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Nutrient dynamics in the Changjiang and retention effect in the Three Gorges Reservoir

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ABSTRACT

2009 ~ 2010 was a critical period for the Three Gorges Reservoir (TGR) transition from staged impoundment to full operation. This study reports on the composition of nutrients in the whole Changjiang and retention effect of the reservoir during the transitional period, and the potential impact of the reservoir impoundment on the eutrophication of the TGR and estuary. Water samples were collected in the mainstream and tributaries of Changjiang from August to October 2009 and June 2010 to analyze the concentrations of dissolved and particulate nutrients, and suspended particulate matter (SPM). The Changjiang was enriched with dissolved inorganic nitrogen (DIN), dissolved silicate (DSi) and SPM, but depleted in PO_4^{3-} and biogenic silica (BSi), with higher DIN:PO_4^{3-} and DSi:PO_4^{3-} ratios. DIN and PO_4^{3-} concentrations were lower in the Jinshajiang, but increased in the Mid-downstream of the Changjiang due to high human activities and nutrients import from major tributaries. DSi concentration varied little along the Changjiang, and was relatively low in the TGR. Particulate inorganic phosphorus (PIP), total particulate phosphorus (TPP) and BSi concentrations were very high in the Jinshajiang, and then dramatically decreased with the SPM in the TGR. The northern tributaries contributed more nutrients to the Changjiang than the southern tributaries. Depending on the nutrients input-output mass balance model, the retention of nutrients in the TGR were higher for TPP and BSi, lower for dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP). Total dissolved nitrogen (TDN), total phosphorus (TP) and DSi retained in the reservoir accounted for 15%, 12% and 1%, respectively of the TDN, TP and DSi fluxes in the Datong station near the estuary. Historical data showed that the impoundment of the TGD greatly contributed to the eutrophication of the reservoir and estuary. Since 2003, algal blooms were likely to occur in the TGR, estuary and adjacent seas, but the outbreak frequency and area of red tides in the East China Sea (ECS) dramatically decreased. Therefore, further study is required to estimate the response of estuarine ecosystem on the dispatching mode of the TGR.

1. Introduction

Riverine transport represents a vital pathway of particulate matter and dissolved elements from land to sea within the global biogeochemical cycles (Liu et al., 2016; Tong et al., 2016; Diaz et al., 2008). Excessive nutrient discharges and changes in nutrient ratios, which are caused by intense anthropogenic activities and land-use changes, affect the dynamics of nutrients in the river systems (Whitney et al., 2005; Hessen et al., 2010; Tong et al., 2016; Seitzinger et al., 2010). Eutrophication, frequent harmful algal blooms and seasonal hypoxia have been observed in the estuaries and coastal marine ecosystems due to the delivery of river nutrients (Armon et al., 2015; Garnier et al., 2010; Romero et al., 2013).

The Changjiang (Yangtze) is the largest river flowing into the West Pacific Ocean with a drainage area of 1.8×10^6 km^2, annual mean runoff of 9.0×10^{11} m^3 and sediment load of 4.7×10^8 ton (t) (Fan et al., 2014; Li et al., 2007). With growing populations and rapid industrialization in the Changjiang Basin, anthropogenic activities, including industrial discharge, city sewage, agricultural and domestic run-off, have increasingly led to water quality deterioration (Gao et al.,

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2016). Nitrogen and phosphorus, as the essential nutrients that support aquatic primary productivity, have exhibited remarkable upward trends in the Changjiang over the past 50 years (Li et al., 2007) and approximately 1.43×10^6 t of DIN, including 1.28×10^6 t of nitrate (NO_3^-), and 2.35×10^5 t of TP are annually transported to the Ocean (Shen et al., 2003; Yan et al., 2003; Tong et al., 2015). Moreover, about 3.17×10^6 t/a of DSi is transported into the ECS (Liu and Shen, 2001).

The Three Gorges Dam (TGD) began to impound water and sediment discharge on 1st June 2003. When the TGD experimental storage water level reached 175 m in 2009, the water storage capacity of the TGR was 39.3 km^3, about 4.5% of the Changjiang's annual discharge (Xu et al., 2009). Although the amount of sediment transported by the Changjiang has gradually decreased due to the construction of the TGD, the amount of water entering the sea has not decreased significantly but basically maintained at 9.0×10^{11} m^3 over the past 50 years (Dai et al., 2011). The TGR has been reported to have influenced nutrient and freshwater discharges of the Changjiang, leading to reduction of primary productivity, abnormal salinity and changes in other ecological parameters such as reduction of heterotrophic bacteria in the Changjiang estuary and coastal area (Gong et al., 2006; Yan et al., 2008; Jiao et al., 2007). So, it is very urgent to study the long-term effects of the TGD operational mode on the ecosystems of reservoir, estuary and ECS. 2009 ~ 2010 is a critical period for TGR's transition from staged impoundment to full operation. At this stage, studying the nutrients composition of the Changjiang and the nutrients retention in the TGR will have a key guiding significance for nutrients transport from the Changjiang to the ECS, as well as for the eutrophication of the TGR and estuary under the full operation of the reservoir since 2010. But at present, most of the researches have focused on the changes of nutrients (Huang et al., 2014; Lou et al., 2016; Xia et al., 2018), distribution of algae composition (Zeng et al., 2006a), the estimation of retention effects (Zhang et al., 1999, 2003; Ran et al., 2009; Ran et al., 2013) in the reservoir and the changes of estuarine ecosystems, etc. (Chai et al., 2009; Jiang et al., 2014; Zhou et al., 2008) before and after TGR impoundment. Few studies have focused on the nutrients in the entire Changjiang basin and nutrients retention in the TGR during this transitional period. Since 2003, the long-term potential impact of the TGR impoundment on eutrophication of the reservoir, estuary and ECS is rarely known.

Based on the observations in 2009 ~ 2010, this study aims to provide a deeper and systematic understanding of nutrient dynamics and biogeochemistry in the Changjiang. The box model is used to estimate the retention effect of TGR on nutrients in the river. Combined with the historical data of the reservoir and estuary, the potential impacts of the TGR staged storage in 2003–2009 and normal storage since 2010 on the eutrophication of reservoir, estuary and ECS are further evaluated, in order to provide a certain historical and theoretical basis for the coordination between the TGR regulation model and sustainable ecological health of the estuary in the future.

2. Materials and methods

2.1. Study area

The Changjiang extends over 6300 km from its headwaters in the Qinghai-Tibet Plateau to the East China Sea. Generally, the area from the source to Yichang in Hubei is defined as the upstream of the Changjiang. It is 4500 km long with a basin area of 1.0×10^6 km^2 (Fig. 1). The midstream, 955 km long, is the reach from Yichang to Hukou (HK) in Jiangxi, and the downstream segment is defined as the reach from Hukou to the Changjiang estuary (Shanghai). The TGD is located about 44 km upstream of Yichang (Fig. 1). The Jinshajiang lies on the upper stream of the Changjiang, which is the region of 3000 ~ 6300 km from the river mouth. Some tributaries such as Yalongjiang (YLJ), Minjiang (MJ), Jialingjiang (JLJ), Tuojiang (TJ), Fujiang (FJ), Daduhe (DDH) and Hanjiang (HJ) are in the north. Other tributaries including Wujiang (WJ), Niulanjiang (NLJ) and Chishuihe (CSH) are in the south. In addition, the Dongting Lake (DTL) connecting the Xiangjiang (XJ), Yuanjiang (YJ) and Zishui (ZS) and the Poyang Lake (PYL) connecting the Ganjiang (GJ) and Fuhe (FH) are located in the south of the main channel. The sampling stations are shown in Fig. 1.

2.2. Sample collection

From August to October 2009 and June 2010, water samples in the mainstream and tributaries of the Changjiang were collected with 20 L Niskin bottles at three different depths (surface, intermediate and near-bottom) at each station. Dissolved nutrient samples were filtered in situ using 0.45 μm cellulose acetate membranes that had been pre-soaked for 24 h with 1: 1000 HCl and then washed to neutral pH with Milli-Q water. The filtrates were preserved by the addition of saturated $HgCl_2$. On return to the laboratory, the filters were dried at 50 °C for 72 h and reweighed to determine the mass of SPM. SPM was analyzed for PIP, TPP and BSi.

2.3. Chemical analyses

Nutrients (NO_3^-, NO_2^- and DSi) were analyzed using an autoanalyzer (Skalar SANplus system) (Liu et al., 2012). PO_4^{3-} was measured manually by phosphomolyb-denum blue method (Grasshoff et al., 1999). NH_4^+ was measured manually by sodium hypobromite oxidation method (Gao et al., 1980). TDN and TDP were measured using alkaline potassium persulfate oxidation method (Grasshoff et al., 1999). The analytical precision was 0.06 μmol/L for NO_3^-, 0.01 μmol/L for NO_2^-, 0.15 μmol/L for DSi, 0.03 μmol/L for PO_4^{3-}, 0.09 μmol/L for NH_4^+, 0.68 μmol/L for TDN and 0.02 μmol/L for TDP. DIN concentration was the sum of NO_3^-, NO_2^- and NH_4^+. DON and dissolved organic phosphorus (DOP) were the difference between TDN and DIN, and between TDP and PO_4^{3-}, respectively.

SPM was ashed at 550 °C for 2 h and then was extracted with HCl (1 M, 16 h) for TPP analysis (Aspila et al., 1976). PIP was determined by extraction of uncombusted samples for 16 h in 1 M HCl (Aspila et al., 1976). POP was the difference between TPP and PIP. TP was the sum of TPP and TDP. The analytical precision was < 0.5% for PIP and TPP ($n = 5$). BSi was measured in our laboratory with modifications to the methods of Ragueneau et al. (2005). Briefly, SPM was subjected to three steps digestion (0.2 M NaOH, pH 13.3) at 100 °C for 40 min. In the first and second leach, all the BSi was converted into $Si(OH)_4$. Si and Al concentrations ($[Si]_1$, $[Al]_1$, $[Si]_2$ and $[Al]_2$) in the supernatant were analyzed. In the third leach, after the filter was rinsed and dried, the $(Si:Al)_3$ ratio of silicate minerals present in the SPM was determined. So the corrected BSi concentration was given by $[BSi] = [Si]_1 + [Si]_2 - ([Al]_1 + [Al]_2) \times [Si]_3/[Al]_3$. Here, the Al concentration was determined by the modified aluminum-fluorescent gallium (Al-LMG) complex fluorescence spectrophotometry (Ren et al., 2001; Hydes and Liss., 1976). The analytical precision was 5% for BSi.

