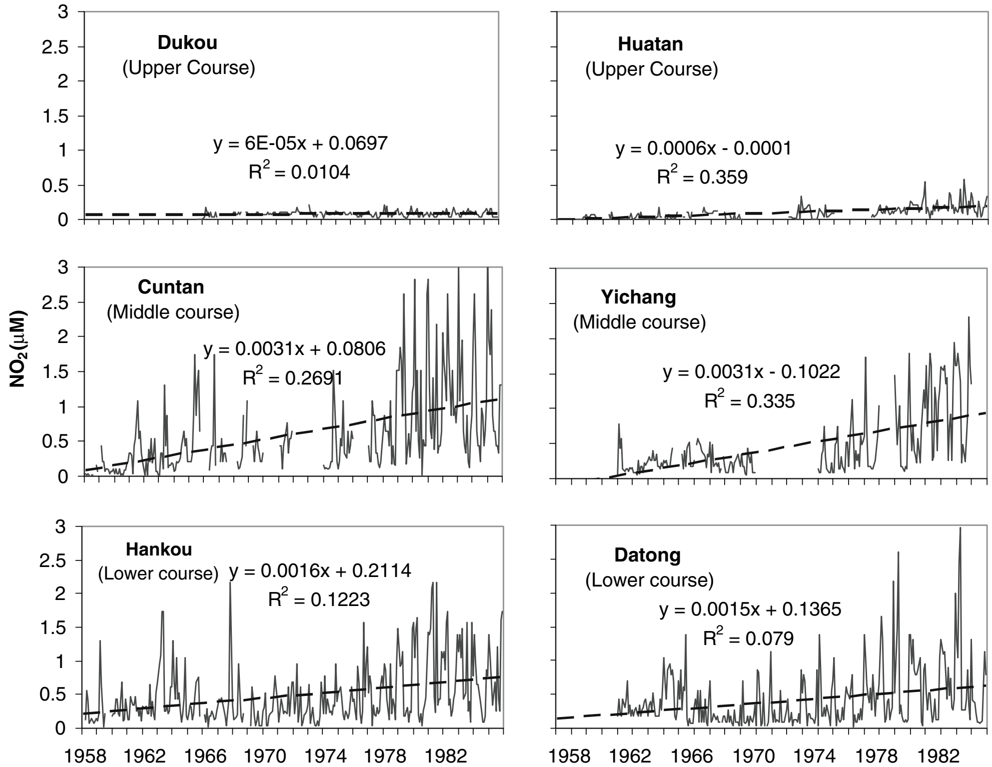


Fig. 4 Concentrations of nitrite in the mainstream hydrological stations of the Changjiang River from 1958 to 1985. Trend of long-term changes in nitrite are also indicateded with *straight lines* and *equations*

high throughout the Changjiang River system, with little spatial variability (6–11) (Fig. 11). Increasing variability appeared during 1980–1985, with a drop in the highest values in the upper Changjiang sites (8.9) to the lowest in the middle reaches (1.7), and then a slight increase (2.4) in the lower reaches.

Nutrient budgets for Changjiang River and Lakes Poyang and Dongting

The budgets of annual water discharge (Q), DIN, SRP, and DSi in the upper, middle, and lower Changjiang River are listed in Table 1 for the period 1980–1985. The upper, middle, and lower courses contributed to 12, 37, and 51% of the water discharge of the Changjiang River, respectively. Compared to water discharge, the primary tributaries of the middle Changjiang contributed relatively more DIN, and the whole upper basin accounted for 52% of the Changjiang's DIN flux; the tributaries of the upper Changjiang and Lake Poyang provided relatively less DIN than water to the Changjiang River. The distribution pattern of SRP and DSi resembled to that of water discharge, but the upper Changjiang contributed relatively more DSi while the lower basin exported relatively more SRP to the Changjiang River compared with water discharge. The DIN budget was not balanced in the middle and lower Changjiang and SPR in the all three courses, with the inputs from tributaries (water discharge-normalized) less than outputs to downstream. The DSi budget was only balanced in the lower Changjiang River.

To calculate nutrient retention in Lake Poyang and Dongting, nutrient inputs budgets of the two lakes were also calculated for 1980 when all nutrient data were available (Table 2). According to our results, 1.007×10^9 moles of DIN and 3.169×10^9 moles of DSi were retained in Lake Poyang, accounting for 26 and 17% of their inputs to the lake, respectively. The budgets for Lake Dongting showed that 2.821×10^9 moles of DIN, 0.055×10^9 moles of SRP and 0.93×10^9 moles of DSi were trapped in the lake in 1980, accounting for 18, 69, and 3% of their total inputs to the lake, respectively.

