

From the water sources of the Tibetan Plateau to the ocean: State of nutrients in the Changjiang linked to land use changes and climate variability

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Abstract Anthropogenic activity is an important driver of changes in the chemistry of nutrients (N, P, and Si) over watersheds at the sub-continental scale (e.g., 10^6 km²) and can markedly modify their seaward fluxes to the global ocean. In the present study, we reviewed the current status of nutrient chemistry in Changjiang (Yangtze River) based on data collected through 11 expeditions along a river course spanning 4,500 km and 15–20 major tributaries during 1997–2016 as well as monthly monitoring at the river mouth since 1980. The data were analyzed together with published results in the literature to synthesize the recent developments and current state of nutrients in the Changjiang. Previously published results from the Qinghai-Tibetan Plateau head waters were included to realize the systematics of nutrients for the whole drainage basin. Here, we showed that tributaries of the upper reaches of watersheds collectively determine the regime with high concentration and skewed species ratio of nutrients in the Changjiang mainstream, producing profound effects over a water course of 2,000–2,500 km further downstream and until the river mouth. Moreover, using data across the Three Gorges Reservoir (TGR) during 2003–2016, we evaluated the trapping and/or amplifying effects of the Three Gorges Dam (TGD) on nutrient chemistry. Tide-influenced river delta contributed an additional 20% dissolved inorganic phosphorus and 5–10% dissolved inorganic nitrogen and dissolved silicates to the seaward flux, dramatically affecting the stoichiometry of nutrients at the river mouth. Next, based on compiled data on supply and export, legacy nutrients were evaluated. Both nitrogen and phosphorus are in the accumulation phase over the watersheds, and the legacy nutrient fluxes are much higher than the annual riverine seaward fluxes. Finally, we demonstrated that the seaward fluxes of anthropogenic nutrients from the Changjiang exceed those from other top 10 largest rivers on this planet, which can be attributed to land use changes in the China over the last three to four decades.

Keywords Changjiang, Nutrient chemistry, Species ratio, Fluxes, Global river systems, Hysteresis effect, Legacy contributions

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1. Introduction

The nutrient chemistry of global river bridges changes in land use, surface water quality, and coastal ecosystem functions, producing profound effects on the sustainability of human societies and feedbacks to the atmosphere and ocean. Typically, the global riverine nutrient fluxes are estimated from hydrographic network data and/or using modeling approaches (Turner and Rabalais, 2003; Seitzinger et al., 2005; Gallo et al., 2015). Historically, riverine monitoring networks are set up in the mainstream and major tributaries, and the lowest gauge station is located in area beyond the tide-affected limit of the river course, considering the logistic difficulties of measuring current and hydrographic parameters (e.g., conductivity and total suspended matter) in areas affected by tide modulation, where water level variability and reversing flow are dominated by changes in tidal phase (Milliman and Farnsworth, 2011). Hence, nutrients from tide-affected coastal and/or deltaic areas are not properly evaluated in global land-ocean interaction analyses.

Another approach to understand riverine nutrient fluxes is through modeling studies (e.g., numerical simulation). As such, the link between driving forces and system responses can be parameterized and validated with observational data. However, although models can be finetuned to match field results, parameterizations based a few laboratory experiments and/or a limited number of observations as well as using data from different watersheds may generate outputs that are seriously biased with uncertainties, which are usually poorly constrained (Seitzinger et al., 2005; Yan et al., 2010). Moreover, the validation of model behaviors using data that cover limited spatial and temporal dimensions does not mean that numeric simulations can reproduce well what is expected in terms of nutrient biogeochemistry, such as the variability of chemical yields and changes in species ratio. In particular, in large rivers, such as Changjiang (here, “jiang” means “river” in Chinese), which has a drainage of sub-continental scale (i.e., $1.81 \times 10^6 \text{ km}^2$) and high diversity in terms of climate, landscape and human activities, there is a compromise between what we can expect from simulation outputs (e.g., annual fluxes of nutrients) and what would be the payoff (e.g., details of nutrient regime affected by ungauged areas) in numeric modeling, and the results must be viewed with caution (cf. Yan et al., 2010). Moreover, in numerical studies, parameterization is generally developed based on a limited number of case experiments and/or through data statistics, and the results are then extrapolated to the whole drainage basin at the sub-continental scale; hence, the potential bias of this approach remains unknown and can be significant.

Therefore, considering the diversity of land use types and

evolution of anthropogenic activities in watersheds, it can be difficult, if not impossible, to constrain the variability in temporal and spatial distribution of nutrient fluxes for a given river, and modeling approaches can generate results that are difficult to validate because of the lack of observational data. In other words, our ability to predict the future chemistry of riverine nutrients and their seaward fluxes in the context of global change remains limited.

The Changjiang (Yangtze River) stands out as a significant river system in the world for a number of reasons.

(1) It is the fourth largest river in terms of annual water flow (ca. $1 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$) on this planet. Changjiang has a vast catchment extending over an area of $1.81 \times 10^6 \text{ km}^2$ in the subtropical areas of the North Hemisphere. During 1950–2000, the seaward flux of total suspended matter (TSM) from Changjiang was $0.5 \times 10^9 \text{ tons yr}^{-1}$.

(2) The watersheds nourish 0.45×10^9 inhabitants, as they cover five of the world’s top 20 super-mega cities, namely Chengdu, Chongqing, Wuhan, Suzhou, and Shanghai, each with a population of $>10 \times 10^6$ people. The per capita GDP of Changjiang watersheds is approximately 50% higher than the Chinese national average (<http://data.stats.gov.cn/>).

(3) The watersheds have been extensively engineered for tributaries. As such, over 50×10^3 dams have been constructed in the drainage basin of Changjiang since the 1950s, including 200 large reservoirs, each with a capacity of $>0.1 \text{ km}^3$. The combined water storage of the reservoirs reaches $300 \times 10^9 \text{ m}^3$, accounting for nearly one-third of the annual water flow of Changjiang (Yang et al., 2005). Of the top 100 high dams worldwide, 15 are located in the sub-basins of Changjiang.

(4) The catchment areas of Changjiang are intensively farmed. Cultivated land extends across $309 \times 10^3 \text{ km}^2$ of the basin, and annual crop production reaches $0.29 \times 10^9 \text{ tons}$ (Bao and Fang, 2007; Ouyang and Zhu, 2011). Annual rice production and fresh water fisheries in this area account for 70% and 60%, respectively, for the whole China (<http://zh.wikipedia.org/wiki>).

To this end, we explored the contributions of nutrients from different parts of Changjiang catchments to evaluate anthropogenic impacts on riverine nutrient dynamics and examine the link between the seaward fluxes of nutrients and changes in land use over the last four decades. In the present study, hydrologic/hydrographic and chemical data were collected for the main channel and major tributaries of Changjiang since 1980. Integrated modeling was applied to examine these time-series data in greater detail and identify the different anthropogenic drivers, which allowed to compare nutrient sources and sinks and understand the nature of hysteresis of nutrient chemistry. Finally, we reviewed the trends of seaward fluxes of nutrients in Changjiang since the early 1960s and compared these with those in other large rivers worldwide.

2. Materials and methods

2.1 Sampling protocol

The present study is based on two types of observations: (1) field expeditions to the upstream area of Changjiang watersheds and (2) monitoring surveys close to the river mouth. Since 1997, 11 expeditions were undertaken from the river mouth upstream covering different hydrographic regimes, with three surveys each from the river mouth upstream over a water course of ca. 4,500 km plus 15 major tributaries and the remaining eight surveys of the middle and lower reaches, mostly from the Three Gorges Reservoir (TGR) down to the river mouth (Tables 1 and 2, Figure 1). This field work was aimed at collecting a series of water samples across Changjiang catchments, which would allow us to assess the temporal and spatial variability of the physical and chemical properties of the river. Moreover, three of these expeditions represented the critical stages of the Three Gorges Dam (TGD): (1) April to May 1997 before the enclosing of two coffer dams of TGD, (2) April to May 2003, a month before the lowering of TGD gates to store water in June 2003, and (3) August to October 2009, before the water level of TGD reservoir rises up to 175 m, entering full operation afterward.

At each sampling point, surface water was collected from the main channel using acid-cleaned 1-L HDPE bottles attached to a 5-m-long fishing rod from the bow side of boats. The bottles were rinsed five times with river water before collecting the samples. Depth profile samples were collected using a 5-L Niskin bottle attached to a nylon cable, and near-

bottom water was sampled at approximately 1 m above the riverbed. When sampling in the area of tributary confluence with the mainstream, we collected water samples from the tributary before it joins Changjiang, from the main channel before it receives the confluent inflow, and from downstream reaches of ca. 1 to 2 km to assess the influences of tributaries.

The *in situ* measurements included hydrographic parameters (i.e., temperature, depth, conductivity, and turbidity) and chemical (e.g., pH and dissolved oxygen) properties. The samples were filtered immediately through pre-cleaned polycarbonate membranes (pore size: 0.4 μm) in the field laboratory in a clean plastic tent under a HEPA filter with clean laminar airflow of Class 100. The filtrate used for nutrient analysis was fixed using saturated HgCl_2 solution and preserved in the dark at 4°C. Samples for particulate nitrogen (PN), total particulate phosphorus (TPP), and biogenic silica (BSi) were collected in pre-cleaned 2.5 L LDPE bottles. Samples for PN were filtered through pre-combusted GF/F filters and those for TPP and BSi through polycarbonate membranes. Water samples for oxygen and hydrogen isotope analyses (i.e., $\delta^{18}\text{O}$ and δD) were collected in 30 mL brown glass bottles with air-tight caps. Before collection, the bottles were rinsed *in situ* with water three times. Then, the bottles were immersed in the water, filled, and capped without air bubbles. After collection, the bottles were wrapped with parafilm and stored in the dark at 4°C.

In 1980, our monitoring surveys began in Nantong—a site close to the river mouth. Surface water samples were collected at three stations across the main channel of Chang-

Table 1 Summary of eleven expedition campaigns in the Changjiang drainage basin along the mainstream and major tributaries in 1997–2016

Time (MM–MM/YY)	Observation area	Water regime	Chemical measurements
04–05/1997	Panzhihua to Nantong	Transition	DIN, DIP, DSi, DON, DOP, PN, PP
04–05/2003	Lijiang to Nantong	Transition	DIN, DIP, DSi
10–11/2006	Yichang to Jiangyin	Transition	DIN, DIP, DSi
01/2008	Yichang to Xuliujing	Dry season	DIN, DIP, DSi
09/2008	Jiujiang to Xuliujing	Flood season	DIN, DIP, DSi
08–10/2009	Lijiang to Xuliujing	Floods to transition	DIN, DIP, DSi, DON, DOP, PN, PP, BSi
06/2010	Yichang to Xuliujing	Transition	DIN, DIP, DSi, DON, DOP, PN, PP, BSi
07–08/2010	Wanzhou to Jiangyin	Flood season	DIN, DIP, DSi, BSi
06–07/2011	Yichang to Jiangyin	Transition to floods	DIN, DIP, DSi
07–08/2012	Yichang to Xuliujing	Flood season	DIN, DIP, DSi
03–04/2016	Wanzhou to Xuliujing	Transition	DIN, DIP, DSi

Table 2 Summary of monitoring activities at river mouth (i.e., Nantong and Xuliujing) area of the Changjiang in 1980–2015

Area	Period (MM/YY)	Sampling frequency (Month)	Station (s)	Chemical measurements
Nantong	01/1980–12/1989	03, 08, 10	3	DIN
Nantong	01/1990–06/1996	01, 03, 05, 07, 09, 11	3	DIN
Nantong	07/1996–09/2003	01, 03, 05, 07, 09, 11	3	DIN, DIP, DSi
Xuliujing	After 05/2003	Monthly	1	DIN, DIP, DSi

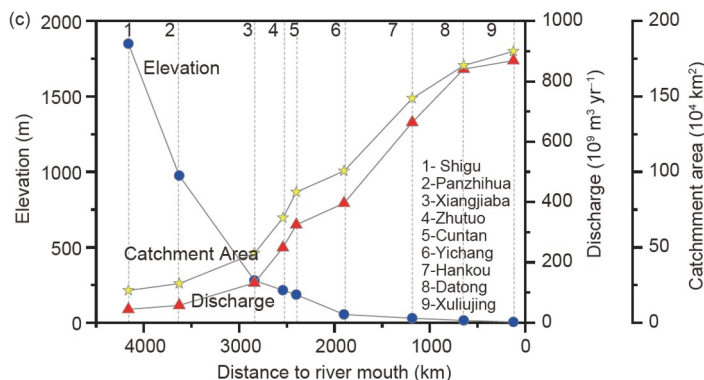
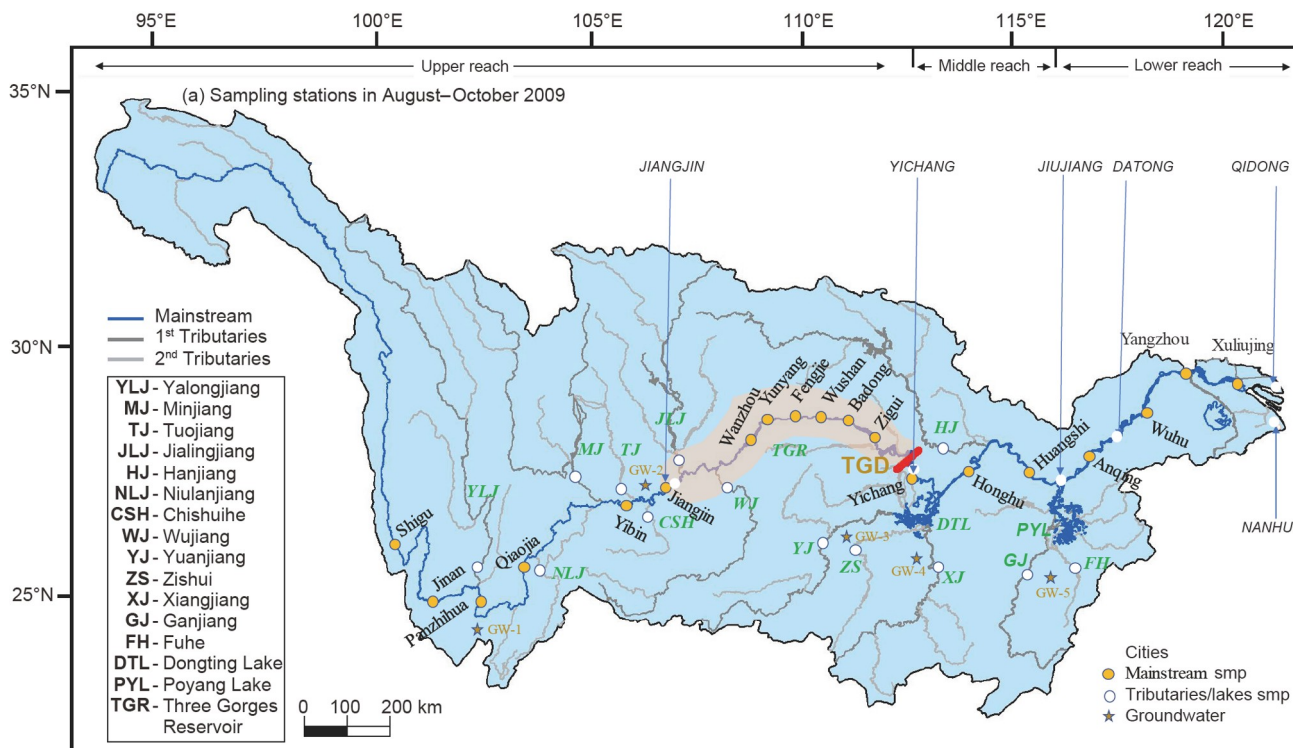


Figure 1 (Color online) (1a) Watersheds of the Changjiang (Yangtze River), with important sampling sites and the major tributaries sampled during field expeditions in 1997–2016, and the Nantong and Xuliujing (XLJ) monitoring stations are marked. (1b) Connection of the Qinghai-Tibetan Plateau (Qingzang Gaoyuan) and the watersheds of Changjiang, the figure is modified from the Ministry of Natural Resources (Web-site: <http://bzdt.ch.mnr.gov.cn/browse.html?picId=%224028b0625501ad13015501ad2bfc0065%22>). The pink and orange areas represents Qinghai-Tibetan Plateau and the watersheds of Changjiang, respectively. (1c) Changes in riverbed elevation, water discharge, and catchment area along the river course sampled. The geographic separation between the Changjiang and the East China Sea is defined by the line between the tips of Qidong (QD) to the north and Nanhui (NH) to the south at river mouth. Stations and name abbreviations include: SG (Shigu), JH (Jinhe), PZH (Panzhuhua), XJB (Xiangjiaba), YB (Yibin), JJ (Jiangjin), CD (Chengdu), CQ (Chongqing), CT (Cuntan), WZ (Wanzhou), YC (Yichang), YY (Yueyang), CS (Changsha), WH (Wuhan), NC (Nanchang), HK (Hukou), AQ (Anqing), HF (Hefei), DT (Datong), NJ (Nanjing), ZJ (Zhenjiang), SZ (Suzhou), XLJ (Xuliujing and Nantong), QD (Qidong), SH (Shanghai), and NH (Nanhui). Black letters show the geographic locations, and blue circles indicate the sampling stations along the river mainstream. The area marked by orange color indicates the water surface area of the Three Gorges Reservoir (TGR) with the dam (i.e., TGD) site that is ca. 30 km upstream the Yichang.

jiang in March, August, and October over the period from 1980 to 1989. Thereafter, the sampling frequency was increased to bi-monthly (i.e., January, March, May, July, September, and November) during 1990–2003 (Tables 1 and 2, Figure 1). Since May 2003, monthly surface and near-bottom water samples were collected from Xuliujing, which is nearly 20 km downstream from Nantong (Tables 1 and 2,

Figure 1). In the field, sample collection was completed during the ebb phase of neap tides to minimize the influence of seawater intrusion. *In situ* measurements included the same hydrographic and chemical properties as for the watershed samples described above; however, the samples were filtered upon return to the home laboratory, which is at 1-h drive from the sampling site.

2.2 Laboratory analysis and methods

In the laboratory, concentrations of dissolved inorganic species, including NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} (dissolved inorganic phosphorus, DIP), and silicates (dissolved silicates, DSi), in water samples were measured photometrically. Then, the concentration of dissolved inorganic nitrogen (DIN) was calculated as $\text{DIN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$ (Zhang et al., 1999; Liu et al., 2003). Further, samples were wet-digested to measure total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) using the boric acid-persulfate oxidation method (Grasshoff et al., 1999); the differences between the respective total concentrations and inorganic fractions were considered dissolved organic nitrogen (DON) and phosphorus (DOP). Samples collected before 2001 were measured manually, and those collected after 2001 were analyzed using the SKALAR SAN^{plus} continuous flow instrument.

Particulate inorganic phosphorus (PIP) in TSM was measured through extraction with 1.0 mol L^{-1} HCl at 25°C for 24 h. Total particulate phosphorus (TPP) was measured through extraction with 1.0 mol L^{-1} HCl following the combustion of particulate matter at 550°C for 2 h. Particulate organic phosphorus (POP) fraction was determined as the difference between TPP and PIP. The different forms of particulate phosphorus (PP) were measured spectrophotometrically (Liu et al., 2003). Our analysis of the Chinese coastal sediment standard (GBW 07314) revealed the total phosphorus concentration of $19.68 \pm 0.08 \mu\text{mol g}^{-1}$, which is close to the certified value (i.e., $20.85 \pm 1.97 \mu\text{mol g}^{-1}$). The analytical precision for phosphorus extraction was $<0.1\%$ for PIP and $<0.5\%$ for TPP (Liu et al., 2003). Nitrogen in total suspended matter (PN) was measured using a CHNOS (Vario EL III) analyzer.

Biogenic silica (BSi) in TSM was analyzed using alkaline leaching with correction for lithogenic silica (LSi) interference (Ragueneau et al., 2005; Liu et al., 2008). Briefly, the method involved quadruple wet alkaline digestion, followed by molybdate-blue spectrophotometry for Si (Grasshoff et al., 1999) and fluorometry for Al (Ren et al., 2001).

Isotope analyses ($\delta^{18}\text{O}$ and δD) of water samples were conducted a mass spectrometer (Delta^{plus} XP, Thermo Fisher Scientific Co.). The Vienna Standard Mean Ocean Water (V-SMOW) was used to calibrate the instrument. The isotope ratios were expressed as per mil (‰) deviation, with precision of 0.3‰ for $\delta^{18}\text{O}$ and 3.0‰ for δD .

Quality assurance (QA) and quality control (QC) procedures were realized via inter-laboratory comparisons, determination of national standards, and repeat measurements on selected samples, which showed a precision of $<5\%$ for all dissolved nutrient species. For detailed procedures of QA/QC in the present study, please refer to Appendix 1: Methods

(<https://link.springer.com>).

2.3 Data processing and statistics

The original data were collated in a Microsoft Excel spreadsheet for further processing. Regarding the temporal trends of nutrients, since data for water flow at Xuliujing were not officially available before 2004 and Datong is 650 km upstream from the river mouth, we used 12 sets (i.e., January to December) of monthly measurements to calculate the annual average for 2004–2015 in the present study.

Statistical analyses were performed using SPSS 10.0 and R Software, and the results were plotted using Excel, ArcGIS, and Kriging tools. We used multivariate statistical methods (i.e., cluster analysis, principal component analysis, multiple regression analysis, and factor analysis) to determine the significance of specific parameters in the data sets. Other data processing procedures used included time-series analysis and nonparametric statistics. We set statistical significance at 95% confidence interval throughout the data analysis, unless specified otherwise. We used additional more complex statistical methods as appropriate (e.g., one-way analysis of variance). Pearson correlation coefficient was used to examine the associations among the parameters, and two-tailed p values at 95% confidence intervals were used to infer the significance of results.

2.4 Estimation of riverine fluxes

Water flow data from Xuliujing became officially available after 2004 and were obtained from the Changjiang River Estuary Bureau of Hydrological and Water Resources Survey (Shanghai) of the Changjiang Water Resources Commission (CWRC). As Xuliujing is in the tide-affected area near the river mouth, water discharge was calculated by the integration of acoustic Doppler current profiler (ADCP) data from across the channel rather than using the conventional method based on discrete flow rate relative to the area of the transect section, which is used at Datong Hydrographic Station even today (Zhu et al., 2008; Yan et al., 2013). To calculate the annual nutrient fluxes, we multiplied the average of the surface and near-bottom nutrient concentrations by the monthly water discharge, all from Xuliujing, and then used the sum of each 12-month period.

2.5 Modeling

In the present study, we used a generalized additive model (GAM) to discriminate various factors affecting DIN and DIP in the Changjiang and selected variable candidates for simulation. Moving averages were used to smooth out the occasional sections of missing data, as required (Hopke et al., 2001; Peng and Dominici, 2008). Compared with the

other types of models, GAM offers a number of advantages, such as identifying the effect of hysteresis and eliminating co-linearity between variables, which is particularly important when analyzing anthropogenic drivers, because at the spatial scale of $1.81 \times 10^6 \text{ km}^2$, driving forces and response terms interact in a complex manner with uncertainties. Moreover, auto-regression enables the discrimination of unobserved factors and over-fitting in the analysis of time-series data, and the outliers and disturbance in the original data sets can also be identified.

Because dependent variables change with time and the trend may not be in parametric (e.g., linear) form, we introduced a nonlinear function to deal with the “time effect”. Specifically, we used nonparametric methods to constrain the inter-relationship between inputs and outputs at the seasonal and inter-annual scales, thereby elucidating the hysteretic nature of nutrient concentrations in the Changjiang. The GAM used in the present study can be expressed as follows:

$$y_t = \alpha + \beta x_{t-l} + s(t) + \varepsilon_t, \quad (1)$$

where y_t is the annual DIN and DIP concentration; α is the intercept; βx_{t-l} represents the effects of input factors of the model; subscript t is the time (year); l is the lag of year; $s(t)$ is the nonlinear time effect; and ε_t is the random error.

Before model application, we assigned x_{t-l} for different input factors, such as synthetic and organic fertilizers, atmospheric deposition, harvest, and aquaculture, among others (see Appendix 2: Atmospheric Depositions and Appendix 3: Source vs. Sink). The hysteresis factor “ l ” ranged from 0, indicating no lag, to 5 years in model runs. We then used a correlation coefficient matrix to examine the association between factors and stepwise regression to select the most important input variables for model simulation. Consequently, synthetic fertilizer and atmospheric deposition for DIN as well as synthetic and organic fertilizers for DIP were selected as parameters to simulate the impacts of drivers on nutrient chemistry in Changjiang.

Both concentrations and fluxes of nutrients in the river are affected by various factors in the watersheds, which interact and/or are cross-linked (i.e., auto-correlated relationship) and also change over time. These associations were analyzed using the ARIMAX (autoregressive integrated moving average with exogenous variables) model (Hamjah and Chowdhury, 2014):

$$y_t = \beta_1 x_{1,t-l_1} + \beta_2 x_{2,t-l_2} + \dots + \beta_k x_{k,t-l_k} + n_t, \quad (2)$$

where n_t represents the ARIMAX part of time series analysis.

$$\text{Let } w_t = \Delta^d n_t = (I - B)^d n_t,$$

then,

$$w_t = \delta + \phi_1 w_{t-1} + \phi_2 w_{t-2} + \dots + \phi_p w_{t-p} + \varepsilon_t - \theta_1 \varepsilon_{t-1} - \theta_2 \varepsilon_{t-2} - \dots - \theta_q \varepsilon_{t-q}, \quad (3)$$

where d is the order of difference; p is the order of the auto-

regression part; and q is the order of the moving average part. These three parameters were estimated from the analysis of time-series data.

In the ARIMAX model, $\beta_1 x_{1,t-l_1} + \beta_2 x_{2,t-l_2} + \dots + \beta_k x_{k,t-l_k}$ represents the impact of exogenous variables on the dependent variable and n_t is the inter-dependency of time-series data. We applied ARIMAX (p , d , and q) to model time-series data that were auto-correlated. Here, p is the degree of auto-regression (AR), which can be determined by observing the PACF (partial autocorrelation) function chart; q is the degree of moving average (MA), which can be determined by observing the ACF chart; and d is the difference parameter, which can be determined using the ADF (Augmented Dickey-Fuller) unit root test (Shumway and Stoffer, 2010).

3. Results

In the present study, we integrated three types of information resources to demonstrate the biogeochemistry of nutrients in Changjiang watersheds, including (1) data of hydrographic gauge at Datong issued by the CWRC and previously published results in the literature; (2) our monitoring data from field stations at Nantong and Xuliujing (XLJ) since 1980; and (3) data collected through 11 expeditions along the river course and its major tributaries between 1997 and 2016. These 11 expeditions encompassed both dry and wet seasons as well as drought and flood years. Altogether, the data sets enabled us to comprehensively examine the changes in nutrient regimes, compare and quantify the impacts of anthropogenic activities, and offer guidance to constrain the fluxes of nutrients from Changjiang to the NW Pacific Ocean via the East China Sea.

Moreover, in the Changjiang, the concentrations of NO_2^- and NH_4^+ are much lower than that of NO_3^- ; as such, in 95% water samples, NO_3^- accounted for >90% of DIN. Hence, in the present study, we focus hereafter on data interpretations of DIN.