2.4. Nutrient budgets for the TGR and data source

As shown in Fig. 1, there are three major input rivers in the upstream of the TGR, including the Changjiang mainstream, Jialingjiang and Wujiang (Han et al., 2016). It was reported that the sum water flux of the three upstream input rivers accounted for 90.8% of the total water flux of the TGR (Wang et al., 2009). Therefore, Fuling is regarded as the control station of three major input rivers entering the TGR in this study.

A box model is adopted to estimate the nutrient input-output mass balance for the TGR (Fig. 2, Ran et al., 2013 & 2015). It is hypothesized that the total input to the reservoir, including the upstream inflow at the Fuling, the lateral input from the sub-catchment of the TGR, urban domestic sewage, industrial and agricultural pollution, and atmospheric

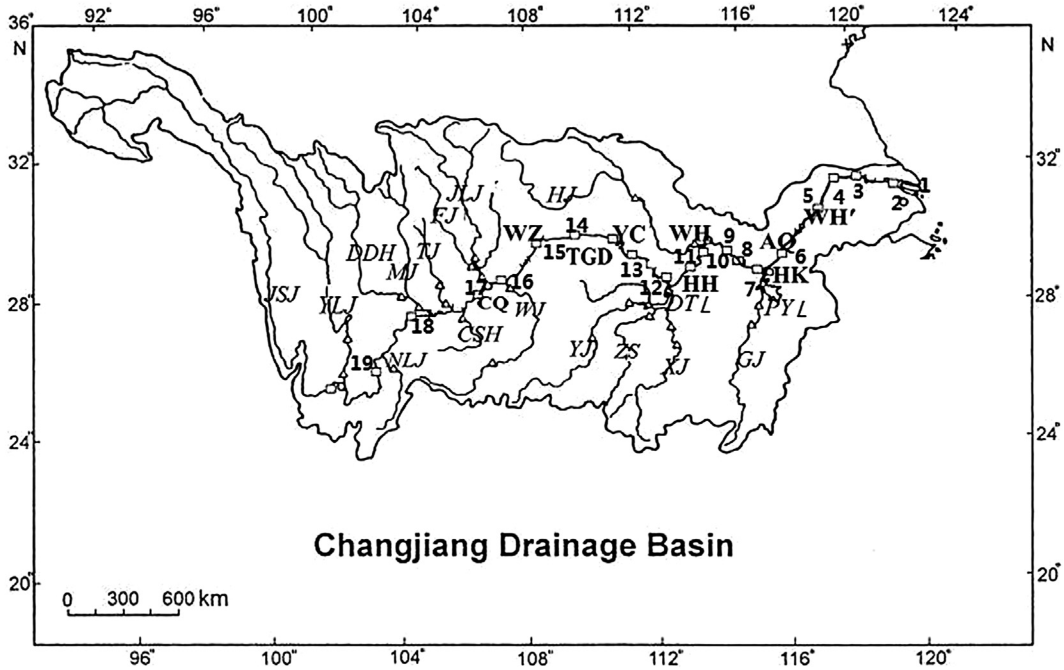

Fig. 1. Map of the Changjiang drainage basin which shows the main stream and its large tributaries. Two big lakes including Dongting Lake (DTL) and Poyang Lake (PYL) are illustrated. Sampling sites: (1) Shanghai (2) Xuliujing (3) Dayun (4) Yangzhou (5) Wuhu (6) Anqing (7) Hukou (8) Huangshi (9) Huanggang (10) Wuhan (11) Honghu (12) Yueyang (13) Yichang (14) Fengjie (15) Taibaiyang (16) Fuling (17) Jiangjin (18) Nanxi (19) Qiaojia-Jinshajiang.

deposition must be equal to the losses, including the output at the dam (Yichang) and the reservoir retention. The equation is as follows:

$$L_I + L_T + L_P + L_D + L_S = L_O + L_R \quad (1)$$

where L_I represents the upstream nutrients input load of TGR, including the Changjiang mainstream, Jialingjiang and Wujiang; L_T represents the lateral nutrients input load from the sub-catchment of the TGR. Here, to avoid the pseudo retention effect caused by freshwater discharge difference, the water discharge of the lateral input is the difference between upstream inflow and downstream outflow of the TGR (Kelly, 2001; Ran et al., 2013); L_P represents the industrial and agricultural pollution load; L_S represents urban domestic sewage; L_P and L_S only considers the part that is directly discharged into the main stream of the reservoir. L_D represents atmospheric deposition nutrient load, L_O represents the downstream output loads of the TGR and L_R is the net retention of the reservoir. Data sources are shown in Table 2.

The retention efficiency is considered as a parameter to evaluate and identify the retention effect of the dam or reservoir on nutrients. Here, the retention efficiency is defined and calculated as follows (Harrison et al, 2009; Ran et al, 2009):

$$\text{Retention efficiency} = \frac{L_I + L_T + L_P + L_D + L_S - L_O}{L_I + L_T + L_P + L_D + L_S} \times 100\% \quad (2)$$

3. Results

3.1. Hydrographic features

Fig. 3A showed that the Changjiang carried a large volume of water to the East China Sea during the study period. An increasing trend was observed within the main channel from the upper to lower reaches. At the upstream hydrographic station of Fuling, the monthly average water flow between 2009 and 2010 respectively exceeded 509×10^8 and $323 \times 10^8\ m^3$ due to the inflow from several large tributaries including the Yalongjiang, Minjiang, Jialingjiang and Wujiang (Table 1). After the TGD, the monthly mean water discharge at Yichang in August to October 2009 was comparable to that at Fuling. However, in June 2010, the water discharge at the Yichang increased by 44% than that at Fuling (Fig. 3A, Table 1), and then the monthly mean water discharge respectively increased to 812×10^8 and $1305 \times 10^8\ m^3$ at Datong after the inflow from the Hanjiang and Dongting Lake connecting Zishui,

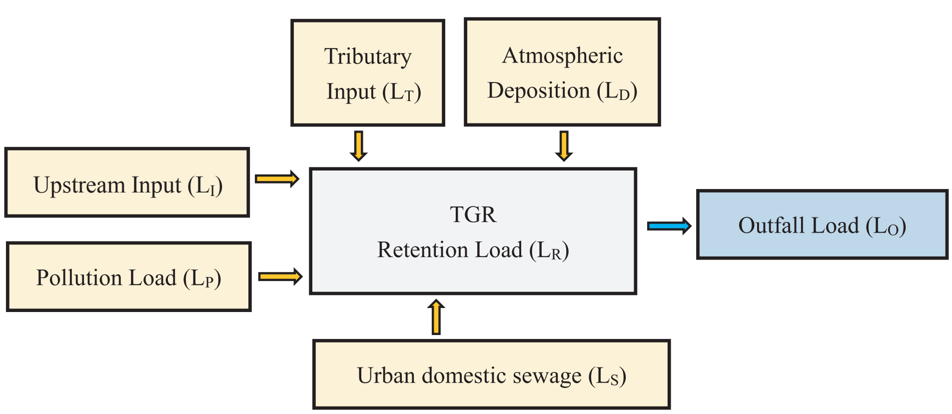

Fig. 2. Mass balances of nutrients in the TGR.

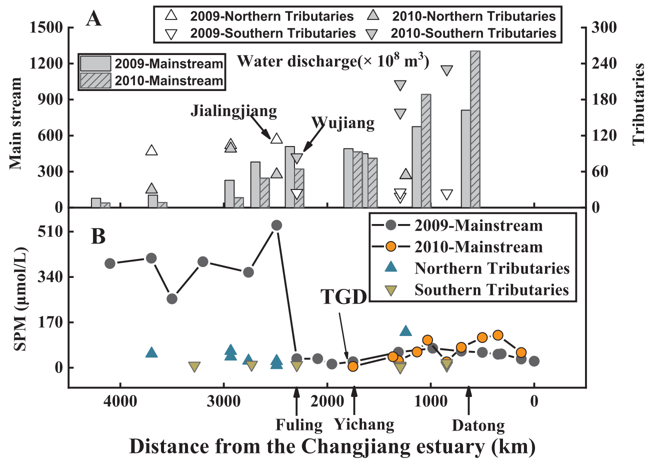

Fig.3. Distribution of the Water discharge (A) and SPM (B) in Changjiang mainstream and its main tributaries.

Yuanjiang and Xiangjiang and Poyang Lake connecting Ganjiang and Fuhe (Table 1). In addition, the mean water discharge in the Mid-downstream section increased by 39%~60% in 2010 than in 2009 from the impact of concentrated heavy rainfall during the study period (Wang, 2010).

The SPM concentrations had a significant negative correlation ($P < 0.05$, $R = -0.816$, $n = 8$) with water discharge along the Changjiang. The SPM concentrations varied between 4.49 and 534 mg/L with an average of 124 mg/L in the main channel. A decreasing trend was observed within the main channel from the upper to middle reaches (Fig. 3B). In 2009, SPM concentration decreased to 33.7 mg/L at Fuling due to the deposition of suspended particulate matter and the dilution of water discharge. After the TGD, SPM concentration at Yichang (22.3 mg/L) decreased by 34% compared to that at Fuling, then slowly increased to 50.3 mg/L at Datong. Besides, the concentrations of SPM from Datong station to the estuary in 2010 were significantly higher than that in 2009 due to heavy rainfall (Fig. 3B).

3.2. Spatial patterns of nutrient concentrations

In the mainstream of the Changjiang, the distributions of NH_4^+ and NO_2^- were similar to each other (Fig. S1 D and C). The average level of NH_4^+ and NO_2^- accounted for 5.4% and 0.7% of TDN, respectively. In 2009, the nutrient concentrations in the upper reaches slowly increased to 6.69 μmol/L for NH_4^+ and 0.90 μmol/L for NO_2^- at Fuling, and then decreased to 1.07 μmol/L for NH_4^+ and 0.15 μmol/L for NO_2^- at Yichang, respectively. In the middle reaches, the concentrations of NH_4^+ and NO_2^- increased by one order of magnitude than those in the upper reaches. Further downstream, the nutrient concentrations decreased to fairly stabilization in the region of 350 ~ 700 km from the river mouth, and then the average level respectively increased to 8.12 μmol/L for NH_4^+ and 1.06 μmol/L for NO_2^- in the area 0 ~ 300 km from the estuary.