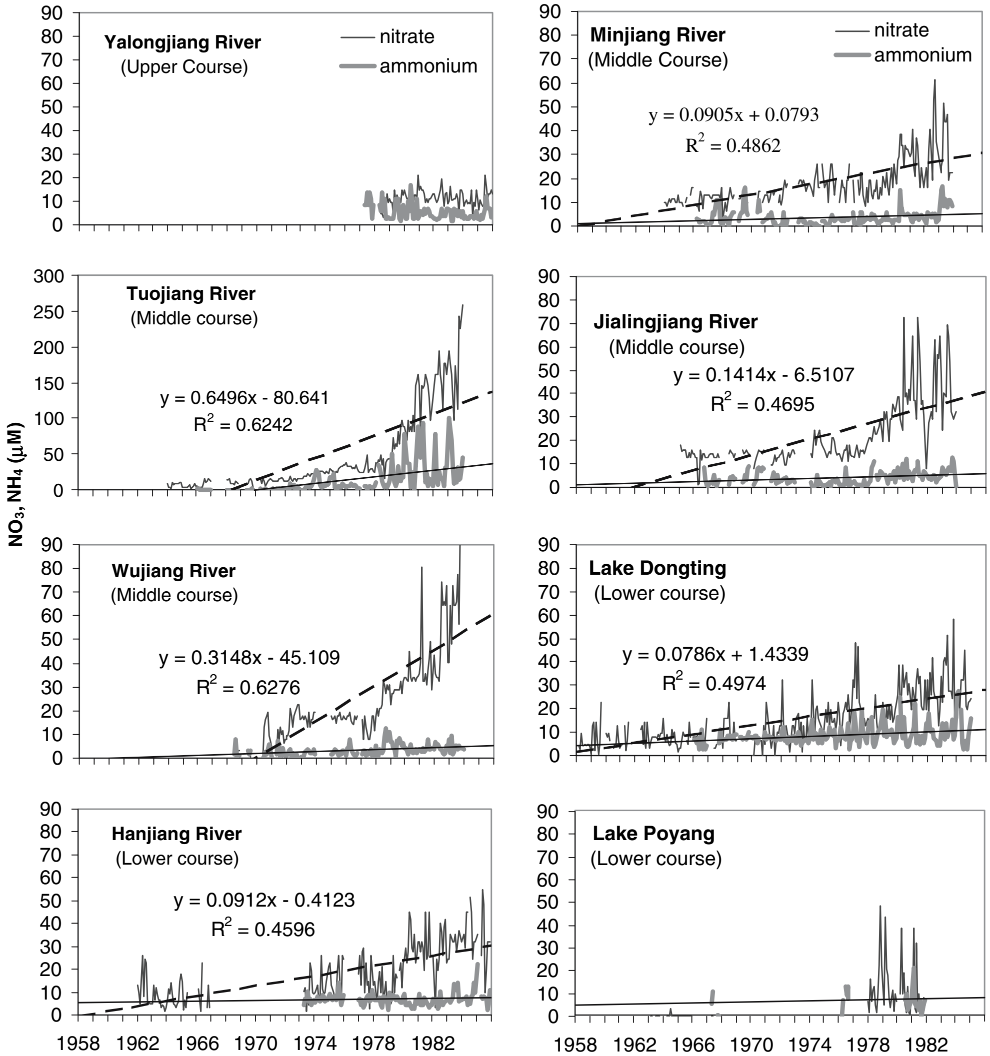


Fig. 5 Concentrations of nitrate and ammonium in the eight primary tributaries or lakes of the Changjiang River from 1958 to 1985. Trend of long-term changes in nitrate and ammonium are also indicated with *straight lines* and *equations* (for nitrate)

Nutrient yields and basin parameters for primary tributaries

Nutrient yields and possible controlling parameters of the drainage basins of the principal tributaries (the upper Changjiang–Jinshajiang is also listed) are listed in Table 3. In general, the upper Changjiang basins (Jinshajiang and Yalongjiang) were characterized by the lowest DIN yields, percentage of arable land, population density, and chemical fertilizer use and the highest forest + grassland%. The smallest basin of the Tuojiang River showed the opposite trend. The middle Changjiang watersheds (Tuojiang, Wujiang and Jialingjiang, Minjiang) were significantly higher in terms of DIN yield and lower in water area% than the watersheds of the lower Changjiang (e.g., Lakes Dongting and Poyang), but there were no significant differences in the other basin characteristics.

For the watersheds of upper Changjiang and eight primary tributaries (n = 9), DIN yield was negatively correlated with forest + grassland% (R = −0.84), and positively correlated with arable land% (n = 0.88) and population density (R = 0.95) (Table 4). Although DIN yield increased with chemical fertilizer use, chemical fertilizer use accounted only for 36% of the

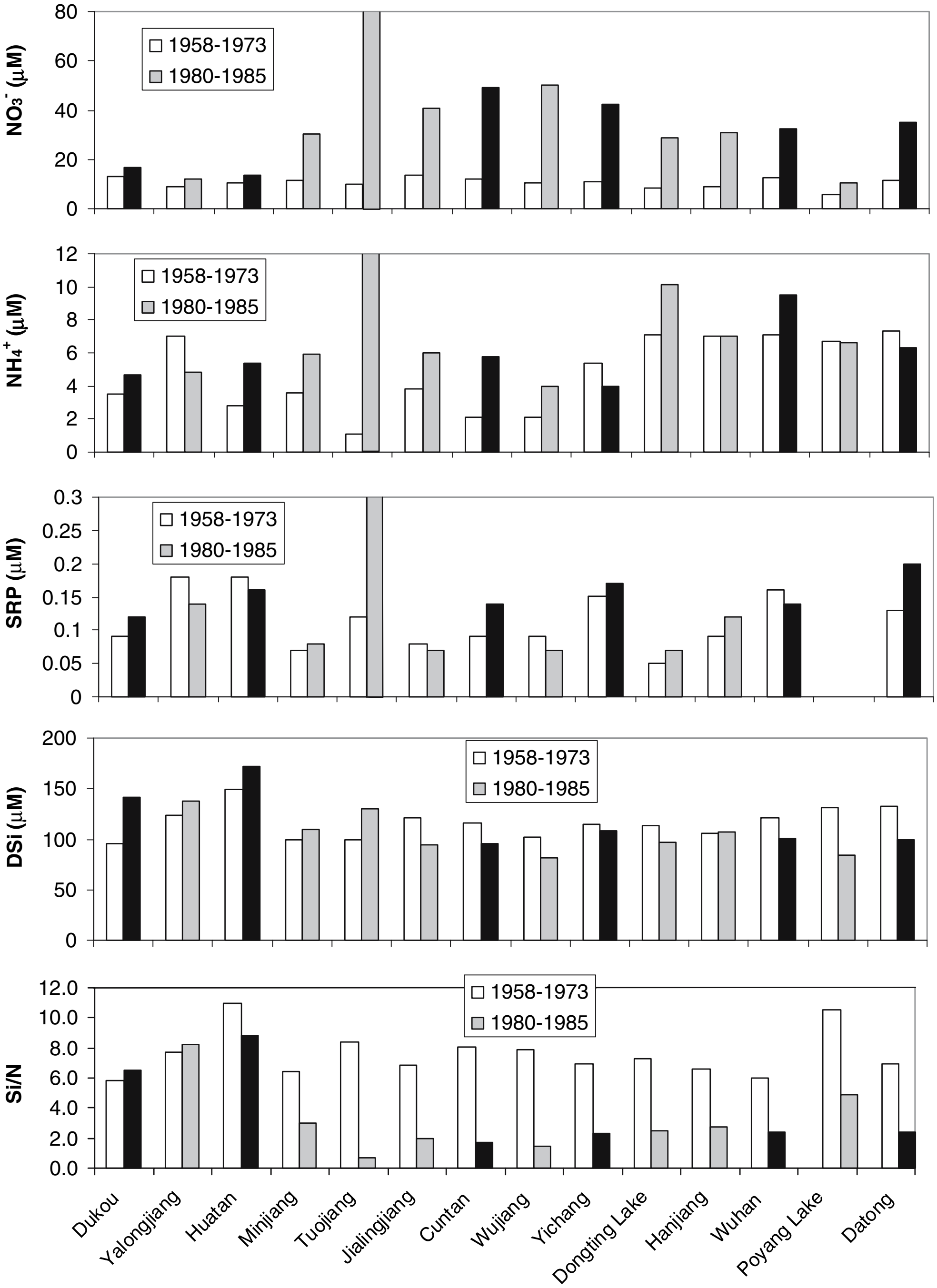


Fig. 6 Downstream variations in the concentration of nitrate, soluble reactive phosphorus (*SPR*), dissolved silica (*DSi*), and Si:N ratios along the mainstream of the Changjiang River during the periods of 1958–1973 and 1980–1985. The concentrations and ratios are the means of the corresponding periods. The average nitrate and SRP concentrations in the Tuojiang River were above the maximum of the *y*-axis, 144 and 0.62 μM, respectively. *Black columns* Mainstream stations, *gray columns* principal tributaries or lakes