3.1 Impacts of the Qinghai-Tibetan Plateau and head-water composition

Our field sampling sites cover over 70% of the river course and 88% of the drainage area from the river mouth of Changjiang upstream to Yunnan Province. Shigu (SG) in Lijiang County is located ca. 4,500 km from the river mouth and at 2,500–3,000 m above sea level (asl), where Changjiang flows out of Qinghai-Tibetan Plateau in the western part of China (Figure 1). Here (i.e., Shigu of Lijiang), the river bed is approximately 1,850 m asl in the deep valleys. Similarly, the sampling sites at Yalongjiang upstream and Jinhe (JH) in Xichang City are located in the deep valley,

with an altitudinal difference of nearly 1,000 m compared with the high plateau. These river stations are located in Qinghai-Tibetan Plateau and carry the finger prints of source waters, shown in Figure 1. In the Jinshajiang and Yalongjiang upstream, DIN, DIP, and DSi concentrations in the main channel and tributaries were in the range of 10–30, 0.1–0.4, and 100–120 $\mu\text{mol L}^{-1}$, respectively (Figure 2). These values are comparable to previously reported concentrations in the source waters of Changjiang even further upstream (Shen, 1997; Wu et al., 2007), indicating that in this area of watershed, the riverine nutrient chemistry remains essentially undisturbed. At Shigu and Jinhe, DIN/DSi and DIP/DSi were in the range of 0.1–0.3 and 0.001–0.003, respectively; these ratios are comparable to previously reported values in the literature for pristine river systems, such as headwaters of the Qinghai-Tibetan Plateau.

Surface water runoff (e.g., rivers and creeks) from the

Qinghai-Tibetan Plateau is considered pristine, because it is at a high altitude and the land area is far from the direct impact of anthropogenic activities. Likewise, in samples collected from surface waters further upstream of Shigu, DIN and DSi were in the range of 2–31 $\mu\text{mol L}^{-1}$ for DIN, 78–143 $\mu\text{mol L}^{-1}$ for DSi, respectively, during 2003–2014 (Wu et al., 2008; Ding et al., 2014; Lu et al., 2016). Data on DIP in the headwaters of Changjiang are limited; however, in samples collected from lakes in the Qinghai-Tibetan Plateau, DIP was reported to be in the range of 0.23–0.81 $\mu\text{mol L}^{-1}$ (Lu et al., 2016). These values are consistent with our measurements from upstream areas, including Shigu of Jinshajiang and Jinhe of Yalongjiang, particularly during our first upstream field expedition in 1997.

Surface waters (i.e., river and lake) at the high Qinghai-Tibetan Plateau represent a catchment area of $0.2 \times 10^6 \text{ km}^2$. Recent studies have shown that this area is characterized by

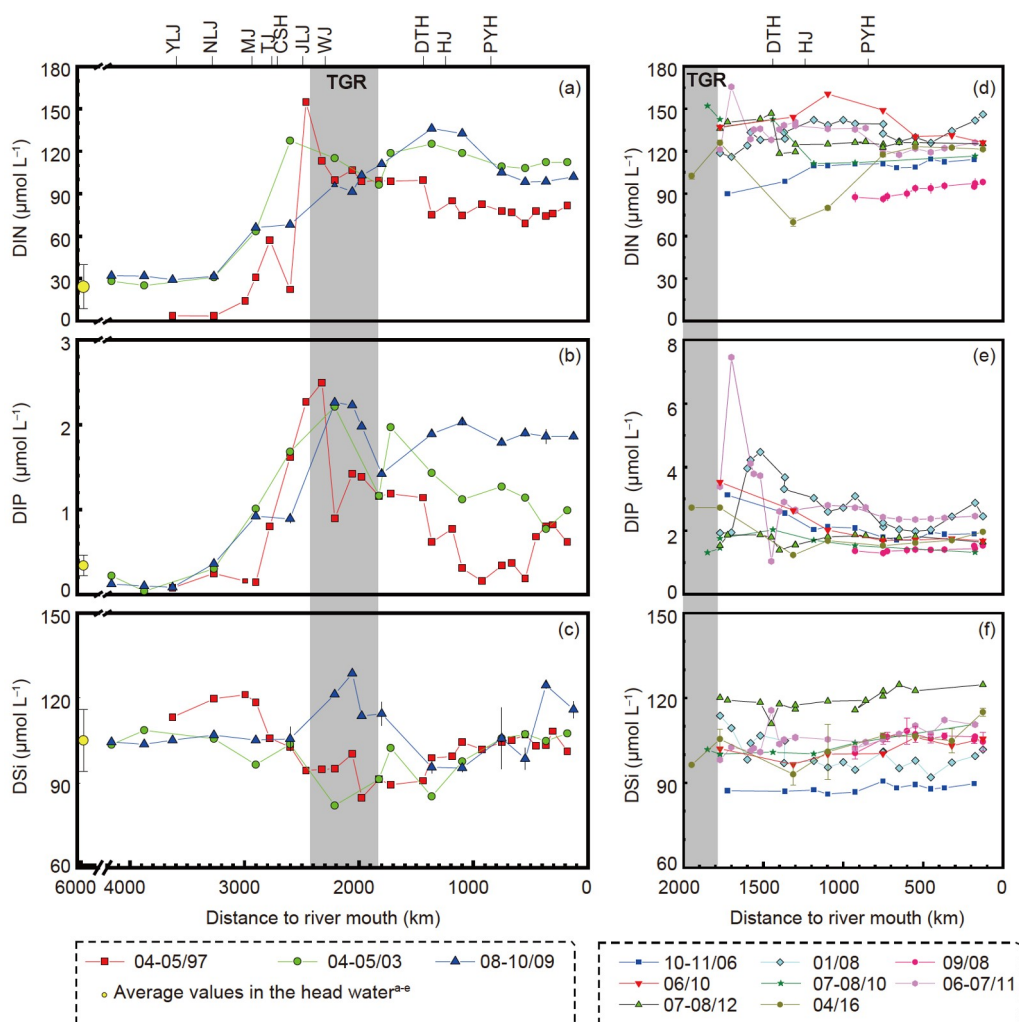


Figure 2 (Color online) Concentrations of DIN, DIP, and DSi along the mainstream of the Changjiang from the river mouth upstream to Shigu of Yunnan Province ((a)–(c)), and from the TGR down to the river mouth ((d)–(f)) in the period of 1997–2016. Data from 2009 shows the average of concentrations in the water column plus the standard deviation (sd), and the error bars are smaller than the sample symbols. The shaded area indicates the location of TGR. Concentrations for DIN, DIP and DSi in the source/head waters of the Changjiang watersheds (i.e., Qinghai-Tibetan Plateau) are cited from Fu et al. (1998), Zhao et al. (2003), Wu et al. (2007), Ding et al. (2014), and are also plotted for comparison in (a)–(c).

high chemical weathering rates than other parts of the world, which is attributed to strong runoff and steep gradient of the river course as well as the geological (uplifting) settings. Furthermore, evaporates and carbonates are abundant outcrops in the Qinghai-Tibetan Plateau, which increase the concentrations of major anions and cations (Wu et al., 2008; Ding et al., 2014). Moreover, from the tectonic point of view, continuous uplifting of the Himalayas accelerates weathering and erosion over the Qinghai-Tibetan Plateau, which can explain the markedly higher DSi in the headwaters of Changjiang than in its tributaries further downstream and at the river mouth (shown later). Moreover, the catchment area of Qinghai-Tibetan Plateau is located at 4,500–5,000 m asl and is home to an overall low density of inhabitants (i.e., 1–25 persons km⁻²), with very limited agriculture activity and practically no industrial facilities, as opposed to the densely populated lowland regions of Changjiang drainage basin with great anthropogenic load. Anthropogenic activities, such as chemical fertilizer and pesticide applications in agriculture as well as domestic waste drainage, produce rather a limited impact on the level of nutrients (e.g., nitrogen and phosphorus) in surface waters of this headwater area.

3.2 Upper reaches 3,600–2,200 km upstream of the river mouth

Downstream of the Qinghai-Tibetan Plateau and starting from Panzhihua (PZH) to Chongqing (CQ), the upper reaches span a water course of 3,600–2,200 km upstream the river mouth. In this area, Changjiang flows through the Sichuan Province, Chongqing Municipality, and Guizhou Province, and the main channel receives large quantities of nutrients from tributaries in this part of catchment areas. Here, DIN and DIP concentrations were increased over five times but the DSi concentration remained more or less stable (Figures 2 and 3). In major tributaries (e.g., Minjiang, Tuojiang, Jialingjiang, Chishuihe, and Wujiang) in this area, DIN and DIP concentrations exceeded 100 and 1 $\mu\text{mol L}^{-1}$, respectively, while DSi concentration remained high at around 110 $\mu\text{mol L}^{-1}$ (cf. Liu et al., 2003). These trends were confirmed subsequent observations in other studies (Shen and Liu, 2009; Ding et al., 2014). Collectively, tributaries in Sichuan, Chongqing, and Guizhou contribute an additional three- to four-fold of the annual flow of Changjiang; consequently, water discharge increases from 100×10^9 to 350×10^9 m³ yr⁻¹ on average (Ministry of Water Resources, 2015). In addition, the mainstream of Changjiang in this region shows high conductivity and DSi concentration, presumably indicating extensive leaching of soils from watersheds (Figure 3). Furthermore, this part of the Changjiang drainage basin is densely populated, and extensive area of forest has been cleared for agriculture. The large population and intensive agricultural activities have previously been

identified as important anthropogenic drivers of elevated nutrient levels in surface runoff from this region (Ju and Gu, 2014). For instance, the concentration of anthropogenic nutrients (Box 1) in some tributaries in this area is as high as several hundred of micromoles per liter for DIN, and in Minjiang and Tuojiang, DIP reaches up to 4–8 $\mu\text{mol L}^{-1}$ (Liu et al., 2003; Ding et al., 2014). As a result of high nutrient load in this part of Changjiang, DIN/DSi increased up to 0.6–1.4 and DIN/DIP exceeded 40–50 in the main channel. Thus, fluxes from tributaries in Sichuan, Chongqing, and Guizhou collectively increase the nutrient load in the main channel of Changjiang, which further significantly affects the riverine nutrient chemistry further downstream. The considerable increase in nutrient concentrations in the main channel of Changjiang in this area can be attributed to not only high levels of nutrients in surface waters but also the abundant water flow of tributaries, which is related to high water yield (i.e., mm km⁻² yr⁻¹) in their catchment areas.

3.3 The Three Gorges Reservoir

The TGR is located between Chongqing and Yichang over a distance of ca. 600 km along the mainstream of Changjiang and has a water storage capacity of ca. 40×10^9 m³ and a dam height of 185 m. Briefly, construction of the TGD started in 1994, and two cofferdams were closed in 1997. Subsequently, the dam was constructed, and water gate was closed in 2003, with a water level up to 135 m asl. In 2009, full operation of the TGD started, with the water level of reservoir being further raised up to 175 m asl during the period (e.g., October to April) of water storage. Regarding the policy of dam operation, water level of TGR reduces to ca. 145 m during April to September before the summer floods of Changjiang in the upstream and then elevated up to 175 m during the dry season from October to April of the next year (Tang et al., 2018). As shown in Figure 3, water samples from TGR presented a lower pH and dissolved oxygen level than samples from the river course either upstream or downstream of TGD or both, whereas DIP and DSi were higher.

Our observations since 1997 indicated that over ca. 600 km distance of the TGR, nutrient data did not show any systematic trends, although concentrations varied among different species and among surveys (e.g., dry vs. wet seasons). For instance, before the enclosure of TGD (e.g., April to May 2003), DIN decreased by 25% downstream of TGD compared with that upstream of the reservoir, while DIP was altered by 30%. Meanwhile, DSi remained rather stable throughout the TGR, with a difference of ca. 10% (Figures 2 and 3). Furthermore, monthly water discharge during the dry season (e.g., April to May 2003) was increased by ca. 50% from Cuntan, which is upstream of the TGR, to Yichang, which is 30 km downstream of the TGD (CWRC, 2004).

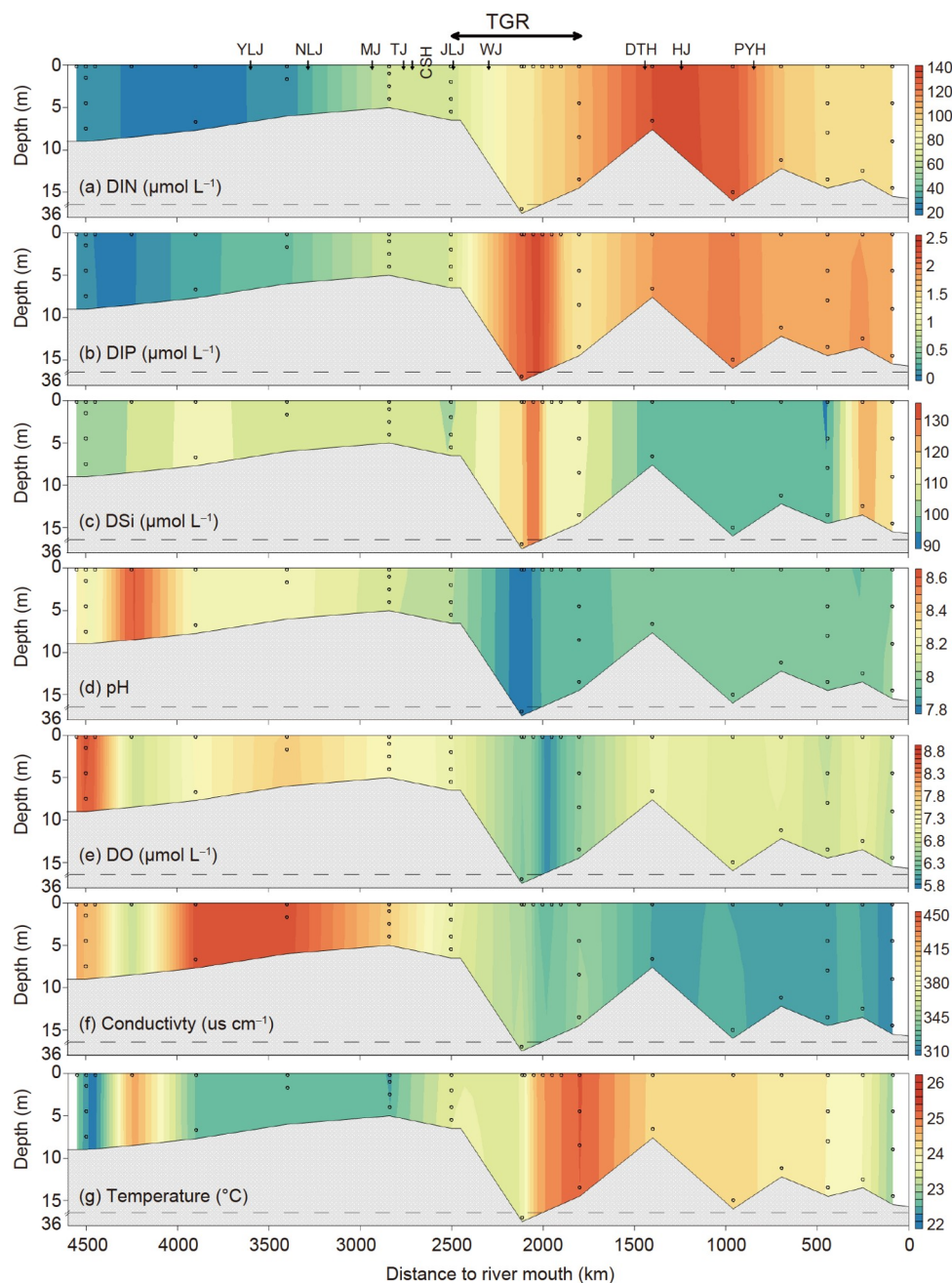


Figure 3 (Color online) Vertical section of nutrients from Shigu to the river mouth in 2009 expedition, which shows profiles of nutrients and other water properties measured *in situ*. The confluence points of major tributaries, together with location of the TGR are indicated in the figure, with abbreviation for tributaries shown in Figure 1.

Following the enclosure of TGD (e.g., August to October 2009), DIN downstream the dam was 50% higher than that upstream the reservoir. Similarly, DIP was higher downstream the TGD. During this period, the monthly water flow at Yichang was 10–30% lower than that at Cuntan because samples were collected from the impoundment stage of the reservoir (CWRC, 2010). Similar to that during the dry season of 2003, DSi during the flood period of 2009 was comparable between upstream and downstream stations across the TGR, although data showed variabilities. In 2016,

observational data indicated that DIN in the TGR was 20% higher than that at Yichang, a downstream station of TGD, whereas DIP was comparable between stations within and downstream the reservoir (Figures 2 and 3). During the spring of 2016, DSi was 10% higher within the reservoir than further downstream (Figures 2 and 3). Compared with previous observations in 1997 and data in the literature, our measured nutrient concentrations in the TGR showed temporal variability at the seasonal and inter-annual scales. Apparently, the overall distribution pattern over the last

20 years (1997–2016) can be characterized by the increasing trends of DIN and DIP from upstream to downstream the TGR and the relatively stable DSi.

Of note, the catchment area around the TGR itself has been historically ungauged in the hydrographic monitoring network of CWRC. However, across the length ca. 600 km of the TGR, there are a number of tributaries, including Xiangxihe and Daninghe (here “he” means “river” in Chinese), discharging a considerable amount of nutrients at the annual scale into the TGR. For instance, based on a study of 13 tributaries around the TGR, Zhang S et al. (2008, 2009) claimed that eight river/creek systems in this area present eutrophic characteristics, with total nitrogen (TN) and total phosphorus (TP) levels reaching up to 500 and 15–20 $\mu\text{mol L}^{-1}$, respectively. These reports were further supported by studies on five other tributaries in the TGR area, although the reported values for TP (ca. 3 $\mu\text{mol L}^{-1}$) and TN (ca. 150 $\mu\text{mol L}^{-1}$) were lower (Zhang et al., 2005). Subsequent studies reported that DIN and DSi in local tributaries emptying into the TGR were comparable to the values in the mainstream of Changjiang, while DIP was either high (2–6 $\mu\text{mol L}^{-1}$) or low (0.5–1.0 $\mu\text{mol L}^{-1}$) and showed significant variations depending upon the sampling period (Cao et al., 2015; Zhang et al., 2015; Wang et al., 2016). Overall, results in the literature indicate that tributaries around the TGR exhibit strong characteristics of seasonality and inter-annual variability in terms of nutrient fluxes. Moreover, tributaries in this area present generally high concentrations of phytoplankton pigments (Chl *a* >25 $\mu\text{g L}^{-1}$) in surface waters, which can be five-fold higher than those in the Changjiang mainstream (Zhang et al., 2015; Wang et al., 2016). Using the box model approach, Ran et al. (2009) examined the retention of nutrients within the TGR and found that respectively 8%, 15%, and 20% DIN, DIP, and DSi were retained upstream the TGD at the annual scale. The relatively low retention of nutrients within the TGR was attributed in part to the leaching of soil nutrients in the catchment areas around the reservoir during the impoundment period and influx from the ungauged tributaries in this region (Ran et al., 2009; Zhang et al., 2015; Wang et al., 2016).

3.4 Downstream the TGD and to Datong

The river mouth of Changjiang is another 1,800 km downstream from the TGD. In this section of the river course, nutrient concentrations in the main channel are further regulated by inflows from Hanjiang (HJ), an important tributary in the north, and from two large lakes, namely Dongtinghu and Poyanghu (here “hu” means “lake” in Chinese), in the south (Figure 1). This part of the mainstream is characterized by relatively high nutrient concentrations that remain stable over a rather short-term (i.e., for a given

expedition) down to Datong. For instance, during 1997–2006, DIN and DIP in this region were in the range of 100–120 and 1–2 $\mu\text{mol L}^{-1}$, while DSi remained at ca. 100 $\mu\text{mol L}^{-1}$ (Figures 2 and 3). This pattern can be explained by the higher concentrations of nutrients in the Hanjiang, Dongtinghu, and Poyanghu, comparable to those in the mainstream, which will be discussed later.

Historical overview of existing data revealed that although in the middle and lower reaches (i.e., sections downstream from Yichang) of Changjiang, DIN and DIP augmented throughout the study period (1997–2016), the increase tended to slowdown and/or level-off more recently, that is, after the TGD became fully operational in 2009.

Furthermore, vertical water profiles obtained at each station during the 11 expeditions in 1997–2016 indicated no significant trends of nutrient species with depth (Figure 3). The surface and near-bottom concentrations were typically similar over the 4,000–4,500 km course of the river sampled, indicating that nutrient concentrations and other chemical properties in the water column of Changjiang are uniform. In addition, samples collected and analyzed from the main channel show no systematic trends of nutrient concentrations between downstream urban sites and upstream stations ($p < 0.05$), because we collected all samples from the fast-flowing area of the mainstream to minimize the effects of local drainage of pollutants (e.g., nutrients) from urban areas.

At a given station, DIN has shown a slow but steady increase over the last 30 years, although the data are scattered (Figure 4). However, samples collected from the same cruise demonstrate a rather smooth distribution along the main channel without a significant trend from the middle to the lower reaches over the distance of approximately 2000 km (Figures 2 and 3). Overall, DIP has followed a similar distribution pattern to DIN during 1997–2016, but there was a 5 times downstream increase for DIP compared with the up-trend of DIN at between 50% and 100% over the last 20 years, indicating that DIP is steadily ascending in this area. Exceptionally high concentrations of DIP in the main channel were recorded in October to November 2006, when Changjiang was affected by an extraordinary dry period in the middle and lower reaches, as well as in January 2008, when a severe winter led to extremely low water flow. Therefore, climate and anthropogenic forces over the drainage basin produce different impacts on DIP and DIN in the middle and lower reaches of the watershed. As shown in Figure 4, DSi is the most stable nutrient species in Changjiang at the temporal scale, and the systematic change, if any, was within 20% to 40% over last two decades.

Data reported in the literature are consistent with our measurements, taking into account the different temporal and spatial dimensions of the observations. For instance, Shen et al. (2003) and Shen (2006) investigated nutrient concentrations in Changjiang between 1997 and 1998 and reported that

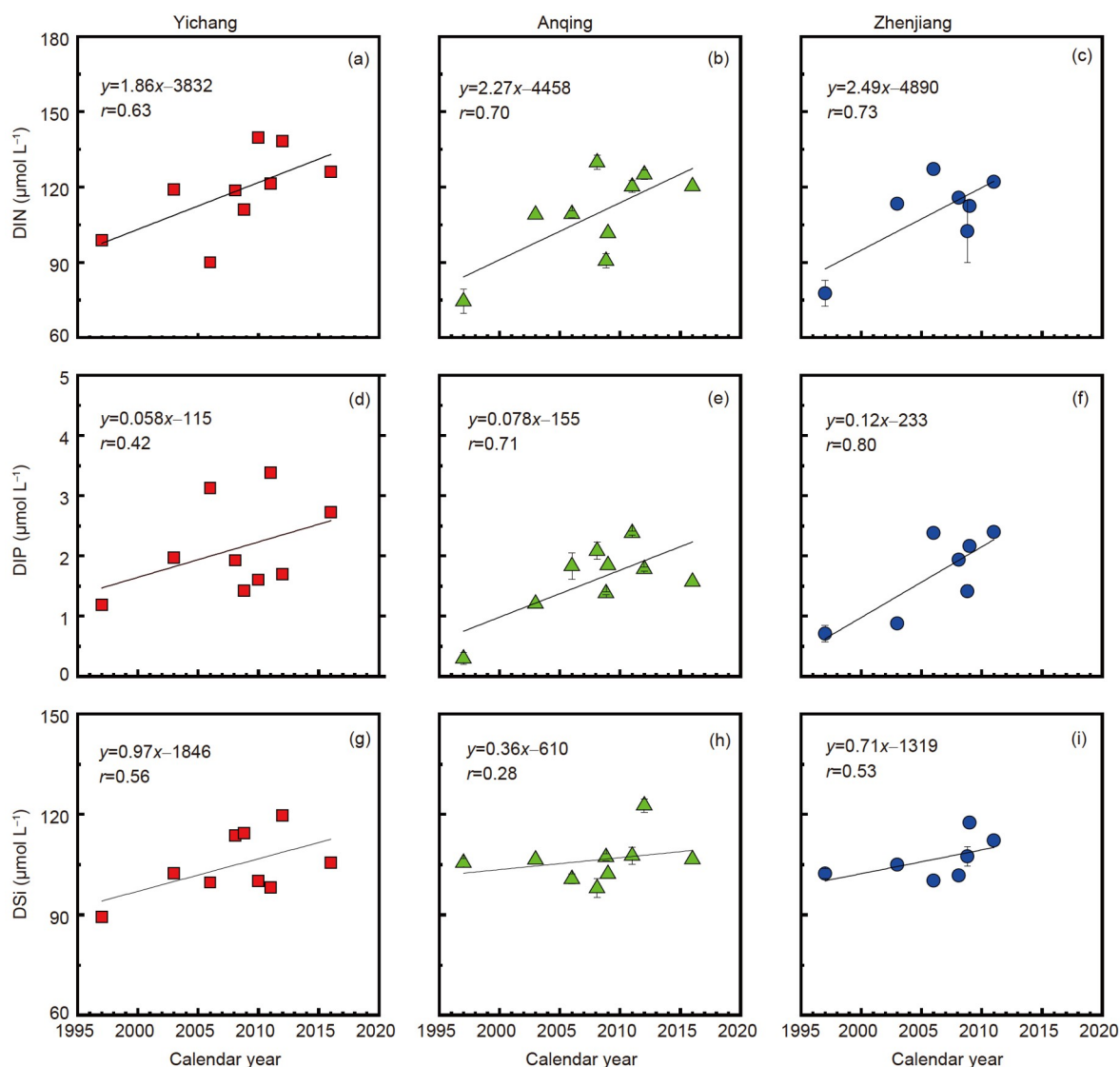


Figure 4 (Color online) Nutrient data from selected stations in the middle and lower reaches of the Changjiang (mainstream) for DIN, DIP and DSi at Yichang, Anqing and Zhenjiang in the period of 1997–2016, and the samples represent different hydrographic conditions with lines showing linear trend. In the figure, when several samples were collected and analyzed from sites close to the given station, average and standard deviation are both provided. Note that concentrations of DIN and DIP at these stations have increased by more than 100% in last twenty years, whereas DSi changed by 20–40% in this period.

DIN, DIP, and DSi values downstream of Yichang were similar to our data from 1997. More recently, other research teams have reported DIN and DIP data from the middle and lower reaches, and their results were either similar to our observations, when obtained in the same season, or slightly higher, when samples were collected during periods of extreme drought and/or affected by urban sites nearby (cf. Müller et al., 2008; Jiang et al., 2012a).

3.5 Downstream Datong and to the river mouth

For the purpose of discussion and data integration in the present study, the river mouth of Changjiang and hence its separation from the East China Sea are defined by the line connecting Qidong in the north to Nanhui in south, as shown

in Figure 1.

Datong is a hydrographic gauge station of the CWRC network, which is upstream of the limit of tide-influenced pan-delta and ca. 650 km upstream of the river mouth. Downstream of Datong is another drainage area covering $95 \times 10^3 \text{ km}^2$ to the river mouth and accounts for ca. 5% of the whole surface area of the drainage basin. Compared with the upper and middle reaches, several important characteristics of the drainage area downstream of Datong and to the river mouth can be summarized as follows:

(1) Individual tributaries in this area, such as Qingyijiang and Shuiyangjiang, Yuxihe, Chuhe, Qinhuaihe, Jing-Hang Great Canal, and Huangpujiang, are usually small in terms of annual water flow, and their water flow and chemistry are not gauged by CWRC. However, these small tributaries collec-

tively account for 5% of the annual water discharge of Changjiang into the East China Sea on average, particularly from Anhui and Jiangsu (Zhang and Chen, 2003; Zhang E F et al., 2009). Moreover, there are no time-series data on the nutrient status of most of the tributaries, creeks, and canals in this tide-influenced deltaic area.