NO_3^-, DIN and TDN had a similar tendency (Figs. 4A; S1A and B). The nutrient concentrations were quite low in the Jinshajiang with averages of 29.2 μmol/L for NO_3^-, 30.3 μmol/L for DIN and 35.9 μmol/L for TDN, respectively, and increased significantly to 135 μmol/L for NO_3^-, 142 μmol/L for DIN and 152 μmol/L for TDN at Fuling, respectively, subsequently decreased to 97.5 μmol/L for NO_3^-, 98.3 μmol/L for DIN and 112 μmol/L for TDN at Fengjie, respectively. Further Mid-downstream, NO_3^- concentration basically remained stable except in the region of 300 km from the river mouth in 2009 (Fig. 4A). However, DIN and TDN concentrations slightly increased in the midstream and decreased to fairly stable in the downstream with a similar tendency to nitrate (Fig. S1 A and B). NO_3^- was the main form of nitrogen in the Changjiang, accounting for 84.1% of TDN. Fig. S1 A also indicated that the average concentration of inorganic N in the tributaries of Changjiang was significantly higher than that of the main stream, including the Jialingjiang, Minjiang, Tuojiang and Hanjiang in the north and Wujiang in the south, while the inorganic N concentration in the Yalongjiang was the lowest in all tributaries.

The average DON concentration (Fig. S1E) was relatively high compared with that of NH_4^+ and NO_2^-, which accounted for 9.8% of TDN. The concentration ranged from 0.65 to 17.13 μmol/L with an average of 7.23 μmol/L in the mainstream. The DON concentration was rather low in the upper reaches, significantly increased to 12.43 μmol/L by average in the TGR, and decreased further in the Mid-downstream

Table 1
Characteristics of hydrology in the Changjiang.

Chang jiang	River	Sampling station	Hydrological control station	Drainage area /km^2	Distance from the estuary /km	Water discharge ($\times 10^8$ m^3)					
						/month		/a			
						2009.8–10	2010.6	1997	2005	2007	2009
Mainstream	Jinshajiang		Shigu	232,651	4190	78	40				
			Panzhihua	284,540	3640	104	43				
		Nanxi	Pingshan	458,592	2900	228	83				
		Jiangjin	Zhuotuo	694,725	2650	381	246	2385	2844	2384	2431
		Yichang	Yichang	1,005,501	1751	492	465	3680	4606	4004	3822
		Huangshi	Hankou	1,488,000	1090	675	944				
		Wuhu	Datong	1,705,400	615	812	1305				
		Yangzhou	Datong	1,705,400	615	812	1305				
Northern tributaries	Yalongjiang		Tongzilin	128,400	3698	94	30				
	Minjiang		Gaochang	135,378	2933	104	98				
	Jialingjiang		Beibei	156,142	2489	113	55	310.8	802.9	665.3	671.9
	Hanjiang		Huangzhuang	142,100	1241	54	54				
Southern tributaries	Wujiang		Wulong	83,053	2294	25	84	536.6	377.2	524.8	361.4
	Ganjiang		Waizhou	80,900	845	24	231				
	Fuhe		Lijiadu	15,800	845	–	–				
	Zishui		Taojiang	26,700	1295	–	–				
	Yuanjiang		Taoyuan	85,200	1295	18	158				
	Xiangjiang		Xiangtan	81,600	1295	26	206				

Drainage area and distance from the estuary (Shanghai) are from the report of Xu and Tong (2012).
Water discharges are from Changjiang Sediment Bulletin, 2009 & 2010.

Table 2
Data sources of nutrient budgets in the TGR.

	DIN	TDN	DON	DSi	BSi	PO_4^{3-}	TDP	DOP	TPP	TP	Source (time of investigation)
Fuling (μmol/L)	113			94.8		2.50					Liu et al., 2003 (1997)
	102			123		1.48					Zeng, 2006 (2005)
	128			108		1.50					Ran et al., 2017, 2013 &2015 (2007)
	142	152	9.78	119	7.47	2.20	2.91	0.71	1.10	4.01	This Study (2009)
Jialingjiang (μmol/L)	59.2			48.4		0.99					Liu et al., 2003 (1997)
	110					1.00					Cao et al., 2008 (2005)
	135			96.0		1.50					Ran et al., 2007; Ran et al., 2013a,b,2015 (2007)
	124	130	6.17	119	0.63	1.39	1.82	0.43	0.91	2.73	This Study (2009)
Wujiang (μmol/L)	92.7			68.3		6.06					Liu et al., 2003 (1997)
	152					0.97					Cao et al., 2008 (2005)
	139			95.0		1.15					Ran et al., 2007; Ran et al., 2013a,b,2015 (2007)
	222	226	4.10	99.2	1.09	1.80	1.93	0.13	0.23	2.16	This Study (2009)
Yichang (μmol/L)	99.2			91.3		1.16					Liu et al., 2003 (1997)
	108			126		1.02					Zeng, 2006 (2005)
	118			107		0.83					Ran et al., 2007; Ran et al., 2013a,b,2015 (2007)
	111	123	12.0	112	3.26	1.40	2.26	0.86	0.61	2.87	This Study (2009)
Lateral input (μmol/L) average	62.7			91.5		1.80					Ye 2006 (1997)
	99.4			83.0		1.39					Fang et al., 2006; Ran et al., 2013b (2005)
	89.3			67.5		0.75					Ran et al., 2013a,b,2015; Ran et al., 2017 (2007)
	92.1	108	16.3	93.4		0.81	1.64	0.83		1.64	Tan et al., 2010 (2009)
Atmospheric deposition ($\times 10^2$ ton)	3.43	6.86	3.43			0.10	0.23	0.13		0.23	State Environmental Protection Administration of China,
Industrial and agricultural pollution load ($\times 10^2$ ton)	132	224	92.3			17.0	47.6	30.6		47.6	2010 (2009)
	90.0					14.0					Hu et al., 2013 (1997)
	154					28.0					Hu et al., 2013 (2005)
	154					26.0					Hu et al., 2013 (2007)
Urban domestic sewage ($\times 10^2$ ton)	0.76	1.51	0.75			0.10	0.21	0.11		0.21	Huang and Li, 2006 (1998)

except for the region of 500 ~ 700 km from the estuary. Meanwhile, the average concentration of DON in the Mid-downstream of the Changjiang in 2009 was almost three times that of 2010 (Fig. S1E).

In the main stream of the Changjiang, the distribution of PO_4^{3-} (Fig. 4B) was similar to that of TDP (Fig. S1F). PO_4^{3-} averagely accounted for 73.3% of TDP and 35.4% of TP, respectively. Like NO_3^-, DIN and TDN, PO_4^{3-} concentrations were quite low in the Jinshajiang with an average of 0.21 μmol/L, and increased by a factor of more than 10 in the TGR, decreased to lower value after the TGD, and then slightly increased to stable concentrations basically in the Mid-downstream in 2009 (Fig. 4B). But in 2010, there was a large fluctuation for PO_4^{3-} concentrations in the midstream.

DOP was considered to be a smaller part of the TDP, about 26.7%. The DOP concentration ranged from 0.19 to 1.19 μmol/L with an average of 0.61 μmol/L in the mainstream. The DOP concentration decreased significantly in the area 4100 ~ 3200 km from the river mouth, increased to the highest value at Fuling probably due to the effect of the tributaries such as the Yalongjiang, Daduhe and Minjiang (Fig. S1G), and gradually decreased in the Mid-downstream. In the lower reaches of the Changjiang, the average DOP concentration in 2010 was twice that in 2009.

The concentrations of PIP and TPP varied from 0.22 to 9.50 μmol/L and 0.32 to 13.36 μmol/L with averages of 2.05 μmol/L and 2.69 μmol/L in the main channel, respectively. The average PIP and TPP concentrations in the upstream of TGR in 2009 were 5–7 times as high as that of the middle and lower reaches of the Changjiang, and reached the lowest values with 0.43 and 0.66 μmol/L in the TGR, respectively (Figs. S1 I and 4C). In 2010, PIP and TPP concentrations in the Mid-downstream were lower than those in 2009. Besides, in the region of 2400–4200 km from the river mouth, PIP and TPP concentrations in the tributaries were significantly lower ($P < 0.01$) than that in the mainstream.

Like DOP, the POP was also considered to be an important fraction of the TPP. POP averagely accounted for 24.0% of TPP and 12.4% of TP. POP concentrations were between 0.04 and 3.86 μmol/L with an average of 0.65 μmol/L in the mainstream. The average concentrations of POP and PIP in the Mid-downstream in 2010 were smaller compared with 2009 (Fig. S1J and I). The concentrations of TP were between 1.51 and 14.67 μmol/L on average of 4.87 μmol/L in the main channel. Its concentrations in 2009 were quite higher in a region of 2400–4200 km from the river mouth, decreased by a factor of about 3 in the TGR, increased in the midstream due to the inflow of Hanjiang and then decreased gradually in the downstream (Fig. S1H). The average TP concentration in the northern tributaries was almost 2 times higher than that in the southern. The concentration of particulate P (PP) in the Jinshajiang was significantly higher than that of dissolved P (< 1 μmol/L), and PP accounted for more than 85 ~ 95% of TP.

DSi concentration ranged from 70.8 to 127 μmol/L with an average of 105 μmol/L in the mainstream. The average concentration of DSi in the Mid-downstream was almost similar to that in the upstream (Fig. 4D). The average concentration of silicate in the northern tributaries was comparable to that of the southern tributaries, but somewhat higher than that of the mainstream of the Changjiang.

The BSi concentrations were between 0.11 and 29.4 μmol/L with an average of 11.07 μmol/L in the Changjiang. The average concentration of BSi was relative high in a region of 2400–4200 km from the estuary, decreased by a factor of 3 in the TGR, increased to the maximum value of 13.24 μmol/L, and then decreased at the lower reaches of Changjiang in 2009 (Fig. 4E). In 2010, The BSi concentration in the downstream was significantly higher than that of the midstream ($P < 0.01$, Fig. 4E). In addition, the distribution of BSi in 2010 was closely related to that of SPM ($R = 0.685$, $n = 43$, $P < 0.01$). In 2009, the concentrations of BSi in most of the tributaries were lower than that of the mainstream of the Changjiang (Fig. 4E).

