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Nutrient budgets for large Chinese estuaries

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Abstract. Chinese rivers deliver about 5–10% of global freshwater input and 15–20% of the global continental sediment to the world ocean. We report the riverine fluxes and concentrations of major nutrients (nitrogen, phosphorus, and silicon) in the rivers of the contiguous landmass of China and Korea in the northeast Asia. The rivers are generally enriched with dissolved inorganic nitrogen (DIN) and depleted in dissolved inorganic phosphate (PO_4^{3-}) with very high DIN: PO_4^{3-} concentration ratios. DIN, phosphorus, and silicon levels and loads in rivers are mainly affected by agriculture activities and urbanization, anthropogenic activities and adsorption on particulates, and rock types, climate and physical denudation intensity, respectively. Nutrient transports by rivers in the summer are 3–4 times higher than those in the winter with the exception of NH_4^+. The flux of NH_4^+ is rather constant throughout the year due to the anthropogenic sources such as the sewer discharge. As nutrient composition has changed in the rivers, ecosystems in estuaries and coastal sea have also changed in recent decades. Among the changes, a shift of limiting nutrients from phosphorus to nitrogen for phytoplankton production with urbanization is noticeable and in some areas silicon becomes the limiting nutrient for diatom productivity. A simple steady-state mass-balance box model was employed to assess nutrient budgets in the estuaries. The major Chinese estuaries export <15% of nitrogen, <6% of phosphorus required for phytoplankton production and ∼4% of silicon required for diatom growth in the Chinese Seas (Bohai, Yellow Sea, East China Sea, South China Sea). This suggests that land-derived nutrients are largely confined to the immediate estuaries, and ecosystem in the coastal sea beyond the estuaries is mainly supported by other nutrient sources such as regeneration, open ocean and atmospheric deposition.

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1 Introduction

The coastal ocean represents an area of only 10% of the global ocean surface, but accounts for ∼25% of global ocean primary production and 80% of global organic carbon burial (Berner, 1982; Smith and Hollibaugh, 1993). Drastic increases in delivery of river-borne nutrients owing to land-use changes and anthropogenic emissions are known to result in eutrophication, modifying aquatic food webs and provoking more severe hypoxic events in coastal marine environments (Humborg et al., 1997; Ragueneau et al., 2002; Pahlow and Riebesell, 2000; Turner and Rabalais, 1994; Turner et al., 2003). Estuaries, seaward continuum of rivers, modify riverine nutrient fluxes to the sea significantly through biogeochemical processes. The estuarine processes in turn affect the sustainability of near-shore ecosystems, and perhaps over long periods of time, the open ocean ecosystems as well (Nixon et al., 1986).

About 5–10% of global freshwater input and 15–20% of the global continental sediment (Table 1) are delivered to the ocean by the Chinese rivers (Zhang, 2002). Their drainage area covers a region between 5 to 55° N latitude, ranging from tropical to cold temperate climate. Under tectonic control, most of the major Chinese rivers originate in the western part of the country, the Himalayan glacial plateaus above 4000 m altitude, and flow eastward zonally, notably the Huanghe (Yellow River) and Changjiang (Yangtze River),

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Table 1. Length, drainage area, long-term average water and sediment loads of large rivers discharging into the Chinese Seas.

River	Length (km)	Drainage area ($\times 10^4$ km^2)	Water discharge ($\times 10^9$ m^3 yr^{-1})	Sediment load ($\times 10^6$ t yr^{-1})
Huanghe	5463[a]	75.2[a]	42.6[d]	1089.3[d]
Luanhe	877[a]	5.4[b]	4.7[e]	22.2[e]
Daliaohe	891[m]	2.66[m]	4.66[m]	17.1[f]
Shuangtaizihe	961[m]	19.24[a]	3.95[m]	20.0[j]
Yalujiang	795[g]	6.3[b]	32.8[b]	1.1[b]
Huaihe	1000	27	26.4[h]	9.87
Daguhe	179	0.56[c]	0.5[c]	0.96[c]
Changjiang	6300	180.9[b]	928.2[h]	500[h]
Han	469.7[i]	2.62[i]	20.9[i]	12.42[i]
Keum	401.4[i]	0.99[i]	5.8[i]	3.95[i]
Yeongsan	115.8[i]	0.28[i]	2.1[i]	1.24[i]
Qiantangjiang	494[l]	4.1[j]	34.2[j]	4.4[j]
Yongjiang	121[l]	0.43[k]	3.45[m]	0.36[k]
Jiaojiang	198	0.65[m]	6.66[m]	1.2[j]
Oujiang	376	1.79[k]	14.6[k]	2.67[k]
Minjiang	2872	6.1[j]	53.6[j]	7.5[j]
Jiulongjiang	258	1.5[b]	11.7[j]	2.5[j]
Zhujiang	2214	59.0[j]	482.1[j]	95.9[j]

Note: [a] Ren et al. (2002); [b] Zhang (1996); [c] Liu et al. (2005a); [d] National Compilation Committee of River and Sediment Communiqué (2000); [e] Feng and Zhang (1998); [f] National Compilation Committee of Hydrology Almanac (1982); [g] Liu and Zhang (2004); [h] Liu et al. (2003a); [i] Hong et al. (2002); [j] Zhang (2002); [k] Ministry of Hydrology Power of People's Republic of China (2004); [l] Gao et al. (1993); [m] Chinese Compilation of Embayment (1998b).

emptying into the Northwest Pacific Ocean (Fig. 1). Therefore, the Chinese rivers are ideal place for investigating latitudinal climate influence on weathering and erosion of the continent across the climate zones. The Changjiang may be regarded as a boundary which separates the hot and wet climate in the south (annual average air temperature: >15°C, annual precipitation: >1000 mm, aridity: <0.75) from the cool and dry climate in the north (annual average air temperature: <15°C, annual precipitation: <1000 mm, aridity: >0.75). The estuaries along the coast of China are heavily inhabited including several megacities (>1.6 million) and human alterations of the coastal environment and ecosystems are easily seen.

The present work attempts to provide holistic view on the material fluxes from rivers to sea via estuaries and their transformations along their paths and the ecosystem effects using previous biogeochemical surveys in major Chinese rivers and estuaries, including the Changjiang, Zhujiang (Pearl River), and Huanghe during the last 20 years. Several rivers emptying into the Yellow Sea from South Korea are also included. This work will provide practical database to solve some environmental problems in coastal ecosystems in the region (Dennison, 2008).

2 Study areas

Studied estuaries for nutrient budgets are shown in Fig. 2. The Yalujiang is the boundary system between China and North Korea, of which 50–60% is in China. The Yalujiang drains a region with well-developed vegetation upstream and extensive cultivation in the lower reaches. The Yalujiang estuary is characterized by semi-diurnal tides, with tidal current of 1.5–2.0 m s^{-1}, and tidal range of 4–6 m at spring tide and 2–4 m at neap tide. The semi-diurnal tides affect a region 40 km inland from the river mouth. The turbidity maximum zone stretches over a distance of ca. 10 km in the upper estuary of Yalujiang, where concentration of total suspended matter reaches 1.0–2.0 g l^{-1} and has significant impact on the pathways of terrigenous materials to the Yellow Sea (Zhang et al., 1997). Moreover, industrial and urban areas in the lower reaches introduce ca. 20–30$\times 10^3$ t d^{-1} of liquid wastes to the Yalujiang (Zhang et al., 1997).