(2) The level of urbanization in this area is higher than that in other parts of China. For instance, there are 15 mega-cities in the tide-influenced pan-delta of Changjiang, each with population exceeding a million, such as Hefei, Anqing, Nanjing, and Wuxi. Two super mega-cities, namely Suzhou and Shanghai, each with a population exceeding 10 million, are also in this tide-affected delta.

(3) The capacity of water extraction from the river course of Changjiang downstream of Datong is very high. Apparently, ca. $25 \times 10^9 \text{ m}^3$ of water can be extracted annually from Changjiang downstream of Datong (Zhang et al., 2012). Of note, most of the extraction facilities along the river course can discharge into Changjiang during flood periods.

(4) The progress of economic reform in this tide-influenced delta is very rapid, taking the lead for the entire country over the last four decades. For instance, the per capita GDP of this tide-influenced area is up to 10×10^3 USD, which is two- to four-fold higher than that of other provinces and/or autonomous cities in the upstream region (<http://data.stats.gov.cn/>).

Close to the river mouth (e.g., Xuliujing), time-series data showed comparable nutrient concentrations between surface and near-bottom samples ($p < 0.05$). In the lower reaches of Changjiang, including the tide-influenced delta, NO_3^- accounted for 90–95% of DIN in the mainstream, with minor contributions of NO_2^- and NH_4^+ , similar to the pattern in the upper and middle reaches.

Statistics based on the whole data sets of Xuliujing during 2003–2016 did not indicate simple relationships between nutrients and water flow at the monthly scale. Zooming into the annual scale, however, nutrient concentration in water samples tended to be higher during the dry than the wet season, providing evidence that seasonality is important for long-term trends at the inter-annual scale. This can be explained by the limited variability (10–20%) in the water flow of Changjiang at the annual scale but marked seasonal fluctuations with continuous increase in nutrient load in the drainage area. A systematic increase in anthropogenic nutrient species, such as DIN and DIP, has been noted annually in this area (Figure 4).

Downstream of Xuliujing, Huangpujiang is the most important tributary that drains into Changjiang in the estuarine area. Huangpujiang spans a drainage area of $24 \times 10^3 \text{ km}^2$ and has a water flow of 10×10^9 to $18 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$, including contribution of another $0.3 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ from Suzhouhe. Both tributaries drain through the municipality of Shanghai

before emptying into the Changjiang Estuary, further downstream of Xuliujing and to the river mouth (Figure 1). Therefore, the evaluation of seaward export of nutrients in Changjiang must consider contributions from estuarine sources (e.g., Huangpujiang) as well. To avoid the back-flush effect of Changjiang into Huangpujiang on nutrient concentrations in its tide-influenced deltaic area, samples were collected during the ebb tide phase of neap-tide periods (cf. Cui et al., 2011).

Table 3 summarizes the data of monthly sampling and measurements of nutrients in Huangpujiang. In the present study, nutrient concentrations in water samples from four stations in Huangpujiang and Suzhouhe were measured in 2002, 2006–2007, and 2015–2016. At the time, the flux of nutrients in Huangpujiang could only be estimated at the monthly scale based on data in Table 3 and information from the literature, as shown in Figure 5.

During November 2006 to November 2007, the monthly observations in the downstream reaches of Huangpujiang revealed DIN, DIP, and DSi ranges 93–342, 1.9–5.0, and 51–160 $\mu\text{mol L}^{-1}$, respectively (Cui et al., 2011). Earlier, measurements during March to July of 2002 with sampling frequency of two weeks revealed DIN, DIP, and DSi ranges of 73.4–291, 2.6–22, and 43.9–133 $\mu\text{mol L}^{-1}$, respectively (Zhu et al., 2004). Hence, monthly and inter-annual variations in nutrient levels in Huangpujiang can be important factors affecting riverine nutrient fluxes into the estuary, because the small tributaries of Changjiang are more sensitive to water flow variability linked to rainfall and anthropogenic perturbations over their watersheds. Measurements during 2007 represent the most comprehensive study of nutrients in Huangpujiang to date. Using the monthly concentrations and water discharge during 2006–2007, Zhang et al. (2021) calculated the annual nutrient flux from Huangpujiang into Changjiang, as shown in Table 3 for comparison. Their observations were subsequently confirmed by measurements during 2015–2016, which revealed DIN, DIP, and DSi in the ranges of 92.6–228, 1.28–3.79, and 53.0–129 $\mu\text{mol L}^{-1}$, respectively, in the Huangpujiang before it affluxes into the Changjiang Estuary (Ye, 2019).

Considering the drainage area of Huangpujiang and annual nutrient fluxes, chemical yield can be estimated. Based on this, $129 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ DIN, $3.5 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ DIP, and $56 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ DSi can be produced from the catchment area of Huangpujiang during the period of first 10 years of this century. These nutrient yields from Huangpujiang are higher than those from other tributaries in the upstream area of Changjiang, which will be addressed later.

3.6 Stable isotopes

In the Changjiang, stable isotopes of dissolved silicates (e.g., $\delta^{30}\text{Si}$) showed an upward trend along the mainstream from

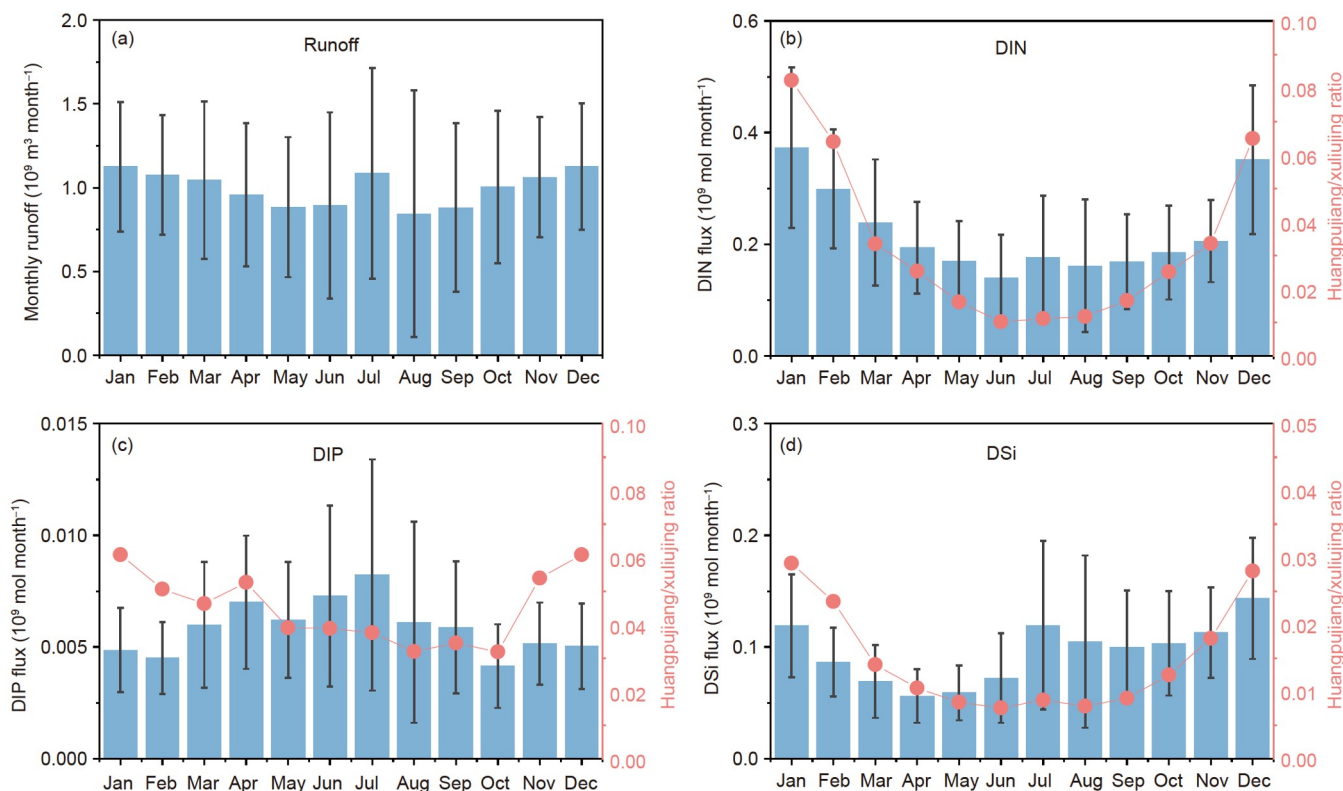


Figure 5 (Color online) Changes in monthly water discharge and flux of nutrients of the Huangpujiang in histogram with error bars showing the impact of water flow variability and comparison with the Changjiang in terms of nutrient export relative to the mainstream at Xuliujing (i.e., line).

Table 3 Concentrations of nutrients from the Huangpujiang, which flows through the Shanghai Municipality and empties directly into the Changjiang Estuary, shown in Figure 1^{a)}

Period	DIN ($\mu\text{mol L}^{-1}$)	DIP ($\mu\text{mol L}^{-1}$)	DSi ($\mu\text{mol L}^{-1}$)	Data sources
2002	73–291	2.6–22	44–133	Zhu et al., 2004
2006–2007	93–345	1.9–5.0	51–160	Cui et al., 2011
2015–2016	92.6–228	1.25–3.80	53–129	Ye, 2019

a) Samples for nutrient measurements were collected at monthly scale from four stations across the Huangpujiang and its tributary, the Suzhouhe.

the upper part (i.e., 4,500 km) down to the river mouth. For instance, the $\delta^{30}\text{Si}$ of water samples from the mainstream was 1.0–1.3‰ in the river course above the TGD, and it increased up to 1.9‰ downstream to the river mouth (Zhang, 2016; Zhang et al., 2020). Moreover, $\delta^{30}\text{Si}$ values for tributaries in the middle and lower reaches and downstream of TGD, such as Dongtinghu, Poyanghu, and Hanjiang, were higher than those for tributaries above the TGR and further upstream, including Yalongjiang, Minjiang, Wujiang and Jialingjiang (Zhang, 2016). This pattern of $\delta^{30}\text{Si}$ can be explained by the enrichment of heavy (i.e., ^{29}Si and ^{30}Si) versus light (i.e., ^{28}Si) isotopes of silicon in the solution of rivers and lakes from the lower part of drainage basin. Statistically, the $\delta^{30}\text{Si}$ composition in water sample can be 0.5–1‰ heavier in tributaries from the middle and lower reaches than those draining through the upper part of drainage basin, which is related to 50–100% increase in DSi in the surface runoff of

tributaries from the southern part of Changjiang watersheds (Zhang et al., 2020). Agriculture based on rice paddies in the Changjiang drainage basin may increase $\delta^{30}\text{Si}$ in surface runoff, particularly in the middle and lower reaches of watersheds, where wet rice cultivation in paddy fields is ubiquitous and a very important activity in agriculture (Ding et al., 2004). Similarly, blooms of fresh water diatoms in lakes and rivers of middle and lower reaches can increase $\delta^{30}\text{Si}$ further downstream, which is consistent with the positive correlation between dissolved $\delta^{30}\text{Si}$ and biogenic silica (BSi) in Changjiang (Zhang, 2016; Zhang et al., 2020).

In the upstream area, $\delta^{18}\text{O}-\text{H}_2\text{O}$ of tributaries (e.g., Jinshajiang) reflected melted ice and/or snows from glacial source. Water samples from this area carry finger prints of glacial stable isotopes of oxygen and hydrogen. For instance, in the summer, water samples from Panzhuhua (PZH) to Yibin (YB) mainstreams presented $\delta^{18}\text{O}$ of -10% to -15%

and δD of -100% to -120% , which are comparable to the reported values of snow and ice samples from the Qinghai-Tibetan Plateau (Li et al., 2010). Although comparison revealed seasonality and/or inter-annual variations in $\delta^{18}\text{O}$ - H_2O between dry (May of 2003) and wet (August of 2006) periods, the overall trend along the river course remained stable (Figure 6). Compilation of surface runoff and rainfall data in the Qinghai-Tibetan Plateau showed $\delta^{18}\text{O}$ of -10% at the altitude of 1,500 m asl and -15% at the altitude of 4,500 m asl, indicating a strong linear correlation between $\delta^{18}\text{O}$ and altitude (Sun et al., 2018). Water samples from the upstream area of Changjiang reflected contribution from the glaciers of source area. Nitrate concentration in source waters in this area is ca. $10 \mu\text{mol L}^{-1}$ in the river, with 12% $\delta^{15}\text{N-NO}_3^-$, indicating the dominance of nitrogen from the leaching of soil in the upstream areas of Changjiang (Li et al., 2010). In previous studies, the contribution of source waters from the Qinghai-Tibetan Plateau to the seaward flux of Changjiang was estimated in samples from the river mouth, which also shows strong seasonality (Zhang et al., 1990b).

Downstream of TGD, $\delta^{18}\text{O}$ of water samples in the mainstream of Changjiang increased up to ca. -8% , consistent with values in rainfall samples in the middle and lower reaches and reflecting the effect of atmospheric precipitation on the water budget. In the water course downstream Yichang, $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ were reduced, with a weak but negative correlation between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-H}_2\text{O}$ (Figure 6). Moreover, in the middle and lower reaches of Changjiang, $\delta^{15}\text{N-NO}_3^-$ was 7% to 10% in the mainstream, compared with 7.7% in Dongtinghu, 12.3% in Poyanghu, and 4% to 7% further downstream to the Taihu in the tide-influenced deltaic area (Townsend-Small et al., 2007; Li et al., 2010). This reduction in $\delta^{15}\text{N-NO}_3^-$ demon-

strates the greater contribution of fertilizer nitrogen into the river course in the middle and lower reaches because of extensive agriculture in the watersheds (Townsend-Small et al., 2007; Li et al., 2010). These results are consistent with an increase in NO_3^- concentration downstream of Yichang in the Changjiang mainstream relative to the source region (i.e., Qinghai-Tibetan Plateau) and low $\delta^{15}\text{N-NO}_3^-$ values obtained in surface waters of the tide-influenced deltaic area.

In the Changjiang mainstream, $\delta^{15}\text{N}$ of particulate nitrogen (PN) in TSM was 1.8% to 7.4% , corresponding to -27.1% to -24.2% for $\delta^{13}\text{C}$ in particulate organic matter (POM) over the river course of ca. 4,500 km (Zhang et al., 2002). Moreover, the observed $\delta^{15}\text{N}$ of PN tended to decrease from upstream down to the river mouth, which is consistent with the fact that tributaries draining into the Changjiang below Yichang have lighter $\delta^{15}\text{N}$ (range: 0% to 3%) for PN than those discharging into the mainstream above the TGR, with $\delta^{15}\text{N}$ of 3% to 8% (Zhang et al., 2002). These results are in line with the observations for $\delta^{15}\text{N-NO}_3^-$ in water samples.

Regarding the sources of organic matter (OM) in TSM, soil samples from the Changjiang drainage basin showed $\delta^{15}\text{N}$ of -1.7% to 7.0% with $\delta^{13}\text{C}$ of -31.2% to -23.7% for southern tributaries and $\delta^{15}\text{N}$ of 1.7% to 5.6% with $\delta^{13}\text{C}$ of -28.2% to -21.3% for northern tributaries (Zhang et al., 2002). Similarly, plant samples collected from the Changjiang drainage basin showed $\delta^{15}\text{N}$ of -2.7% to 14.6% with $\delta^{13}\text{C}$ of -30.4% to -14.2% in the southern part and $\delta^{15}\text{N}$ of -1.0% to 6.3% with $\delta^{13}\text{C}$ of -30.7% to -27.0% in the northern part of drainage basin, depending upon the species of interest (Zhang et al., 2002).

In summary, the isotopic data of particulate organic matter in Changjiang watersheds indicated that although nitrogen composition can markedly vary across different parts of

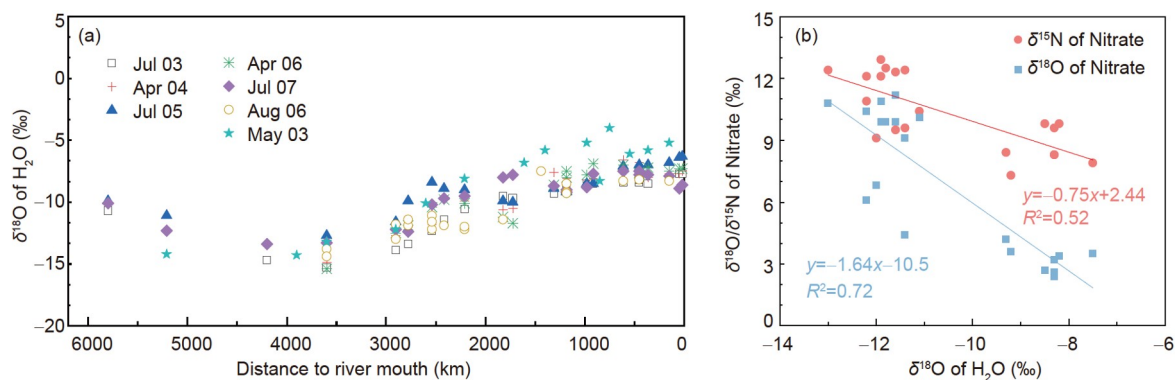


Figure 6 (Color online) Changes in $\delta^{18}\text{O}$ - H_2O along the mainstream of the Changjiang from the Qinghai-Tibetan Plateau to the river mouth (a), and stable N and O isotopes for nitrate between upper and lower parts of the river course for the Changjiang (b). Data of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ are from Li et al. (2010), those of $\delta^{18}\text{O-H}_2\text{O}$ are from Li et al. (2010) and Ding et al. (2014) and the expedition in 2003. Note that when samples in the river are affected by the source waters from the Qinghai-Tibetan Plateau, the observed $\delta^{18}\text{O-H}_2\text{O}$ is -10% to -15% in the upstream, the corresponding $\delta^{15}\text{N-NO}_3^-$ is in the range of 10% to 15% . In the lower part of river course, where low land rainfall has $\delta^{18}\text{O-H}_2\text{O}$ of ca. -8% , $\delta^{15}\text{N-NO}_3^-$ of the Changjiang in mainstream reduces to 5% – 10% , indicating an increase in contributions from chemical fertilizers.

drainage basin (e.g., south vs. north and upstream vs. tide-influenced river delta), these data illustrate the systematics along the water course from upstream down to the river mouth. Evidently, in the source area (i.e., Qinghai-Tibetan Plateau), DIN in the river is related to soil nitrogen under pristine conditions, and $\delta^{15}\text{N}$ in the river reflects OM decomposition and leaching from soil profiles through snow and/or ice melt. Further downstream and to the river mouth, contribution from nitrogen with anthropogenic finger prints (e.g., chemical fertilizer application) becomes gradually more important, eventually being the dominant source of DIN in the river. In Changjiang, $\delta^{15}\text{N}$ in particulate matter shows a similar distribution pattern to $\delta^{15}\text{N}\text{-NO}_3^-$ in water samples.

3.7 Trends of nutrients in the estuary and at the river mouth of Changjiang

In the literature, seaward nutrient fluxes from Changjiang have been reported based on data from the Datong Hydrographic Station of CWRC (cf. Shen, 2001; Duan et al., 2007; Yan et al., 2010; Dai et al., 2011; Liu et al., 2015); however, this gauge site is located beyond the tidal limit and is still ca. 650 km upstream the river mouth. Historically, seaward water discharge from Changjiang and, hence, the management of nutrient over-enrichment has also been through Datong Hydrographic Station in Anhui Province.

Downstream of Datong, the tide-dominated and ungauged water course of Changjiang, that is its tide-influenced pan-delta, covers a catchment area of ca. $0.1 \times 10^6 \text{ km}^2$, similar to the headwaters at the Qinghai-Tibetan Plateau in terms of area but markedly different in terms of the natural (e.g., landscape and land-use) and socioeconomic aspects. Moreover, a number of tributaries downstream of Datong discharge directly into the tide-influenced deltaic area, such as Huangpujiang, and their contributions to the Changjiang nutrient flux should be assessed based on observational data.

In the present study, we start with nutrient data from Nantong and Xuliujing, which demonstrate variability at the monthly, seasonal, and inter-annual scales as well as long-term trends compared with results at Datong available from CWRS monographs/reports and studies in the literature (Figure 7). Relative to Datong, Nantong and Xuliujing were selected as monitoring sites for river chemistry owing to a number of considerations. First, geographically, Nantong and Xuliujing are located just before Changjiang bifurcates into different branches and passages in the estuary, and water salinity is still zero even in the spring tide period during the dry season; in other words, sampling is not affected by seawater intrusion up to the estuary. Second, the main channel at Xuliujing is narrow and deep (i.e., up to 40 m) in the water course between Datong and the river mouth; thus, it

is an ideal location to examine the structure of vertical profiles of chemistry. Third, the sampling site at Xuliujing is approximately an hour drive from the home laboratory, which allowed sample processing in a clean room/condition immediately after collection. Another advantage of Xuliujing relative to Datong is that the river course between these two locations is ca. 500 km long, representing over 75% of the river path downstream Datong to the river mouth, which provided an opportunity to examine the effects of anthropogenic activities in this stretch of the pan-deltaic area on river chemistry and refine the calculation of seaward flux of nutrients in Changjiang. Moreover, after the mid-1990s, water flow data become available through the integration of ADCP measurements at Xuliujing, allowing for the estimation of nutrient fluxes taking contributions from this previously un-gauged and tide-influenced pan-deltaic area into account.

Changes in nutrient concentrations and species ratios in the studied tide-influenced delta have recently been reported by Zhang et al. (2021). Herein after, the major findings are summarized in more details.

DIN concentrations at Nantong and Xuliujing have increased steadily ($\gamma^2=0.55$, $p<0.01$) since 1980—from 30–40 $\mu\text{mol L}^{-1}$ in the early 1980s to $>100 \mu\text{mol L}^{-1}$ in 2016. The rapid increase in DIN at the river mouth of Changjiang in the early 1980s can be explained by the large-scale application of synthetic fertilizers and pesticides, which overpassed conventional manure-N in agriculture over watersheds (Appendix 3: Source vs. Sink). DIP concentrations remained relatively stable at 0.4–0.5 $\mu\text{mol L}^{-1}$ prior to 1995 but increased 5-fold ($\gamma^2=0.61$, $p<0.01$) over the next 20 years, reaching 2.0–2.5 $\mu\text{mol L}^{-1}$ during 2010–2015 (Figure 7).

Similarly, the systematic increase in DIP at the river mouth in the mid-1990s can be a result of increased application of synthetic fertilizers compared with that of manure-P in agriculture, which promoted significant retention of phosphorus in the watersheds of Changjiang (cf. Appendix 3: Source vs. Sink). Although the application of synthetic fertilizers in Chinese agriculture increased since the early 1980s, the response of DIP in Changjiang appeared much later. Apparently, DIP exhibits a different behavior from DIN, and there is a gap between external forces (e.g., synthetic fertilizer application) and system responses of DIP. As mentioned above, a systematic increase in DIP in Changjiang occurred when the amount of synthetic fertilizers applied exceeded that of organic manure used in agriculture. Consequently, DIN/DIP molar ratio in Nantong and Xuliujing increased up to 100–300 from the 1980s to the 1990s, followed by a two-factor decrease between 2000 and 2015 (Figure 7). This change reflects in part the higher affinity of DIP than of DIN to particulate phase. Zhang (2007) reported that a reduction in TSM concentration in Changjiang from 500 mg L^{-1} during 1950–2000 to 100 mg L^{-1} after 2003 in-

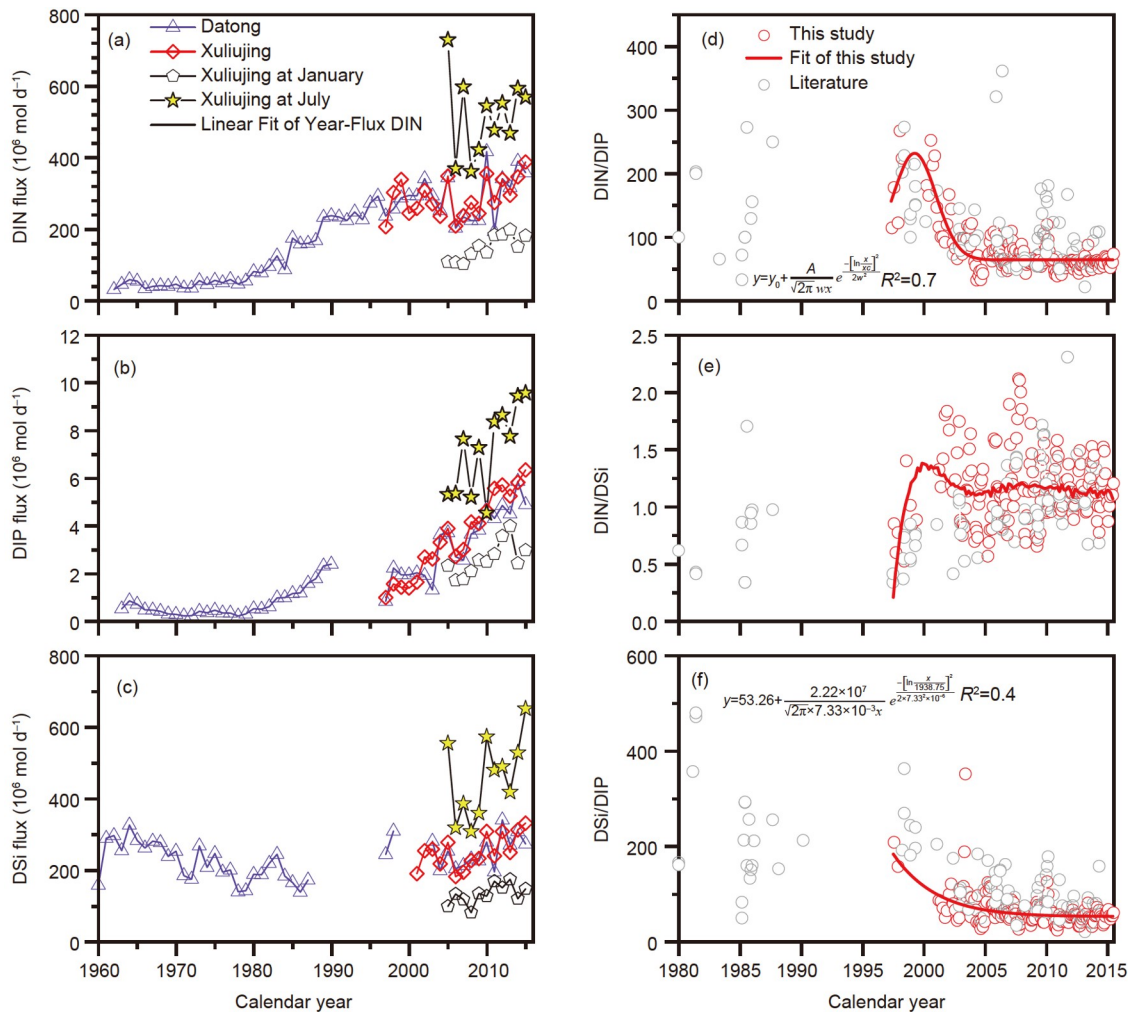


Figure 7 (Color online) Water flux weighted DIN, DIP, and DSi recorded at Nantong and Xuliujing ($\mu\text{mol L}^{-1}$), plotted together with published results in the literature (Zhang et al., 2021). Data of flood (July) and dry (January) periods at the Xuliujing are compared to the reported results at Datong (left panel), and changes in DIN/DIP, DIN/DSi and DSI/DIP at Xuliujing are shown for comparison (right panel). Note that the daily fluxes in July (flood period) can be 4 folds higher than those in dry season (January) because of changes in water flow and nutrient concentrations in combination. Before 2000 when the Changjiang suffered a rapid increase in DIN, the corresponding DIN/DIP ratios were high at the Xuliujing, then DIN/DIP decreases and tends to stabilize in this century. Annual water loads from the Xuliujing are publically available after 2004, and those for the period 1997–2004 were collated from published studies (cf. Yan et al., 2013). Nutrient concentration data in the lower reaches of the Changjiang were collated from previous studies and used to compile and calculate nutrient fluxes at Datong, including Wang et al., 1983; Edmond et al., 1985; Huang et al., 1986; Zhang, 1996; Shen, 1997; Ye et al., 2000; Fu and Shen, 2002; Shen et al., 2003; Ding et al., 2004; Xu et al., 2004; Li et al., 2006; Yu et al., 2006; Gao and Song, 2007; Chetelat et al., 2008; Guo, 2008; Müller et al., 2008; Shi and Liu, 2009; Guo et al., 2015; Li et al., 2015; Ma, 2015; Meng, 2015, and Zhang, 2015. Note that the rapid increase in DIN at the river mouth after 1980 followed the large-scale application of synthetic fertilizers over the watersheds. Similarly, the increase in riverine DIP after 1995 corresponds to the higher amount of chemical than traditional manure fertilizers used in agriculture, shown in Appendix 3: Source vs Sink.

creased DIP concentration by over 10% when the original phosphate level was at $1\text{--}2 \mu\text{mol L}^{-1}$ through partitioning between solid and liquid phases. This phenomenon can be linked to changes in suspended sediment load of the river. Hence, the depletion of TSM in the lower reaches of Changjiang in the post-TGD period (i.e., after 2003) may indicate the lower capacity of suspended sediments to combine with anthropogenic DIP. However, the increase in DIP of water column at the river mouth (i.e., downstream of Xuliujing) cannot solely be explained by the reduction in TSM because of the trapping of sediments behind TGD.