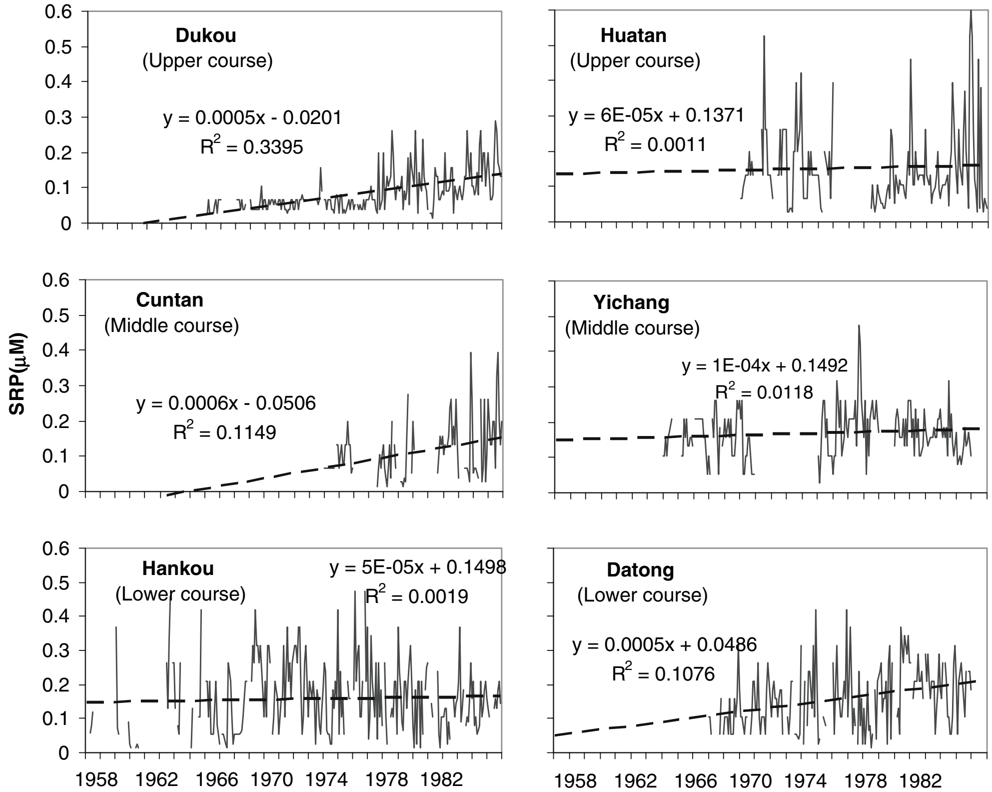


Fig. 7 Concentrations of SRP at the six mainstream hydrological stations of the Changjiang River system from 1958 to 1985. Trend of long-term changes in SRP are also indicated with *straight lines* and *equations*

variations in DIN yield. Compared to DIN, SPR and DSi yields in the watersheds of the Changjiang primary tributaries were in a relatively narrower range (Table 3), and their correlation with basin parameters was generally not as significant as DIN (Table 4). However, the correlation between DSi yield and runoff was more significant than that with DIN and SRP, and the correlation coefficient would be greatly improved (R = 0.87) if the data of the Tuojiang were excluded.

Discussion

Effects of chemical fertilizer use on long-term changes in NO_3^- and NO_2^- concentrations

The overall increases in NO_3^- and NO_2^- concentrations in the Changjiang River system during the 1958–1985 study period was largely attributed to the increasing use of chemical fertilizer in the drainage basin. This conclusion is partly based on the positive relationship between watershed chemical fertilizer use and annual NO_3^- and NO_2^- concentrations at Datong (R^2 = 0.63 and 0.44, respectively; n = 20). This relationship became much stronger (R^2 = 0.966, n = 30) when more recent data (1986–1997) were added (Yan et al. 2003), indicating that chemical fertilizer use has become a more important control measure for NO_3^- concentration of the Changjiang River in recent years. This seems plausible because chemical fertilizer accounted for 80% of the total N inputs to the basin in 1997, compared to 60% in the early 1980s and 20% in the 1960s (Yan et al. 2003). In addition, the lack of correlation between NO_3^- concentration and arable land (this study) or green manure area (Yan et al. 2003) excludes the possibility that watershed N fixation by crops accounted for the increase in NO_3^- in the Changjiang River. On the other hand, the positive relationships between NO_3^- concentration at Datong and population (R^2 = 0.72, n = 20) or human and animal manure (Yan et al.

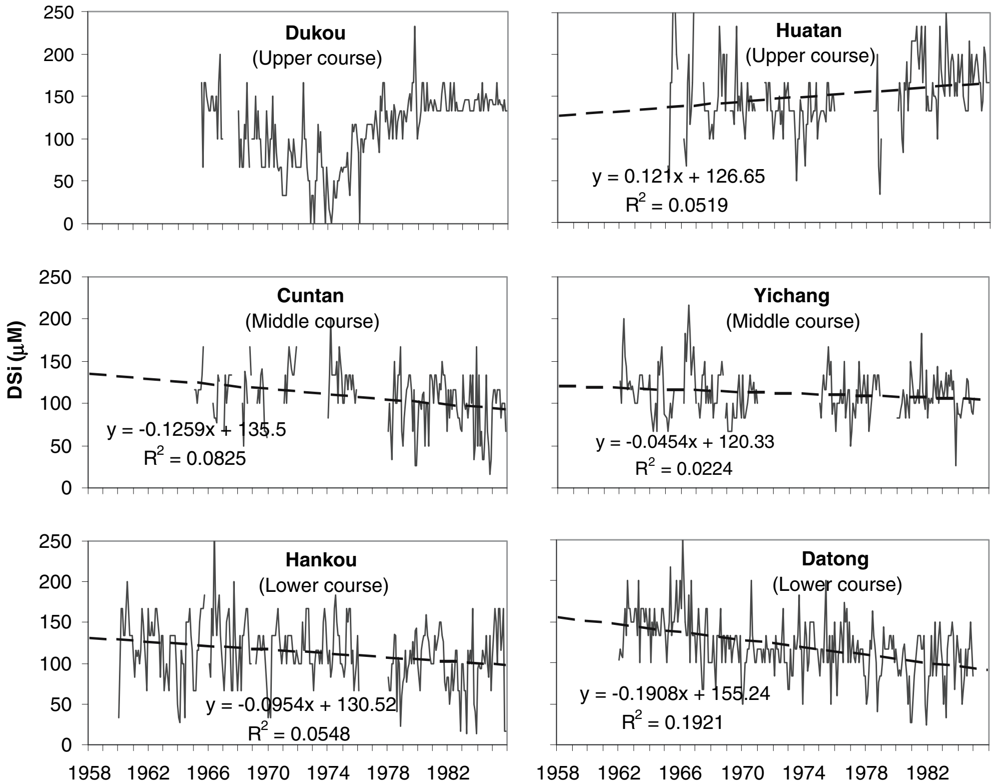


Fig. 8 Concentrations of DSi in the six mainstream hydrological stations of the Changjiang River from 1958 to 1985. Trend of long-term changes in DSi are also indicated with *straight lines* and *equations*