The Daliaohe drains the Quaternary subsidence region of Northeast China to the Bohai in Yingkou, Liaoning Province and it is composed mainly of two tributaries: Hunhe and Taizihe. Its watershed is one of the most important heavily industrialized and densely populated areas of China. The Daliaohe estuary is characterized by semi-diurnal tides, with average tide of 2.7 m and maximum tide of 4.3 m. The tidal influence extends up to 98 km from the river mouth. The

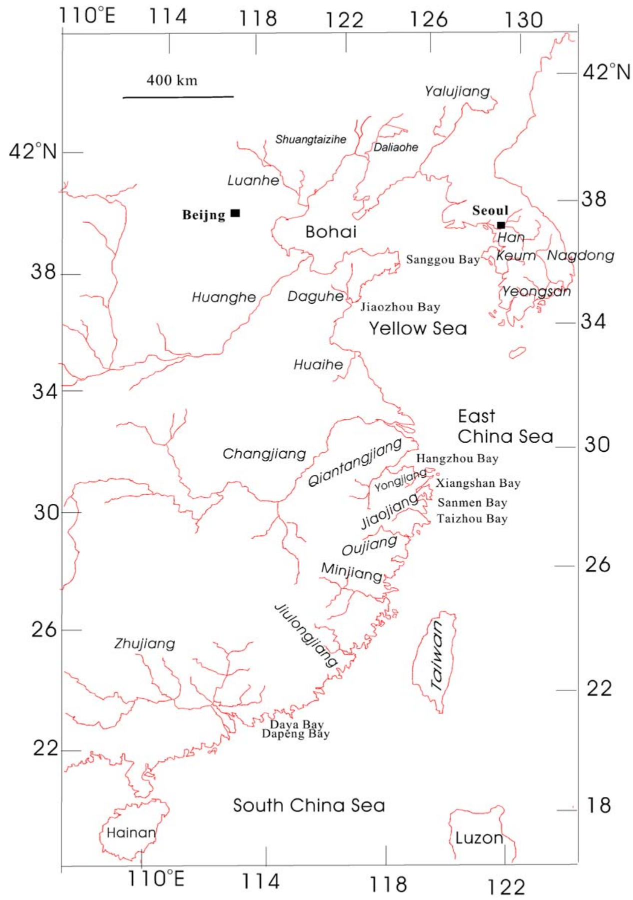

Fig. 1. Map of the east China and South Korea, showing the location of large rivers and adjacent shelf regions from north to south in the Chinese Seas dealt with in this study.

Daliaohe estuary is a typically frigid-temperate zone system: it is dry in the winter and wet in the summer.

The Huanghe originates on the eastern Qinghai-Tibet Plateau at an altitude of 4500 m, and it flows eastward through northwestern China. It drains a wide basin that exhibits a variety of geological and climatic features. The Huanghe is regarded as the second largest river of the world in terms of sediment load over the last several thousand years, with a widely cited annual sediment load, which represents 6% of the estimated global river sediment flux to the ocean. However, in the last 6 years (2000–2005) the Huanghe sediment load decreased, reverting to its pristine levels of the middle Holocene, prior to human intervention (Saito et al., 2001; Wang et al., 2007a). Historically, the Huanghe has shifted between the Yellow Sea and the Bohai. It changed its course from the Yellow Sea to the Bohai in 1855; since then the river has been emptying into the Bohai, except for the period between 1939 and 1947 when it reverted to the Yellow Sea as a result of man-made diversion. The Huanghe now enters directly into the Laizhou Bay located in the southern part of the Bohai. The decline of the Huanghe sediment load, as well as synchronous decreases in water discharge has had profound physical, ecological, and geomorphological effects on the lower reaches of the river and the coastal areas of the Bohai (Liu et al., 2008b; Wang et al., 2007a). The Huanghe estuary is characterized by irregular semidiurnal tides with the tidal current attaining speeds of 1.5–2.0 m s^{-1}.

The Changjiang originates in the Qinghai-Tibet Pleateau at an altitude >5000 m and flows eastwards to the East China Sea. The Changjiang is the largest river in Euro-Asian continent. Its drainage basin is characterized by large industrial and agricultural activities, which provides 24% of the national arable land, 35% of the national crop production, 32% of the national gross output of agriculture and industry. It passes through high densely populated areas with about 35% of the national population living in the Changjiang drainage basin in 1992 (Liu et al., 2003a). The "Three Gorges Project" will have far-reaching effects on environment and human health over the drainage basin and adjacent East China Sea (Zhang et al., 1999).

The Minjiang has its origin in the Wuyishan in southeast China. It is the largest river in Fujian Province, which flows to the East China Sea. It is a mountainous stream system significantly affected by typhoons. About 75% of total annual water flow in this river occurs during the wet season from April to September. The area of cultivated land in the Minjiang drainage is 55×10^4 ha, with irrigated area of 38×10^4 ha and forestland of 350×10^4 ha. About 150–200 hydropower stations have been constructed over the drainage basin (Xiong et al., 1989). The Minjiang estuary is a macro-tidal delta where tidal influence extends up to 59 km from the river mouth. The estuary is mainly affected by freshwater flow and tidal current.

The Jiulongjiang is the second largest river in Fujian Province. The river catchment is politically administrated by six counties and two cities. Of the land uses in the catchment, 12% is arable land, 7% horticultural, 66% forestland, and 1% urban. Physiographically, the Jiulongjiang estuary is a relatively enclosed system. The Jiulongjiang estuary is a typically subtropical system, with temperate climate and average annual rainfall of 1200 mm. The water temperature fluctuates from 13 to 32°C and pH from 7.77 to 8.47 (Cao et al., 2005).