In Nantong and Xuliujing, DSi concentrations have re-

mained relatively stable and/or have increased slightly over the past 20 years (Figure 7). For instance, DSi concentration in Xuliujing after 2005 was comparable to concentrations reported in the 1970s and 1980s, that is, during the period well before the construction of TGD (Zhang et al., 2006). Consequently, DIN/DSi of Changjiang has increased systematically and exceeds 1.0 at present, indicating that relative to that in the headwaters from the Qinghai-Tibetan Plateau (i.e., Shigu), and DIN/DSi has been increased by over four-folds close to the river mouth over a river course of 4,500 km because of anthropogenic nitrogen emissions (e.g., fertilizer application) over the watersheds. However, data

examination in greater details indicated that DSi concentration at the river mouth has increased slowly but rather steadily after 2000. This trend may be related to the changes in water flow proportions of DSi between the upper parts of drainage basin (i.e., upstream the TGD) and the middle and lower reaches. As mentioned before, tributaries and lakes in areas downstream of TGD have higher DSi and $\delta^{30}\text{Si}$ than waters exported from the TGR. Hence, the regulation of upstream water flow by TGD alters the proportions of water from the upper and middle/lower reaches in the measured river samples. The higher the proportion of tributaries from the middle and lower reaches, the higher the concentration of DSi and heavier the value of $\delta^{30}\text{Si}$, as evidenced in Nantong and Xuliujing.

Another important aspect of nutrient regimes is changes in species ratios. The observed species ratios at Nantong and Xuliujing illustrate an overall trend of reduction for DIN/DIP but increase for DIN/DSi at the annual scale because of continuous increase in DIN and DIP with a relatively stable DSi in the Changjiang drainage basin (Figure 7). The observed increase in DIP is also faster than the increase in DIN at the river mouth over last two decades. This re-emphasizes the modification of nutrient structure by human activities through the enrichment of anthropogenic nutrients (i.e., nitrogen and phosphorus) relative to dissolved silicate, inducing a continuous increase in DIN/DSi and DIP/DSi of the river water. Moreover, the trends of nutrients differed between Datong and Nantong/Xuliujing, as indicated by time-series data. For instance, the measured DIN/DSi was 0.73 at Datong and 0.80 at Nantong/Xuliujing in 1997 and 1.09 at Datong and 1.06 at Xuliujing in 2016. Of note, wastewaters from areas downstream of Datong have much higher DIN/DIP (up to 400) and DIN/DSi (up to 3–4) (Zhang et al., 2021), and drainage of wastewaters into the estuary can modify the DIN/DIP of samples, further affecting the implementation for management based merely on riverine compositions measured at Datong (cf. Lui and Chen, 2012).

3.8 Major tributaries at sub-basin dimensions

In Table 4, the annual water discharge and nutrient composition of the major tributaries of Changjiang over the whole drainage area are compared. At the sub-basin scale, a considerable spatial variability was noted between different tributaries in terms of the concentration of nutrients and species ratio changes from upstream down to the confluence with the mainstream for a given tributary. Such comparisons can offer some important clues, as summarized below.

Data in Table 4 cover a wide drainage area, from 10×10^3 to $215 \times 10^3 \text{ km}^2$, with an annual water load of 5×10^9 to $70 \times 10^9 \text{ m}^3$, both differing by more than one order of magnitude among the tributaries. Regarding nutrients, DIN in these tributaries of the Changjiang watershed ranged from

<10 to $>600 \mu\text{mol L}^{-1}$, DIP from 0.02 to $20 \mu\text{mol L}^{-1}$, and DSi from 20 to $200 \mu\text{mol L}^{-1}$. In Table 4, three important lakes are also compared, including Dongtinghu and Poyanghu in the middle reaches and Taihu in the tide-influenced deltaic area. These lakes are eutrophicated, as reported in the literature for their high concentrations of nutrients, and show elevated DIN/DIP and DIN/DSi molar ratios.

As mentioned earlier, tributaries draining through the source areas of the Qinghai-Tibetan Plateau, such as Jinshajiang and Yalongjiang, present low DIN and DIP levels in their upstream parts (i.e., Shigu and Jinhe), with a low DIN/DSi (0.1–0.2) but moderate DIN/DIP due to the retention of phosphorus and silicon relative to nitrogen from erosion (e.g., leaching of soils). Thereafter, concentrations increase downstream, reaching high values at confluence with the mainstream, due to increase in perturbations from human activities, such as urbanization and agriculture. Typically, tributaries draining through agricultural areas present high DIN and DIP concentrations, with a DIN/DIP of >50 and DIN/DSi of >1.0 because of different chemical properties of nitrogen and phosphorus in the catchment areas. As opposed to phosphorus, nitrogen has no natural mineral resources in the watersheds from the literature. Moreover, nitrogen salts are readily soluble and hence easily leached from soil profiles, whereas phosphorus tends to form insoluble compounds with Al, Ca, and Fe and can be retained in the watersheds.

Two large lakes in the middle reaches of Changjiang, namely Dongtinghu and Poyanghu, present high concentrations of DIN and DIP because of embracing tributaries with high nutrient loads. Moreover, when the tributaries drain through urbanized areas, such as Wujiang and Hanjiang, phosphorus loading can increase considerably with a reduction in DIN/DIP, although both concentrations are still high. Further, the DIN/DIP of water samples can be affected by wastewater treatment processes in urban and domestic areas, and the removal of nitrogen through denitrification and aeration can reduce the nitrogen-to-phosphorus ratio of post-treatment waters. Similar to that in the mainstream of Changjiang, DIN and DIP concentrations have tended to increase since the mid-1990s in these tributaries, whereas DSi in the river systems did not exhibit any long-term trend between 1997 and 2016.

Another factor to be considered is the spatial yield of nutrients in these tributaries. Among the top 17 tributaries of Changjiang, the spatial yield for DIN ranged from 5×10^3 to $10 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ for the upstream tributaries Jinshajiang (JSJ) and Yalongjiang (YLJ) and from 140×10^3 to $150 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ for Tuojiang (TJ) and Qingjiang (QJ), indicating a difference of more than one order of magnitude. Further, DIP yield ranged from $<0.1 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ for Jinshajiang (JSJ) and Chishuihe (CSH) to 1.5×10^3 – $2.0 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ for Tuojiang,

Table 4 Comparison for nutrient concentrations among major tributaries of the Changjiang drainage basin^{a)}

Tributaries	Drainage area ($\times 10^3 \text{ km}^2$)	Water flow ($\times 10^9 \text{ m}^3 \text{ yr}^{-1}$)	DIN ($\mu\text{mol L}^{-1}$)	DIP ($\mu\text{mol L}^{-1}$)	DSi ($\mu\text{mol L}^{-1}$)	DIN/DIP	DIN/DSi
Jinshajiang	214.2	44	2.39–38.3	0.08–0.36	100–118	87–382	0.22–0.49
Yalongjiang	128.4	55.5	13.6–25.9	0.07–1.24	68–170	15–230	0.12–0.23
Niulanjiang	13.2	5.5	14.5–132	0.05–2.3	94.7–123	57–394	0.12–1.32
Minjiang	135.4	78.7	80.3–242	1.06–11.8	49.0–156	16–76	0.87–2.3
Daduhe	82.7	48.6	19.8–46.9	0.06–0.70	81.6–93.3	34–163	0.21–0.57
Tuojiang	27.9	12.7	268–608	4.01–19.2	70.0–164	30–68	1.6–7.2
Chishuihe	20.4	8.2	92.8–127	0.02–0.49	57.6–61.8	259–724	1.7–2.2
Fujiang	36.4	15.4	85.7–186	0.80–1.74	19.6–156	50–151	1.2–2.9
Jialingjiang	156.7	67.6	59.2–131	0.99–1.44	45.7–129	56–91	1.0–2.7
Wujiang	83	41.3	96.7–245	1.1–10.4	47.0–138	14–123	1.1–2.8
Qingjiang	17	14.3	146–187	0.17–2.73	60.5–95.6	58–107	1.7–2.4
Yuanjiang	85.2	58	28.7–136	0.16–17.3	48.8–180	7.4–188	0.22–1.4
Zishui	26.7	20.5	50.1–169	0.20–3.35	81.8–149	15–394	0.33–1.7
Xiangjiang	81.6	62.1	66.2–229	0.23–1.20	76.5–186	98–288	0.67–1.9
Hanjiang	142.1	43.9	80.6–122	0.20–2.34	71.9–133	52–403	0.81–1.4
Ganjiang	80.9	66.2	43.3–67.9	0.15–0.36	110–154	187–289	0.29–0.53
Fuhe	15.8	11.7	39.7	1.2	194	33.1	0.21
Dongtinghu			38.1–158	0.42–3.25	46.1–161	39–323	0.47–3.4
Poyanghu			49.5–124	0.31–1.01	111–150	61–401	0.38–0.89
Taihu			2.21–466	0.03–7.00	2.77–143	8.8–1203	0.18–13

a) In the table, annual water discharges are for the period of 2005–2014. To compare with measurements at the river mouth (i.e., Xuliujing), data from three lakes, i.e., the Dongtinghu, Poyanghu and Taihu, are also shown.

Minjiang (MJ) and Wujiang (WJ), all of which drain in Sichuan and Guizhou. Finally, the DSi yield ranged from 20×10^3 to $30 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ in Jinshajiang and Chishuihe in the upper stream, and the values were elevated to 100×10^3 – $150 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ in Ganjiang and Fuhe, which empty into Poyanghu in the middle reaches. These trends may be explained by increased silicate weathering and erosion from the northern to the southern parts of the Changjiang drainage basin. Moreover, chemical yields of nutrients (e.g., DSi) can be regulated by the petrology of watersheds as well, for example, carbonates vs silicates; tributaries with abundant carbonates in their drainage basin, such as Wujiang and Chishuihe, have relative low yield for DSi.

In the tide-influenced delta downstream of Datong, surface runoff may exhibit different nutrient regimes. Compared with tributaries from the upstream, where agriculture in highlands increases nutrient concentrations and DIN/DIP in river waters, surface waters in coastal areas (e.g., Taihu) may present a higher rate of increase in the concentration of DIP than of DIN, when surface waters (e.g., river) are affected by domestic and/or aquaculture activities that reduce the DIN/DIP value downstream. Indeed, in the watershed of Taihu, the amount of aquaculture and domestic sewage drainage has increased nearly 30-fold from 1980 to 2014, with a 40–50%

decrease in DIN/DIP of lake water (<http://data.stats.gov.cn/>).

Considerably high concentrations of anthropogenic nutrients (i.e., nitrogen and phosphorus) have been recorded in tributaries in Sichuan Province (e.g., Tuojiang), resulting in eutrophication, which is attributed to surface runoff from cultivated lands and drainage of mining waste (Tao et al., 2016). Moreover, elevated concentrations of nutrients have been detected in ground waters of the watersheds of these tributaries, increasing nutrient levels in the base flow of river (Xue and Zhang, 2009).

3.9 Nutrient speciation and partitioning between particulate and dissolved phases

In 1997, DON in the Changjiang was 10 – $20 \mu\text{mol L}^{-1}$, compared with 50 – $100 \mu\text{mol L}^{-1}$ for DIN over the water course of ca. 4,000 km from the river mouth upstream (Liu et al., 2003). During the same period, DOP of the river was ca. $0.5 \mu\text{mol L}^{-1}$ in the middle and lower reaches, which was comparable to DIP, although the concentration was $1 \mu\text{mol L}^{-1}$ at some stations (Liu et al., 2003). During this period, the areal yield of DON was nearly one-third of the yield of DIN in major tributaries, whereas the yield of DOP was comparable to that of DIP (Liu et al., 2003). This resulted in a DON/DOP value of 10–20 in the mainstream of

Changjiang, while the ratio varied over a wide range, at 25–160, for the major tributaries, with values exceeding 40 in Sichuan Province (Liu et al., 2003).

Twelve years later and in 2009, DON in the mainstream ranged from 5 up to 20 $\mu\text{mol L}^{-1}$ in the mainstream, consistent with DON in the northern (5–20 $\mu\text{mol L}^{-1}$) and southern (4–15 $\mu\text{mol L}^{-1}$) tributaries (Chen, 2012). High levels of DON at >10 $\mu\text{mol L}^{-1}$ were noted between Chongqing and Wuhu; this can be linked to the high DON level of tributaries draining through this area, such as the Minjiang and Chishuihe, which join the mainstream with a DON of >15 $\mu\text{mol L}^{-1}$. Regarding DOP in Changjiang watersheds, concentrations of 0.2–1.0 $\mu\text{mol L}^{-1}$ were noted in the mainstream over the river course of ca. 4,500 km, with values in the range of 0.4–2.0 $\mu\text{mol L}^{-1}$ for northern and 0.2–3.0 $\mu\text{mol L}^{-1}$ for southern tributaries. Consequently, the observed DON/DOP ratio in 2009 was 6–25 for the mainstream, 3–28 for northern tributaries, and 2–45 for southern tributaries. Thus, in 2009, DON/TDN was in the range of 2–28%, while DOP/TDP was in the range of 7–90% in Changjiang watersheds, indicating that DOP is relatively more important than DON in the dissolved pool of anthropogenic nutrients. Overall, the dissolved organic fraction of nutrients, particularly DOP, tended to increase from 1997 to 2009, which can be linked to more frequent algal blooms in the reservoirs and lakes during the post-TGD period (Tang et al., 2018).

Furthermore, comparison of values between 1997 and 2009 indicated that on average, DON/DOP, DON/TDN, and DOP/TDP were significantly higher in 1997 than in 2009, which was true for both the main water course as well as northern and southern tributaries in the drainage basin (Table 5). One of the plausible explanations for this difference is the increase in organic fraction relative to the total dissolved nutrient pool due to spring plumes of photosynthetic species (e.g., phytoplankton) in the aquatic environments in 1997, as opposed to that during the late summer and autumn expeditions in 2009. In addition, the amount of TSM in the Changjiang mainstream during the expeditions of 2009 was twice as high as that during the expeditions of 1997 in the upstream area, due mainly to the floods of northern tribu-

aries. Another interesting finding is that PP, after normalizing to TSM, in the Changjiang was much higher in 2009 than in 1997. This can be a result of increased retention of nutrients in the TGR because of dam construction, which promoted 20–25 events of phytoplankton blooms per year and consequent changes (transfer) in speciation from inorganic to organic forms in the water column (Zhang et al., 2015; Wang et al., 2016). In recent years, increased eutrophication of lakes in the middle and lower reaches has been reported.

Comparison of values between 1997 and 2009 indicated that DON in the watersheds remained relatively stable, whereas DOP tended to increase from 1997 to 2009, thereby accelerating lacustrization and reservoirization in the middle and lower reaches of the drainage basin and reducing the DON/DOP of the mainstream in 2009.

Changes in nutrient speciation are associated with variability in the amount of TSM in the water column. Historically, seaward sediment load of Changjiang was 0.45×10^9 tons yr^{-1} , and the suspended sediment load has considerably reduced to 0.1×10^9 tons yr^{-1} , particularly after the enclosure of TGD in 2003 (CWRC, 2010). Among the various species of nutrients, phosphorus shows a higher affinity toward particulate matter (e.g., TSM) than nitrogen in aquatic environments. Phosphorus partitioning between particulate and dissolved phases increases with the amount of TSM in Changjiang, indicating that the capacity of the river to buffer changes in nutrient concentration can be enhanced by higher TSM levels (Zhang, 2007). Moreover, such a partitioning of nutrients between dissolved and particulate phases is not reversible. For instance, phosphorus adsorbed to solid phases in the river will not be completely released into water (Zhang, 2007). Since the sediment load of Changjiang has decreased by over a quarter since the beginning of this century, such changes in riverine TSM may generate a greater impact on the partitioning of DIP than of DIN, leading to the retention of more DIP in the dissolved phase. This can explain in part the observation that DIP has increased faster than DIN over the last several decades. Hence, along with the reduction in sediment load during the post-TGD period, the buffering capacity of suspended particles in

Table 5 Comparison of nutrient data between major tributaries and the mainstream of the Changjiang for 1997 (dry season) and in 2009 (flood season)^{a)}

Year	River	DON	DOP	DON/DOP	DON/TDN	DOP/TDP
1997	Mainstream	0.25–23.4	0.12–1.21	27±21 (9–115)	0.14±0.06 (0.07–0.29)	0.46±0.21 (0.14–0.89)
	Southern Tributaries	7.66–68.0	0.14–0.84	79±145 (24–493)	0.28±0.20 (0.08–0.82)	0.64±0.27 (0.10–0.94)
	Northern Tributaries	4.75–163	0.15–3.91	61±49 (18–165)	0.24±0.06 (0.16–0.34)	0.50±0.30 (0.02–0.81)
2009	Mainstream	4.5–17	0.2–1.5	18±7 (7–33)	0.11±0.04 (0.06–0.18)	0.34±0.22 (0.16–0.90)
	Southern Tributaries	4–16	0.1–3.5	14±16 (2–46)	0.10±0.09 (0.03–0.28)	0.45±0.26 (0.07–0.90)
	Northern Tributaries	5–18	0.4–2.5	12±9 (3–28)	0.11±0.07 (0.05–0.20)	0.39±0.20 (0.17–0.74)

a) These two surveys were both carried out from river mouth upstream over a water course of 4000 to 4500 km. In the table, data are shown average plus sd, and range in brackets (concentration unit: $\mu\text{mol L}^{-1}$).

the river on DIP has considerably reduced in the middle and lower reaches of Changjiang.

4. Discussion

4.1 Did dam construction (i.e., TGD) significantly affect nutrient trapping in Changjiang?

Trapping of nutrient species, particularly DSi, in reservoirs has been reported in many aquatic ecosystems worldwide, such as Danube and Mississippi rivers (Humborg et al., 1997; Goolsby et al., 1999; Turner and Rabalais, 2003). Likewise, in the case of Changjiang, previous studies have argued that changes in DSi may be related to the trapping effect of the TGR (Zhang et al., 2006).

To evaluate the impact of TGR on the nutrient chemistry of Changjiang, the efficiency of nutrient retention (R_{nu}) was defined as follows:

$$R_{\text{nu}} = \frac{\text{NU}_{\text{in}} - \text{NU}_{\text{ou}}}{\text{NU}_{\text{in}}}, \quad (4)$$

where NU_{in} and NU_{ou} are the nutrient concentration and/or flux into the TGR and export across the TGD, respectively.

In the present study, we compared water quality at Yichang (YC), which is 30 km downstream of the TGD (NU_{ou}), and Jiangjin (JJ) to Cuntan (CT) (Figure 1), which are stations upstream of the TGR (NU_{in}), taking contributions from ungauged tributaries around the watershed into account. We investigated nutrient data at upstream sampling sites between Jiangjin and Cuntan and a downstream sampling site at Yichang during 2003–2016 to examine whether the TGD produced significant effects on nutrient concentration in Changjiang; in other words, we explored nutrient “trapping” and/or “retention” in the reservoir (*t*-test, $p=0.05$). In total, 27 datasets were available from upstream stations (i.e., Jiangjin and Cuntan) and another 23 from Yichang were obtained in the present study and from the literature, covering both flood and dry seasons (Ding et al., 2004; Chetelat et al., 2008; Guo, 2008; Müller et al., 2008; Yao et al., 2009; Bao et al., 2010; Jiang et al., 2012a). As shown in Figure 8, at Yichang, which

is downstream of TGD, DIN increased by 13% on average compared with values at Jiangjin and/or Cuntan, which are upstream of the reservoir, and the difference for nitrate alone was 23%. During the same period, DIP increased by 40% at the upstream stations compared with that at the downstream stations of TGR. In contrast, DSi concentration at Yichang was 12% lower than that at Jiangjin and Cuntan (Figure 8), and albeit without a systematic trend. Consequently, DIN/DIP and DSi/DIN at Yichang were respectively 27% and 22% lower than those at sections upstream of TGR. Furthermore, data from the wet season (May–October) showed a similar pattern of nutrients to average values over the study period. However, during the dry season (November–April), that is, at the impoundment stage of TGD, DIN and DIP at Yichang were lower than those at sections upstream of TGR, whereas DSi increased across the reservoir (Figure 8). Comparison with results in the literature confirmed our interpretations, proving the robustness of our diagnostic analysis of nutrient dynamics in the Changjiang (cf. Ding et al., 2019). Considering the water residence time of approximately a month on average for TGR, which can be estimated based on the capacity of reservoir and water flow at Yichang, biological removal of inorganic nutrient species through phytoplankton uptake can be modest; hence, a rather limited “trapping” effect can be expected because of rapid flushing processes in the reservoir.

As an independent check, we further examined the primary production of TGR and linked it to nutrient fluxes of Changjiang in the section between Cuntan and Yichang. The mean observed gross primary productivity (GPP) of TGR was $0.070 \text{ mol C m}^{-2} \text{ day}^{-1}$ (range: $0.014\text{--}0.15 \text{ mol C m}^{-2} \text{ day}^{-1}$), cited by Xiong et al. (2015). This value of GPP is within the reported range for major lakes from the middle and lower reaches of Changjiang (Zeng et al., 2007). Using the mean ratio of net primary productivity (NPP) to GPP of 0.67 (range: 0.50–0.80) for lakes in China (Yi et al., 2014) and the stoichiometric ratio (e.g., Redfield Value of C:N:P=106:16:1) between carbon and nutrients, nitrogen and phosphorus fixed by the NPP of TGR were estimated to be

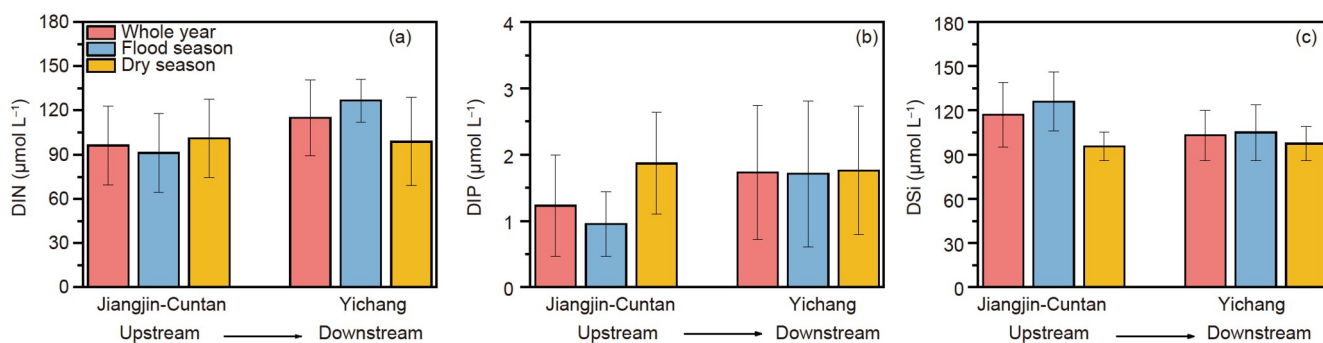


Figure 8 (Color online) Comparison of nutrient concentrations between upstream of the TGR at Jiangjin-Cuntan Sector across the mainstream of the Changjiang and downstream TGD at Yichang Station for the period of 2003–2016. (a) DIN; (b) DIP; (c) DSi.

respectively 5–10% and 10–20% of nutrient fluxes from Changjiang entering the reservoir. These results are consistent with our above-mentioned observations.

In summary, by collating the data obtained from 11 expeditions and time-series data from the river mouth, together with previously published results, we observed that the so-called “nutrient trapping” in TGR does not play a significant role in modifying nutrient regimes further downstream in Changjiang and should not therefore be exaggerated. Overall, TGR produces a rather limited effect on the regulation of nutrient fluxes from Changjiang into the East China Sea at the annual scale based on a number of considerations. First, our field samples showed that nutrient concentrations were similar in sections upstream and downstream of the reservoir (i.e., TGR). Moreover, nutrient species, specifically DIN and DIP, continued to increase downstream of TGD (e.g., at Yichang) and further to the river mouth, even after the dam was closed in 2003 and then became fully operational in 2009. In addition, DSI remained somewhat stable and/or tended to increase downstream of TGR further in the lower reaches of Changjiang and at the river mouth after the construction of TGD. Over the last three to four decades, DSI did not exhibit any systematic reduction at the river mouth based on monthly sampling and data from the literature (Figure 7). These results are contrary to the trends observed in many other global river-sea systems, for example the Danube River and Black Sea (Humborg et al., 1997). Nevertheless, the increase in DIN and DIP at Yichang relative to that at Cuntan and Jiangjin is in part related to nutrient remobilization and/or legacy nutrients (Box 2) from watersheds around TGR, influx from various rivers, and/or even waste drainage in ungauged watersheds in this region (Yang et al., 2014). Another reason that the nutrient trapping effect of TGD was not as significant as expected at the river mouth (i.e., at Xuliujing) based on the literature is that previous reports were drawn from sporadic sampling and measurements at a few sites, which did not permit the extraction of concentration trends and/or systematic examination of response. Furthermore, the retention of nutrients in the TGR is compensated by tributaries, such as Dongtinghu, Poyanghu, and Hanjiang, and other surface runoff (e.g., lake and reservoir) with high nutrient concentration over a 2,000 km river course downstream the reservoir (i.e., TGR). More recently, Ding et al. (2019) argued that the retention of nutrients behind the TGD should not be misinterpreted, and the nutrients retained in the TGR can be compensated by influxes from lakes and tributaries downstream of Yichang until the river mouth. Further, Ding et al. (2019) indicated that TDN, TP and DSI retained in the TGR accounted for 15%, 12%, and 1% of the respective fluxes measured at the Datong Hydrographic Station, which is the limit of tide-influenced river course, emphasizing once again that the retention of nutrients within the TGR is rather limited compared to the annual nutrient fluxes from

Changjiang to the East China Sea.