3.3. Nutrient fluxes and areal yields

Nutrient fluxes in the main channel and main tributaries were calculated as follows (Ran et al., 2013 & 2015):

$$F_{load} = C \times Q \tag{3}$$

where F_{load} is the monthly flux of nutrients, C is the average

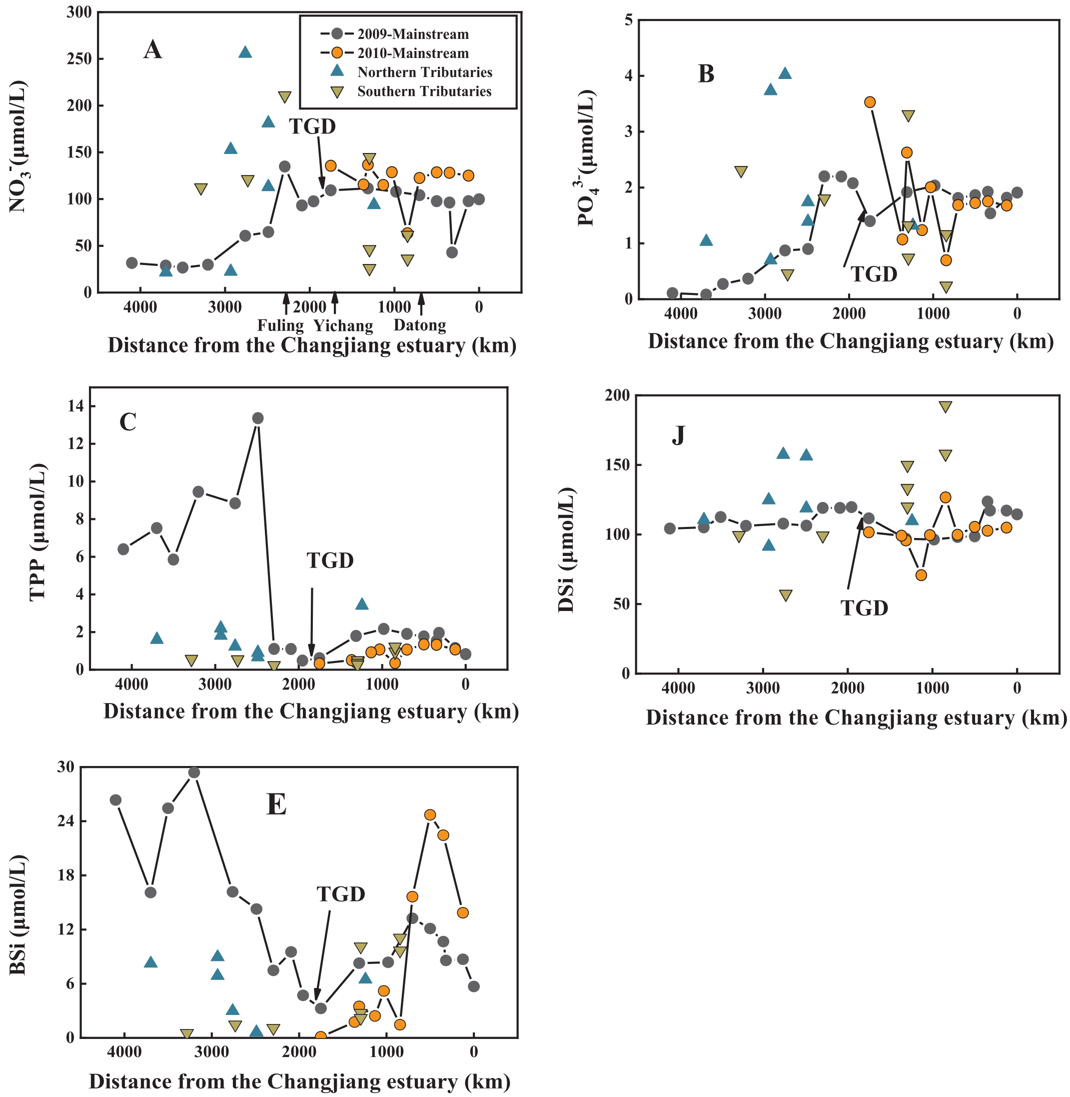

Fig.4. Distribution of the nutrients concentration in Changjiang mainstream and its main tributaries: (A) NO_3^-; (B) PO_4^{3-}; (C) TPP; (D) DSi (E) BSi.

concentration of nutrients, and *Q* is the monthly average freshwater discharge at the hydrological control station (Table 1). The monthly yields of nutrients were estimated based on the average monthly fluxes of nutrients and drainage area (Liu et al., 2009).

The monthly fluxes and area yields of nutrient in the Changjiang mainstream and its main tributaries in 2009 are shown in Tables 3 and 4. Affected by the monthly average water discharge along the Changjiang, the fluxes of NO_3^-, DIN and TDN increased from the upstream to

Table 3
Nutrient fluxes (mol/month) in the Changjiang and its main tributaries in 2009.

Station	NO_2^-	NH_4^+	NO_3^+	DIN	TDN	DON	DSi	PO_4^{3-}	TDP	DOP	PIP	TPP	POP	TP	BSi
	$\times 10^6$	$\times 10^7$	$\times 10^8$	$\times 10^8$	$\times 10^8$	$\times 10^7$	$\times 10^8$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$	$\times 10^7$
Jinshajiang	0.50	0.37	2.47	2.51	2.95	4.39	8.13	0.08	0.72	0.64	4.09	4.99	0.90	5.71	20.5
Jinshajiang	0.49	0.37	3.00	3.04	3.70	6.63	11.0	0.09	0.85	0.77	7.16	7.84	0.68	8.69	16.8
Nanxi	13.3	10.0	13.8	15.0	16.1	11.6	24.5	1.99	3.29	1.30	18.3	20.1	1.86	23.4	36.8
Jiangjin	11.0	8.17	24.6	25.6	28.3	27.6	40.5	3.42	4.97	1.55	36.2	50.9	14.7	55.8	54.3
Yichang	6.83	5.25	53.8	54.3	60.2	58.8	54.9	6.87	11.1	4.24	1.83	3.00	1.17	14.1	16.0
Huangshi	203	156	72.8	90.5	97.7	72.4	65.0	13.7	17.9	4.14	8.99	14.6	5.60	32.5	56.5
Wuhu	8.30	6.37	79.3	80.1	94.0	139	80.1	15.1	19.3	4.19	9.91	14.3	4.42	33.7	98.3
Yangzhou	19.2	14.7	78.2	79.8	87.2	73.1	100	15.6	18.7	3.08	9.13	12.4	3.27	31.1	86.6
Yalongjiang	0.94	0.75	2.03	2.11	2.63	5.20	10.3	1.00	2.34	1.38	0.80	1.50	0.69	3.84	7.70
Minjiang	10.1	7.62	15.9	16.7	18.5	17.5	13.0	3.88	6.03	2.15	1.50	2.29	0.78	8.33	7.15
Jialingjiang	14.6	10.8	12.8	14.0	14.7	6.97	13.4	1.57	2.06	0.49	0.46	1.03	0.57	3.08	0.71
Hanjiang	2.58	1.98	5.05	5.27	5.56	2.89	5.90	0.71	1.09	0.38	1.01	1.83	0.83	2.92	3.48
Wujiang	3.10	2.33	5.18	5.44	5.55	1.01	2.44	0.44	0.48	0.03	0.03	0.06	0.02	0.53	0.27
Yuanjiang	0.39	0.28	0.48	0.51	0.61	1.05	2.45	0.14	0.43	0.29	0.02	0.05	0.03	0.48	0.40
Ganjiang	1.34	1.01	1.47	1.59	1.73	1.43	3.78	0.06	0.35	0.29	0.09	0.23	0.14	0.58	2.66

Table 4
The monthly yields of nutrients ($mmol·m^{-2}·month^{-1}$) in the Changjiang and its main tributaries in 2009.

Station	NO_2^-	NH_4^+	NO_3^+	DIN	TDN	DON	DSi	PO_4^{3-}	TDP	DOP	PIP	TPP	POP	TP	BSi
	$\times10^{-3}$	$\times10^{-2}$				$\times10^{-1}$		$\times10^{-2}$	$\times10^{-2}$	$\times10^{-2}$	$\times10^{-2}$	$\times10^{-2}$	$\times10^{-2}$	$\times10^{-2}$	$\times10^{-2}$
Jinshajiang	2.14	1.61	1.06	1.08	1.27	1.89	3.49	0.36	3.10	2.73	17.6	21.4	3.85	24.5	88.3
Jinshajiang	1.71	1.29	1.05	1.07	1.30	2.33	3.85	0.30	3.00	2.70	25.2	27.5	2.39	30.5	58.9
Nanxi	29.0	21.8	3.01	3.26	3.51	2.52	5.35	4.33	7.17	2.84	39.8	43.9	4.06	51.1	80.3
Jiangjin	15.9	11.8	3.54	3.68	4.08	3.98	5.83	4.92	7.15	2.23	52.1	73.2	21.1	80.4	78.2
Yichang	6.79	5.22	5.35	5.40	5.99	5.85	5.45	6.83	11.1	4.21	1.82	2.98	1.16	14.0	16.0
Huangshi	137	105	4.89	6.08	6.57	4.86	4.37	9.22	12.0	2.79	6.04	9.81	3.76	21.8	37.9
Wuhu	4.86	3.74	4.65	4.69	5.51	8.15	4.70	8.87	11.3	2.46	5.81	8.40	2.59	19.7	57.7
Yangzhou	11.2	8.64	4.58	4.68	5.11	4.28	5.89	9.15	11.0	1.81	5.35	7.27	1.92	18.2	50.8
Yalongjiang	7.29	5.83	1.58	1.64	2.05	4.05	8.06	7.51	18.2	10.7	6.25	11.7	5.41	29.9	60.0
Minjiang	74.5	56.3	11.7	12.4	13.7	12.9	9.57	28.6	44.5	15.9	11.1	16.9	5.78	61.5	52.8
Jialingjiang	93.4	69.1	8.18	8.96	9.41	4.47	8.60	10.1	13.2	3.11	2.92	6.59	3.67	19.8	4.57
Hanjiang	18.2	14.0	3.55	3.71	3.91	2.04	4.15	5.00	7.65	2.65	7.07	12.9	5.83	20.6	24.5
Wujiang	37.3	28.1	6.24	6.56	6.68	1.21	2.93	5.33	5.74	0.41	0.42	0.68	0.26	6.42	3.23
Yuanjiang	4.53	3.26	0.56	0.60	0.72	1.23	2.88	1.60	5.05	3.45	0.24	0.56	0.32	5.61	4.74
Ganjiang	16.6	12.4	1.82	1.96	2.14	1.76	4.68	0.71	4.29	3.58	1.10	2.81	1.71	7.11	32.8

the mouth in the mainstream ($P < 0.01$), except at the Huangshi, where the values of DIN and TDN fluxes were higher due to higher fluxes of NH_4^+ and NO_2^- (Table 3). However, the changes of DON flux in the mainstream were controlled by both concentration and water discharge ($P < 0.01$, Table 3). Additionally, NO_3^-, DIN and TDN yields from upstream to Huangshi had increased significantly by a factor of 4 than that in upstream, and NO_3^- yield remained relatively stable from Huangshi to Yangzhou (Table 4). Although the monthly mean fluxes of NH_4^+ and NO_2^- in tributaries were much lower than those in mainstream, their monthly yields were about 1.4 times higher than that of mainstream (Tables 3 and 4). The DON yields increased by more than 6 times from the upper to the Wuhu, but decreased sharply in the Yangzhou (Table 4). The average DON yields in the tributaries were comparable to that of the main stream.