The Zhujiang is the second largest river in China next to the Changjiang and ranks 13th in the world in terms of freshwater discharge. The Zhujiang drains nearly entirely in the subtropical region and it is composed mainly of three tributaries, namely Xijiang, Beijiang and Dongjiang. The Zhujiang water empties itself via eight major channels into the South China Sea. The Zhujiang delta is one of the most densely populated areas in China having several major economic and industrial centers, like Hong Kong, Macao and Guangzhou. The Zhujiang estuary is a semi-enclosed area located along a micro-tidal coast with an average tidal range

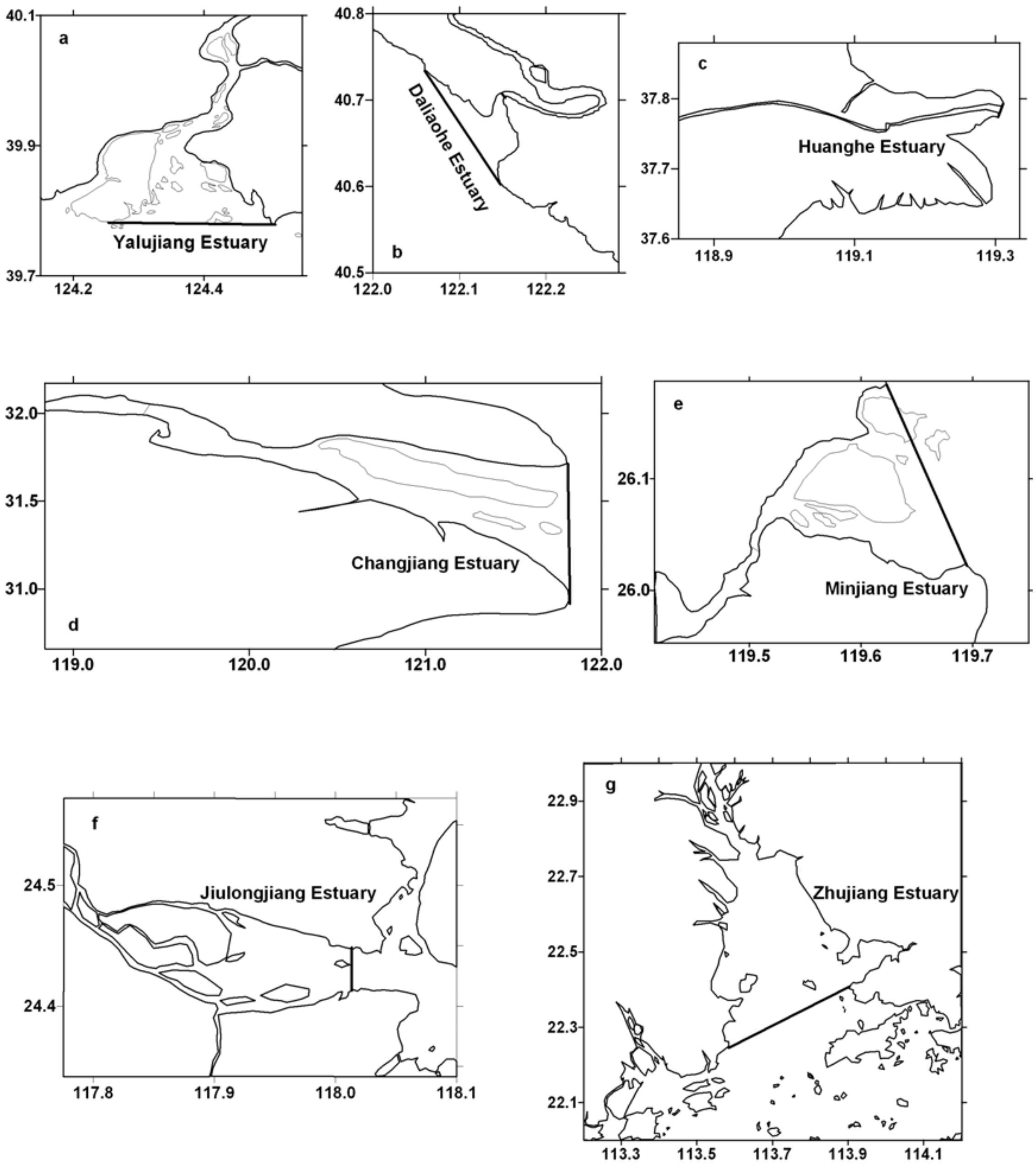

Fig. 2. Studied estuaries with bars showing boundaries of the budgeted systems, including: Yalujiang Estuary **(a)**, Daliaohe Estuary **(b)**, Huanghe Estuary **(c)**, Changjiang Estuary **(d)**, Minjiang Estuary **(e)**, Jiulongjiang Estuary **(f)**, and Zhujiang Estuary **(g)**.

of about 1 m (Su, 2004) on the south coast of China, and connects to the northern part of the South China Sea. The estuary serves as an important waterway to contact the main land with Hong Kong and Macao and from South China to other economic centers in the world and hence is characterized by heavy traffic. About 70–80% of total annual water flow in the river occurs during the wet season from April to September.

3 Materials and methods

Eighteen rivers including Huanghe and Changjiang, four coastal seas of Bohai, Yellow, East China and South China were subjected to our analysis (Fig. 1, Tables 1, 2, and 5). Korean rivers discharged into the Yellow Sea were also included here to complement our basin wide survey. Nutrient budgets were focused on 7 estuaries (Fig. 2).

Rainwater and aerosol samples were collected from Changdao island in the Bohai Strait in 1995 (Zhang et al.,

Table 2. Concentrations (μM) of various nutrient species in the major Chinese and Korean rivers discharging into the Chinese Seas, in which the given values in parentheses are the average.

River	Season	NO_3^-	NH_4^+	NO_2^-	PO_4^{3-}	$Si(OH)_4$	Reference
Daliaohe	May 1992	146–183 (159.2)	12.9–18.6 (17.1)	10.7–13.6 (12.1)	0.90–1.39 (1.19)	70.2–74.1 (71.2)	Jiang et al. (1995)
Daliaohe	Aug 1992	35.7–75.0 (52.1)	1.14–4.14 (3.14)	5.57–16.4 (8.56)	1.68–2.81 (1.71)	29.2–37.8 (34.2)	Jiang et al. (1995)
Shuangtaizihe	Aug 1993	120–240 (181)	0.40–4.0 (3.0)	(0.05)	0.10–0.76 (0.40)	82–123 (105)	Zhang et al. (1997)
Luanhe	Aug 1991	63–81 (74.4)		(0.2)	0.37–0.66 (0.51)	63–84 (87.2)	Zhang (1996)
Huaihe	Dec 2004–Feb 2005	45–104 (76.3)	1.2–21.7 (16.5)	0.5–3.2 (1.71)	0.1–9.9 (4.02)	17–70 (38.1)	Unpublished data
Huanghe[a]	Winter	224–252 (238)	15–48 (36.8)	4.9–10 (7.42)	0.56–0.70 (0.62)	111–121 (115)	Tan (2002)
Huanghe[a]	Summer	166–268 (225)	2.6–9.2 (5.14)	0.8–10 (3.93)	0.1–0.4 (0.33)	90–110 (99.8)	
Yalujiang	Aug 1992, 1994	146–559 (268)	0.6–18.7 (2.38)	0.3–1.2 (0.37)	0.1–1.0 (0.30)	98–187 (127)	Liu and Zhang (2004)
Yalujiang	May 1996	70–89 (76.3)	0.2–6.3 (5.78)	0.1–0.3 (0.17)	0.06–0.11 (0.09)	65–163 (146)	
Daguhe	Mar 2002, 2004	34–251 (142.8)	7.8–25.4 (16.6)	0.6–0.7 (0.65)	<0.1	<20	Liu et al. (2005, 2007b)
Daguhe	Aug 2002, 2004	1.4–312 (156.5)	12–20 (15.7)	<1.2	0.5–0.7 (0.58)	46–156 (101.1)	
Han	June 1992	(57.1)	(75.8)	(2.0)	(3.5)	(36.9)	Hong (unpublished)
Han	June 2000	(97.6)	(217.5)	(12.7)			Kim et al. (2004a)
Keum	1997–1998	(160)	(26.5)	(1.5)	(1.4)	(85)	Yang et al. (1999a)
Yeongsan	1998–2000		(37.1)		(3.9)	(72.2)	Cha and Cho (2002)
Changjiang	Jan 1997–2001	13–130 (62.7)	4.8–30 (16.0)	<1.8	<0.77	22–166 (112.0)	Unpublished data
Changjiang	Jul 1997–2001	21–188 (70.2)	1.0–13.6 (4.64)	<0.3	<0.89	27–200 (100.2)	
Qiantangjiang	Aug 2004	(101)	(0.70)	(1.54)	(1.00)	(128)	Unpublished data
Yongjiang	May 2002	(119)		(11.1)	(3.2)	(183)	Unpublished data
Jiaojiang	Oct 1994	(123)	(0.59)		(2.21)	(162)	Zhang (2002)
Oujiang	Aug 2004	(72.3)	(3.21)	0.44	(0.30)	(150)	Unpublished data
Minjiang	Oct 1986	(65)	(4.13)	(1.65)	(1.45)	(208)	Hu et al. (1996)
Minjiang	Jun 1986	(45)	(3.61)	(0.84)	(0.50)	(156)	
Jiulongjiang[b]	Summer	23.5–47.0 (36.2)	(10.7)		(0.61)	252–270 (261)	Chen et al.(1985, 1997); Wang et al. (2006)
Jiulongjiang[b]	Winter	24.5–49.3 (36.2)	(19.6)		(0.91)	189–377 (279.4)	
Zhujiang	Aug 1999	50–94 (78.6)	0.9–3.4 (2.15)	0.05–7.7 (1.71)	0.3–1.5 (0.85)	102–134 (116.3)	Unpublished data
Zhujiang	Jan 2000	44–63 (58.1)	10–30 (22.0)	1.4–2.5 (2.06)	0.2–0.8 (0.66)	100–108 (106.2)	