2003) indicate that manure N was also an important source for the Changjiang River NO_3^-. However, manure N was not a new N source but was converted from chemical fertilizer N (Yan et al. 2003), and thus the increase in manure N was eventually derived from increasing chemical fertilizer use.

Regional similarities in the long-term changes in NO_3^- and NO_2^- concentrations between the Changjiang mainstream and nearest upstream tributaries of the upper, middle, and lower courses (Figs. 4–6) suggested that these tributaries were the main providers of DIN to the Changjiang River. This assumption was confirmed by the nutrient budget of the Changjinag River (Table 1). Therefore, the three patterns of long-term changes in NO_3^- and NO_2^- concentrations of the Changjiang mainstream can be explained by chemical fertilizer use and the basin characteristics of the nearest upstream watersheds. For example, the lowest concentrations and minimal long-term changes in NO_3^- and NO_2^- in the stations of the upper Changjiang River likely resulted from the extremely low fertilizer use in the upper drainage basins. The upper Changjiang watersheds consist mainly of plateau and high mountains and were in a less-disturbed state (e.g., high forests + grasslands%, small area of arable lands, and lowest population density; Table 3). This lower degree of disturbance and extremely lower chemical fertilizer use indicated that these watersheds were likely N-limited. As a result, chemical fertilizer loss and, consequently, DIN yield in the upper Changjiang watersheds were the lowest among the areas studied, and NO_3^- and NO_2^- concentrations in the upper Changjiang River were the lowest and did not change during the study period. Additionally, the average NO_3^- concentration of the upper Changjiang River between 1980 and 1985 was comparable to that reported by Zhang et al. (1999) and Liu et al. (2003) (<20 μM) in May 1997. Thus, the level of NO_3^- in the upper Changjiang did not change during the subsequent 12 years even though chemical fertilizer use in the watershed tripled (Annual Reports of China, 1986–1997, Beijing, PRC), furthering suggesting the N-limited state of this region.

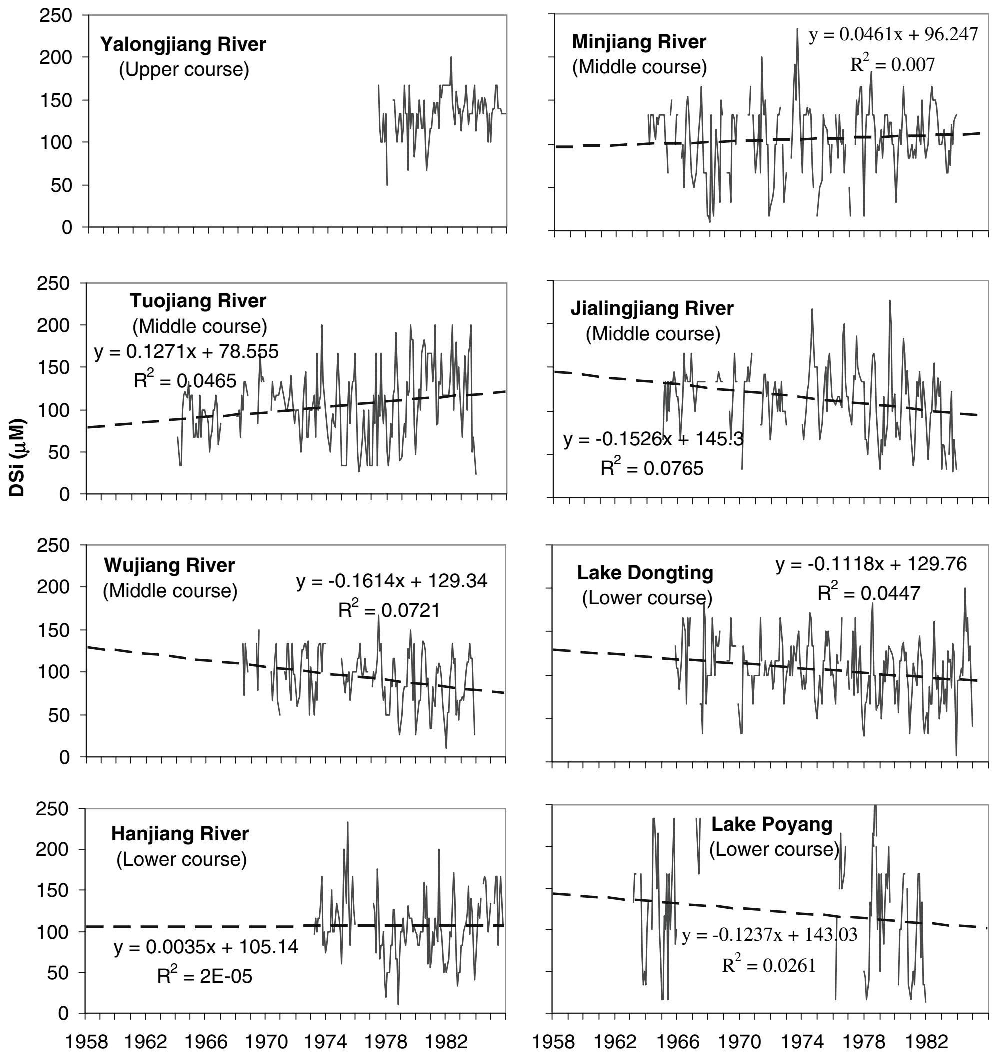


Fig. 9 Concentrations of DSi in the eight principal tributaries or lakes of the Changjiang River from 1958 to 1985. Trend of long-term changes in DSi are also indicated with *straight lines* and *equations*