Affected by the changes of water discharge along the Changjiang, the monthly fluxes of PO_4^{3-} and TDP were much lower in the upstream and increased significantly in the Mid-downstream, but the DOP fluxes were relative low in the upstream, increased rapidly from the Jiangjin to Wuhu, and then decreased suddenly in the Yangzhou (Table 3). DOP inputs to mainstream from the Yalongjiang and Minjiang were estimated to be respectively 1.38×10^7 and 2.15×10^7 mol/month, which had important impact on the fluxes of DOP in the upstream. Besides, the average yields of PO_4^{3-} and TDP increased first and then gradually stabilized from the upstream to downstream (Table 4), and the average yields of PO_4^{3-} and TDP were comparable in the northern and southern tributaries, and were almost twice that of the mainstream (Table 4). However, DOP yields decreased at Jiangjin in the upstream, increased to the highest value at Yichang and significantly decreased in the Mid-downstream (Table 4). All DOP yields in the tributaries were higher than those in the mainstream, except for Hanjiang and Wujiang (Table 4). In contrast, the fluxes of PIP, POP, TPP and TP in the mainstream were more affected by concentration ($P < 0.01$). Their fluxes increased from the upstream to Jiangjin, sharply decreased at the Yichang, and then increased in the lower reaches (Table 3). Meanwhile, the trend of their yields were similar to their fluxes (Table 4). Interestingly, their maximum fluxes and yields were closely related to the particulate matter in the Jiangjin area, where concentration of SPM was the highest (Fig. 3B). Besides, the fluxes of PIP, POP, TPP and TP in all the tributaries were less than those in the mainstream (Table 3).

The DSi flux increased from the upstream to the mouth, but BSi flux increased to 54.3×10^7 mol/month at Jiangjin, sharply decreased to 16.0×10^7 mol/month at the Yichang, and then increased in the Mid-downstream (Table 3). The fluxes of DSi and BSi in all the tributaries were less than those in the mainstream. Besides, silicate yields were rather low in the upstream, and then increased by a factor of 0.6 from the Yichang to Yangzhou (Table 4). The BSi yields in the upstream were significantly higher than that of the Mid-downstream. Interestingly, BSi yields was the lowest at the Yichang after the TGD (Table 4). However, the DSi yields in all tributaries were at least 1.3 times than that of the mainstream, except for Hanjiang and Wujiang (Table 4). The monthly average BSi yield of the tributaries was 45% of that of the mainstream (Table 4).

3.4. Nutrients retention of the TGR in 2009

The monthly average water discharge at Zhutuo, Beibei, Wulong, which are the control sections in the Changjiang mainstream, Jialingjiang, Wujiang, and Yichang accounted for 15.7%, 16.8%, 6.8% and 12.9% of the annual average water discharge, respectively during the survey period in 2009 (Table 1). Because of seasonal changes of the nutrient concentrations and water discharge in the reservoir, the retention of nutrients in the TGR also had obvious seasonality. Therefore, in order to avoid the pseudo retention effect caused by freshwater discharge difference, the annual retention load and efficiency of nutrients in the TGR in 2009 were further estimated. Although there is great uncertainty in this estimate and difficulty in assessing the uncertainty, the estimation lay a good theoretical foundation and data support for evaluating the response of nutrients in the Changjiang to the operation scheme of TGR in the future.

The total inflow load of DIN and TDN were 77.29×10^4 t/a and 83.25×10^4 t/a, respectively, in which about 91% of the DIN and TDN input came from the upstream of the TGR and approximately 6% of this input came from the lateral load from the sub-catchment of the TGR. The total outflow load of DIN and TDN were 59.16×10^4 t/a and 65.56×10^4 t/a, respectively. So, DIN and TDN retained in the TGR would be 23.5% and 21.2% of the total inflow load, respectively (Table 5). However, total DON input load (5.96×10^4 t/a) was significantly lower than the total output load (6.41×10^4 t/a). About 0.45×10^4 t/a of DON was produced in the TGR, which accounted for 7.5% of the total inflow load (Table 5).

PO_4^{3-} was the main TDP retained in the TGR, and accounted for 61.9% of the retained TDP load. The retention of DOP (1.4%) observed was clearly lower than that of PO_4^{3-} (31.2%) (Table 5). The input (10.36×10^3 t/a) and output (10.21×10^3 t/a) loads of DOP were comparable, which showed that the retention of DOP in the reservoir was relatively weak. The differences between input and output load of TDP and TPP were 7.66×10^3 t/a and 3.21×10^3 t/a, respectively. This differences accounted for 22.2% and 30.8% of the TDP and TPP inflow loads, respectively. The retention of TPP was obvious. However, TDP retained in the TGR was dominant, which was about 70.5% of the retained TP (Table 5).

The total inflow load of DSi from the upstream and lateral input of

Table 5
Retention of nutrients in the TGR.

Time (Retention)	Water level (m)	DIN	DON	TDN	PO_4^{3-}	DOP	TDP	TPP	TP	DSi	BSi
1997(%)	~70 (before impoundment)	1.9			60.5					−5.4	
2005(%)	135 (after the first impoundment in 2003)	1.7			33.9						
2007(%)	156 (after the second impoundment in 2006)	8.9			48.1					−7.1	
2009(%)	175 (the third impoundment)	23.5	−7.5	21.2	31.2	1.4	22.2	30.8	24.2	2.8	34.3
2009($\times 10^4$ ton)	175 (the third impoundment)	18.14	−0.45	17.69	0.75	0.02	0.77	0.32	1.09	3.42	1.82

the TGR was 122.84×10^4 t/a (Tables 1 and 2), in which approximately 92% of DSi input came from the upstream of TGR. The total outflow load of DSi was 119.42×10^4 t/a. Thus, 3.42×10^4 t/a of DSi was retained by the TGR, which accounted for 2.8% of the total inflow load (Table 5). The BSi inflow and outflow load were respectively 5.31×10^4 and 3.49×10^4 t/a (Tables 1 and 2). For BSi, approximately 1.82×10^4 t/a was trapped by the TGR, which accounted for 34.3% of the total inflow load (Table 5). Obviously, the retention of BSi was higher than that of DSi, but the retained BSi accounted for 34.7% of retained total silicon (BSi + DSi) in the TGR, and BSi/(BSi + DSi) decreased from 4.1% at the inflow to 2.8% at the outflow. This indicated that DSi was the main contributor to total silicon retained in the TGR.

4. Discussion

4.1. Biogeochemistry of nutrients in the river

Nutrient levels showed a wide range of variation along the Changjiang. Generally, the excess DIN was derived from intense anthropogenic activities, such as municipal sewage discharge, extensive agricultural land leaching and aquaculture water discharge, etc. (Liu et al., 2011). Most previous studies (e.g. Shen et al., 2003; Hao et al., 2006; Yan et al., 2010) indicated that N-fertilizer was the main source of DIN in the Changjiang from the 1970s to 1990s. However, the growth rate of N-fertilizer application dropped significantly after 2000, and domestic sewage, a major DIN source, had dramatically driven up DIN loads in the Changjiang from 2000 to 2010 (Xu et al., 2013). In this study, the mean level of DIN (100.8 μmol/L, Fig. S1A) in the Changjiang was comparable with those reported for polluted waters (110 μmol/L) (Smith et al., 2003) and Pearl River (113.8 μmol/L), less than those in the Yellow River (318.4 μmol/L), but higher than those in the Mississippi-Atchafalaya River (94.5 μmol/L), Congo River (14.8 μmol/L), Amazon River (10.4 μmol/L), Yenisey River (26.0 μmol/L) and Mekong River (12.6 μmol/L) (Table 6). PO_4^{3-} (1.57 μmol/L) concentrations in the Changjiang were higher than those in the Yellow River (0.38 μmol/L) and Pearl River (0.70 μmol/L), but lower than those in the Mississippi-Atchafalaya River (2.50 μmol/L), Nile (2.40 μmol/L) and Congo River (2.20 μmol/L) (Table 6). However, PO_4^{3-} concentrations had a significant negative correlation with the concentrations of SPM ($P < 0.01$). Due to abundant SPM (average of 124 mg/L) in the Chanjiang, PO_4^{3-} was easily adsorbed by the suspended particulates (Liu et al., 2009). Besides, DSi in rivers was mainly released from phytolith dissolution and silicate weathering (Ma et al., 2017). The weathering was constrained by the interaction of tectonic activities, rock type and climate (Liu et al., 2011). During the study period, the mean level of DSi (104.8 μmol/L) in the mainstream was comparable to that of the Yellow River (108.8 μmol/L), Mississippi-Atchafalaya River (108.0 μmol/L), Amazon (117.6 μmol/L) and Congo River (115.8 μmol/L), and much lower than that of the Mekong River (245.5 μmol/L) (Table 6). Therefore, the Changjiang was enriched with DIN and DSi and depleted with respect to PO_4^{3-}, with very high DIN: PO_4^{3-} (43 ~ 356) and DSi:PO_4^{3-} (29 ~ 1281) molar ratios, while the DSi:DIN ratios was in the range of 0.52–3.94 (Fig. 5A, B and C). According to the critical ratios of Redfield et al. (1963) and Justic et al. (1995), Changjiang still is potentially P limited, which is similar to previous studies (Liu et al., 2016).