4.2 Input via atmospheric pathways

To evaluate whether atmospheric depositions can serve as an important external source of nutrients, we calculated the deposition fluxes of nutrients based on ca. 430 observational data sets from 153 stations across the entire Changjiang watershed during 1983–2014 retrieved from over 100 publications in the literature and government reports. Details of the assessment of atmospheric depositions are available in Appendix 2: Atmospheric Depositions, and results are summarized and discussed in this section.

4.2.1 Nitrogen input

Regarding atmospheric depositions of DIN, there are important spatial and temporal dimensions across the entire watersheds of Changjiang, with an overall distribution of higher fluxes at urban/suburban sites (Group 1) in the middle and lower reaches than at remote sites in the upstream areas (Group 2), such as the Qinghai-Tibetan Plateau (Figure 9). For instance, the observed concentrations of NO_3^- were 1.69–198 $\mu\text{mol L}^{-1}$ and those of NH_4^+ were 8.70–263 $\mu\text{mol L}^{-1}$ in wet depositions. The $\text{NO}_3^-/\text{NH}_4^+$ molar ratio was 0.1–2.4 for atmospheric wet depositions, with an average of 0.49 ± 0.38 (1sd), indicating the dominance of NH_4^+ in depositional events. DON concentration and its flux in wet depositions were reported from only 31 stations over the entire watershed of Changjiang, and the DON/DIN ratio was 0.01–1.19. Specifically, the DON/DIN ratio was 0.01–1.19 in urban/suburban areas and 0.01–0.41 in remote areas.

Data on atmospheric dry depositions for nitrogen for the watersheds of Changjiang are scarce. Xu et al. (2015) compiled dry deposition data of nitrogen from 43 stations across China and reported dry-to-wet deposition ratios of nitrogen in the range of 0.79–2.35 in urban/suburban areas and 1.17 ± 0.93 in remote areas.

Consequently, atmospheric wet deposition fluxes of DIN over the Changjiang watershed show marked spatial variability, ranging from $14.5 \times 10^3 \text{ mol N km}^{-2} \text{ yr}^{-1}$ in remote and upstream stations to $535 \times 10^3 \text{ mol N km}^{-2} \text{ yr}^{-1}$ at coastal and urban sites, indicating a difference of over one order of magnitude. Our results showed that DIN deposition was $(257 \pm 160) \times 10^9 \text{ mol N yr}^{-1}$ (1sd) over the entire watershed of Changjiang, with values in urban/suburban areas being 70% higher than those in remote areas (Figure 9).

Furthermore, the total deposition flux (i.e., dry plus wet depositions) of nitrogen via atmospheric pathways was $(594 \pm 367) \times 10^9 \text{ mol N yr}^{-1}$ (1sd) over the entire drainage basin of Changjiang, with 52% contributed by dry depositions. In Table 6, atmospheric wet and dry pathways as well as the total depositions over the watersheds of Changjiang are

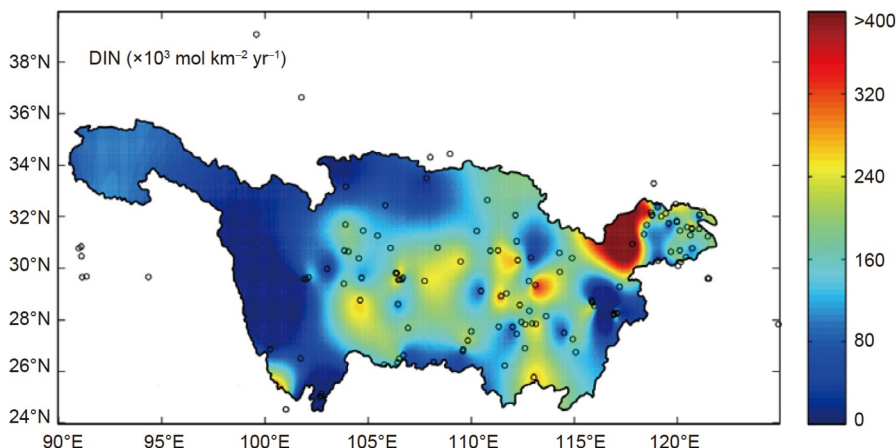


Figure 9 (Color online) Distribution of DIN flux (unit: mol N km⁻² yr⁻¹) of atmospheric wet depositions over the Changjiang watersheds. Data in the figure show the average of 1983–2014, taking into consideration of temporal and spatial dimensions of observations. Observational sites for atmospheric wet depositions in this study are illustrated as open circles in this figure. Details of data compilation can be found in Appendix 2: Atmospheric Depositions (SI2).

compared. Spatial gradients were noted between Group 1 and Group 2 sites across the whole study area.

As shown in Figure 10, in samples from urban and suburban areas (Group 1), the concentration of NO₃⁻ + NH₄⁺ continued to increase during 1983–2014 at a rate of 0.91 × 10⁹ mol N yr⁻¹. However, samples collected from remote area (Group 2) did not exhibit any significant trend for NO₃⁻, NH₄⁺, or both during the same period (1983–2014).

4.2.2 Phosphorus input

As reported in the literature, the ratio of dissolved inorganic phosphorus (DIP_{wet}) to dissolved organic phosphorus (DOP_{wet}) in rainwater is 1.46, and the ratio of soluble phosphorus (TDP_{dry}) to total phosphorus (TP_{dry}) in aerosols is 0.48 (Bi, 2006; Jiang, 2009; Zhu, 2011; Han, 2013). Variations in P-fluxes of atmospheric wet (range: 67–1,900 mol P km⁻² yr⁻¹) and dry (range: 65–6,900 mol P km⁻² yr⁻¹) depositions throughout China are presented in Table 7. Furthermore, the total deposition of phosphorus via atmospheric pathways ranges from 0.68 × 10⁹ to 16.4 × 10⁹ mol P yr⁻¹, with an average of (3.44 ± 4.43) × 10⁹ mol P yr⁻¹ (1sd); of this, 0.06 × 10⁹–2.20 × 10⁹ mol P yr⁻¹ are derived from urban/suburban sites and 0.62 × 10⁹–14.2 × 10⁹ mol P yr⁻¹ from remote areas (Table 7).

4.2.3 DSi

Data of DSi in atmospheric depositions were even more scarce than those of phosphorus, and most of the available information was based on studies in the coastal areas of China. In the present study, DSi deposition over Changjiang watersheds was elaborated, as shown in Table 8. To our best knowledge, atmospheric DSi fluxes at the time of the study ranged from 0.10 × 10³ to 7.40 × 10³ mol Si km⁻² yr⁻¹ in wet depositions and from 0.30 × 10³ to 8.50 × 10³ mol Si km⁻² yr⁻¹

in dry deposition (Note: water and/or acid soluble fractions only). The first-order estimate of total atmospheric depositions of soluble silicate based on the sum of dry and wet depositions integrated over the entire drainage basin of Changjiang was 0.82 × 10⁹–32.8 × 10⁹ mol Si yr⁻¹, with an average of (9.64 ± 9.84) × 10⁹ mol Si yr⁻¹ (1sd). In the present study, the observed concentrations and estimates of atmospheric pathways indicated that ca. 10% of DSi flux from Changjiang is exported to the East China Sea.

Compilation and comparison of the depositional fluxes of nutrients indicated that atmospheric pathways as a whole are an important source to sustain the ecosystem of the Changjiang drainage basin. Moreover, it is one of the pivotal external forces driving nutrient export from Changjiang to the global oceans. However, nutrients supplied via atmospheric pathways combine with other external sources (e.g., chemical fertilizers) and actively interact with autotrophic organisms in the ecosystem (e.g., forest and grassland) across the Changjiang watershed, in turn regulating the riverine fluxes of nutrients, which is discussed later.

4.3 Analysis of sources and sinks for nutrients

To assess the collective impacts of natural processes and anthropogenic activities on nutrient chemistry over the entire drainage basin of Changjiang, we investigated and compared sources and sinks and evaluated the retention of nutrients since 1979 (Appendix 3: Source vs Sink). At the annual scale, spatial yields (Y_{nu}) of nutrients (mol km⁻² yr⁻¹) across the drainage area can be assessed using the following equation:

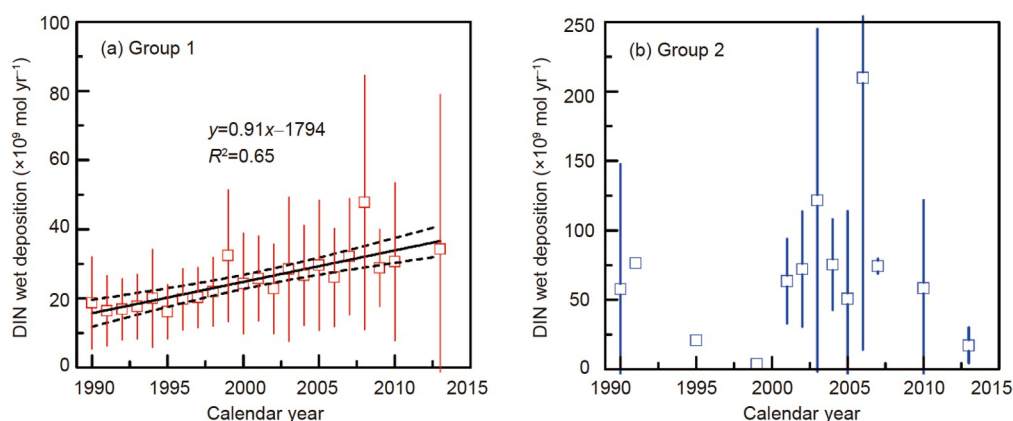
$$Y_{nu} = \frac{1}{A} \left[W_{nu} - R_{nu} + \sum_{i=1}^n (I_i \times M_i) \right], \quad (5)$$

where A is the catchment area; W_{nu} represents weathering;

Table 6 Summary of atmospheric pathways for nitrogen deposition over the watersheds of the Changjiang in the period of 1983–2014^{a)}

Categories	Group 1	Group 2	Changjiang watersheds
Drainage area (%)	21.7	78.3	100
Deposition flux of DIN ($\times 10^3$ mol N km ⁻² yr ⁻¹)	174	107	
Total DIN depositions ($\times 10^9$ mol N yr ⁻¹)	77.8	173	250
Deposition of DON ($\times 10^9$ mol N yr ⁻¹)	20.2	13.8	34.0
Dry deposition of N ($\times 10^9$ mol N yr ⁻¹)	101	202	303
Total depositions of N via atmosphere ($\times 10^9$ mol N yr ⁻¹)	199	390	588

a) Based on the locations and characteristics of sampling site, data are classified into two groups: urban/suburb (Group 1) and remote/upstream (Group 2), respectively. Details of data compilation are in the Appendix 2: Atmospheric Depositions (SI2).

**Figure 10** (Color online) Trend analysis for DIN in atmospheric wet depositions for Group 1 (a) and Group 2 (b) samples, respectively, in the period of 1983–2014. The error bars show the standard deviation of annual average. The solid line and dashed curves refer to the linear regression and 95% confidence level for DIN in wet depositions. Details of data compilation are in the Appendix 2: Atmospheric Depositions (SI2).**Table 7** Summary of atmospheric deposition pathways for phosphorus over the watersheds of the Changjiang in the period of 1983–2014^{a)}

Items	Group 1	Group 2	Changjiang watersheds
Drainage area (%)	21.7	78.3	100
Wet deposition flux of P (mol P km ⁻² yr ⁻¹)	908	1103	
Dry deposition flux of P (mol P km ⁻² yr ⁻¹)	513	634	
Wet and dry deposition flux of P (mol P km ⁻² yr ⁻¹)	1421	1737	
Total depositions of P via atmosphere ($\times 10^9$ mol P yr ⁻¹)	0.63	2.80	3.44

a) Details of data compilation are from Appendix 2: Atmospheric Depositions (SI2).

Table 8 Estimation on wet and dry deposition fluxes of dissolved silicates via atmospheric pathways in China^{a)}

Locations	Wet deposition of Si (mol DSi km ⁻² yr ⁻¹)	Dry deposition of Si (mol DSi km ⁻² yr ⁻¹)
Qingdao	2650–3500	400–8500
Qianliyan	2000–7400	320–2300
Zhoushan	1950–4130	300
Shanghai	100	

a) Details of data compilation are from Appendix 2: Atmospheric Depositions (SI2).

R_{nu} is the retention of nutrients in the watersheds; M_i represents other contributions (e.g., human activities and river export); and l_i is positive for sources and/or inputs and negative for sinks and/or outflow.

Using a box model with the assumption of steady state, Y_{nu}

can be linked to riverine fluxes of nutrients through specific surface runoff F_{nu} (unit: m³ km⁻² yr⁻¹), catchment area A , and nutrient concentrations (unit: mol m⁻³) measured at the river mouth.

Compiled data for 1979–2014 are presented in Appendix

3: Source vs. Sink. Data for 2003–2014 are summarized and compared in Tables 8 and 9. In this section, discussion is focused on data for 2003–2014 to compare with the seaward nutrient export from Changjiang measured at Nantong/Xuliujing.

4.3.1 Nitrogen

During 2003–2014, the total nitrogen input to the Changjiang drainage basin reached 2.2×10^{12} mol yr⁻¹. Atmospheric deposition accounted for 26% of input and was, therefore, an important external source of nitrogen, together with synthetic

fertilizer application, which represented another 30%. These were closely followed by the input of organic fertilizer in the form of manure and crop residues (20%) and combined nitrogen fixation in forests, grasslands, farmlands, and wetlands (8%). Waste drainage from aquaculture and domestic sectors accounted for 9%, and the products of fossil fuel combustion accounted for 6% (Appendix 3: Source vs. Sink). During this period (i.e., 2003–2014), the total output and retention of nitrogen across the drainage basin of Changjiang was approximately 5% higher than its influx, due partly to the uncertainties in data compilation and statistics.

Table 9 Summary of nitrogen budget of the Changjiang watersheds with percentage in parentheses^{a)}

Categories	This study	Bao et al. (2006)		Xing and Zhu (2002)	Yan et al. (2010)	Jiang et al. (2012b)
Study period	2003–2014	1980	1990	1996	2000–2002	2005
<i>Input of N</i>						
Synthetic fertilizer-N	675±40 (31±2%)	184	402	521	419	436
Organic fertilizer-N	439±18 (20±1%)	296	412	411	359	404
Manure-N	394±18 (18±1%)	269	342	380	359	374
Straws-N	45±3 (2±0.2%)	27	70	31		30
Atmospheric depositions-N	587±16 (27±1%)	36	36	268	300	239
Fixation-N	158±9 (7±0.5%)	46	46	93	139	158
Wastewaters-N	208±20 (9±1%)	–	–			
Aquaculture wastewaters-N	120±20 (5±1%)	–	–	65		21
Domestic wastewaters-N	88 (4%)					
Fossil fuel-N	131±40 (6±2%)			65		
Subtotal	2198±65 (100%)	571	927	1423	1220	1259
<i>Output of N</i>						
Harvests and culture products-N	575±34 (26±2%)	–	–	–	–	–
Harvest crop-N	411±32 (19±2%)	185	239	310	139	–
Production of land-based animal-N	115±10 (5±1%)	–	–	–	–	–
Production of aquatic animal-N	49±8 (2±0.4%)	–	–	–	–	–
Emission-N as gas species	547±15 (25±1%)	–	–	–	–	–
Denitrification-N	240±11 (11±1%)	66	131	153	–	251
Volatilization-N	306±10 (14±1%)	64	119	166	–	–
Open water N ₂ O emission ^{*1}	0.6 (0.03%)	–	–	–	–	–
Export by river as TN	138±22 (6±1%)	–	–	–	–	–
Export by river as DIN	107±19 (5±1%)	149 ^{*2}	241 ^{*2}	271 ^{*2}	121 ^{*2}	251 ^{*2}
Export by river as DON	13±8 (0.6±0.4%)	–	–	–	–	–
Export by river as PN	18±8 (0.8±0.4%)	–	–	–	–	–
Subtotal	1260±49 (57±3%)	571	921	1150	260	251
<i>Retention of N</i>						
Retention in farmland-N	374±12 (17±1%)	108	191	251	–	–
Retention in forest and grass-N	351±25 (16±1%)	–	–	–	–	–
TGR trap of sediments -N	28±18 (1.3±1%)	–	–	–	–	–
Subtotal	753±23 (34±1%)					
Differences	185±82 (8±4%)	0	6	276	1078	1259

a) ^{*1} Data from Zhao et al., 2006; ^{*2} DIN transported into water bodies. Unit: $\times 10^9$ mol yr⁻¹. Data from the literature are also shown in the table for comparison. Details of data compilation are shown in Appendix 3: Source vs Sink (S13).

Nitrogen retention in soils and sediments trapped by the TGD as particulate nitrogen, and nitrogen fixation by forest biomass and grasses in the watersheds collectively accounted for 34% nitrogen input to the Changjiang drainage basin. Crop harvest as well as animal and aquatic products (e.g., fishery) represented 26% of the total input, and denitrification plus losses through the volatilization of chemical fertilizers accounted for another 29%. Based on nutrient data at Xuliujing, the seaward flux of nitrogen from Changjiang was estimated to be $0.138 \times 10^{12} \text{ mol yr}^{-1}$, accounting for approximately 6% of the total input from the watersheds. Further examination of nitrogen loads from different sub-basins (i.e., at the tributary level) revealed that the load from Taihu (lake) was the highest, particularly in terms of DON. Meanwhile, the contribution to nitrogen load of sewage from aquaculture activities was higher in the Taihu sub-basin than in the other parts of the Changjiang drainage basin.

4.3.2 Phosphorus

During 2003–2014, the total phosphorus input to the Changjiang drainage basin was $155 \times 10^9 \text{ mol yr}^{-1}$, of which 87% was attributed to synthetic fertilizers and organic-P from manure and crop residues. Phosphorus inputs from atmospheric deposition accounted for only 2% of the total input, which is much less than the share for N. Meanwhile, waste drainage from aquaculture and domestic sectors accounted for approximately 11%. Phosphorus generated through weathering and erosion over the entire drainage basin was $0.2 \times 10^9 \text{ mol yr}^{-1}$, accounting for 0.1% of the total phosphorus influx in the catchment areas.

The total phosphorus output from the watersheds plus retention in the drainage basin of Changjiang was 2% higher than the input, presumably because of uncertainties in data compilation. The retention of phosphorus in the watersheds was $126 \times 10^9 \text{ mol yr}^{-1}$ on average, accounting for 81% of the total input, which is twice as high as the corresponding percentage for retained nitrogen. This result is consistent with the fact that phosphorus is less soluble during weathering and erosion, because it can interact with Al, Ca, and Fe to form insoluble complexes and is thus retained in watersheds. For the same reason, phosphorus from chemical fertilizers is retained in soils compared with nitrogen. Crop harvest as well as animal and aquatic products accounted for a phosphorus output of $23 \times 10^9 \text{ mol yr}^{-1}$. Fluvial export of phosphorus, including DIP, DOP, and PP to the East China Sea reached $7.7 \times 10^9 \text{ mol yr}^{-1}$, accounting for 5% of the total input. Phosphorus trapped in the TGR was mostly in the particulate form (i.e., trapped in sediments) and reached $4.7 \times 10^9 \text{ mol yr}^{-1}$, accounting for 3% of the total input to the drainage basin. Again, this discussion implies that the effect of DIP retention within the TGR is rather limited and the effect of “trapping” should not be exaggerated.

Of note, however, the above mentioned source *versus* sink

associations for nitrogen and phosphorus across the entire drainage basin of the Changjiang include internal cycles of anthropogenic nutrients (Appendix 3: Source vs. Sink). For example, a certain amount of crop uptake and harvest removal can be linked to manures (i.e., organic fertilizer) through food trade and waste treatment within the drainage basin. Additionally, straw and husks are used as fertilizer in agriculture, accounting for 20–40% of the input. Loss through the evaporation of chemical fertilizers (e.g., ammonia and urea) can be recycled to the watersheds via atmospheric depositions (30–40%). Biomass fixation can be used during timber processing and papermaking. Overall, these pathways of internal cycling in watersheds can effectively reduce the impacts of external forces. Therefore, the retention of anthropogenic nutrients in Tables 9 and 10 becomes rather conservative, which must be further refined based on new data sets in the future studies. Nevertheless, the data in Tables 9 and 10 provide up-to-date information on major pathways of nutrients in the vast drainage area of Changjiang.

4.4 Quantifying nutrient drainage and extraction between Datong and Xuliujing

Recently, Zhang et al. (2021) summarized trends of nutrients in the tide-influenced delta of Changjiang downstream of Datong. Here, we extend the discussion with information in greater details. Watersheds downstream of Datong to the river mouth add another 4–10% to water discharge at the annual scale relative to the water flow of the Changjiang measured at Datong (Yang, 2013). Therefore, the water flow of Changjiang significantly differs between Datong and Xuliujing at the seasonal as well as inter-annual scales (Wang et al., 2006; Tang et al., 2011; Zhao et al., 2012).

The capacity of water extraction along the mainstream of Changjiang between Datong and Xuliujing reaches up to ca. $0.6 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$. Sluices and pumping facilities in this area can discharge water backward into Changjiang during flood seasons (Zhang and Chen, 2003; Zhang E F et al., 2009; Zhang et al., 2012). Comparison of nutrient concentrations between Datong and Xuliujing indicated that two sets of data were statistically different (Figures 5 and 8), as reported by Zhang et al. (2021). Currently, information on the water flow and nutrient chemistry of tributaries and sluices/pumping stations between Datong and Xuliujing is still limited, restricting the examination of seasonality. Thus, only collective assessments are plausible, although not for individual cases (systems) and at the annual scale.

4.4.1 Water drainage and extraction between Datong and Xuliujing

From Jiangsu Province, 6.4×10^9 – $79.2 \times 10^9 \text{ m}^3$ water is discharged into Changjiang annually (WRDJP, 2002–2014).

Table 10 Summary of phosphorus budget for the Changjiang watersheds with percentage in parentheses^{a)}

Categories	This study	Li et al. (2011)	Powers et al. (2016)
Study period	2003–2014	2003	2003–2010
<i>Input of P</i>			
Synthetic fertilizer-P	73±8 (47±6%)	69	56±3
Organic fertilizer-P	62±3 (40±3%)	108	–
<i>Manure-P</i>	59±3 (38±4%)	108	–
<i>Straws-P</i>	2.8±0.2 (2±0.2%)	–	–
Atmospheric depositions-P	3.4 (2%)	–	–
Weathering-P	0.2 (0.1%)	–	–
Wastewaters-P	16±2 (11±1%)	–	–
<i>Aquaculture wastewaters-P</i>	12±2 (8±1%)	–	–
<i>Domestic wastewaters-P</i>	4.5 (3±1%)	–	–
Subtotal	155±8 (100%)	177	56
<i>Output of P</i>			
Harvests and culture products-P	23±2 (15±1%)	–	–
<i>Harvest crop- P</i>	18±2 (12±1%)	–	–
Production of land-based animal-P	4±0.3 (2±0.2%)	–	–
<i>Production of aquatic animal -P</i>	1±0.2 (1±0.1%)	–	–
Export by river as TP	7.7±2.2 (5±1%)	–	3.9±0.6
<i>Export by river as DIP</i>	1.6±0.3 (1±0.2%)	0.82*	–
<i>Export by river as DOP</i>	1.5±1.7 (1±1 %)	–	–
<i>Export by river as PP</i>	4.5±1.4 (3±1%)	–	–
Subtotal	31±3 (20±2%)	–	–
<i>Retention of P</i>			
Retention in farmland-P	101±6 (65±5%)	–	–
Retention in forest and grass-P	20±2 (13±1%)	–	–
TGR trap of sediments P	4.7±3 (3±2%)	–	–
Subtotal	126±7 (82±6%)	–	–
Differences	–3±11 (–2±7%)	–	–

a) * DIP transported into water bodies. Unit: $\times 10^9 \text{ mol yr}^{-1}$. Data from the literature are also shown in the table for comparison. Details of data compilation are shown in Appendix 3: Source vs Sink (SI3).

Meanwhile, from Anhui Province, annual water drainage into Changjiang reaches 10.5×10^9 – $27.0 \times 10^9 \text{ m}^3$ (WRDAP, 2003–2013). Here, we used annual water drainage and measured concentrations of nutrients from tributaries in this area, taking into account the seasonality of amount of nutrients extracted/drained through sluices/pumping stations to obtain a conservative estimate of nutrient budgets between Datong and Xuliujing for the Changjiang mainstream (Tables 11 and 12).

In the present study, nutrient influx (i.e., $17.4 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ on average) from Huaihe to Changjiang was also included in the calculation, and over 95% of confluences in this area occur between Nanjing and Nantong (e.g., Yangzhou). However, water discharge from Huaihe to Changjiang, among other tributaries, is highly variable even at the annual scale. For instance, the measured water discharge at Wan-fuzha (here “zha” means “gate” in Chinese), a pumping

station in Yangzhou, which is one of main sluices connecting Huaihe and Changjiang, ranged from $2.1 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ in 2013 to $13.7 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ in 2010, differing by a factor of >6. Historical records indicated that during 1961–1981, water flow was $15.5 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$, adding another uncertainty to the estimation of nutrient influx from tributaries in this region (WRDJP, 2002–2014). Of note, our estimate is rather conservative and modest, since other sources, such as direct waste drainage and groundwater discharge, were not included because of the lack of data.

Zhang et al. (2021) reported that water flux-weighted average concentration of DIN, DIP, and DSi was 104, 1.53, and $108 \mu\text{mol L}^{-1}$, respectively, in the mainstream of Changjiang between Datong and Xuliujing. These values are comparable to data reported in the literature for the period of 1997–2015. During 2002–2014, the annual water extraction from Changjiang varied between 15.0×10^9 and $24.1 \times 10^9 \text{ m}^3$,

Table 11 Estimation of flux for nutrients along the mainstream and in the watersheds of the Changjiang between Datong and Xuliujing^{a)}

Area	Period	Water flow ($\times 10^9 \text{ m}^3 \text{ yr}^{-1}$)	Nutrient fluxes ($\times 10^9 \text{ mol yr}^{-1}$)		
			DIN	DIP	DSi
Drainage					
Jiangsu	2002–2014	27.5	3.9	0.152	2.83
Anhui	2003–2013	16.8	2.2	0.064	1.73
Sum		44.2	6.1	0.214	4.56
Extraction					
Jiangsu	2002–2014	18.4	1.9	0.028	1.99
Anhui	2003–2013	6.83	0.7	0.01	0.74
Sum		25.23	2.6	0.038	2.73
Extraction					
Jiangsu	2002–2014	18.4	1.9	0.028	1.99
Anhui	2003–2013	6.83	0.7	0.01	0.74
Sum		25.23	2.6	0.038	2.73

a) Flux of nutrients into the mainstream from tributaries and other surface runoffs and comparison with water extraction from Jiangsu and Anhui. Original data are cited from Zhang et al. (2021).