The drastic increases in NO_3^- and NO_2^- concentrations in the tributaries and mainstream of the upper Changjiang River toward the end of the1970s were likely attributive to the rapid increase in chemical fertilizer use during the same period due to agricultural reforms in China. These reform, which began in 1978, distributed croplands that used to be cultivated by village communities to individual households (Prosterman et al. 1996) and resulted in an explosive increase in chemical fertilizer use – almost double within the first 3 years (1978–1980) (Fig. 2) – that exactly matched the rapid increases in NO_3^- and NO_2^- concentrations at the end of 1970s in the tributaries and mainstream of the middle Changjiang River (Figs. 3–5); in addition, NO_3^- and NO_2^- concentrations in the middle Changjiang River at Cuntan were highly correlated with chemical fertilizer use during 1958–1985 ($R^2 = 0.93$ and 0.78, respectively; $n = 20$). This matching was expected, considering the fact that the Chinese farmers were probably lack of skills in managing chemical fertilizer application in the first few years of agricultural reform. Enhanced chemical fertilizer use and this lack of fertilizer management skill consequently resulted in the enhanced loss of chemical fertilizers from croplands and consequent rapid increases in NO_3^- and NO_2^- concentrations in

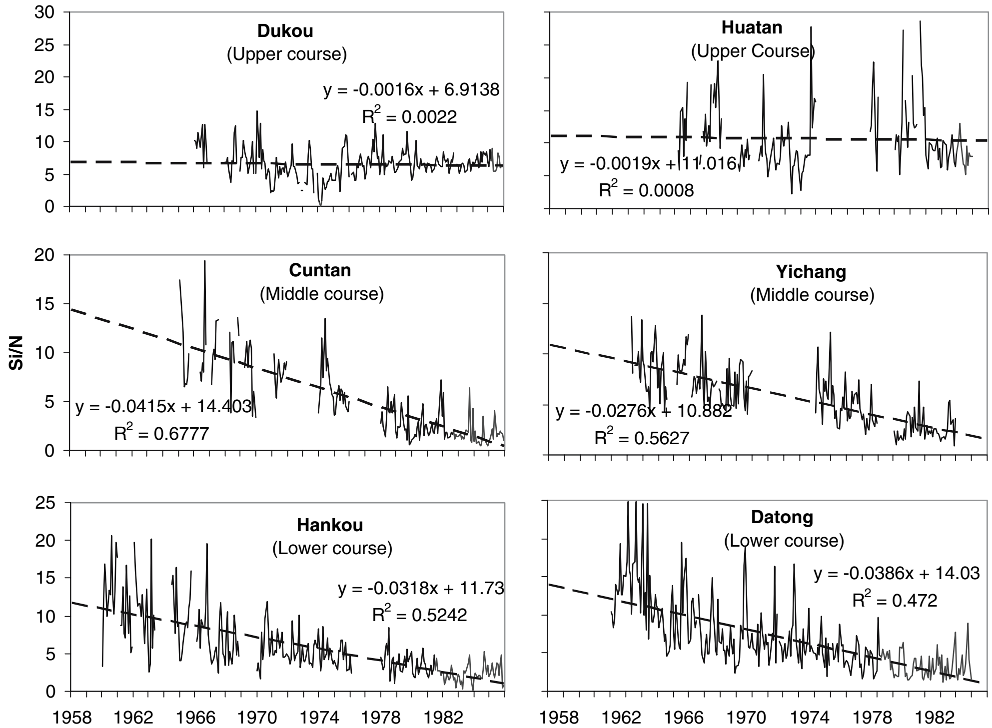


Fig. 10 Atomic ratio of DSi to dissolved inorganic N (DIN) (*Si:N*) in the six mainstream hydrological stations of the Changjiang River from 1958 to 1985. DIN includes nitrate, nitrite and ammonium. Trend of long-term changes in Si:N are also added with *straight lines* and *equations*

the middle Changjiang tributaries and mainstream towards the end of the 1970s.

Chemical fertilizer use seems not the sole controlling measure for the long-term changes in NO_3^- and NO_2^- concentrations in the Changjiang mainstream and tributaries. For example, NO_3^- and NO_2^- concentrations in the lower Changjiang River at Datong were not so highly correlated with chemical fertilizer use ($R^2 = 0.63$ and 0.44, $n = 33$) as those in the middle Changjiang at Cuntan. In particular, the gradual increases in NO_3^- and NO_2^- in the lower Changjiang mainstream and tributaries did not match the drastic increase in chemical fertilizer use at the end of the 1970s. Of course, gradual increase in chemical fertilizer use in the lower drainage basin could have contributed to these gradual increases, but there is no reason to assume that the change in chemical fertilizer use in the lower watersheds differed from that over the whole drainage basin. Lastly, chemical fertilizer use explained only 36% of the variations in DIN yield, and DIN yield of the watersheds of the upper Changjiang was significantly higher than those of the middle/lower Changjiang, although their chemical fertilizer use was not significantly different, suggesting an effect from other parameters.

Effects of basin characteristics on the long-term changes in NO_3^- and NO_2^-

The drastic increases in NO_3^- and NO_2^- toward the end of 1970s and the highest NO_3^- and NO_2^- levels in the middle Changjiang River also likely resulted from the steep slopes and alkaline soils in the upper drainage basin. For example, the middle Changjiang River drains a combination of hills, mountains, and highlands, and a large portion of croplands in the middle watersheds is located on hilly or steep mountainous slopes (see Fig. 1). Prior studies showed that chemical fertilizers applied to cropland in large-slope watersheds can be readily eroded or leached out to rivers (Yavtushenko et al. 1999; Fu et al. 2004; Teixeira and Misra 2005). Additionally, the main types of bed rock in this region are carbonate rock