Froelich (1988) suggested that the adsorption of PO_4^{3-} by particles proceeds via a two-step mechanism, the first involving rapid PO_4^{3-} adsorption/desorption at the particle surface, and the second involving slow solid-state diffusion of the adsorbed PO_4^{3-} from the surface of the particle to the interior. So the K_d (partitioning coefficient, given as $K_d = P/C$, where P (μmol/g) and C (μmol/L) are the particulate and dissolved concentrations, respectively.) approach can be used to quantify the partitioning of P between the particle and dissolved phase, and the evaluation of its particle reactivity (Fang et al., 2000). The $LogK_d$ values for inorganic P in the mainstream of the Changjiang ranged from 0.48 to 2.31 with an average of 1.12, which were obviously less than the value (4.80) in the Pearl River Estuary, 4.59 in the Humber estuary and 4.62 in the Amazon estuary (Li et al., 2017; Prastka et al., 1994). In 2009, the $LogK_d$ values in the mainstream significantly decreased in the upstream 2400–4200 km from the river mouth and then remained around 1 in the downstream (where concentrations of SPM were between 22.29 and 72.73 mg/L) (Fig. 6A). It has been demonstrated that the K_d values exhibited an inverse relationship with SPM (< 20 mg/L) and remained fairly constant when the SPM concentration was higher than 20 mg/L (Li et al., 2017; Fang, 2000). Therefore, the dependence of phosphate particle-dissolved interactions on SPM decreased in the Mid-downstream with high SPM concentrations (> 20 mg/L).

During the survey period, the Changjiang was depleted with DON, DOP and POP (Fig. S1E, G and J). Dissolved organic nutrients were less bioavailable than dissolved inorganic forms (Cotner and Wetzel, 1992), but DOP and PO_4^{3-} may be used by the phytoplankton (Huang et al., 2005). Although microbial N uptake was generally dominated by DIN

Table 6
Comparison of the nutrient concentrations in the Changjiang with other national and world rivers (μmol/L).

River	DIN	PO_4^{3-}	DSi	BSi	Time	Reference
Yenisey River	26.0	0.34	78.0		2003 ~ 2009	Gordeev, 2000; Bessudova et al., 2014
Mekong River	12.6	0.84	245.5		1985 ~ 2011	Li and Bush, 2015
Amazon River	10.4	0.60	117.6	73.90		Araujo and Noriega, 2014
Congo River	14.8	2.20	115.8	9.70		Araujo and Noriega, 2014; Hughes et al., 2011
Nile River		2.40				Nixon, 2003
Mississippi-Atchafalaya	94.5	2.50	108.0		1995 ~ 2005	Dagg et al., 2004; Lohrenz et al., 2008
Pearl River	113.8	0.70			2005–2006	Lu et al., 2009
Yellow River	318.4	0.38	108.8	40.20	2012–2013	Wu et al., 2017
Yangtze River	100.8	1.57	104.8	11.07	2009–2010	In this study
Rhine River				23.40		Conley, 1997

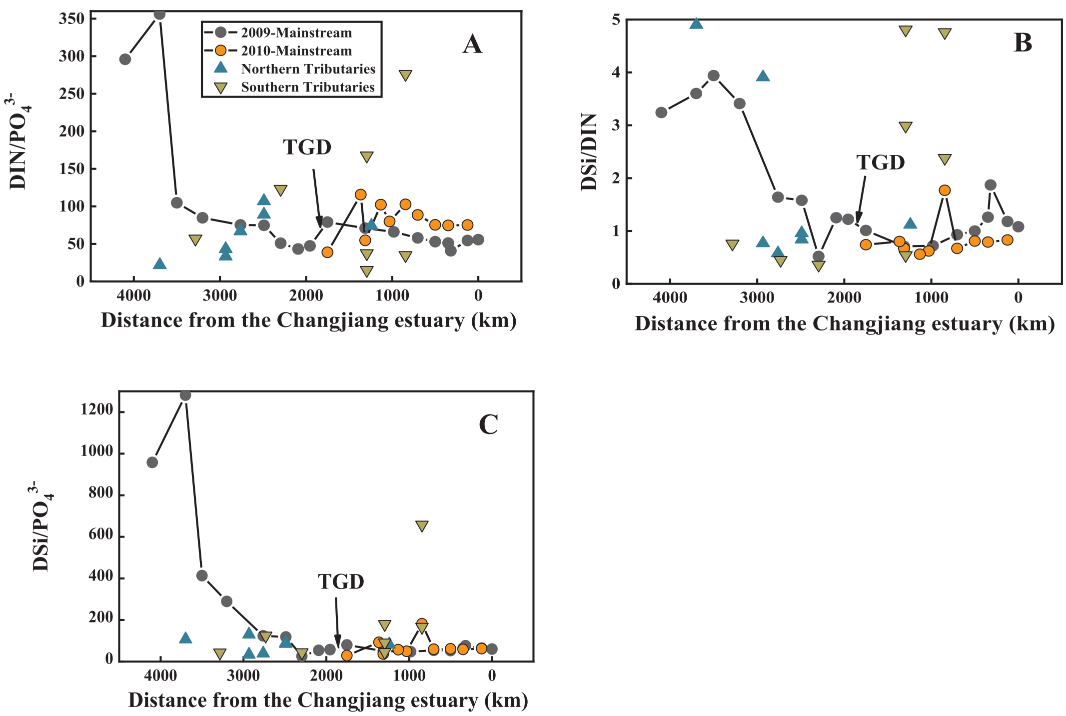

Fig.5. Potential nutrient limitation in the Changjiang mainstream and its main tributaries. (A) DIN/PO_4^{3-}; (B) DSi/DIN; (C) DSi/PO_4^{3-}.

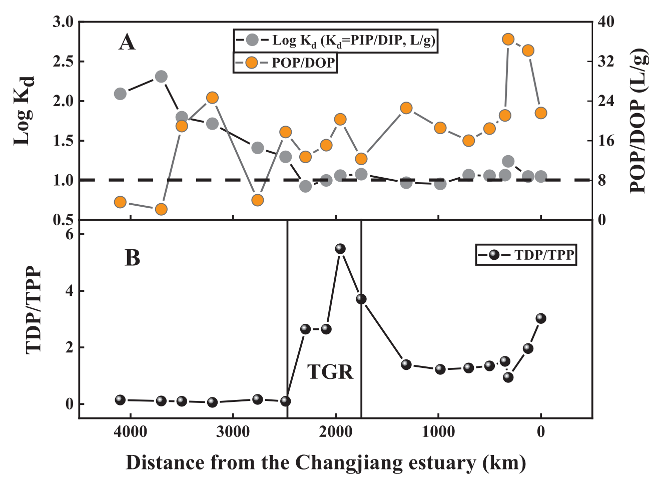

Fig.6. Distribution of LogK_d and POP/DOP (A) and TDP/TPP (B) in the Changjiang mainstream in 2009.

(especially NH_4^+), DON (both urea and dissolved free amino acids) also served as an important N source and could fueled bacterial production and remineralization (Veuger et al., 2004; Pomeroy, 1974). In the present study, DON concentrations in the region before the TGD were higher than that in the upstream of the TGR (Fig. S1E), and might contribute to the composition of the microbial plankton community in the region before the TGD. Besides, in the case of phosphate limitation in the water column, microorganisms may obtain phosphate by utilizing Alkaline Phosphatase Activity (APA) to degrade organic phosphorus (POP or DOP) compounds (Artigas et al., 2012). In 2009, POP/DOP (L/g) in the mainstream increased along the river and reached to the highest value in the estuary (Fig. 6A), which could promote APA synthesis of particle-attached microorganisms (Dyhrman et al., 2006), and APA degraded POP to produce PO_4^{3-} into the water, may have a potential impact on receiving coastal marine ecosystems.

The value of TPP/TP decreased by 66% from the upstream to the TGR and the concentration of TP also decreased by 61%, which indicated that the particulate phosphorus was the major type of component among the phosphorus species in the upstream (TPP/TP, 90%) (Ding et al. 2010; Huang et al., 2014). In addition, the average level of SPM decreased by 93% from the upstream to the TGR (Fig. 3B), which further indicated that PP accompanied with SPM was intercepted and retained in the TGR. Even during the flood season in 2017, the TGR trapped nearly 76% of SPM and 75% of PP (Tang et al. 2018).

The main sources of BSi in aquatic ecosystems were the erosion input of terrestrial ecosystems and the production of phytoplankton (Ma et al., 2017). The average BSi concentrations in the Changjiang were 11.07 µmol/L, lower than that of the Rhine River (23.40 µmol/L), Amazon River (73.90 µmol/L) and Yellow River (40.20 µmol/L), but slightly higher than that of the Congo River (9.70 µmol/L) (Table 6). Obviously, the BSi level in the Changjiang was at a low level in the world's rivers (average, 28.00 µmol/L) (Conley, 1997).

4.2. Nutrients retention in the TGR

The retention efficiency of DIN and TDN in the TGR were 23.5% and 21.2%, respectively (Table 5). In the present study, NO_3^-/TDN at Yichang (89.3%) was compared to that at Fuling (88.6%) (Fig. 4A), but NO_2^-/TDN and NH_4^+/TDN at Yichang respectively decreased by 81% and 80% compared with that of Fuling (Fig. S1C and D), while DON/TDN increased by 52% (Table 2). This implies that the composition of nitrogen in the TGR had changed because of the reservoir effect. Generally, when reactive N enters the reservoir, it would be faced with a variety of potential fates such as nitrification, denitrification, burial, uptake by aquatic plants (eg. diatoms) and adsorption on particulates, etc. (Harrison et al, 2009; Wang et al., 2010). The reduction of NH_4^+ and NO_2^- at Yichang may partly be as a result of algal assimilation to produce DON (Sun et al., 2013). Therefore, based on our mass balance calculation, TGR served as a DON source in the river (Table 5). Besides, denitrification at the surface sediments was considered to be the main mechanism of nitrogen removal in the reservoir, but N removal via denitrification was much lower in the main stream of the Changjiang before the construction of the TGD (Yan et al., 2004). If denitrification in the TGR was estimated based on 7 ~ 16% of total input TDN load (8.32×10^5 t) in the reservoirs at the global scale (Seitzinger et al., 2006), after the full operation of the TGR, 33 ~ 75% of retained TDN (Table 5) would be removed via denitrification. Furthermore, according to the denitrification and the surface area of TGR (1080 km^2, Xu et al., 2011), the denitrification rate (54 ~ 123 $g\,N\,m^{-2}\cdot a^{-1}$) would be similar to the observed 108 $g\,N\,m^{-2}\cdot a^{-1}$ in Lake Shelbyville, Illinois, U.S.A. (David et al., 2006), where the NO_3^- content was comparable to that of the TGR. However, although longer residence time accelerated denitrification, it was difficult to evaluate the strength of denitrification depending on our available data.