[a] For the Huanghe, monthly cruises between March 2001 and February 2002.
[b] For the Jiulongjiang, NO_3^-, $Si(OH)_4$: monthly cruises during November 1982–December 1983; NH_4^+: July 2003 and January 2003; PO_4^{3-}: monthly cruises during March 1995 to February 1996.

2004), Fulongshan in Qingdao during 2004–2005, Qianliyan Island in the northwest of the Yellow Sea during 2000–2005, and Shengsi Archipelago in the East China Sea during 2000–2004 (Bi, 2006; Zhang et al., 2007a). The wet depositional fluxes of nutrients were determined from volume-weighted average concentration and rainfall rate. Dry depositional fluxes of nutrients were estimated from nutrient concentration in the aerosol and the estimated dry deposition velocity (Zhang et al., 2007a).

Water samples were taken with Niskin water samplers in estuaries and adjacent seas and 2 l acid-cleaned polyethylene bottles attached to the end of a fiber-glass reinforced plastic pole in the rivers. Water samples were filtered immediately through acid-cleaned 0.45 μm pore size acetate cellulose filters in a clean plastic tent, and the filtrates were poisoned with saturated $HgCl_2$ solution. All nutrient concentrations were measured using spectrophotometric methods. NO_2^- was measured using diazo-azo method. NO_3^- was measured using the zinc-cadmium reduction method before 1993 and using the cadmium-copper reduction method thereafter. These two NO_3^- reduction methods were comparable (Chen et al., 1998a; Yu et al., 1998). NH_4^+ was measured using the sodium hypobromite oxidation method. PO_4^{3-} was measured using phosphomolybdenum blue method and $Si(OH)_4$ with the silicomolybdic complex method (Liu et al., 2003a; Zhang et al., 2007b; State Oceanic Administration (SOA), 1998). The analytical precision of NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, and $Si(OH)_4$ were 0.006 μM, 0.06 μM, 0.09 μM, 0.03 μM, and 0.15 μM, respectively. Salinity was measured using induction salinometer in the upper reaches of the rivers and Sea-Bird CTD in the estuaries and adjacent seas with accuracy of 0.01.

4 Estuarine nutrient budgets-LOICZ approach

Constructing nutrient budgets facilitate evaluation of the relative importance of external nutrient inputs versus physical transports and internal biogeochemical processes within a water body (Savchuk, 2005), including denitrification (Gordon et al., 1996; Chen and Wang, 1999). We adopt a box model devised by Land Ocean Interactions in the Coastal Zone (LOICZ) (http://nest.su.se, Gordon et al., 1996; Webster et al., 2000; Hung and Kuo, 2002; Hung and Hung, 2003; de Madron et al., 2003; Souza et al., 2003; Simpson and Rippeth, 1998). In this model, estuary is treated as a single box,

Table 3. Nutrient fluxes ($\times 10^6$ mol/day) from rivers to the Chinese Seas.

River	Season	NO_3^-	NH_4^+	NO_2^-	PO_4^{3-}	$Si(OH)_4$
Daliaohe	May 1992	1.80	0.19	0.14	0.013	0.80
Daliaohe	Aug 1992	2.39	0.14	0.39	0.078	1.57
Shuangtaizihe	Aug 1993	1.96	0.032	0.0005	0.004	1.14
Luanhe	Aug 1991	0.96		0.003	0.007	1.12
Huaihe	Dec 2004–Feb 2005	5.52	1.19	0.12	0.29	2.76
Huanghe	Winter	1.23	0.19	0.038	0.003	0.59
Huanghe	Summer	2.54	0.058	0.044	0.004	1.12
Yalujiang	Aug 1992, 1994	29.2	0.26	0.040	0.033	13.8
Yalujiang	May 1996	4.81	0.37	0.011	0.006	9.21
Daguhe	Mar Aug 2002, 2004	0.22	0.001	0.024	0.0005	0.08
Han	Jun 1992, 2000	4.43	8.40	0.42	0.20	2.11
Keum	1997–1998	2.54	0.42	0.024	0.022	1.35
Yeongsan	1998–2000	–	0.21	–	0.022	0.42
Changjiang	Jan 1997–2001	65.9	16.8	0.64	0.51	117.7
Changjiang	Jul 1997–2001	277.4	18.3	0.28	1.34	395.9
Qiantangjiang	Aug 2004	9.46	0.066	0.14	0.094	12.0
Yongjiang	May 2002	1.12		0.11	0.030	1.73
Jiaojiang	Oct 1994	2.24	0.011		0.040	2.96
Oujiang	Aug 2004	2.89	0.13		0.012	6.00
Minjiang	Winter	4.48	0.28	0.11	0.10	14.3
Minjiang	Summer	12.5	1.00	0.23	0.14	43.2
Jiulongjiang	Summer	2.6	0.78		0.04	19.1
Jiulongjiang	Winter	0.5	0.30		0.01	4.2
Zhujiang	Aug 1999	117.1	3.20	2.55	1.27	173.3
Zhujiang	Jan 2000	17.2	6.51	0.61	0.20	31.4

which is well-mixed both vertically and horizontally and assumed to be at a steady-state.