Table 12 Estimation of flux for nutrients along the mainstream and in the watersheds of the Changjiang between Datong and Xuliujing^{a)}

Observations	Period	DIN	DIP	DSi
Datong to Xuliujing	1997–2015	120±31.6	1.21±0.55	107±30.5
Dayunhe	2003–2016	29–210	0.50–2.32	46.5–117
Qingyijiang	2003–2016	98.6–129	1.52–2.66	98.6–113
Yuxihe	2016	63.9	0.31	74.5
Qinhuaihe	2016	464	8.25	84.8
Chuhe	2016	188	1.33	46.7
Tongqiyunhe	2016	142	2.73	160
Renganghe	2016	126	3.53	140
Jiuweiganghe	2016	824	0.32	135
Ruhaiyunhe	2016	91.1	2.13	141
Tonglvyunhe	2016	114	5.96	151
Xuliujing	2005–2015	122±24.4	1.91±0.62	109±18.1

a) Concentration ($\mu\text{mol L}^{-1}$) of nutrients measured between Datong and Xuliujing. Data in the table show the average and standard deviations for the mainstream cited from Zhang et al. (2021), plus concentrations from major tributaries between Datong and the river mouth.

with an average of $18.4 \times 10^9 \text{ m}^3$ in the Jiangsu Province, and another $0.13 \times 10^9 \text{ m}^3$ was extracted under the national “South-to-North Water Diversion” Program from Jiangsu and northward to the Shandong Province (WRDJP, 2002–2014).

Similarly, from the Anhui Province, an amount of $6.83 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ water was extracted on average during 2003–2013 (WRDAP, 2003–2013). As an independent check, four municipalities (i.e., districts) downstream of Datong in the Anhui Province, namely Maanshan, Chaohu, Wuhu, and Tongling, use water resources from Changjiang. Collectively, these municipalities extracted 4.49×10^9 to $7.68 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ water from the mainstream during 2005–2013, with an average of $6.23 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$, which is well consistent with value from the water budget. Of note, the

water budget of extraction and drainage from watersheds between Datong and Xuliujing in Tables 11 and 12 (i.e., $19.1 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$) is consistent with the difference in annual loads at these two hydrographic stations (i.e., Datong and Xuliujing), which is $(23.3 \pm 18.9) \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ during 2004–2015.

4.4.2 On the base-flow and background concentrations

In the literature, the influx of groundwater to a stream is considered a type of base-flow (i.e., background concentration), cited by Wittenberg (2003) and Dai et al. (2010). In the present study, we used a rather simple but straightforward method to estimate base-flow contributions to the observed nutrient flux in the upper parts of estuary (e.g., Xuliujing). Assuming that the observed flux ($C \times Q$) for a given nutrient

species is the sum of base-flow component ($C_b \times Q$) and contributions from other sources (P), the equation of nutrient budget can be given as:

$$C = C_b + \frac{1}{Q} \times P, \quad (6)$$

where C is the nutrient concentration; Q is the water flow; subscript b represents the base-flow; and P includes point sources. When data of nutrients are plotted against monthly discharge (Q_m), no simple relationships could be identified between nutrient concentration and water flow at Xuliujing, with a correlation coefficient (r^2) of <0.1 ($p < 0.05$). In fact, the plot of monthly nutrient data against the reciprocal of water flow ($1/Q$) provided a y -intercept (i.e., an estimate of “base-flow”) that was lower than and/or even somewhat comparable to the nutrient level measured in the Changjiang mainstream during the dry seasons. Perhaps, in the Changjiang drainage basin, at least in the lower parts of the river course, background level (i.e., base-flow contribution) can be comparable to the measured concentrations in the mainstream. This observation is supported by results in a review of groundwater status by Xue and Zhang (2009), who reported that some pollutants (e.g., nutrients) can be abundant in ground water connecting to streams/canals, including tributaries of the Changjiang. Since base-flow can be potentially high for nutrients, during the flood period, concentrations in the mainstream of Changjiang may be somewhat diluted. In the present study, a few samples from wells in the upper and middle reaches showed wide ranges of nutrient concentrations across the drainage basin (note: $10\text{--}620 \mu\text{mol L}^{-1}$ for DIN, $0.25\text{--}1.2 \mu\text{mol L}^{-1}$ for DIP, and $130\text{--}490 \mu\text{mol L}^{-1}$ for DSi). Since well samples represent the composition of groundwater that sustains the base-flow

across the watershed, these results confirm that base-flow for anthropogenic nutrients can be high in the Changjiang drainage basin. Importantly, the variation range of the annual water load of Changjiang is rather limited, whereas both DIN and DIP concentrations have increased continuously, albeit with different trends, over the past three to four decades, depending upon the species of interest (Figure 7). This limits a simple correlation between monthly water flow and nutrient concentrations at Xuliujing during 2003–2015.

4.5 Constrains to seaward nutrient fluxes downstream of Xuliujing to the river mouth

Downstream of Xuliujing bifurcation, the distance until the river mouth is ca. 150 km. Here, at the line joining the tips of Qidong (QD) and Nanhui (NH), the area is affected by seawater intrusion along with tides. In this area, seaward fluxes of nutrients from Changjiang are further influenced by the input of tributaries (i.e., Huangpujiang), extraction of freshwater resources by the reservoir, and drainage of treated wastewater into the Changjiang Estuary (Figure 11). All these processes are affected by anthropogenic activities and must be properly evaluated to quantify the seaward fluxes of nutrients with certainty.

As shown in Table 3, observations at Huangpujiang revealed DIN, DIP, and DSi values of 73–345, 1.9–22, and 44–160 $\mu\text{mol L}^{-1}$ across four stations at the monthly scale (Zhu et al., 2004; Cui et al., 2011; Ye, 2019). Based on the data of water discharge, flux of nutrients from the Huangpujiang into the mainstream of the Changjiang can be calculated (Table 13).

As shown in Figure 5, although water discharge from Huangpujiang represented only 1–2% of that from Chang-

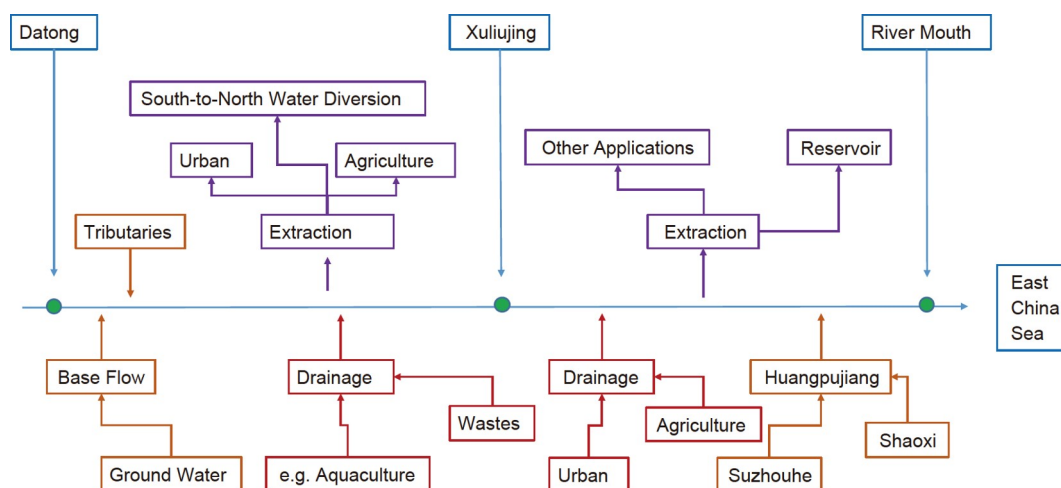


Figure 11 (Color online) Carton illustrations of contribution pathways that induce changes in seaward flux of nutrients in the tide-influenced delta downstream the Datong of the Changjiang. Those pathways are elaborated in this study after Zhang et al. (2021), shown in the main text and Appendix. Note that the distance between the Datong and Xuliujing (ca. 500 km) and then from the Xuliujing downstream to the river mouth (ca. 150 km) is not proportional in this illustration.

Table 13 Influx to the Changjiang Estuary from the Huangpujiang and extraction of fresh water by reservoirs downstream Xuliujing and to the river mouth^{a)}

River	Water flow ($\times 10^9 \text{ m}^3 \text{ yr}^{-1}$)	DIN ($\times 10^9 \text{ mol yr}^{-1}$)	DIP ($\times 10^9 \text{ mol yr}^{-1}$)	DSi ($\times 10^9 \text{ mol yr}^{-1}$)
Huangpujiang	14.12	3.10	0.084	1.34
Reservoirs	2.657	0.3241	0.005075	0.2896

a) For the estimation of extraction of nutrients by the reservoir, concentrations measured at Xuliujing were used. Data of water discharge for the Huangpujiang are from the Water Authority of Shanghai, and monthly concentrations of nutrients are from Zhu et al. (2004), Cui et al. (2011), and Ye (2019).

jiang (i.e., $905.1 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$) at Datong during 1950–2000, nutrient fluxes from Huangpujiang accounted for 4–5% of those from the mainstream. Elevated flux of nutrients relative to the water flow of Huangpujiang can be attributed to elevated DIN and DIP concentrations, which were more than twice higher than those in the Changjiang mainstream. However, the concentration of dissolved silicates in the Huangpujiang was comparable and/or even lower relative to that in the Changjiang mainstream.

Another important aspect is the different patterns of monthly fluxes between Huangpujiang and the Changjiang mainstream. For instance, during the dry season (i.e., December to February), the monthly water flow was 10.9×10^3 – $14.3 \times 10^3 \text{ m}^3 \text{ s}^{-1}$ for Changjiang during 1950–2000, which was ca. 20% of that during the flood period (i.e., June to September), when the monthly water discharge at Datong is 40.4×10^3 – $50.6 \times 10^3 \text{ m}^3 \text{ s}^{-1}$. Monthly water discharge from Huangpujiang is 420 – $445 \text{ m}^3 \text{ s}^{-1}$ during the winter, which is 10–30% higher than that during the summer (i.e., 315 – $405 \text{ m}^3 \text{ s}^{-1}$ from June to August). In addition, the flux of nutrients from Huangpujiang to Changjiang (compared with that from Xuliujing) increases by a factor of 4–5 (5–10%) during the winter (Figure 5). Thus, the proportion of nutrient flux from Huangpujiang to the Changjiang mainstream increases during the winter and/or spring relative to that during the summer each year. Since Huangpujiang discharges nutrients directly into the Changjiang Estuary, the seasonality of nutrients in Huangpujiang drastically affects the estuarine ecosystem as well as the adjacent coastal environment of the East China Sea. However, this effect has not been properly assessed in previous studies on the seaward fluxes of Changjiang (cf. Duan et al., 2007; Yan et al., 2010; Dai et al., 2011).

Recently, Zhang et al. (2021) evaluated the impact of five major reservoirs from downstream of Xuliujing to the river mouth, which extract fresh water from the pan-delta of Changjiang. The results indicated these reservoirs extract

DIN, DIP, and DSi of 0.324×10^9 , 5.1×10^6 , and $0.29 \times 10^9 \text{ mol yr}^{-1}$, respectively, from the Changjiang. Collectively, these five reservoirs extract fresh water from the Changjiang mainstream with an annual capacity of ca. $2.7 \times 10^9 \text{ m}^3$. By 2020, the water extraction capacity of reservoirs from the Changjiang Estuary is expected to increase by another 50–100% (Lu et al., 2010; Le, 2012). Simultaneously, it is difficult, if not impossible, to estimate the extraction of nutrients by these reservoir from the Changjiang mainstream at monthly resolutions, because in the estuarine area, the operation of impoundment for a given reservoir is affected by tidal phases for avoiding the influence of seawater intrusion.

Downstream of Xuliujing, four districts from the Jiangsu Province, including Changshu, Taicang, Haimen, and Qidong, are located. The amount of treated wastewater from this area can be estimated based on the relationship between economic growth and wastewater drainage (Li et al., 2006; Chen and Lu, 2008). In other words, the ratio of GDP of these four districts to that of the whole Jiangsu Province is multiplied by the total wastewater released, and these values are available from the national statistical data network (<http://data.stats.gov.cn/>). Zhang et al. (2021) calculated nutrient fluxes based on measured concentrations and amount of treated wastewater discharged directly into the Changjiang Estuary (Table 14). Notably, however, ca. 50% of treated wastewater from Qidong directly drains into the coastal environment, which is excluded in the calculation hereafter, because we consider waste drainage only at the river mouth. In Table 14, wastewater compositions from coastal urban areas may show a very different DIN/DIP (e.g., DIN/DIP > 400) compared with water samples from the river and coastal environment. Therefore, different mitigation strategies must be implemented across the estuary, such as managing the spatial distribution of eutrophication, considering that riverine and marine waters contain different limiting nutrient species and salinity plays a role in reg-

Table 14 Wastewater drainage and flux for nutrients from water treatment facilities in the area downstream Xuliujing of the Changjiang Estuary^{a)}

Provinces	Period	Water drainage ($\times 10^9 \text{ m}^3 \text{ yr}^{-1}$)	DIN ($\times 10^9 \text{ mol yr}^{-1}$)	DIP ($\times 10^9 \text{ mol yr}^{-1}$)	DSi ($\times 10^9 \text{ mol yr}^{-1}$)
Jiangsu	2005–2014	0.3837	0.2548	0.000587	0.07521
Shanghai	2005–2014	1.3578	0.9016	0.002077	0.2661

a) Drainage of nutrients from wastewater treatment facilities in the table represents Jiangsu and Shanghai, respectively. Original data are from Zhang et al. (2021).

ulating system characteristics (Lui and Chen, 2012).

In Shanghai, we considered the facilities that directly drain treated wastewaters into the Changjiang Estuary. Thus, those discharging into coastal environment (e.g., Hangzhou Bay) are not included for the same reason mentioned above for comparison with the Jiangsu. Further, waste drainage into Huangpujiang is not included to avoid duplications in calculation. Collectively, direct wastewater drainage from Jiangsu and Shanghai into the Changjiang Estuary reaches 1.57×10^9 to 1.90×10^9 t yr⁻¹ on average, as reported by Zhang et al. (2021).

The implications of our work are as follows. Majority of the developing maritime countries aim to advance their economics in coastal areas, such as tide-influenced river deltas, which entails increase in the fluxes of nutrients and other pollutants from these areas into the ocean, as evidenced in the pan-deltaic region of Changjiang (Zhang et al., 2021). However, hydrography and water quality monitoring networks are typically set-up further upstream to avoid tidal influences, as in the case of the Datong Hydrographic Station of Changjiang, which is 650 km upstream the river mouth. Thus, the effects of tide-influenced deltaic and adjacent coastal areas on nutrient concentrations, species ratios, and seaward fluxes are often “ignored” and excluded from management by governments owing to the lack of knowledge and logistic difficulties.

In summary, our results indicate that Changjiang has witnessed a steady increase in the fluxes of nutrients and unprecedented changes in their species ratio (e.g., DIN/DIP) since the epoch of the Cultural Revolution (i.e., after 1980). This change is particularly important in the tide-influenced river delta downstream of Datong, which is over 650 km upstream of the river mouth. Economic boom (e.g., land-use changes) and rapid urbanization (i.e., mobilization of population) in this delta have attracted the movement of people from inland areas to the coast (Zhang et al., 2021). Since water flow data at the Xuliujing Hydrographic Station were officially available only after 2004, we focused here on the comparison with Datong for data during 2004–2015. Compared with that at Datong, the annual nutrient flux at Xuliujing increased by 2% for DIN and 3% for DSi but significantly by 13% for DIP on average during 2004–2015 (Table 15 and Figure 7). The different patterns of temporal variability of nutrient fluxes at Datong and Xuliujing were

also noted. For instance, based on results in the literature, the DIP flux at Datong has tended to slow down in recent years, while the flux of DIN appears to have phased off after 1995. Meanwhile, our data indicate that at Xuliujing, the annual nutrient fluxes continued to increase during 2004–2015 (Figure 7).

At the river mouth (i.e., line joining the tips of Qidong and Nanhui), the annual nutrient flux during 2004–2015 was further increased by 4% for DIN, 5% for DIP, and ca. 2% for DSi relative to that at Xuliujing (Table 15). Since surface runoff in tide-influenced delta presented a higher DIP than DIN and DSi compared with upstream tributaries, DIN/DIP at the river mouth was decreased by 11% but DIP/DSi was increased by 13%, together with significant changes in seaward fluxes of nutrients during 2004–2015 (Zhang et al., 2021). Indeed, in the tide-influenced delta, DIP increased much faster than DIN in water samples. In conclusion, seaward nutrient fluxes at the river mouth of Changjiang can further increase by 5–10% for DIN and DSi and 15–20% for DIP compared with values at Datong, which is important since the surface area of tide-influenced delta is rather limited (ca. 5%) in the vast drainage basin of Changjiang.

Indeed, wastewater drainage from aquaculture and domestic areas make significant contributions to the spatial yields of nitrogen and phosphorus in catchment areas downstream of Datong; however, more nutrients are carried to the mainstream through creeks, streams, and canals. This has increased the chemical yields of nutrients in this tide-influenced deltaic area by nearly two times higher than the averages of the whole Changjiang watershed, as evidenced from data in Table 4. The observed DIN/DIP of surface runoff in watersheds downstream of Datong was lower than that of upstream tributaries, where anthropogenic sources of nutrients are dominated by agricultural activities (e.g., leaching of nutrients from soil). Nutrients in tide-influenced delta are released from urban and domestic sources, where relatively low DIN/DIP is recorded in surface runoff.

Since the contribution of tide-influenced delta to the mainstream of Changjiang can be important in terms of the fluxes and species ratios of nutrients, ignoring this part of watersheds can result in the underestimation of seaward fluxes and overestimation of DIN/DIP, ultimately guiding inappropriate policies for the mitigation of nutrient over-enrichment in the estuarine and adjacent coastal environ-

Table 15 Comparison of nutrient fluxes of the Changjiang between Datong, Xuliujing and at the river mouth^{a)}

Category	Water flow ($\times 10^9$ m ³ yr ⁻¹)	Nutrient fluxes ($\times 10^9$ mol yr ⁻¹)		
		DIN	DIP	DSi
Datong	841	107	1.50	91.4
Xuliujing	869	108	1.66	94.1
River Mouth (i.e., line between Qidong and Nanhui in Figure 1)	882	115	1.79	96.7

a) Data compilation is for the period of 2004–2015, cited from Zhang et al. (2021).

ments or improper strategies of management against eutrophication at the ecosystem level. As shown in Table 15, DIN/DIP decreased by 10% but DIP/DSi increased by nearly 20% at the river mouth compared with values at Datong.

4.6 How important are seaward nutrient fluxes in Changjiang from the global perspective of land-ocean interactions?

Table 16 lists and compares the nutrient status of the world's 10 largest rivers in terms of annual water discharge, covering a broad climate spectrum from equatorial to the sub-polar regions of this planet. Regarding anthropogenic nutrients, such as DIN and DIP, concentrations recorded in the Changjiang are up to five times higher than those in most of the other large rivers listed in Table 16. Although Mississippi also shows relatively higher concentrations of nutrients (e.g., DIN), the overall nutrient status of Mississippi markedly differs from that of Changjiang. For instance, DIN and DIP levels in the lower reaches of Mississippi River, that is, at St. Francisville, have remained stable after the 1980s, whereas DSi in 1950–1960 was two times higher than during the last decade of the 20th Century (Goolsby et al., 1999). Moreover, among the world's largest rivers listed in Table 16, Changjiang stands first in that the chemical yield of DIN is higher than of DSi, indicating that its watersheds are strongly affected by anthropogenic activities and that these perturbations prevail and exceed natural processes, such as

weathering, petrology, and tectonics (e.g., age and type of rock exposure, soils, landscape, and vegetation) at the scale of the whole drainage basin.

Furthermore, we systematically examined time-series data to compare the trends and pattern of nutrients species ratios (e.g., for DIN and DIP) between the Amazon River and Changjiang over last three to four decades, because the Amazon River is ranked the first in the world in terms of annual water flow (Figure 12). Our comparison revealed that in the early 1980s, DIN flux from the Amazon River was 50–60% higher than that from Changjiang (Edmond et al., 1985); however, during 2004–2015, the seaward flux of DIN from Changjiang surpassed that from the Amazon River by 70–90%, even though the water flow of the Amazon River was six times higher than that of Changjiang. Apparently, the last five years of the 20th Century marked the critical period for this change in DIN flux from Changjiang (Figure 12). Moreover, DIP flux from Changjiang is approaching that from the Amazon River, particularly when taking an additional 20% contributed by tide-influenced deltaic area and adjacent coasts into account. Given the continuously increasing trend of DIP flux from Changjiang, the seaward flux of DIP from Changjiang will possibly exceed that from the Amazon River in the near future. Consequently, Changjiang will soon become the largest riverine source of anthropogenic nutrients (i.e., DIP and DIN) from the continents to the ocean. Comparison against the global budget indicated that Changjiang alone would account ca. 5% DIP and ca.

Table 16 Comparison of annual water flow and nutrient concentrations among the top 10 largest world rivers on this planet^{a)}

River	Drainage area ($\times 10^3$ km ²)	Annual water flow ($\times 10^9$ m ³ yr ⁻¹)	DIN ($\mu\text{mol L}^{-1}$)	DIP ($\mu\text{mol L}^{-1}$)	DSi ($\mu\text{mol L}^{-1}$)	Period	References
Amazon	6300	6300	10–32	0.2–1.0	144–163	1982–2015	Demaster and Pope, 1996; Martinelli et al., 2010; Goes et al., 2014; Kalmbach, 2016; Moquet et al., 2016; Ward et al., 2016
Congo	3800	1300	7.2	0.8	111–240	2006–2008	Dagg et al., 2004; Hughes et al., 2011
Orinoco	1100	1100	6.6–8.2	0.20–0.31	86–108	1982–1985	Lewis and Saunders, 1989; Dagg et al., 2004
Changjiang	1800	715–1044	123–145	1.78–2.95	109–124	2010–2015	This Study
Brahmaputra	670	630	4.8–21	1.3	160	1984–2002	Mahanta, 1999; Mahanta et al., 2002; Uddin et al., 2014
Yenisei	2600	620	5.73–14	0.26–0.42	73–97	2003–2009	Holmes et al., 2012; Bessudova et al., 2014
Mekong	800	550	4.1–22	0.321–1.6	62.8–256	1985–2011	Li and Bush, 2015
Lena	2500	520	4.1–19	0.1–0.7	40.9–164	1989–2006	Cauwet and Sidorov, 1996; Holmes et al., 2012
Ganges	980	490	27–35	2.1–2.6	117–151	1999–2001, 2013	Mukhopadhyay et al., 2006; Frings et al., 2015
Mississippi	3300	490	73–116	1.9–3.1	75–125	1980–2005	Goolsby et al., 1999; Dagg et al., 2004; Lohrenz et al., 2008

a) Data of drainage area and annual water discharge are from Milliman and Farnsworth (2011).

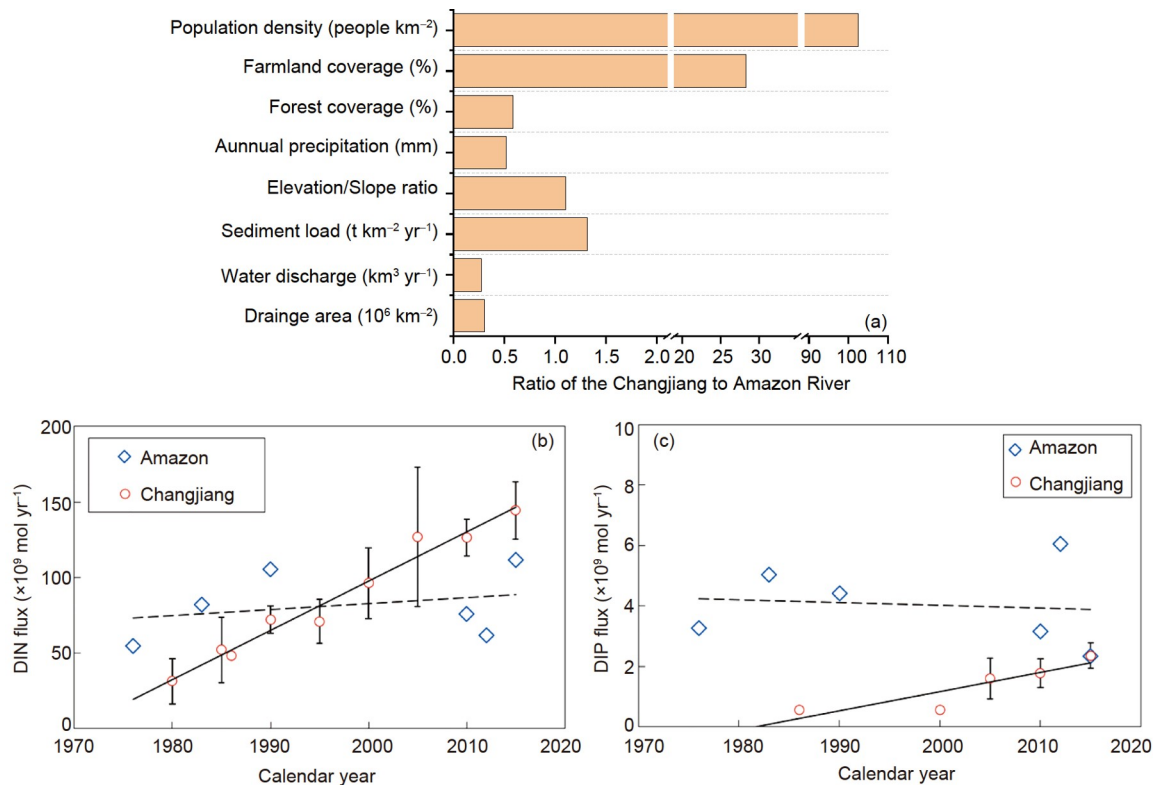


Figure 12 (Color online) Comparisons of drainage basin characters, DIN and DIP fluxes between the Amazon River and the Changjiang. With regards to the Amazon, we used data that show the seasonality of nutrients in estimating the annual flux, such as Edmond et al. (1985), Richey et al. (1986), Demaster and Pope (1996), Goes et al. (2014) and Moquet et al. (2016). In the figure, water flow of $6.3 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ for the Amazon River is used. In comparison, data from Nantong and Xuliujing are used for the Changjiang, and the water flow of $1.0 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ is adopted in the figure. The parameters of drainage basin for the Amazon River are cited from Ludwig et al. (1996) and Qin et al. (2019).

10% DIN of the world's riverine nutrients reaching the open oceans (Sharples et al., 2017; Zhang et al., 2021).

For comparison between the Amazon River and Changjiang, climate and anthropogenic characters over their drainage basins must be taken into account. Annual precipitation in the Amazon River basin exceeds 2,000 mm on average, which is twice as high as that in the Changjiang basin (Qin et al., 2019). However, the elevation-to-length ratio (H/L) of Changjiang is higher than that of the Amazon River, since the former drives water sources in the high plateaus of Qinghai and Tibet. Moreover, as shown in Figure 12, population density across the watersheds of Changjiang is over two orders of magnitude higher than that around the Amazon River. Furthermore, farmland coverage over the drainage basin of Changjiang is more than 20 times greater than that over the Amazon River basin. In contrast, forest coverage over the drainage basin of the Amazon River is nearly two times greater than that over the drainage basin of Changjiang (Figure 12). These differences indicate that compared with the Amazon River, Changjiang has suffered considerably more extensive perturbations from human society and thus experienced stronger anthropogenic than natural drivers.