The retention efficiency of PO_4^{3-} and TDP in the TGR were 31.2% and 22.2% (Table 5), respectively. Like nitrogen, the composition of phosphorus changed significantly due to the reservoir effect of the TGR. In particular, DOP/TP increased from 17.7% at Fuling to 30.0% at Yichang, while PO_4^{3-}/TP decreased from 54.9% at Fuling to 48.7% at Yichang (Table 2). Meanwhile, diatom was observed to be the dominant algae species in the TGR during the study period (Yang et al., 2012). Therefore, the growth of diatom lowered the PO_4^{3-} concentration and increased the DOP concentration in the TGR. In order to study the uptake of PO_4^{3-} by phytoplankton in reservoirs, we made the following estimates. A primary production model (Canfield et al., 1981) output showed that primary production in the TGR was 350 $g\,C\,m^{-2}\cdot a^{-1}$, with a range of 262.5–437.5 $g\,C\,m^{-2}\cdot a^{-1}$ (Zhang et al., 1999). Here, we proposed a way of estimating fixed PO_4^{3-} flux using the typical C:P ratio of 106:1 for phytoplankton assimilation (Redfield et al., 1963). The model output showed that the potential primary production in the TGR would be 0.21 ~ 0.34 $mol\cdot m^{-2}\cdot a^{-1}$, which corresponded to a total annual PO_4^{3-} fixation of $6.91 \times 10^3 \sim 11.52 \times 10^3$ t/a, taking into account the surface area of 1080 km^2 at the water level of 175 m after the impoundment of TGR. In fact, 7.52×10^3 t/a of PO_4^{3-} (Table 5) was retained in the TGR based on our mass balance calculation. In addition, the retention mechanism of phosphorus in the reservoir was mainly based on the sedimentation of PP (Kennedy et al., 1990). In this study, the retention efficiency of TPP (30.8%) was significantly higher than that of TDP (22.2%), and 3.21×10^3 t/a of TPP was trapped in the TGR, which accounted for 30% of TP load retained in the TGR (Table 5). As discussed in Section 4.1, the retention of PP in the reservoir was closely related to the sedimentation of particulate matters. When the impounded water level increased from 135 m in 2003 to 175 m in 2010, the deposition of particulate matters in the TGR dramatically increased from 12.40 million tons in 2003 to 19.60 million tons in 2010 (Changjiang Water Resource Commission, 2000-2016). Therefore, impoundment to 175 m obviously engendered a considerably large amount of particulate matters as well as PP deposition in the TGR (Tang et al., 2018).

After the full operation of the TGD, lower flow velocity, prolonged residence time, high transparency and high nutrient levels (excess N and P) stimulated the growth of phytoplankton, especially diatoms (Yang et al., 2012). Diatoms (i.e., biological uptake DSi and conversion to BSi) were more likely to be deposited than other planktonic algae, and the lower dissolution rate of BSi (siliceous shell) limited the regeneration of silicon, resulting in the removal of silicon in the reservoir (Humborg et al, 2006). Additionally, silicon fixation in the TGR was estimated from the primary production model (Canfield et al., 1981; Zhang et al., 1999). Total primary productivity had been described above in detail. Here, a way of estimating fixed DSi flux was proposed by using the typical C:Si ratio of 106:16 for phytoplankton assimilation (Redfield et al., 1963). The primary productivity of diatoms can be calculated by using the ratio of diatom primary productivity to total primary productivity, which is usually 1:2 in freshwater ecosystems (Chinese Encyclopedia Compilation Committee, 1987). Therefore, the model output showed that the total annual DSi fixation was $4.99 \times 10^4 \sim 8.32 \times 10^4$ t/a, taking into account the surface area of 1080 km^2 at the water level of 175 m after the impoundment of TGR. In fact, 3.42×10^4 t/a DSi was trapped in the reservoir based on our mass balance calculation, which indicates that the retained DSi may be all assimilated by diatoms. Consequently, based on the typical N:P:Si ratio of 16:1:16 for phytoplankton assimilation (Redfield et al., 1963), 6.84×10^4 t/a DIN and 4.28×10^3 t/a PO_4^{3-} were assimilated by phytoplankton.

According to our mass balance estimates, the retention of nutrients in the TGR varied during the three staged impoundment (Table 5). When the first impoundment to 135 m, the retention of DIN (1.7%, 2005) in the TGR had no obvious changes compared with that (1.9%, 1997) before the impoundment. Subsequently, the intercept of DIN increased from 1.7% in 2005 (135 m) to 8.9% in 2007 (156 m) and 23.5% in 2009 (175 m). However, the retention of PO_4^{3-} had no statistical significance at different water levels. Moreover, the TGR had a relatively small retention of DSi and even acted as a source of DSi (Table 5), and the retention of DSi in the TGR at the pre- and post-impoundment were far lower than the level (18–19%) in reservoirs of the global river basins (Beusen et al., 2009). Normally, nutrient loads were mainly controlled by water discharge. Based on the above assumptions (detail in Section 2.4), the annual average water discharge of the lateral input in 1997, 2005, 2007 and 2009 was 12.1%, 12.6%, 10.7% and 9.4% of total inflow of TGR, respectively. If these estimates subtracted the annual water discharges from 11 tributaries (more than 100 tributaries in the TGR) whose drainage area are more than 1500 km^2 (http://www.cqwater.gov.cn), these differences in 1997, 2005, 2007 and 2009 would account for 6.1%, 7.8%, 5.2% and 3.5% of total inflow of TGR, respectively. These estimates were considered valid in this study. Additionally, monthly averages of nutrients were used as annual averages in the estimates due to limited data availability. Thus, there were some uncertainties in this estimate. The most obvious feature was the operational state of the reservoir. The data of nutrient concentrations in 2005 and 2007 mainly came from April to May when the reservoir was in the discharge stage, but the concentrations in 2009 were mainly obtained in September-October when the reservoir was in the impoundment stage. In these different stages of operation, not only the hydrology had obvious changes (such as water level) (Changjiang Sediment Bulletin), but other parameters such as temperature, Chl *a*, dissolved oxygen, pH and algae distribution also had significant changes (Zeng et al., 2006a). Therefore, these uncertainties must be improved in future work.

4.3. Effect of impoundment on eutrophication in the TGR

The impoundment of the TGR had changed the original hydrodynamic conditions of the river. The most obvious feature was the slow flow velocity in the reservoir. When the TGR impoundment reached the height of 175 m, the average water flow rate decreased to 0.09 ~ 2.43 m/s, which was much lower than that (3 ~ 5 m/s) observed in natural Changjiang channels (Tang et al., 2018; China National Environmental Monitoring Centre, 1998–2017). The reduced flow rate led to longer water retention time. During 2003 ~ 2009, monthly residence time of the TGR mainstream ranged from 5 to 77 d (day), with an average of 27 d, while that for Xiangxi Bay (a tributary of TGR) was 26–538 d, with an average of 179 d (Xu et al., 2011). Obviously, monthly residence time was often shorter in the mainstream than in the tributaries. Accordingly, the reduced water flow would also result in the settlement of SPM and the increase of water transparency in the reservoir and tributaries. However, the sedimentation of SPM in the Changjiang was closely related to deposition of TPP ($R = 0.966$, $n = 46$, $P < 0.01$). So, with the decrease of SPM (Fig. 3B), the ratio of TDP/TPP in reservoir would increase (Fig. 6B), changing the partitioning of P between the dissolved and particle phase. In addition, the level of nutrients in the TGR and tributaries had exceeded the internationally recognized threshold of eutrophication (TN 14.29 μmol/L; TP 0.65 μmol/L; Thomann et al., 1987). Therefore, under suitable temperature and light intensity, algal blooms would occur in the reservoir and its tributaries (Zhang et al., 2012). Historical data showed that since 2003, the impoundment of TGR resulted in the water eutrophication in the TGR and its tributaries (China National

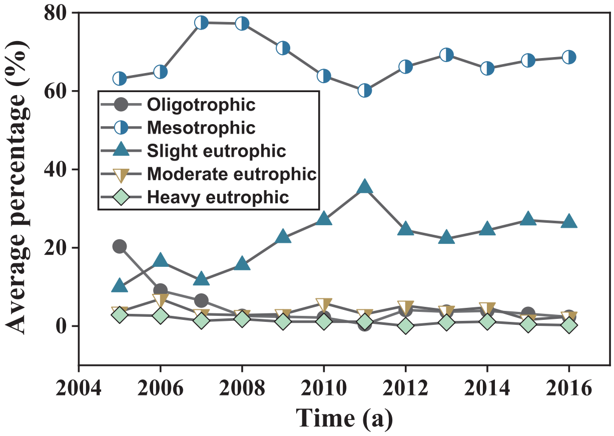

Fig.7. Variation in the trophic status of the water in the TGR when the impounded water level increased from 135 to 175 m.

Environmental Monitoring Centre, 1998–2017). Not only the sensitive period for (the occurrence of) algal bloom extended from March–July in 2004 to March–October after 2007, but the number of tributaries affected by algal blooms also increased from ~3 in 2003 to 11 ~ 22 after 2009 (Tang et al., 2018). More importantly, the trophic status of the TGR was mainly mesotrophic, with the average proportion of 68%, but the proportion of slight eutrophication significantly increased from 10% in 2005 to 27% in 2010, and fluctuated between 22% and 27% after 2010 (except for 2011) (Fig. 7) (China National Environmental Monitoring Centre, 1998–2017). This implies that there was a risk of algal outbreaks in the reservoir and tributaries. In addition, the species composition of phytoplankton in the mainstream of the TGR was basically the same before and after the impoundment, and diatoms, green algae and cyanobacteria were the main species observed from 1999 to 2008 by Qiu et al. (2011).