Nutrient budgets are constructed based on the water and salt budgets. Briefly, the water mass balance was estimated using:

$$V_R = V_{\text{in}} - V_{\text{out}} = dV_S/dt - V_Q - V_P - V_G - V_W + V_E$$
$$= dV_S/dt - V_{Q*} \quad (1)$$

Where V_R is denoted as the residual flow, which is equal to the net input of freshwater; V_S is the volume of the system; V_Q, V_P, V_E, V_G, V_W, V_{in}, V_{out} are the mean flow rate of river water, precipitation, evaporation, groundwater, waste water, advective inflow and outflow of water from the system of interest, respectively. All freshwater inputs minus evaporation are combined into a single term (V_{Q*}). And the system water volume remains to be constant. Thus the derivative (dV_S/dt) becomes zero. V_G in Chinese rivers and coastal areas is relatively small and negligible in this calculation. For example, the contributions of DIN, PO_4^{3-} and $Si(OH)_4$ fluxes from groundwater were 2.5×10^{-4}%–2.0×10^{-3}% of the riverine nutrient fluxes in the Huanghe delta (Tan, 2002), and submarine groundwater nutrient discharge to the Jiaozhou Bay accounts for only 0.06% for PO_4^{3-}, 5% for NO_3^- and 2.6% for $Si(OH)_4$ of the riverine nutrient fluxes due to the construction of a low permeability subsurface dam and excessive groundwater withdrawal (Liu et al., 2007a, b). The volume of wastewater (V_W) directly discharged into the estuaries in China is not considered, as no data are available. However, potential consequences of water and nutrient budgets with waste load are considered (see discussion below). Taking salinity as 0 for fresh water (V_Q, V_P and V_E), the salt balance in the system of interest, therefore, can be derived:

$$V_X(S_{\text{syst}} - S_{\text{ocn}}) = S_R V_R + V_S dS_{\text{syst}}/dt \quad (2)$$

Where S_R=(S_{syst}+S_{ocn})/2 and S_{syst} and S_{ocn} are mean salinity in the system of interest and adjacent system; V_X is the water exchange flow or mixing flow between the system of interest and adjacent system. The total water exchange time (τ) of the system of interest can be estimated from the ratio $V_S/(V_R+V_X)$. The time-dependent term, $V_S dS_{\text{syst}}/dt$, is zero under the steady state assumption. However, it may be ignored, if the following condition holds:

$$V_S|dS_{\text{syst}}/dt| \ll |S_R V_R| \quad (3)$$

If Eq. (3) does not hold, then, it may be assessed through the following approximation:

$$|dS_{\text{syst}}/dt| = (|S_{\text{syst}}(t_2) - S_{\text{syst}}(t_1)|)/(t_2 - t_1) \quad (4)$$

Table 4. The areal yields of nutrients ($\times 10^3$ mol km^{-2} yr^{-1}) in the major Chinese and Korean rivers.

River	NO_3^-	NH_4^+	NO_2^-	PO_4^{3-}	$Si(OH)_4$
Daliaohe	18.5	1.78	1.81	0.25	9.23
Shuangtaizihe	3.72	0.06	0.00	0.008	2.16
Luanhe	6.48		0.02	0.044	7.59
Huaihe	7.46	1.61	0.17	0.39	3.73
Huanghe	13.1	1.19	0.32	0.027	6.08
Yalujiang	89.6	2.12	0.14	0.10	71.1
Daguhe	14.3	0.06	1.54	0.031	5.38
Han	61.7	117.0	5.86	2.79	29.4
Keum	93.7	15.5	0.88	0.82	49.8
Yeongsan		27.8		2.93	54.2
Changjiang	34.1	5.30	0.17	0.21	54.4
Qiantangjiang	84.3	0.58	1.28	0.83	106.8
Yongjiang	95.5		8.93	2.57	146.8
Jiaojiang	125.7	0.60		2.26	165.5
Oujiang	59.0	2.62		0.25	122.3
Minjiang	48.3	3.40	1.09	0.86	159.9
Jiulongjiang	28.2	11.8	11.8	0.59	210.8
Zhujiang	55.9	9.87	1.54	0.62	90.9

where (t_2–t_1) represents the time span of the period examined by the model. In this study, the winter and summer conditions are examined. Therefore the time span is 6 months. Thus Eq. (3) can be expressed as the following:

$$V_S(|S_{\text{syst}}(t_2) - S_{\text{syst}}(t_1)|)/(t_2 - t_1)/|S_R V_R| \ll 1 \quad (5)$$

This condition was examined with the data presented in Table 5. The index expressed as the left hand side of Eq. (5) ($V_S(|S_{\text{syst}}(t_2)$–$S_{\text{syst}}(t_1)|)/ (t_2$–$t_1)/|S_R V_R|$) ranges between 0.00002 to 0.08 for estuaries. If 0.1 is taken as the cut-off point, all cases for the estuary in Table 5 qualify for steady state assumption.

Non-conservative fluxes of nutrient elements (ΔY) can be derived based on water budgets and nutrient concentrations:

$$\begin{aligned}\Delta Y &= \Sigma \text{ outflux } - \Sigma \text{ influx}\\ &= V_R C_R + V_X C_X - V_Q C_Q - V_P C_P \end{aligned} \quad (6)$$

where C_Q, C_{syst}, C_{ocn}, C_P, C_R and C_X denote mean element concentration in the river runoff, system of interest, adjacent ocean system, precipitation, residual-flow boundary (C_R=(C_{syst}+C_{ocn})/2) and mixing flow (C_X=C_{syst}–C_{ocn}). A negative and positive sign of ΔY indicates that the system of interest is a sink and a source, respectively.