In addition to its outstanding seaward flux of nutrients, Changjiang is peculiar among the world's top 10 rivers in

terms of nutrient species ratios (Table 16). For instance, DIN/DIP and DIN/DSi for Changjiang are higher than those for world's other top rivers. Likewise, Changjiang also presents a high DIP/DSi value. These results are consistent with the facts that Changjiang hosts densely populated areas in its watersheds, and its drainage basin is highly disturbed by agricultural (nearly one-sixth of the total drainage area) and aquaculture activities relative to other large river systems.

Nutrient fluxes and species ratios in Changjiang differ from those in other major rivers elsewhere in Europe and North America. For instance, in Mississippi River, DIN and DIP levels were stabilized and DSi started decreasing at the mouth of the river in the 1980s (cf. Goolsby et al., 1999), while in the Danube-Black Sea ecosystem, DSi has decreased since the 1970s following the construction of dams, such as the Iron Gate (Humborg et al., 1997).

In terms of global application, we believe that extensive urbanization and rapid economic growth in coastal areas of many developing maritime countries have considerably improved the welfare of human societies since the 1990s; simultaneously, however, these anthropogenic activities have dramatically increased nutrient loads and altered nutrient species ratio compared with levels in the adjacent coastal environments. These effects differ from the impacts of the

Green Revolution in agriculture, in which nutrient over-enrichment of rivers is related to the application of synthetic fertilizers, whereas sources from urbanized deltaic areas are characterized by a higher DIP/DIN. Nonetheless, these factors remain poorly quantified at the global scale, because the existing monitoring networks are typically established upstream of the limit of tide-influenced river course and exclude downstream deltaic areas, which can be vast in terms of surface and act as hotspots for national economics. In this context, studies of global nutrient chemistry must take into account the conventionally un-gauged coastal and tide-influenced deltas of major rivers to understand the nature of land-ocean interfaces. For instance, if we consider the addition of phosphorus from tide-influenced deltaic areas, as illustrated by studies on Changjiang, the global riverine fluxes of DIP may increase by approximately 10–20%.

4.7 Hysteresis of nutrients in Changjiang and analysis of management strategies

Currently, the concentration of nutrients in Changjiang remains high over the water course of ca. 4,500 km from river mouth upstream, and there is no clear sign that this situation will be considerably ameliorated and/or improved in the immediate future. Using modeling approach, we explored the hysteresis of nutrients in Changjiang, as uncovered through comparison between a unit increase in independent variables at year t and the resultant changes in dependent variables after “ T ” years, i.e., “lag T ” (cf. Section 2: Materials

and Methods). The application of ARIMAX model to time-series data of DIN at the river mouth (e.g., Xuliujing) revealed synthetic fertilizers with lag 3 and atmospheric depositions with lag 0 as the most important driving forces regulating the variability of DIN concentration in Changjiang (Figure 13). As shown in Figure 13, the fitted model explained 91.6% of data variance, including both decadal (i.e., long-term) trends and inter-annual (i.e., short-term) fluctuations. Further, we use the ARIMAX model to predict the response of DIN in Changjiang to various management scenarios over the watersheds, including five cases as follows:

(1)–(3) Synthetic fertilizer application is increased by 1.0% and 1.5% (i.e., average rate in the last 10 years) per year and reduced 5% per year, while atmospheric deposition remains unchanged.

(4) Atmospheric deposition is decreased by 5% per year, while synthetic fertilizer application remains unchanged.

(5) Both atmospheric deposition and synthetic fertilizer application are maintained at the level during 2014–2015 (i.e., control run).

Considering the hysteretic nature of DIN in Changjiang, predictions were made for the next 10 years to understand and estimate the corresponding changes in riverine concentrations following the mitigation actions to reduce nutrient load over the drainage basin. In the above-mentioned scenario analyses, we also considered the action plan of the Ministry of Agriculture of China (MAC) formulated in 2015, which called for stepwise reduction in synthetic fertilizer

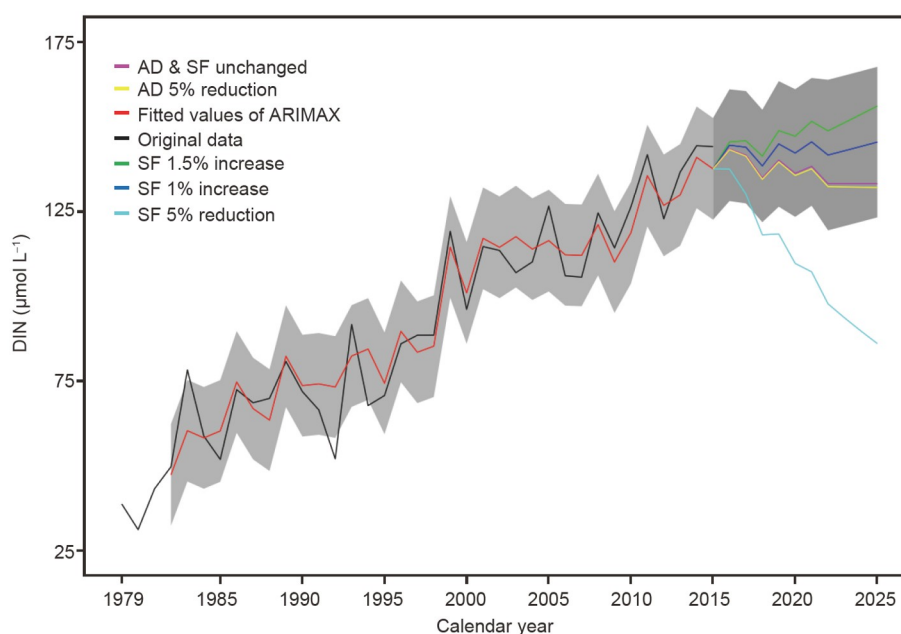


Figure 13 (Color online) Results from GAM and ARIMAX models applied to DIN at the river mouth of the Changjiang. In the figure, black and red lines represent the observed data and model fitted results, respectively, and grey area represents the 95% confidence intervals. For the predictions, five different cases are considered, shown in different colors. The shadowed area represents the range within the 95% confidence interval for the case that the synthetic fertilizer application rate increases by 1% per year while atmospheric depositions remain unchanged.

application rate at 1% per year from 2015 to 2019, with target toward zero growth in the farming of principal crops in 2020 (http://www.moa.gov.cn/zwl/m/tzgg/tz/201503/t20150318_4444765.htm). As shown in Figure 13, predictions for DIN in all scenarios illustrated the significant potential of this management strategy, regardless of data fluctuations of the model output. If the rate of synthetic fertilizer application increases by 1.5% per year, the riverine DIN level will continue to increase over the next decade. However, reducing this rate by 1% per year over the watersheds, which was the target of 2015 MAC action plan, will help stabilize the riverine DIN level within the data resolutions, even though these levels will still be relatively high. In an extreme case, reducing the fertilizer application rate by 5% per year will considerably decrease DIN level in the Changjiang by a factor of approximately two in next decade. Finally, reducing atmospheric depositions by 5% per year over the watersheds will still generate DIN concentration similar to that in the control run (Figure 13). Overall, synthetic fertilizer application in tillage is the major factor to be considered in management options to improve river water quality by ameliorating DIN over-enrichment, followed by an action plan to reduce atmospheric depositions over the watersheds. However, in both cases, excess DIN will still be retained in the watersheds because of the nature of hysteresis.

Regarding DIP in Changjiang, the ARIMAX model revealed synthetic fertilizer with lag 5 and organic manure with

lag 0 as the most important drivers (Figure 14). As shown in Figure 14, the model output explains 88.9% of data variance, including both decadal (i.e., long-term) trend and inter-annual (i.e., short-term) fluctuations. We used the ARIMAX model to examine the future DIP trends in Changjiang and explored the potential of different management considerations over the watersheds, including six cases as follows:

(1)–(3) Synthetic fertilizer application is increased by 1.0% and 2.3% (i.e., average rate over the last 10 years) per year and reduced by 5% per year, while organic manure application remains unchanged.

(4) Organic manure application is increased by 1.4% (i.e., average rate over the last 10 years) per year, while synthetic fertilizer application remains unchanged.

(5) Synthetic fertilizer and organic manure application rates are increased by respectively 2.3% and 1.4% per year.

(6) Synthetic fertilizer application is maintained at the level during 2014–2015 over the next 10 years (i.e., control run).

Again, considering the hysteresis of DIP in Changjiang and the fact that phosphorus is not as readily remobilized as nitrogen over the watersheds, predictions were obtained for the next 10 years (Figure 14). As shown in Figure 14, if the application of synthetic fertilizers continues at the average rate observed over the last 10 years (i.e., 2.3% per year), DIP level in Changjiang will continue to increase in the next 10 years. However, reducing this rate to 1% over the wa-

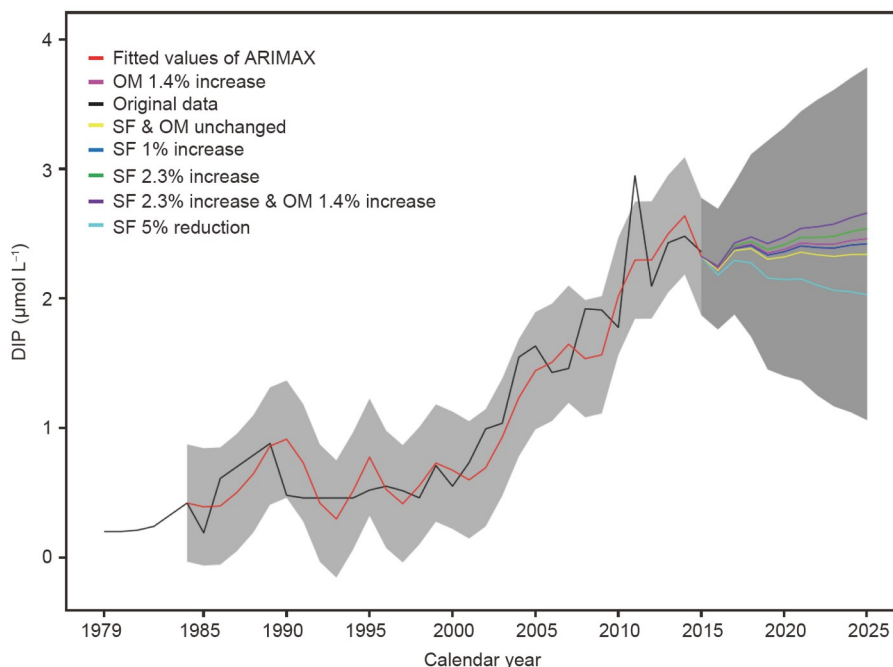


Figure 14 (Color online) Results from GAM and ARIMAX models applied to DIP at the river mouth of the Changjiang. In the figure, black and the red lines represent the observed data and model fitted results, respectively, and grey area represents the 95% confidence intervals. Data before 2000 were not available at the river mouth and results from Datong were used instead, since in 1980s–1990s was expected limited impact of human beings. For predictions, six different scenarios are considered, shown in colors, and the shadowed area represents the range within the 95% confidence interval for the case that synthetic fertilizer application rate increases by 2.3% per year while organic manure remains unchanged.

tersheds, according to the 2015 MAC action plan, will help stabilize the riverine DIP level within the data resolutions, although the DIP level in Changjiang will remain relatively high. While a ban on the use of synthetic fertilizers in tillage will reduce DIN in Changjiang, the outcome remains unclear for DIP, indicating that river is fueled continuously through the remobilization (i.e., legacy) of phosphorus in watersheds because of a more significant hysteresis characteristic of DIP than of DIN. In the extreme case, when the application of synthetic fertilizers is reduced by 5% per year, the river DIP concentration will exhibit an overall and a considerable fall in the near future, although this reduction will not be significant compared with that expected for DIN by 2025. Because the application of manure as organic fertilizers is expected to continue in the near future, DIP level in the river will increase slightly yet steadily.

Currently, the effects of reducing fertilizer application in agriculture on the seaward fluxes of nutrient in Changjiang remain obscure because of the sub-continental size and diverse nature of its watersheds. However, a simple and conservative mixed model can be applied to examine the potential impacts of nutrient reduction from major tributaries based on the findings of the present work. For instance, annual nutrient flux into the limit of pan-deltaic area at Datong can be simplified and described as the sum of export fluxes across the TGD at Yichang and contributions from two lakes, namely Dongtinghu and Poyanghu, plus Hanjiang, and represented as follows:

$$F_{\text{nu}}^{\text{dt}} \approx F_{\text{nu}}^{\text{yc}} + (F_{\text{nu}}^{\text{dh}} + F_{\text{nu}}^{\text{ph}} + F_{\text{nu}}^{\text{hj}}), \quad (7)$$

where F_{nu} is for the annual average nutrient flux. Superscript

dt, yc, dh, ph, and hj represent Datong, Yichang, Dongtinghu, Poyanghu, and Hanjiang, respectively, ignoring the uptake of nutrients by phytoplankton in the river and influx from small tributaries between Yichang and Datong and along the mainstream, because of the lack of data. Since the mainstream is characterized by fast flow (i.e., 1 m s^{-1}) with a rather short residence time in the middle and lower reaches of Changjiang, we believe that the above-mentioned simplification is robust and can be considered as the first-order approach. Here, we consider two simple yet different scenarios of management. In case one, we assume that the management policy for reducing fertilizer application is effective and levels of anthropogenic nutrients (i.e., DIN and DIP) in major tributaries in Sichuan and Guizhou are reduced by 50%, while levels in the major tributaries between Yichang and Datong (i.e., Dongtinghu, Poyanghu, and Hanjiang) remain unchanged. In this case, we reduced nutrient flux at Yichang by 50% and compared the corresponding changes in nutrients at Datong. In case two, we assumed that nutrient fluxes from tributaries between Yichang and Datong, including Dongtinghu, Poyanghu and Hanjiang, are reduced by 50%, while the flux at Yichang remains unchanged. In the assessment, we used annual average during the period of 2004–2015 as the reference value, as shown in Table 17, considering that the drainage area upstream of Yichang covers 60% of the total watershed of Changjiang and the annual water flow at Yichang was approximately half (i.e., 48%) of the flux measured at Datong during 1950–2010.

In case one, simulation results indicated that the corresponding nutrient fluxes at Datong would be reduced by 27–

Table 17 Comparison between upper reaches (i.e., upstream Yichang) and major tributary systems in the middle and lower parts of drainage basin (i.e., Dongtinghu, Poyanghu and Hanjiang) for their collective contributions to the riverine nutrient fluxes measured at the Datong^{a)}

Categories	Water flow ($\times 10^9 \text{ m}^3 \text{ yr}^{-1}$)	DIN ($\times 10^9 \text{ mol yr}^{-1}$)	DIP ($\times 10^9 \text{ mol yr}^{-1}$)	DSi ($\times 10^9 \text{ mol yr}^{-1}$)
Yichang	399.7	44.1	0.693	41.1
Dongtinghu	231.9	23.2	0.33	20.4
Hanjiang	42.8	4.02	0.072	4.31
Poyanghu	145.4	9.74	0.059	19.6
Sum (0)	819.9	81.1	1.2	85.4
Case 1				
Yichang $\times 0.5$		22.1	0.347	20.5
Sum (1)		59.1	0.809	64.9
Sum (1)/Sum (0)		0.73	0.7	0.76
Case 2				
(Dongtinghu+Hanjiang+Poyanghu) $\times 0.5$		18.5	0.231	22.2
Sum (2)		62.6	0.924	63.3
Sum (2)/Sum (0)		0.77	0.8	0.74

a) The scenario analyses are carried out for the purpose of management strategy in order to reduce the seaward fluxes of anthropogenic nutrients from the Changjiang. This includes Case 1 in which the nutrient flux at Yichang is cut-off by a factor of two, and Case 2 in which collective nutrient fluxes from middle and lower reaches is reduced by 50%.

climate forcing, which generally increases from higher to lower latitudes, such as from the north to south across the Changjiang drainage basin. Moreover, the southern parts of China, that is, areas of Dongtinghu and Poyanghu, are affected by more intense monsoons (e.g., East Asian Monsoon) than northern and upstream parts of Changjiang, inducing higher rainfalls at both monthly and annual scales. This climatic pattern also explains the diverse nature of nutrient species across the vast drainage basin of Changjiang. DIN and DIP in the river are mainly contributed from the areas of Sichuan and Guizhou upstream of TGD, which are most likely derived from extensive agriculture activities and high population density over watersheds with moderate surface runoff. Meanwhile, DSI levels are higher in the south and in the middle reaches of the drainage basin downstream of TGD, where erosion is accelerated by intense rainfall (e.g., changes from temperate to subtropical climate zones).

In summary, the need for improving the quality of riverine and marine waters is pressing to protect human health and manage aquatic environments at the ecosystem level in a sustainable manner. Our results suggest that because of the nonlinear characteristics of nutrient chemistry in response to the proposed management strategies over the drainage basin of Changjiang as well as the effects of hysteresis, high concentrations of anthropogenic nutrients in the river will be sustained for a certain period in the near future. Reducing fertilizer application from the average rate over the past 10 years (i.e., 1.5% for nitrogen and 2.3% for phosphorus) to 1% would delay the rate of increase in DIN and DIP in Changjiang over the next 10 years, albeit with strong inter-annual variability (Figures 13 and 14), due partly to hysteresis. Mitigation strategies, such as reducing synthetic fertilizer input and improving air quality, are expected to produce different effects on the load of anthropogenic nutrients in Changjiang, as DIN responds more rapidly than DIP due to their different behaviors as well as the diversity of sources involved. However, this will certainly result in a continuous but slow remobilization of nutrients previously stored/retained in watersheds, which is also regulated by hysteretic effects (Johnson et al., 2016).

Furthermore, data compilation for Datong revealed that the rate of increase in DIP and DIN should have slowed down and/or plateaued during the present century. On the contrary, our results demonstrate that both concentrations and seaward fluxes of anthropogenic nutrients continue to increase further downstream and to the river mouth, such as in the un-gauged stretch at Xuliujing. The seaward flux of DIN would decrease over the long term as synthetic fertilizer application and atmospheric depositions are managed eventually (controlled). Likewise, careful management of the manure-to-fertilizer ratio in agricultural systems will help reduce the DIP load in Changjiang. Our results demonstrate that the reduction in riverine DIN and DIP loads relies on integrated

efforts across the entire watershed, rather than at the local scale. In the case of Changjiang, both upper and lower reaches present comparable contributions of anthropogenic nutrients to seaward fluxes. Regarding DSI, the near linear relationship of chemical yield with rainfall implies control by leaching processes relative to weathering supply in this region (Zhang et al., 1990a). Importantly, since large amounts of nitrogen and phosphorus are retained in watersheds, even a minor external trigger (e.g., climate variability) can generate considerable fluctuations in riverine nutrient fluxes.

4.8 El Niño vs La Niña: Interaction between climate variability and anthropogenic impacts

Previous studies evidenced that the inter-annual variability of water load in Changjiang is related to climate change. For instance, spectrum analysis of hydrographic data for 1950–2010 at Datong revealed variations in water flow during periods of 2–3 and 4–8 years, with the former corresponding to rainfall fluctuations over the middle and lower reaches of the Changjiang drainage basin and the later representing the impacts El Niño and La Niña (Shen and Li, 2011). Over the last five decades, however, both concentrations and fluxes of nutrients have shown a trend of continuous increase at the inter-annual scale (cf. Duan et al., 2007; Yan et al., 2010; Dai et al., 2011). In particular, this uptrend of nutrient concentrations at Datong accelerated after the 1980s, when China launched economic reform and adopted the open market policy. Since information on annual water flow from Xuliujing covers a rather short time span (i.e., after 2004), we examined data of nutrients from the Datong Hydrographic Station and compared to the ENSO index in the present study.

We statistically analyzed nutrient data from Datong to identify whether the periodic nature observed previously for water flow exists because of prolonged observational history. Although the annual water flow at Datong during the El Niño period was 20–40% higher than that during the La Niña period, such a periodic impact would not affect the overall increase in nutrient concentrations in Changjiang, particularly for anthropogenic species (i.e., DIN and DIP). Notably, however, a relatively higher flux of nutrients has been found during some El Niño events compared with values during the preceding La Niña periods, most likely because of regulation by water flow. Another plausible explanation is that during the El Niño period, increased rainfall induces a greater flushing of soil profiles and leads to prolonged flooding, which would release significant amounts of nutrients from watersheds. Nevertheless, increased water flow may also dilute riverine nutrient concentrations; hence, higher nutrient fluxes have been observed in the Changjiang during La Niña years.

Given the nature of continuous increase in anthropogenic nutrients and the inter-annual variability of water discharge over the last several decades, we examined the different effects of El Niño and La Niña on nutrient fluxes (DIM_{E-L}) in Changjiang, which can be defined as follows:

$$DIM_{E-L} = \frac{DIM_{El} - DIM_{La}}{DIM_{No}} \times 100\%, \quad (8)$$

where DIM is the annual flux of DIN and DIP and subscripts El and La indicate El Niño and La Niña periods, respectively. In eq. (8), subscript No represents the annual flux of anthropogenic nutrients (e.g., DIN and/or DIP) in the absence of either El Niño or La Niña, which can be estimated using the data of normal hydrographic situations and/or based on moving averages. During 1960–2015, there were eight pairs of El Niño and La Niña events, and the above-mentioned differences in anthropogenic nutrient fluxes between El Niño and La Niña periods did not exhibit any systematic trends of the inter-annual variability of DIN and DIP ($p < 0.05$). Compared with those of DSI, anthropogenic activities over the watersheds have steadily increased the concentrations of DIN and DIP in the Changjiang, which have significantly narrowed the inter-annual fluctuations in anthropogenic nutrients linked to climate variability, such as El Niño and La Niña, particularly after the 1980s. This phenomenon became evident following China's economic reform since the 1980s, including agricultural progress, when the central government promoted the policy of "Fixing Farm Output Quotas for Each Household" (i.e., privatization of farming land in agriculture) throughout the country in 1979.

In a previous study, nutrient regimes and climate change indices were compared through trend analyses of data, such as z-score standardization (Ioannou et al., 2011). Here, the original nutrient data (X_i) from Datong were standardized and transformed into values (X'_i), as follows:

$$X'_i = \frac{(X_i - \bar{X})}{sd}, \quad (9)$$

where \bar{X} and sd represent mean and standard deviation, respectively.

Moreover, the residual (LR_i) relative to the trend can be estimated as follows:

$$LR_i = V_i - X'_i, \quad (10)$$

where V_i is the value from linear fitting and/or moving average, and X'_i is the observed value for a given year (i). In eqs. (9) and (10), standardized values and fitting residuals are believed to result from climate variability, e.g., El Niño and La Niña.

Using nutrient data from Datong, we compared standardized values and residuals with the ENSO index, such as Niño 3.4 and ONI. Our results indicated that neither Niño 3.4 nor ONI was correlated with the residuals based on nutrient data from Datong, confirming that the variability of nutrient

fluxes in the lower reaches of Changjiang (i.e., Datong) is regulated by not only natural dimensions, such as the inter-annual variability of water flow between El Niño and La Niña period, but also anthropogenic perturbation.

In the long-term, we also compared nutrient data from the Changjiang with the PDO index of this region (i.e., ONI). Nutrient concentrations showed no simple correlations with the PDO index at a confidence level of $p < 0.2$. Similarly, comparison with the PDO index using nutrient species ratios did not improve the correlations between these parameters. Even after the normalization of nutrient concentrations, data did not match the variability of PDO ($p < 0.2$). This is consistent with the results of spectral analysis using nutrient data, which indicated mis-match with the PDO phase (data not shown).

4.9 On the potential impact of legacy nutrients

As discussed earlier, our data compilation based on budgetary approaches and statistics from national archives revealed that considerable amounts of anthropogenic nutrients (i.e., nitrogen and phosphorus) are accumulated in the watersheds of Changjiang (Appendix 3: Source vs Sink). Therefore, this retention of nutrients in watersheds (i.e., a proxy for legacy nutrients) may significantly affect the maintenance of their high concentrations in the river. The annual accumulation rate of anthropogenic nutrients (A_{nu}) in watersheds can be estimated as follows:

$$A_{nu} = \sum IN_{nu} - \sum OU_{nu}, \quad (11a)$$

and/or

$$A_{nu} = \sum (\text{Fertilizer} \times \text{Retention rate}), \quad (11b)$$

where IN_{nu} is the external source of nutrients, and OU_{nu} is the output of nutrients from the watersheds. Recently, Powers et al. (2016) used eq. (11a) to evaluate the trend of phosphorus accumulation in the watersheds of Changjiang and compared these with reported trends for other rivers in Europe and North America. In another study, Bao et al. (2006) used eq. (11b) to examine the budget of nitrogen in agriculture fields in the Changjiang watersheds. In eq. (11a), the so called annual accumulation rate includes not only retention in farmlands but also storage in forests and grasslands, which are part of nature and hence not related to anthropogenic activities. The amount of nitrogen retained in farmlands and that fixed in forests and grasslands can be comparable; however, the amount of phosphorus retained in farmlands can be up to five-fold higher than that in forests and grasslands (Table 9). Thus, in the following discussion, we focus on results based on application of eq. (11b) to avoid over-estimation.

In eq. (11b), the fertilizer is composed of two parts, namely synthetic fertilizer and organic manure, and the later can be

recycled. As described in Appendix 3: Source vs Sink, the retention rates of synthetic fertilizer nitrogen and phosphorus are 23% and 75%, respectively, whereas those for organic nitrogen and phosphorus are 49% and 23%, respectively. Hence, in the long-term trend, accumulation of organic nitrogen would be higher than that of synthetic fertilizer nitrogen. Before 2005, the accumulation of synthetic fertilizer phosphorus was smaller than that of organic manure phosphorus, but the trend has reversed since the beginning of the present century. Variations in the accumulation rates of nitrogen and phosphorus can be explained by differences in the strategies of synthetic fertilizer application in agriculture over last five to six decades and different behaviors of these two elements.

In Figure 16, we examined the amount of nutrients accumulated in the watersheds of Changjiang during 1979–2015. Over the last three to four decades, nitrogen accumulation has increased by over 100% at a rate of ca. $3 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$. Similarly, phosphorus accumulation has increased by three folds at a rate of ca. $1 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ during this period. Therefore, the ratio of N/P accumulation is 1/3 on average over the entire watershed of Changjiang. The ratio of nitrogen and phosphorus accumulation in the watersheds is also rather different from

the ratio of DIN and DIP (64.2) at the river mouth. Of note, these rates are far much higher than the export of nutrients from Changjiang to the global oceans. Furthermore, trend analysis of time-series data revealed that nitrogen accumulation in the watersheds has plateaued in the present century, while phosphorus accumulation has continued to increase over the last four decades (Figure 16).