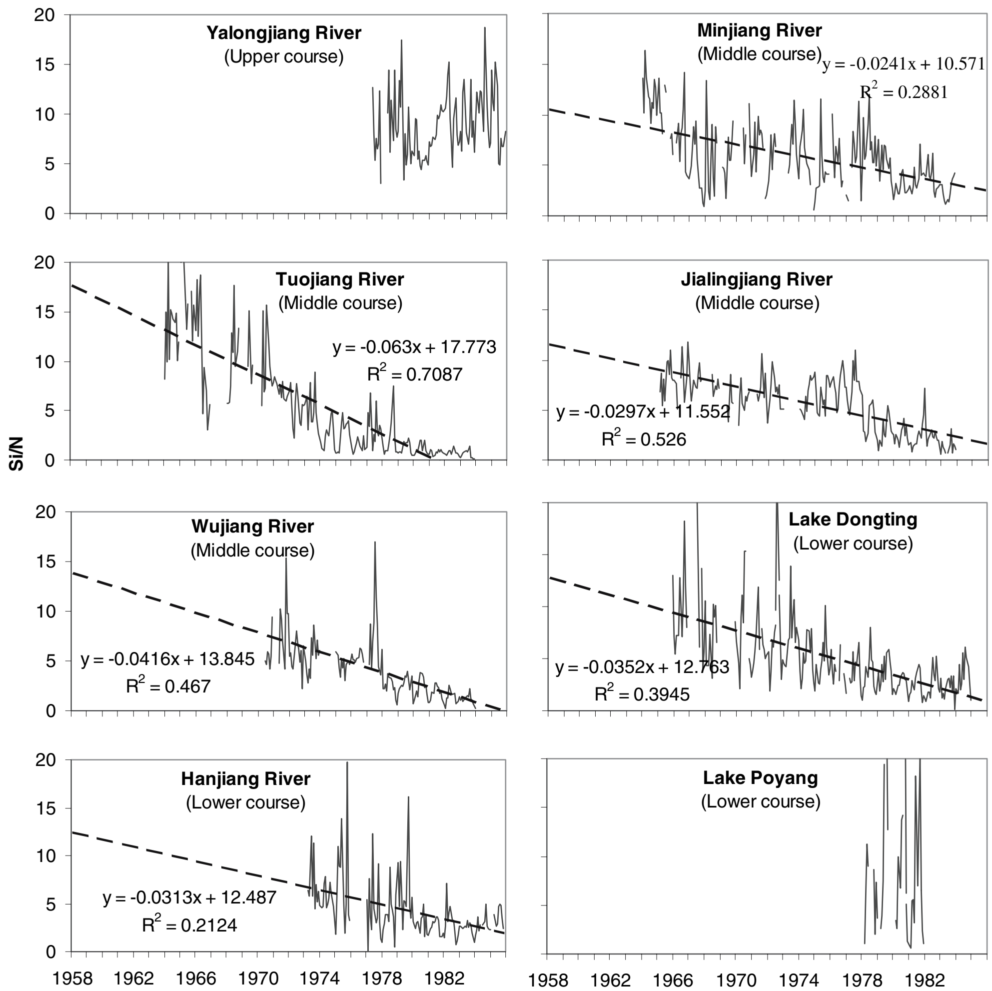


Fig. 11 Si:N ratio in the eight principal tributaries or lakes of the Changjiang River from 1958 to 1985. Trend of long-term changes in Si:N are also added with *straight lines* and *equations*

and alkaline purple shale (China Physical Geography Edit Committee 1981), and the pore water of soils derived from these types of rocks generally has a high pH (Li et al. 1978; Xi and Xu 1994). Field and laboratory studies have reported a significantly higher loss rate of chemical fertilizers (e.g. ammonium bicarbonate) from alkaline soils than from other types of soils because ammonia was more easily lost via volatilization in alkaline environments (Zhu et al. 1989; Roelcke et al. 1996). Since chemical N fertilizers applied to the croplands of the middle Changjiang watersheds was readily lost due to the steep slopes and alkaline soils, it is reasonable expect that the upper Changjiang watersheds would have higher DIN yields and, consequently, that the NO_3^- and NO_2^- concentrations in the upper Changjiang would be higher and more responsive to the drastic increase in chemical fertilizer use in the late 1970s.

Conversely, the flat topography, non-alkaline soils and relatively increased water area in the lower watersheds likely explain the lower NO_3^- and NO_2^- levels and gradual increases toward the end of the 1970s in the lower Changjiang tributaries and mainstream. The lower drainage basins of the Changjiang consist mostly of lowland plains and hills (Fig. 1), and the flat topography would allow for increased NO_3^- accumulation and denitrification in soils, groundwater, and surface water bodies. Investigations of groundwater quality have found a high level of NO_3^- in the lower Changjiang Basin (Xing and Zhu

Table 1 Annual water and nutrient budgets of the upper, and middle, and lower Changjiang River system during the study period 1980–1985

Section		Q[a,b]	%Q[c]	DIN[b]	%DIN[c]	SRP[b]	%SRP[c]	DSi[b]	%DSi[c]
Upper Changjiang	Jinshajiang	54	6	1.2	3	0.007	3	7.7	8
	Yalongjiang	49	5	0.8	2	0.007	4	6.8	7
	Summary	103	11	2.0	5	0.013	7	14.5	15
	Normalized input[d]	113	12	2.2	6	0.014	8	15.9	17
	Output	113	12	2.2	6	0.018	10	19.4	21
Middle Changjiang	Minjiang	86	9	3.2	8	0.007	4	9.4	10
	Tuojiang	14	2	2.7	7	0.009	5	1.8	2
	Jialingjiang	88	9	4.2	11	0.006	3	8.3	9
	Wujiang	53	6	2.9	7	0.004	2	4.3	5
	Summary	241	26	13.0	33	0.026	14	23.8	25
	Normalized input[d]	341	37	18.4	47	0.037	20	33.7	35
	Output	341	37	20.5	52	0.059	31	29.8	32
Lower Changjiang	Dongting[e]	170	18	5.5	14	0.012	6	15.2	16
	Hanjiang	55	6	2.1	5	0.007	4	5.9	6
	Poyang	130	14	2.3	6	–	–	10.9	12
	Summary	355	38	9.9	25	–	–	32.0	34
	Normalized input[d]	483	51	13.4	34	–	–	43.5	46
	Output	483	51	16.7	42	0.110	59	44.5	47

DIN, Dissolved inorganic nitrogen; SRP, soluble reactive phosphorus; DSi, dissolved silica

[a] Q is annual water discharge

[b] The units for water discharge and nutrient fluxes are 10^9 m^3 $year^{-1}$ and 10^9 mol $year^{-1}$, respectively

[c] Percentage of water discharge or nutrient fluxes to those of the Changjiang River at Datong

[d] Calibrated input refers to nutrient inputs calibrated with water discharge

[e] Water discharge and nutrient fluxes of the Lake Dongting system were calculated by subtracting 23% of Yichang's nutrient fluxes from the actually measured fluxes at Chenglingji

2002), and freshwater lakes and reservoirs in this area began to shift from an oligotrophic to a eutrotrophic state in the 1980s (Jin et al. 2005). Moreover, the lower level of ammonia volatilization in these non-alkaline soils, which are typical of this area (Li et al. 1978), facilitated a less direct DIN loss and temporary storage of fertilizer-derived N in the watersheds (Cai et al. 1985; Zhu et al. 1989). Conversely, the retention and sequestration of NO_3^- and NO_2^- in large lakes (e.g. Lake Donting) also likely contributed to their gradual increase in the lower Changjiang River because 20–25% of the discharge of the upper Changjiang River flows into Lake Dongting. A smaller percentage of water also flows to Lake Poyang during the summer high-flow period. Thus, a proportion of the NO_3^- and NO_2^- loads from the upper Changjiang River could be retained or sequestered in these lakes through algal consumption and denitrification in the lake sediments (Windolf et al. 1996; Svensson 1999; Saunders and Kalff 2001; Kaste and Dillon 2003), and the drastic increases in NO_3^- and NO_2^- observed towards the end of 1970s in the upper Changjiang were consequently buffered. The evidence supported these processes is (1) more than 18% of DIN inputs to Lakes Poyang and Dongting were retained or sequestrated (Table 2), and (2) NO_3^- and SRP concentrations of these lakes were significantly lower than those of the Changjiang mainstream (Fig. 6; Xu et al. 2004). Since fertilizer-derived N was more likely retained in the lower Changjiang watersheds and NO_3^- flux from upper Changjiang was partly sequestrated in Lakes Dongting and Poyang, DIN yields in the lower watersheds were lower and, consequently, NO_3^- and NO_2^- concentrations in the