5 Results

5.1 Nutrients in the rivers

Nutrient levels in the Chinese rivers are shown in Table 2. NH_4^+, NO_3^-, PO_4^{3-}, and $Si(OH)_4$ concentrations vary 30–60, 8, 30–60, and 8 times, respectively. In the Korean rivers, the concentrations of NH_4^+ and PO_4^{3-} are higher than those in the Chinese rivers, while NO_3^- and $Si(OH)_4$ concentrations in rivers of the two countries are comparable (Table 2). All considered riverine nutrient fluxes to the Chinese Seas are 125×10^9 mol yr^{-1} for NO_3^-, 2.08×10^9 mol yr^{-1} for NO_2^-, 20.7×10^9 mol yr^{-1} for NH_4^+, 1.11×10^9 mol yr^{-1} for PO_4^{3-} and 186×10^9 mol yr^{-1} for $Si(OH)_4$ (Table 2). The Changjiang and Zhujiang represent more than 80% of total riverine nutrient fluxes to the Chinese Seas except for PO_4^{3-} in the winter and NO_2^- in both winter and summer. Nutrient fluxes in the summer were higher than those in the winter (Table 3) related to seasonal changes in the magnitude of water discharges. There are remarkable correlations among the nutrient loads (R for log DIN versus log PO_4^{3-} is approximately 0.86; R for log $Si(OH)_4$ versus log PO_4^{3-} is approximately 0.87; and R for log $Si(OH)_4$ versus log DIN is approximately 0.93), and these correlations are very similar to the relationship between DIN and PO_4^{3-} loads observed on the global scale (Smith et al., 2003). Even though DIN, PO_4^{3-} and $Si(OH)_4$ follow substantially different biogeochemical cycles, their loading is tightly coupled. The flux ratio of DIN to PO_4^{3-} is approximately 160:1 and the $Si(OH)_4$:DIN loading ratio is 1.3:1. The DIN: PO_4^{3-} loading ratio derived by us (160:1) is 8∼9 times higher than global DIN: PO_4^{3-} loading ratio (18:1) (Meybeck, 1982; Smith et al., 2003). This indicates that the nutrient loading is affected by decomposition of organic matter, different chemical reaction pathways, and human production (such as sewage, waste, and fertilizer).

The areal yield of nutrients was estimated based on nutrient concentrations, river discharge rate, and drainage area (Table 4). Higher areal yields of dissolved nitrogen and phosphorus in the rivers (e.g. Yongjiang and Jiaojiang) reflect intensive domestic and agriculture activities. Although the Korean rivers are characterized by higher concentrations of NH_4^+ and PO_4^{3-} than the Chinese rivers, the Korean rivers have lower NH_4^+ and PO_4^{3-} fluxes than those in the Changjiang and Zhujiang. But the Korean rivers have higher areal yields of NH_4^+ and PO_4^{3-}. The areal yields of dissolved silicate varied from 2.2 to 2108×10^3 mol km^{-2} yr^{-1} in the large Chinese rivers and the yields are higher in the south than in the north of the Changjiang (Table 4). Consequently, rivers in the south (e.g. Minjiang) often have higher levels of dissolved silicate than those in the north of China (e.g. Daliaohe and Huaihe) due to the fact that chemical weathering is much stronger in the hot and wet south than in the cool and dry north of the Changjiang. Higher temperature and greater amount of rainfall lead to development of vegetation, enhancing chemical/biological weathering relative to physical denudation (Qu et al., 1993). The concentrations of dissolved silicate in the Yalujiang and Huanghe are comparable to those in the Changjiang and Zhujiang, and the yield of dissolved silicate in the Yaljiang watershed is comparable

Table 5. Water and salt budgets for the Chinese estuaries.

Estuary	Season	Area (km^2)	Depth (m)	V_S ($\times 10^6$ m^3)	S_{syst} (psu)	S_{ocn} (psu)	V_Q ($\times 10^6$ m^3)	V_P ($\times 10^6$ m^3)	V_E ($\times 10^6$ m^3)	V_R ($\times 10^6$ m^3)	V_X ($\times 10^6$ m^3)	τ (days)
Yalujiang	Summer	170	6	1020	5.59	24.45	113.9	1.3	0.80	−114.4	91	5.0
	Winter	170	6	1020	7.42	26.78	63.1	0.1	0.20	−63	55.6	8.6
Daliaohe	Summer	39.4	4	157.6	14.30	29.49	45.8	0.18	0.27	−45.7	65.9	1.4
	Winter	39.4	4	157.6	10.46	28.14	11.3	0.011	0.047	−11.3	12.3	6.7
Huanghe	Summer	3.6	2	7.2	27.00	31.20	11.67	0.015	0.038	−11.6	81	0.1
	Winter	3.6	2	7.2	26.86	30.70	5.33	0.0007	0.0066	−5.3	40	0.2
Changjiang	Summer	3094	5	15 470	7.66	26.91	3951	13.4	18	−3946.4	3544	2.1
	Winter	3094	5	15470	13.98	28.81	1051	4.6	5.8	−1049.8	1515	6.0
Minjiang	Summer	114	2	228	23.11	33.60	276.9	0.6	0.7	−276.8	748	0.2
	Winter	114	2	228	25.91	33.60	68.9	0.2	0.3	−68.8	266	0.7
Jiulongjiang	Summer	85	6.47	550	27.40	33.97	73.0	0.6	0.7	−72.9	341	1.3
	Winter	85	6.47	550	28.30	32.23	15.1	0.1	0.1	−15.095	116	4.2
Zhujiang	Summer	1180	7	8260	6.30	30.00	1490	11.4	7.4	−1494	1144	3.1
	Winter	1180	7	8260	20.60	33.30	296	1.4	4.4	−293	622	9.0

to that in the Zhujiang affected by bedrock and weathering rate (see discussion below).

5.2 Nutrients in the Chinese estuaries

Nutrients in the Chinese estuaries behave either conservatively or non-conservatively depending on the chemistry of nutrient elements, estuarine circulation system, and season. It appears that river water stages related to dry and flood seasons and in situ biological uptake and regeneration are important factors affecting nutrients distribution in the estuary (Zhang, 1996). The concentrations of nutrients in Chinese estuaries and their adjacent seas are provided in Table 6 to construct nutrient budgets (see discussion below). While $Si(OH)_4$ and NO_3^- appear to be largely subjected to a simple estuarine dilution (Jiang et al., 1995; Zhang, 1996), NH_4^+ and PO_4^{3-} undergo desorption/adsorption from suspended particles along the salinity gradient and/or degradation of organic matter in the estuary (Chen et al., 1985; Zhang et al., 1997, 2007b). For example, in the Yalujiang Estuary, the regenerated nutrient contributed 70–80% for PO_4^{3-} and 75–85% for NH_4^+ fluxes to the sea (Liu and Zhang, 2004). Non-conservative distributions were observed in the upper estuary, where remobilization of nutrients may take place due to the desorption/release of nutrients from solid phases with increase of ionic strength. Although there are very few biological studies conducted in the upper section of the estuary in either the dry or wet seasons, and hence there is a need for further research in this region of the river, high turbidity inhibits biological production and uptake of nutrients. For example, in July 1999, the phytoplankton productivity in the freshwater-dominated estuary was only <2% of that at the edge of the estuarine coastal plume south of Hong Kong possibly due to light limitation as a result of dilution/mixing and turbidity (Harrison et al., 2008; Yin et al., 2004). In high salinity regions, nutrients may become depleted in the surface waters due to consumption by biological uptake and enrichment by decomposition of organic material in deep waters (Zhang, 1996). Direct discharge of municipal wastewater was noted in some estuaries; for example, in the Yalujiang estuary, NO_3^- supply from waste discharge accounted for 30% in the flood and 5% in the dry season (Liu and Zhang, 2004).