4.4. The influence of the TGR on nutrient transports in the estuary and its ecological significance

As a typical reservoir of "sediment retaining and no water retaining", the TGR played a major role in the interception of nutrients transported from the upper reaches to the middle and lower reaches of the Changjiang (Xu et al., 2009). After the impoundment of the TGR reached 135 m in 2003, about 18% of TN, 15% of TP and 20% of DSi were trapped in the reservoir (Ran et al., 2009). However, the amount of retained nutrients only accounted for 6%, 4% and 8% of the total N, P and Si of the Changjiang transported to the sea, respectively (Ran et al., 2009). When the TGR launched a 175 m experimental water storage in 2009, approximately 21% of TDN, 24% of TP and 3% of DSi were retained in the TGR (Table 5) and the amount of retained nutrients accounted for 15%, 12% and 1% of the TDN, TP and DSi fluxes in the estuary, respectively. Comparing the historical data of nutrient fluxes in the Datong (Fig. 8B), it was found that the DIN flux decreased by 30% (except in 2005), PO_4^{3-} flux fluctuated between 11.01×10^8 and 15.04×10^8 mol/a, and the DSi exhibited a U-shaped distribution (lower values appeared in 2006), when the impounded water level increased from 135 m in 2003 to 175 m in 2009. The TGR had been fully operational since 2010 with the water level fluctuating between 145 m (from April to September) and 175 m (From October to mid-April). In 2010 ~ 2016, the average DIN and PO_4^{3-} fluxes in the Datong respectively increased by 23% and 50% than that between 2003 and 2009, while the DSi fluctuated around 10.08×10^{10} mol/a since 2010 (Fig. 8B). This suggested that the changes of DSi concentration after 2010 were not so significant, mainly because the water discharged into the estuary was relatively stable (Dai et al., 2011). In addition, the accumulation of nutrients caused by plankton and sediment deposits in

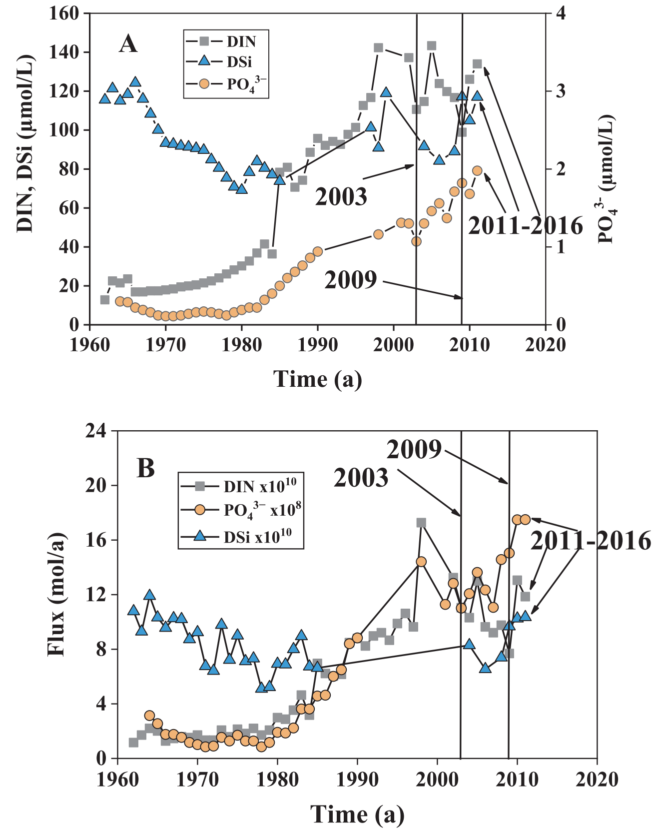

Fig.8. Inter-annual concentration (A) and Flux (B) variations of Nutrients in the Datong station near the Changjiang estuary (Nutrients concentration and load data in 1962–2008, and 2009–2010 are from Dai et al. (2011) and this study, respectively; The average concentration and load of nutrients in 2011–2016 are not published; The DSi concentration and load data in 1997 and 1999 are from Liu et al. (2003) and Xu et al. (2004), respectively.

the reservoir did resulted in a corresponding reduction in the amount of biological elements transported from the Changjiang to the East China Sea. However, the storage capacity of TGR only accounted for 4.5% (Xu et al., 2009) of the annual runoff of the Changjiang, coupled with the interception of the upstream reservoir group and the reduction of sediment entering the TGR, etc. (Huang et al., 2014), such that the impact of TGR on the nutrient flux of the Changjiang into the sea became very limited.

Reduced suspended sediment discharge, elevated nutrient concentrations (e.g., DIN and PO_4^{3-}, Fig. 8A) and changes in the nutrient ratios were found in the estuary and adjacent seas because of the interception in the TGR and human disturbance in the middle and lower reaches of the Changjiang (Gao et al., 2008). The estuary and adjacent seas were likely to become eutrophic because of the changes of nutrient composition, which resulted in the corresponding changes in the phytoplankton composition of the adjacent waters (Jiang et al., 2014). Dai et al. (2011) reported that the decreasing DSi/DIN ratio and the increasing DIN/PO_4^{3-} ratio could cause more frequent red tide in the Changjiang estuary. The concentration of Chl *a* in the estuary and adjacent sea area increased from 1.11 μg/L in 2003 to 3.81 μg/L in 2010 (except for 2009), while dissolved oxygen decreased from 6.80 mg/L in 2003 to 4.29 mg/L in 2010 (Fig. 9). But the historical data showed that the frequency and area of red tides in the ECS decreased significantly since 2003, and maintained a slight fluctuation after 2010 (except for the red tide area in 2016) (Fig. 9). In this study, DIN/PO_4^{3-}, DSi/DIN and DSi/PO_4^{3-} ratios in river water entering the ECS decreased since 2003, and had no obvious correlations with the frequency and area of red tides in the ECS. However, it was found that the DSi ($R = -0.889$, $n = 7$, $P < 0.01$) and PO_4^{3-} ($R = -0.893$, $n = 7$, $P < 0.01$)

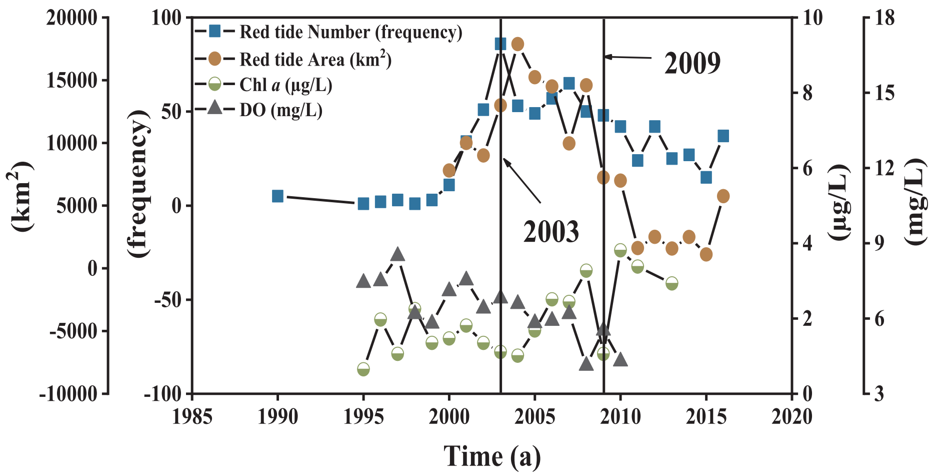

Fig.9. Interannual variation of Chl *a* and DO (dissolved oxygen) in the estuary and adjacent coastal waters and Red tide Number and Area in the East China Sea. (The number and area data of Red tide in the East China Sea in 1990–2002 and 2003–2016 are from Wang et al. (2015) and the East China Sea Environment Monitoring Center of China (http://www.dhjczx.org/), respectively; Chl *a* and DO data in 1995–2010 are from Wang et al. (2015); Chl *a* data in 2011 and 2013 are from Cui et al. (2014) and Li et al. (2016)), respectively.

transported by the Changjiang had significant negative correlations with the area of red tides in the ECS, while DIN did not. This implies that after 2003, PO_4^{3-} and DSi transported by the Changjiang may affected the occurrence of the red tides. In addition, it was also found that after 2003, PO_4^{3-} transported by the Changjiang had positive correlations with Chl *a* ($R = 0.648$, $n = 10$, $P < 0.05$) in the estuary and adjacent sea area, indicating that the enrichment of PO_4^{3-} in the Changjiang may promote the increase of Chl *a* concentrations in the estuary.

So did TGR's storage affect the frequency and area of red tides in the ECS to a certain extent? The assessment was rather difficult at present due to the lack of long- term experimental data such as time series changes of nutrients in the Mid-downstream of the Changjiang. Moreover, the response of shallow lakes in the Mid-downstream on the scheduling model of TGR impoundment was not well understood. Meanwhile, the interception of nutrients in the reservoir should have a seasonal and interannual variations. Therefore, scientifically and comprehensively estimating the relationship between the ecological health of the ECS and the dispatching modes of TGR needed to rely on the accumulation and analysis of longer-term data.

5. Conclusions

This study focused on nutrient dynamics in the Changjiang and retention effect in the TGR. The Changjiang is enriched with SPM, DIN and DSi, depleted with respect to DON, PO_4^{3-}, DOP, POP and BSi. Because of the impoundment, DON and DOP concentrations increased from the inflow to the outflow of the TGR, while other nutrients were on the contrary. The higher POP near the estuary may have a potential impact on receiving coastal marine ecosystems.

Based on input-output mass balance model, the retention of nutrients in the TGR were different. Dissolved nutrient retention was in the order of PO_4^{3-} (31.2%) > DIN (23.5%) > DSi (2.8%). Approximately 3.42×10^4 t/a DSi was assimilated by diatoms, whereas 6.84×10^4 t/a DIN and 4.28×10^3 t/a PO_4^{3-} were assimilated by phytoplankton. The retention of DON and DOP were lower in the TGR, even TGR also served as a source of DON in the river. However, TGR played an important role in the trapping of the incoming TPP (0.32×10^4 t/a TPP) and BSi (1.82×10^4 t/a BSi), which accounted for 30.8% and 34.3% of the total input loads, respectively.

Impoundment of the TGD affected the ecological health of the reservoir and estuary. Since 2003, nutrient status in the TGR was mainly mesotrophic, but slight eutrophication significantly increased during 2005 ~ 2016, which implies that there was still a risk of algal blooms in the reservoir and tributaries. Moreover, the estuary and adjacent seas were likely to become more eutrophic because of the retention of TGR on nutrients in the river and anthropogenic disturbance in the Mid-downstream. Nevertheless, the outbreak frequency and area of the red tide in the ECS significantly decreased after 2003. In order to understand the effect of the operation mode of TGR on red tide in the ECS, a longer time-scale data and effective analytical methods are required to make more scientific and comprehensive assessment.

Declaration of interests

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2019.04.034.

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