Table 2 Nutrient budget for Lakes Poyang and Dongting in 1980

	[DIN][b]	[SRP][b]	[DSi][b]	Discharge[c]	DIN flux[c]	SRP flux[c]	DSi flux[c]
Poyang Lake							
Gangjiang[a]	19	–	107	69	1.709	–	8.186
Fuhe1	18	–	130	17	0.349	–	2.255
Xingjiang[a]	22	–	109	18	0.399	–	2.068
Chang-jiang[a]	16	–	147	5.4	0.090	–	0.936
Leanhe[a]	15	–	110	8.6	0.162	–	1.153
Xiushui[a]	13	–	107	6.8	0.116	–	0.788
Liaohe[a]	102	–	115	3.2	0.372	–	0.397
Total Input				127	3.197	–	15.783
Calibrated input[d]				154	3.862	–	19.069
Output	17		94	154	2.855	–	15.900
Balance[e]					1.007	–	3.169
Dongting							
Tributaries	46	0.28	85	201	9.273	0.056	17.085
Changjiang[f]	51	0.19	110	93	4.759	0.018	10.23
Total Input				294	14.031	0.074	27.315
Calibrated input[d]				320	15.275	0.080	29.730
Output	42	0.09	90	320	12.454	0.025	28.800
Balance[e]					2.821	0.055	0.930

[a] Gangjiang, Fuhe, Xingjiang, Changjiang, Leanhe, Xiushui and Laohe are primary tributaries flowing to Lake Poyang

[b] [DIN], [SRP], and [DSi] represent concentrations of DIN, SRP and DSi in μM

[c] Water discharge is in units of 10^9 m^3, and nutrient fluxes are in units of 10^9 moles

[d] Calibrated input refers to nutrient inputs calibrated with water discharge

[e] The balances are the difference between calibrated inputs and outputs, and positive values mean retaining in the lakes

[f] Nutrient concentrations of Changjiang are the average values at Yichang, and discharge is the summary of four channels connecting the Changjiang River with Lake Dongting

Table 3 Drainage area, average land use, population density, chemical fertilizer use, runoff and nutrient yields of the primary sub-drainage basins of the Changjiang River System

	Area	Arable%	Forest%	Water%	Popul.	Fertilizer	Run-off	DIN yield	SRP yield	DSi yield
Jinshajiang	37	3	49	0.4	39	0.7	30	4.5	0.053	40.1
Yalongjiang	11.8	2	52	1.1	16	0.1	42	7.0	0.058	57.6
Minjiang	13.3	7	58	1.3	104	1.4	68	23.8	0.052	70.5
Tuojiang	2.3	36	9	3.8	557	9.6	58	119.6	0.377	81.0
Jialingjiang	15.8	17	35	2.5	237	3.3	43	26.5	0.039	52.4
Wujiang	8.3	14	34	1.5	195	0.5	60	34.9	0.045	51.7
Dongting	20.7	15	49	5.4	241	4.3	80	26.8	0.057	73.5
Hanjiang	14.0	18	53	1.9	184	2.2	39	15.2	0.047	41.9
Poyang	16.2	14	37	10.3	193	11.0	89	13.9	–	67.6

Area, Drainage area is in units of 10^4 km^2; %arable, %forest, and water% refer to percentage of arable land, forest (including grassland) and water area, respectively; Popul., population density in units of people km^{-2}; fertilizer, fertilizer use per unit area, in units of t km^{-2} $year^{-1}$; runoff refers to river annual total water discharge normalized by drainage area and is in units of cm. Data for land use, population density, chemical fertilizer use, and runoff are adapted from Compilation of Social and Economical Data of the Changjiang Drainage Basin (edited by China State Statistical Bureau 1989, Beijing, PCR); these are available only for 1983 and 1980. Nutrient yields are in units of and 10^3 mol km^{-2} $year^{-1}$, and they are mean values for 1980–1985

Table 4 Correlation between parameters or yields of DIN and DSi of the basins of the nine primary tributaries of the Changjiang River

	Area	Arable%	Forest%	Water%	Popul.	Fertilizer	Runoff	DIN	SRP	DSi
Area	1									
Arable%	−0.60	1								
Forest%	0.49	−0.79	1							
Water%	−0.11	0.31	−0.29	1						
Popul.	−0.58	0.98	−0.84	0.33	1					
Fertilizer	−0.29	0.66	−0.64	0.85	0.69	1				
Runoff	−0.27	0.21	−0.16	0.80	0.27	0.61	1			
DIN	−0.62	0.88	−0.84	0.09	0.93	0.53	0.14	1		
SRP	−0.50	0.80	−0.82	0.39	0.85	0.88	0.15	0.95	1	
DSi	−0.51	0.48	−0.44	0.51	0.59	0.63	0.73	0.62	0.62	1

Area, Total drainage area; %arable, %forest, and water% refer to percentage of arable land, forest (including grassland) and water area, respectively; Popul., population density; fertilizer, chemical fertilizer usage per unit area per year; runoff, water discharge per unit area; DIN, SRP, and DSi are yields of DIN, SRP and DSi, respectively. Original data for this correlation matrix are from Table 3

lower Changjiang tributaries and mainstream were lower and not so responsive as those of the middle Changjiang River to the drastic increase in chemical fertilizer input in the late 1970s.

The downstream change in NO_3^- concentrations in the Changjiang River during 1980–1985, which was characterized by a sharp increase at the middle reaches followed by a slow decrease below Cuntan, were also found by Zhang et al. (1999) and Liu et al. (2003) during the downstream transit in May 1997. This downstream pattern suggested that the upper basin was the main source of NO_3^- in the Changjiang River system. This conclusion is consistent with the DIN budget of the river (Table 1) and the highest DIN yield in the upper watersheds (Table 3). In analogy, the upper watershed is also the principal contributor of yet another DIN-enriched river, the Mississippi, but the reason differs. For the Mississippi River, the upper basin is the highest in terms of chemical fertilizer use (Goolsby et al. 2000), while for the Changjiang River other basin characteristics were also important.