6 Discussion

6.1 Biogeochemistry of nutrients in the river/estuarine systems

6.1.1 River eutrophication

Nutrient levels in the Chinese river/estuarine systems show wide range of variation depending on the system, nutrient and season. The DIN levels in the Chinese rivers are higher than those from the other large and less-disturbed rivers in the world (Meybeck, 1982) such as the Amazon and the Zaire, but comparable to the values of polluted and eutrophic European and North American rivers, e.g., the Loire, Po, Rhine, Seine (Liu et al., 2003a; Zhang, 1996). According to the classification of pollution index based on river DIN concentration devised by Smith et al. (2003), 41% of the rivers emptying into the Chinese Seas are at the levels between the average global conditions (52 μM) to polluted waters (110 μM), and the other 59% are at the levels between polluted to extremely polluted waters (347 μM). The excessive riverine DIN is derived from both extensive agricultural land leaching and municipal sewage discharge over the drainage basins of these rivers. NH_4^+ contribution to the DIN load is relatively high compared to other rivers in the world (Turner et al., 2003). For example, NH_4^+ represented >20% of DIN in the Changjiang and Zhujiang during the winter in China, and accounted for more than 50% of DIN in the Han River in Korea.

Table 6. Box model outputs of nutrient budgets in the Chinese estuaries. C_{sys} and C_{ocn} are nutrient concentrations in the systems and offshore ocean, respectively. $V_P C_P$, $V_Q C_Q$, $V_R C_R$, $V_X C_X$ are atmospheric nutrients deposition, riverine input, the residual nutrients transport out of the system, and mixing exchange fluxes of nutrients, respectively. Δ is nutrients sink and/or source within the system.

		C_{syst} (μM)				C_{ocn}(μM)				$V_R C_R$($\times 10^6$ mol day^{-1})				$V_X C_X$($\times 10^6$ mol day^{-1})			
Estuary	Season	NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$
Yalujiang	Summer	268	2.46	0.53	103	2.96	0.91	0.47	11.9	−15.5	−0.193	−0.057	−6.57	−24.1	−0.14	−0.005	−8.30
Yalujiang	Winter	49.5	3.80	0.164	95.5	4.1	0.973	0.29	8.5	−1.7	−0.150	−0.014	−3.28	−2.53	−0.16	0.007	−4.84
Daliaohe	Summer	47.1	1.00	1.42	22.1	13.6	0.64	0.90	5.34	−1.4	−0.037	−0.053	−0.63	−2.21	−0.02	−0.034	−1.10
Daliaohe	Winter	155.6	7.85	1.52	54.1	77.8	5.57	1.55	9.62	−1.3	−0.076	−0.017	−0.36	−0.96	−0.03	0.000	−0.55
Huanghe	Summer	63.2	2.88	0.20	41.1	9.54	2.29	0.3	24	−0.4	−0.030	−0.003	−0.38	−4.3	−0.05	0.008	−1.38
Huanghe	Winter	69.8	8.0	0.54	30.0	4.19	2.05	0.48	8.15	−0.2	−0.027	−0.003	−0.10	−2.6	−0.24	−0.002	−0.87
Changjiang	Summer	62.8	3.38	0.68	93.0	31.6	0.71	0.57	38.7	−186.3	−8.070	−2.467	−259.8	−110.7	−9.46	−0.390	−192.4
Changjiang	Winter	56.7	7.94	0.79	74.8	26	0.32	0.63	29.6	−43.4	−4.333	−0.747	−54.80	−46.5	−11.5	−0.247	−68.5
Minjiang	Summer	22.3	3.14	0.52	91.5	3.5	0.71	0.17	6.0	−3.6	−0.533	−0.096	−13.50	−14.1	−1.82	−0.262	−64.0
Minjiang	Winter	35	1.96	0.88	99.4	5.6	0.32	0.44	11.0	−1.4	−0.078	−0.045	−3.80	−7.83	−0.44	−0.117	−23.5
Jiulongjiang	Summer	17.3	4.08	0.32	153.3	3.05	0.57	0.2	38.4	−0.7	−0.169	−0.019	−6.99	−4.84	−1.19	−0.041	−39.1
Jiulongjiang	Winter	17.4	2.47	0.74	123.4	12.44	0.39	0.53	57.7	−0.2	−0.022	−0.010	−1.37	−0.58	−0.24	−0.024	−7.64
Zhujiang	Summer	79.2	1.85	0.80	99.1	5.3	1.06	0.19	12.9	−63.1	−2.174	−0.740	−83.69	−84.5	−0.90	−0.698	−98.7
Zhujiang	Winter	34.6	15.1	0.35	56.1	0.38	1.57	0.09	2.13	−5.1	−2.436	−0.064	−8.53	−21.2	−8.39	−0.162	−33.6

Table 6. Continued.

		$V_Q C_Q$($\times 10^6$ mol day^{-1})				$V_P C_P$($\times 10^6$ mol day^{-1})				Δ ($\times 10^6$ mol day^{-1})			
Estuary	Season	NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$	NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$
Yalujiang	Summer	29.2	0.26	0.033	13.8	0.024	0.048	0.000	0.001	10.4	0.03	0.03	1.0
Yalujiang	Winter	3.88	0.083	0.0059	7.42	0.014	0.018	0.000	0.000	0.33	0.21	0.00	0.7
Daliaohe	Summer	2.39	0.14	0.078	1.57	0.009	0.020	0.001	0.001	1.20	−0.099	0.009	0.16
Daliaohe	Winter	1.80	0.19	0.013	0.80	0.002	0.005	0.001	0.001	0.47	−0.091	0.003	0.11
Huanghe	Summer	2.54	0.06	0.004	1.12	0.001	0.001	0.000	0.000	2.2	0.02	−0.01	0.6
Huanghe	Winter	1.23	0.36	0.003	0.59	0.000	0.000	0.000	0.000	1.59	−0.10	0.00	0.4
Changjiang	Summer	277.4	18.3	1.34	395.9	0.188	0.402	0.001	0.024	19.5	−1.20	1.51	56.3
Changjiang	Winter	65.9	16.8	0.51	117.7	0.357	0.641	0.001	0.009	23.6	−1.59	0.48	5.6
Minjiang	Summer	12.5	1.00	0.14	43.2	0.007	0.015	0.000	0.001	5.2	1.34	0.22	34.3
Minjiang	Winter	4.48	0.28	0.10	14.3	0.013	0.024	0.000	0.000	4.7	0.21	0.06	13.0
Jiulongjiang	Summer	2.64	0.78	0.04	19.1	0.005	0.011	0.000	0.001	2.9	0.57	0.02	27.1
Jiulongjiang	Winter	0.55	0.30	0.014	4.22	0.010	0.018	0.000	0.000	0.25	−0.05	0.02	4.8
Zhujiang	Summer	117.1	3.20	1.27	173.3	0.072	0.153	0.000	0.009	30.5	−0.28	0.17	9.1
Zhujiang	Winter	17.2	6.51	0.20	31.4	0.136	0.245	0.000	0.003	9.0	4.07	0.03	10.7

This is due to the application of inorganic N fertilizer (ammonium bicarbonate) in the drainage basins and wastewater discharge (Cao et al., 2005; Sheldrick et al., 2003; Yan et al., 1999; Millennium Ecosystem Assessment, 2005). Phosphate concentrations in 13 rivers are at the pristine level (0.5 μM) and in 5 rivers are at average level (3 μM) compared to the global river data (Smith et al., 2003). The lower concentrations of phosphate in the Chinese rivers are related to adsorption onto particulates (Zhang, 2007, unpublished data), as suspended particulate matters are abundant in the river water. Therefore, N: P ratios varied greatly from 24 to 2000 among Chinese rivers and they also varied seasonally. Very high ratios of N/P might result from very low phosphate values. N/P ratios in Chinese rivers are higher than the other rivers in the world; for example N: P ratio is 24 in Amazon River, 13–38 in Po River, Rhine River and Seine River (Billen and Garnier, 2007).