Based on flux data, the chemical yields for DIN, DIP, and DSI were 63.5×10^3 , 0.99×10^3 , and $53.4 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$, respectively, during 2004–2015 (Table 15). Previously, we estimated the uptrends of concentrations at the river mouth (i.e., Xuliujing) and obtained values of $3 \mu\text{mol L}^{-1} \text{ yr}^{-1}$ for DIN and $0.1 \mu\text{mol L}^{-1} \text{ yr}^{-1}$ for DIP, with a ratio of 30:1 (Zhang et al., 2021). Considering the long term (1957–2015) average water flow of $893.1 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ at Datong issued by CWRC, such a trend of nutrient concentrations would increase annual yield of DIN and DIP by respectively 1.5×10^3 and $0.049 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$. Thus, compared with the accumulation rates of anthropogenic nutrients in the watersheds, on the annual scale, changes in the export of DIN by the river is approximately 50% of the amount of total nitrogen accumulated in the watershed, while the export of DIP is only 5% of the increased accumulation of total phosphorus in the drainage basin. In other words, in management stra-

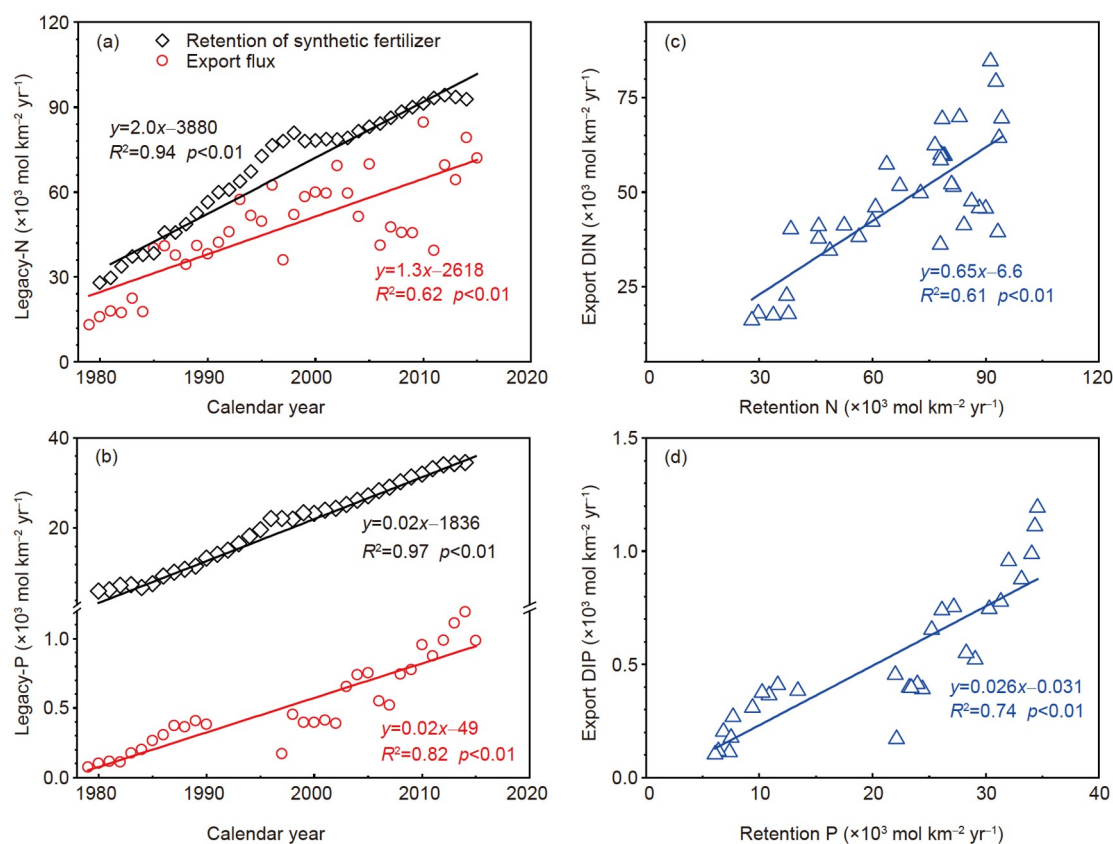


Figure 16 (Color online) Comparison between retention (i.e., legacy-N and legacy-P) of nutrients in the Changjiang watersheds and riverine exports of DIN ((a), (c)) and DIP ((b), (d)) in the period of 1997–2015. The riverine export of DIN and DIP is referred to the Datong Hydrographic Station because of lack of data at Xuliujing before the 1990s.

tegies, reducing chemical fertilizer application in agriculture will induce a rather rapid change in DIN levels of the river (e.g., Changjiang), while there would be a lag of response of export flux for DIP because of different cycling pathways for phosphorus and nitrogen, and the nature of hysteresis (Zhang et al., 2021).

Of note, however, our data compilation and evaluation of “chemical fertilizers” includes not only nitrogen and phosphorus fertilizers but also composite fertilizers that contain either nitrogen or phosphorus or both. As shown in Figure 17, the application of composite fertilizers showed a long-term trend of steady increase during 1980–2015, and the amount is approaching that of synthetic fertilizer phosphorus, which should not be ignored when assessing the retention of nutrients in watersheds and evaluating their impact on river chemistry. Moreover, our data indicate that the application rates of synthetic fertilizer nitrogen and phosphorus have slowed down and even phased off since the beginning of the present century, whereas the application rate of composite fertilizers remains in the state of rapid increase. In previous studies, contributions of composite fertilizers were ignored when evaluating the retention of anthropogenic nutrients in watersheds and their impacts on seaward fluxes (e.g., chemical yields) from the Changjiang (Xing and Zhu, 2002; Bao et al., 2006; Yan et al., 2010; Li et al., 2011; Jiang et al., 2012b; Chen et al., 2016; Powers et al., 2016; Hu et al., 2020). Hence, without considering the role of composite fertilizers, the management strategies of nutrient over-enrichment in aquatic environments (e.g., river) can be ineffective and mitigation policies on nutrient retention in watersheds can be inappropriate.

Regarding river export flux, DIP in Changjiang exhibits a stronger and positive correlation than DIN with the amount of accumulation over the watershed. Moreover, comparison between riverine fluxes and accumulation amounts indicated that seaward export represents only a small proportion of legacy nutrients in the last four decades, underscoring the hysteretic nature of nutrients in the watersheds. As shown in

Figure 18, the total seaward flux from Changjiang reached $138 \times 10^9 \text{ mol yr}^{-1}$ for nitrogen (TN) and $7.7 \times 10^9 \text{ mol yr}^{-1}$ for phosphorus (TP) during 2004–2015. The ratio of linear trend slopes between accumulation and riverine flux was ca. 3 for nitrogen but as high as 50–60 for phosphorus, indicating that phosphorus is more likely to be retained in watersheds than nitrogen. If we consider organic and particulate forms of anthropogenic nutrients, the corresponding total concentrations would be ca. $150 \mu\text{mol L}^{-1}$ for TN and $8.1 \mu\text{mol L}^{-1}$ for TP (Chen, 2012; Ding et al., 2019), corresponding to nutrient yields of $76.7 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ for TN and $4.5 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ for TP, taking into account the water supply of $556 \times 10^3 \text{ m}^3 \text{ km}^{-2} \text{ yr}^{-1}$ from the entire watershed of Changjiang. Further, comparison of data in Figure 18 revealed that the annual river export was 30–40% for TN and 1–2% for TP, relative to the accumulation of nutrients over the watersheds. Thus, the estimated retention time scale of anthropogenic nutrients would be 2–4 years for nitrogen but up to 50–100 years for phosphorus, if the present situation is sustained and if the riverine flux is solely the export pathway in the near future.

The implementation of estimates of potential legacy nutrients in the Changjiang drainage basin lies in that even though the ban on the application of synthetic fertilizers in agriculture is enforced, legacy and/or previously stored nutrients (i.e., nitrogen and phosphorus) will be continuously remobilized to maintain relatively high concentrations in the river mainstream and tributaries for some time, consistent with the output of modeling experiment in the present study. Based on the ratio of nutrient export to accumulation mentioned above, phosphorus can be retained over 10 times longer than nitrogen in the watersheds.

Comparison with world’s other river systems indicated that Changjiang is still in the accumulation phase in terms of anthropogenic nutrients, particularly for phosphorus, as opposed to Maumee in the USA and Thames in the UK (Powers et al., 2016). Furthermore, when nutrient inputs exceed the demand in agriculture and/or biomass of the natural land-

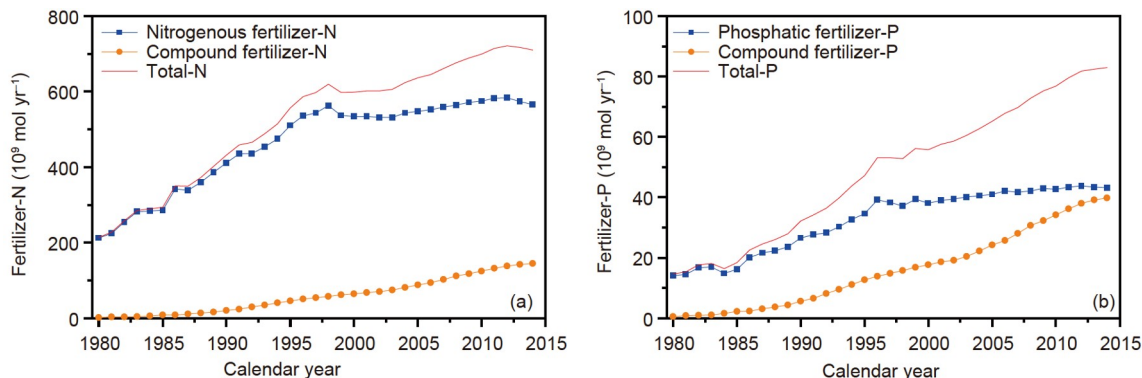


Figure 17 (Color online) The annual input of N and P (Fertilizer-N/P) via synthetic fertilizer applications, including nitrogenous, phosphoric and compound fertilizers in the Changjiang watersheds. Details of data compilation can be found in Appendix 3: Source vs Sink (S13).

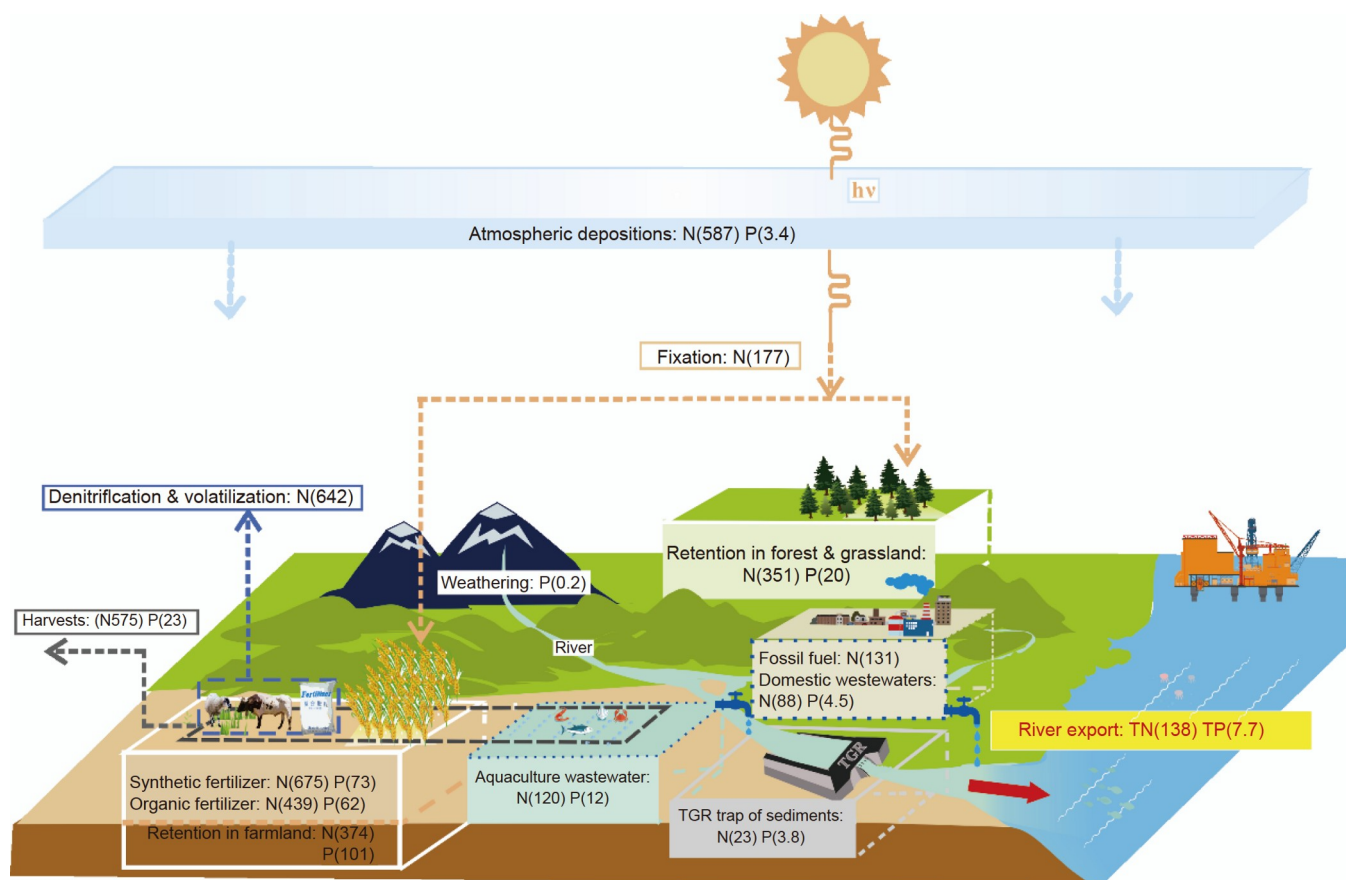


Figure 18 (Color online) Summary of major source and sink terms (unit: $\times 10^9 \text{ mol yr}^{-1}$) as well as retention of nitrogen and phosphorus over the entire watersheds of the Changjiang. Data in this figure show an average for the period of 2003–2015.

scape, river basins undergo a prolonged accumulation phase, and nutrients serve as legacy and potential sources. Our studies in Changjiang indicate that accumulated nutrients may continue to leach out and/or be remobilized from watersheds even after the depletion of anthropogenic sources, such as reduction in both the application of synthetic fertilizers, including composite chemicals, and atmospheric depositions.

Furthermore, variations in the ratio of export flux to accumulation in the Changjiang watersheds revealed the distinction of biogeochemistry between nitrogen and phosphorus. Historically, although the accumulation of nitrogen has been four-to-five-folds higher than that of phosphorus in the river basin, the lower export flux-to-accumulation ratio for phosphorus will lead to prolonged retention. This is presumably related to the more complex speciation of phosphorus in the soil profile and river sediments. For instance, nitrogen in the solid phase of river is essentially in non-mineral forms (e.g., organic detritus), while phosphorus can be either in the organic form or in complexes with Ca, Al, and Fe, which are not readily soluble during the erosion processes of watersheds. Indeed, in the Changjiang and its major tributaries, the proportion of particulate fraction

in river transport is higher for phosphorus (PP) than for nitrogen (PN) along the river course (Liu et al., 2003).

4.10 Comparison with dissolved organic carbon (DOC) in the river

Early data sets of DOC in the Changjiang can be tracked back to the mid-1980s. In water samples analyzed by Cauwet and Mackenzie (1993), DOC was $142 \mu\text{mol L}^{-1}$ during the dry season and $167 \mu\text{mol L}^{-1}$ during the flood period in 1986 at the river mouth. During the same period, the nutrient level in Changjiang was $50 \mu\text{mol L}^{-1}$ for DIN, $0.6 \mu\text{mol L}^{-1}$ for DIP, and $95 \mu\text{mol L}^{-1}$ for DSi. In Figure 19, the concentrations of DOC and nutrients are compared, based on the compilation of data in the literature from the 1980s.

Since the beginning of the present century, DOC at the river mouth of Changjiang has stabilized at ca. $120 \mu\text{mol L}^{-1}$, while DIN and DIP have been increasing rapidly (Figures 7 and 19), resulting in a decline in the ratio of DOC to DIN and DIP. If DSi is considered an index of weathering over the drainage, DOC/DSi decreased by over a factor of two in 2012 relative to that in 1986 (Figure 19). Although changes in the species ratios of DOC to nutrients in the Changjiang

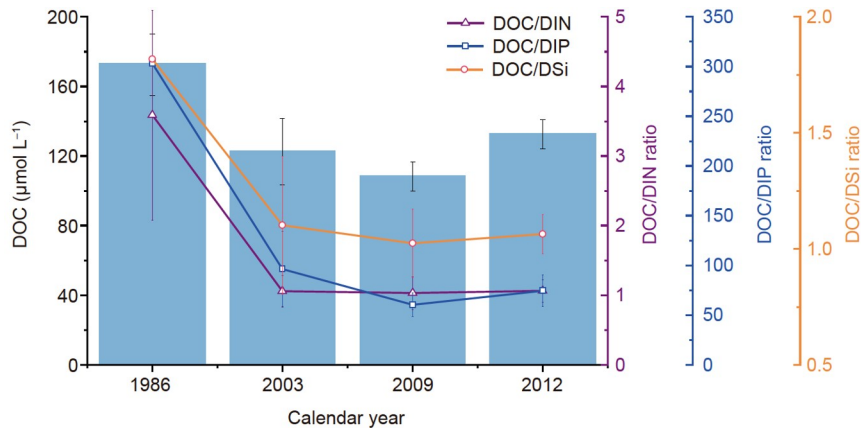


Figure 19 (Color online) Comparison between anthropogenic nutrients and dissolved organic carbon (DOC) in the Changjiang for the period of 1986–2012. In the figure, data of DOC from different observation campaigns and corresponding nutrients to DOC molar ratios are examined. Data of DOC are from Cauwet and Mackenzie (1993), Zhang et al. (2013), Bao et al. (2015) and Wang et al. (2019).

warrant further examination in greater details, the current information indicates that nutrients and DOC can be decoupled in the river systems because of different pathways of cycling involved.

Previous studies indicated that DOC in a river can be supplied via leaching from soil profiles and biological processes (e.g., lysis and exudation of cells) in aquatic environments. In urbanized areas, DOC in a river can also be supplied through waste drainage (Zhang et al., 2013; Bao et al., 2015). Nevertheless, our data indicate that the rapid increase in DIN and DIP in the Changjiang is sustained by the application of chemical fertilizers in agriculture as well as release from domestic centers in coastal and urban areas. Although, the over-enrichment of nutrients (e.g., DIN and DIP) in aquatic environments can promote the proliferation of algal cells, which generate DOC pools, this would produce a rather limited effect in the Changjiang, because DOC can be lost via metabolic processes, such as CO₂ and CH₄ production through respiration and feedback to the atmosphere.

Recently, Liu et al. (2020) reviewed annual variability in DOC flux in the Changjiang based on remote sensing. Using data assimilation techniques, the authors could track the trends of DOC back to the 1950s–1960s. Based on their data, the annual flux of DOC in Changjiang has shown a slow but rather steady increase over last six decades of (Liu et al., 2020). However, the DOC concentration reported in that study (Liu et al., 2020) was 40–50% higher than that measured at the river mouth in the present study. Lack of hydrography and time-series data at the river mouth may lead to either over- or under-estimation of fluxes depending on the chemical parameters of interest. In the case of nutrients, the present study showed that DIP fluxes at the river mouth are 15–20% higher than values reported at Datong, and similar outcomes may be obtained for other chemical properties, such as dissolved organic matter.

5. Conclusions and future prospects

In the present study, we examined the biogeochemistry of nutrients in Changjiang based on data from field observations between the river mouth and upstream reaches over a water course of ca. 4,500 km along the mainstream as well as along major tributaries during 1997–2016. In addition, monthly sampling surveys were conducted in lower reaches and close to the river mouth (i.e., Nantong and Xuliujing) for a period of three to four decades. This allowed us to compare our observations with literature reports in detail.

Based on available information, we noted that although the head waters of Changjiang from the Qinghai-Tibetan Plateau remain in a relatively pristine state, high concentrations of nutrient species are recorded from upstream parts after the river flows out of deep valleys in the source region because of inflows of tributaries in Sichuan, Chongqing, and Guizhou, where surface runoff is strongly influenced by agricultural and other anthropogenic activities (e.g., land-use changes). This contribution of nutrients by upstream tributaries produced profound impacts on the riverine concentrations and species ratios up to 2,000 km downstream until the river mouth. Our data analysis and comparison with literature reports revealed that the TGR produces a rather limited effect on the so-called trapping of nutrients from the upstream areas. In fact, DIN and DIP concentrations increase downstream of TGD, while DSi is slightly reduced (i.e., 10–20%). This pattern can be attributed to the considerable and collective contributions of rivers/streams in un-gauged areas around TGR, which were ignored in previous studies. Moreover, the retention of DSi in the reservoir can be compensated by supply from two large lakes and other tributaries over the next thousands of kilometers; hence, the “trapping” effect of the dam may not be evident at the river mouth.

The concentration of DIN since the early 1960s and, subsequently, that of DIP since the 1980s have steadily increased in the lower reaches of Changjiang, while DSi has remained somewhat stable at Datong. Contrary to previous studies estimating the seaward fluxes of nutrients based on measurements at Datong, we evaluated the additional input of nutrients downstream of Datong and in the entire tide-influenced delta. Our results indicate that despite covering a rather limited fraction (ca. 5%) of the entire Changjiang drainage basin, the tide-influenced delta downstream of Datong can considerably increase the fluxes and alter the specie ratios of nutrients. This pan-deltaic area contributes an additional 20% to the seaward flux of DIP and 5–10% to the seaward fluxes for DIN and DSi, thereby considerably altering the molar values of DIN/DIP and DIP/DSi. Taking direct drainages to the coast into account, the contribution of the tide-influenced delta can be even higher than the fluxes estimated in the present study. This finding highlights the significant role of tide-influenced delta in regulating water chemistry, which was previously underestimated. Specifically, the over-enrichment of nutrients from this area adds value to the seaward fluxes and species ratios of nutrients in global river systems. This global issue is exemplified in the case studies on Changjiang, which is among the top five largest rivers in this world. Earlier, the effects of tide-influenced deltas were not considered when formulating management strategies and policies aimed at the reduction of nutrient over-enrichment in river drainage basins. Such mitigation approaches against coastal eutrophication may not be effective if contributions from tide-influenced deltaic areas are not properly managed.

In [Figure 18](#), critical pathways and budgets for anthropogenic nutrients (i.e., nitrogen and phosphorus) in the entire Changjiang drainage basin are summarized, with comparison to export fluxes to the ocean. Evidently, nitrogen and phosphorus present very different source *versus* sink terms across the entire watersheds, driving distinct biogeochemical cycles in the watersheds. Thus, different mitigation and adaptation policies must be considered to manage nutrient over-enrichments in this aquatic ecosystem.

Using GAM and ARIMAX modeling on the data of nutrients from the drainage basin, we found that synthetic fertilizer and atmospheric depositions are the major sources for DIN and synthetic fertilizer and organic manure are the major external drivers for DIP. These factors induce and maintain high nutrient burdens in Changjiang ([Figure 18](#)), producing profound impacts on the sustainability of coastal ecosystems. Moreover, both DIN and DIP present hysteretic characteristics in the Changjiang relative to their sources *versus* sink terms over the entire drainage basin. Therefore, the effectiveness of action plans for the mitigation of nutrient over-enrichments in the river must be assessed considering the nature of nonlinearity and hysteresis of individual nu-

trients, and different adaptive strategies should be implemented in upstream and tide-influenced deltaic areas. Otherwise, the applied management strategies will be ineffective and implementation results will not be as expected. Overall, the mitigation of anthropogenic nutrient over-enrichment warrants effort over the entire drainage basin rather than at the local scale.

Finally, over the last three to four decades, anthropogenic activities in the Changjiang drainage basin have considerably increased the concentrations of nutrients in this river. Consequently, Changjiang has become an outstanding river system compared with the other top 10 largest river systems on this planet and serves as the largest source of anthropogenic nutrients from the land to global oceans.

Experiences and lessons learnt from studies in Changjiang will be beneficial to other developing and maritime countries, because the common goals of supplying clean water, healthy food, and green energy represent the three critical aspects of sustainable policies for human societies worldwide. In this context, river watersheds bridge the land, atmosphere, and oceans, thereby playing pivotal roles in the evolution of economies and human cultures. River systems should not be considered a passive conduit between the land, atmosphere, and oceans, but rather a bridge between the natural and human dimensions and an intricate matrix of interactions between these three compartments of the Earth. The behavior of a river provides profound feedbacks to human societies in its drainage basin as well as in the adjacent coastal environment, such as the future of the river drainage basin and its deltaic area. Without strict control and careful management, the functions of river systems may be threatened by the environmental impacts of socio-economic growth at the global level. Therefore, human societies will suffer from changes in services provided by rivers. This is particularly important for maritime countries, which experience severe nutrient over-enrichment of rivers, including coastal eutrophication, hypoxia, and pH reduction, among other threats.

The impact of future climate change on the nutrient chemistry of global rivers remains unclear. However, based on lessons learnt from the Changjiang, the functions of coastal ecosystems rely on the behavior of human societies in watersheds. Thus, sustainable solutions are warranted, as these areas are likely to become increasingly populated in the near future, regardless of the increase in global fluvial nutrient fluxes. To this end, successful action plans would rely on how well we understand the nutrient biogeochemistry of rivers.

Box 1. Anthropogenic nutrients

Nutrients in the river can be supplied from various sources over the catchment area, and their behaviors are regulated by

biogeochemical and hydrodynamic processes in different temporal and spatial dimensions, including natural and anthropogenic ones.

The natural sources of nutrients in rivers can be related to different pathways, such as the weathering of minerals containing phosphorus in their crystal structure. Nitrogen is not part of crystal lattices during rock-forming processes; hence, nitrogen lacks its own mineral phases in nature. However, certain types of plants, such as legumes on the land and cyanobacteria in the aquatic environments, can directly use nitrogen in the atmosphere for primary production through a mechanism called nitrogen fixation. Although nutrients are also delivered via atmospheric depositions, their concentrations can be significantly affected by air pollution. Nowadays, the major sources of nitrogen and phosphorus in river watersheds are related to anthropogenic activities. Therefore, DIN and DIP in rivers are sometimes referred to as “anthropogenic nutrients” in studies of aquatic biogeochemistry.

In the case of Changjiang, over 95% supply of nitrogen and phosphorus in the entire drainage basin is regulated by anthropogenic activities as external drivers. Therefore, DIN and DIP concentrations in Changjiang are essentially sustained by these anthropogenic sources.

Box 2. Legacy nutrients

Significant differences between the accumulative supply (i.e., inputs) and export (i.e., outputs) will induce a net storage or depletion of nutrients in a given drainage basin. When input is smaller than export, the river is considered in the phase of nutrients depletion. Conversely, when input is greater than export, the river is considered to be on the accumulation phase, and nutrients are accumulated in the watershed. This difference produces a profound effect on river chemistry, such as the long-term trends of nutrient concentrations at the river mouth.

Nutrients previously accumulated/stored in watersheds are called “legacy nutrients” or “legacy concentrations” in a broader sense when used for other elements in geochemical studies. Legacy nutrients can be remobilized through processes in soil profiles and hence contribute to the high nutrient concentrations in rivers. Such a contribution can be linked to climatic variability (e.g., ENSO) and/or anthropogenic activities (e.g., changes in plant type in agriculture).

In practice, the concentrations of legacy nutrients can be estimated through various approaches, such as differences between external sources and removal over the watershed or the amount of anthropogenic supplies multiplied by the retention rate of nutrients in a given drainage basin. Nutrients may present markedly different legacy concentrations even within a given drainage basin, because elements are subjected to various sources and sink pathways and exhibit di-

verse behaviors.

In Changjiang, both nitrogen and phosphorus are in the accumulation phase and act as the so-called “legacy nutrients,” potentially forming important nutrient pools, which can be two-to-five fold larger than their riverine export fluxes at the annual scale.

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