Long-term changes in NH_4^+ and SRP

Relatively smaller changes in NH_4^+ and SRP concentrations in the Changjiang River mainstream and tributaries suggested that these were not so affected as NO_3^- by the increasing chemical fertilizer use in drainage basin. Although NH_4^+ fertilizers were the main types of N fertilizers and chemical P fertilizer use in the Changjiang basin has also increased substantially in the study period (Fig. 2), fertilizer NH_4^+ and SRP were more likely to be absorbed onto soil particles or oxidized to NO_3^-, without much leaching out of the croplands (Ward 1996; Follett and Delgado 2002; Mainstone and Parr 2002). Actually, riverine NH_4^+ and SRP were more likely to be derived from industrial wastewater and urban effluent from urban area along rivers (Meybeck 1982; Antweiler et al. 1995). This is consistent with the higher SRP concentrations found at the mainstream stations of the Changjiang River than at the primary tributaries (Fig. 6). The apparent increase in NH_4^+ and SRP in the Tuojiang River probably resulted from high domestic effluent inputs because the watershed of the Tuojiang River was the highest in terms of human population density (Table 3). The reason for the increases in NH_4^+ and SRP in the Changjiang mainstream (Dukou, Cuntan and Datong) and other tributaries (e.g. Wujiang River) is not clear. A recent investigation in the Changjiang River system (Liu et al. 2003) found significantly higher SRP concentrations in the Tuojiang, Minjing, Jialingjiang and Wujiang Rivers (≥ 1 μM) than we did in this study, indicating that these rivers have been polluted in recent years in association with the development of urban area and industry in their drainage basins. They also found that NH_4^+ and SRP concentrations in the Changjiang mainstream reached their highest levels approximately 2200 km before the river mouth (a site in Three Gorges) – after these four tributaries had joined the Changjiaj River system – and then decreased quickly to very low levels in the lower reaches (Zhang et al. 1999; Liu et al. 2003). However, the concentration peaks of SRP and NH_4^+ at this location (2200 km) were not found during the period of 1958–1985 in this study (Fig. 6).

Decreases in DSi and Si:N ratio

The decrease in DSi in the Changjiang River mainstream and tributaries was likely attributable to damming in the drainage basin as well as diatom consumption in the large lakes. The positive correlation between DSi yield and surface runoff (Table 4) indicates a natural source of DSi and the control of chemical weathering in the Changjiang River System. Dam construction has caused a substantial decrease in suspended sediment and DSi load in many rivers in the world due to the particle active character and the lower generation rate of DSi in aquatic environments (Whaby and Bishara 1980; Turner and Rabalais 1991; Humborg et al. 1997; Duan and Bianchi 2006). Approximately 50,000 dams were constructed along the tributaries of the Changjiang River basin during the study period (Xu et al. 2006), and there was a concurrent decrease in both suspended sediment and DSi load ($R = 0.6$, $n = 23$) at the Datong hydrological station (Fig. 2). We also observed a long-term reduction in DSi concentration in the tributaries (the Wujiang and Jialingjiang Rivers) where large dams were build and in their downstream stations (Cuntan and Yichang) at the Changjiang River (Figs. 8, 9), highlighting the effect of dam construction on DSi concentration of the Changjiang River system. Additionally, increasing diatom consumption in large lakes appears to be another reason for DSi decrease in the Changjiang River. The decrease in DSi concentration in Lakes Poyang and Dongting (Fig. 9) along with a larger decrease rate in Datong than Hankou and Yichang (Fig. 8) suggests that changes in DSi concentration in these two lakes have affected DSi concentration in the mainstream of the Changjiang River. Our observation of no changes in the level of suspended sediment inputs into these lakes (data not shown) excluded the possibility of damming effect, while the increases in NO_3^- level in these lakes suggested diatom consumption might be a possible reason because diatom growth could be enhanced in high nutrient environments. The DSi budget in this (Table 2) and prior studies (Li et al. 2007) suggested that Lakes Poyang and Dongting were two sinks for riverine DSi and that the sequestration of DSi by diatoms in these lakes was possible.

The changes in the ratios of Si:N in the Changjiang River system during the study period was largely the result of the increase in NO_3^- concentration as well as – but to less degree – the decrease in DSi, with the underlying reason that DIN increased by several fold while DSi reduction was relatively small (<20%). The Si:N ratio in the lower Changjiang River continued to decrease from 2:1 in the 1980s (this study) to 1:1 in 1997 (Liu et al. 2003), with a further increase in NO_3^- (Yan et al. 2003) and minimal change in DSi (Liu et al. 2003). In recent years, sediment discharge of the Changjiag River (at Datong Station) has decreased by nearly half due to the completion of Three-Gorge Dam on the Changjiang mainstream in 2003 (Xu et al. 2006). As a result, large decreases in DSi and the Si:N ratio (from 1.5 in 1998 to 0.4 in 2004) were found in the Changjiang River plume. These decreases are similar to those found in other major rivers affected by dam constructions, such as the Nile (Whaby and Bishara 1980), the Mississippi (Turner and Rabalais 1991) and the Danube (Humborg et al. 1997). The decrease in DSi and Si:N ratio has greatly affected the ecosystem of the Changjiang River plume and East China Sea. For example, primary production in this region declined by 86% between 1998 and 2003, and the phytoplankton assemblage changed from being diatom-dominated to flagellate-dominated (Gong et al. 2006). Moreover, Li et al. (2007) estimated that 4.6×10^9 moles of DSi would consumed by diatoms in Three-Gorges Reservoir each year. Thus, with any further development of the phytoplankton population in the Three-Gorges Reservoir in the near future, the decreases in DSi concentration and Si:N ratio of the Changjiang River would continue and the ecosystem in China Sea would be further influenced.

Conclusions and implications

1) The three patterns of long-term changes in NO_3^- and NO_2^- concentrations in the Changjiang River mainstream and tributaries (upper, middle, and lower) reflect the different responses of the

watersheds to rapid increases in chemical fertilizer application that resulted from agricultural reform in the late 1970s in China.

2) The middle drainage basin was the main contributor of DIN to the Changjiang River in the 1980s. Heavy leaching of chemical fertilizers from croplands, due to the steeper slopes and alkaline soils, explain the higher DIN yields and rapid increases in NO_3^- and NO_2^- in the tributaries in middle drainage basin.
3) A significant increase in DIN concentration as well as a slight decrease in DSi in the Changjiang River system due to damming and diatom consumption has resulted in several-fold decreases in the Si:N ratio in the Changjiang mainstream and tributaries. With the full development of the Three-Gorges Dam, the decreases in DSi concentration and the Si:N ratio in the Changjiang River will continue, and the ecosystem of the Changjiang River Plume and East China Sea will be affected yet further.

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