The Korean rivers draining into the Yellow Sea have received little attention and sufficient data are not available to construct nutrient budgets. As South Korea is a relatively small country (99 585 km^2) with rugged terrain, less than 30% of the land is habitable or cultivable, and with a large population (48.4 million), the land use is extremely demanding. Most agricultural and population centers are concentrated in the lower reaches of the rivers flowing into the Yellow Sea. Regional climate – summer wet monsoon, typhoons in the autumn, dry in the winter-spring, and uneven rainfall – causes heavy soil erosion of the watershed. Therefore, the concentration of dissolved nutrients as well as other materials in the rivers increases with water discharge rate. In the Han River, concentration of NH_4^+, NO_3^-, NO_2^-, and PO_4^{3-} may depart by as much as 30, 98, 101, 196 percent from the mean values (Hong, 1988). It was noted that ammonium fluxes varied little compared to other nutrients as they were largely from human settlements. Recently Millennium Ecosystem Assessment argued that nitrogen fluxes in the rivers to the sea over the past four decades have increased 17 times in South Korea, mostly due to the application of fertilizers, which is the largest change in the world (Millennium Ecosystem Assessment, 2005, Table 4-1). Baskin et al. (2002) had also asserted that a doubling of N content in the Yellow Sea occurred every 3 years during 1994–1997 due to the human derived N inputs. These two assessments need to be appraised independently for clear understanding of nutrient dynamics in the Yellow Sea in future.

6.1.2 Dissolved silicate

Dissolved silicate is mainly delivered via weathering, which is constrained by the interaction of tectonic activities, rock type and climate. Dissolved silicate levels in the rivers and areal yields in their watersheds in general are higher in the warm and wet south than in the cold and dry north of the Changjiang. The solute discharge flux is widely used in the literature as an indicator of chemical weathering rate (White and Blum, 1995; Gaillardet et al., 1999). For the studied river systems, the dissolved loads of rivers indicated a carbonate weathering origin except in the Yalujiang, Yongjiang, Oujiang, Minjiang, Jiulongjiang, Dongjiang (a tributary of the Zhujiang), and Ganjiang (a tributary of the Changjiang) where the dissolved loads indicated a silicate weathering origin (Li, 2003) with high concentrations of dissolved silicate. The total weathering rate is obviously higher than that of major world watersheds and in general with higher erosion rates in the southern China than in the northern China. The chemical weathering rate is always far less than the mechanical denudation rate in the same watershed. The highest physical denudation rate is observed in the Huanghe (Li and Zhang, 2003). Although chemical weathering rates were mainly determined by the rock type and regional climate, the topography (relative elevation) driven mechanical denudation has been greatly accelerated by human activities, e.g., road construction (Li, 2003). For example, $Si(OH)_4$ in the Yalujiang largely originated from Si-bearing granite basin (Li and Zhang, 2003), and $Si(OH)_4$ in the Huanghe largely originated from mechanical denudation and a much higher evaporation over precipitation rate in a large part of its river basin (Cai et al., 2008; Li and Zhang, 2003) which enhances $Si(OH)_4$ concentrations. As a result, the concentrations and areal yield of $Si(OH)_4$ in the Yalujiang are comparable to those in the Changjiang and Zhujiang. The $Si(OH)_4$ level in the Huanghe is similar to those in the Changjiang and Zhujiang.

6.1.3 Natural nutrient load estimation in the Chinese rivers

Information on nutrient composition and concentrations in pristine state rivers are needed to evaluate quantitatively the anthropogenic influence on them with time. We estimated naturally generated nutrient concentration in each river assuming that biological N_2 fixation for DIN and chemical weathering for PO_4^{3-} and silicate are the dominant mechanisms. Additionally we assumed that the nutrient levels observed in the upper reaches of the rivers are reflecting the natural (pristine) background levels for their respective rivers. The nutrient concentrations (3.59 μM for DIN, 0.16 μM for PO_4^{3-}, 116.5 μM for $Si(OH)_4$) 3300–3600 km upstream from the Changjiang river mouth were regarded here as the natural levels, which are 4.6% for DIN, 21.9% for PO_4^{3-}, and 112% for $Si(OH)_4$ of those within 500 km of the river mouth (Liu et al., 2003a). Historical data in the Changjiang river mouth were estimated to be 10–20 μM for DIN and $\sim$120 μM for $Si(OH)_4$) in the early of 1960s, and 0.1–0.2 μM for PO_4^{3-} before 1980s (Li et al., 2007). These values are similar to PO_4^{3-} and $Si(OH)_4$ levels but higher for DIN levels than in the upper reaches of the Changjiang indicating that our assumption of pristine data are acceptable. In the upper reaches of the Yalujiang, 32.7 μM for DIN, 0.13 μM for PO_4^{3-}, and 102.2 μM for $Si(OH)_4$ were observed (Liu and Zhang, 2004). The averages of these two rivers are 18.1 μM for DIN, 0.15 μM for PO_4^{3-}, and 109.4 μM for $Si(OH)_4$). The natural loads estimated from the natural nutrient concentrations and the total annual water discharge for all considered rivers (1650.2×10^9 m^3 yr^{-1}) are 29.9×10^9 mol yr^{-1} for DIN, 0.25×10^9 mol yr^{-1} for PO_4^{3-}, and 180.5×10^9 mol yr^{-1} for $Si(OH)_4$. While these extrapolations are inevitably rough, they give some indication that anthropogenic activities have increased DIN and PO_4^{3-} loading above natural fluxes by more than a factor of 3–4. $Si(OH)_4$ loads originated from rock weathering, however, are similar to present average values with little additional $Si(OH)_4$ entering downstream, and $Si(OH)_4$ losses from large dam construction are not obvious on national scale. For individual rivers, $Si(OH)_4$ losses from large dam construction can not be compensated for as river water flows to the sea (such as the Changjiang) (Li et al., 2007).

6.1.4 Changing nutrient composition and fluxes in the Chinese rivers for recent decades

On global average, approximately 65% of DIN and PO_4^{3-} in the coastal zone are derived from anthropogenic sources, mainly from diffused agricultural sources and point-sources (sewage), respectively (Seitzinger et al., 2005). DIN or PO_4^{3-} yields in the Chinese and Korean rivers are affected by natural and anthropogenic sources of nutrients within the catchments, such as runoff, fertilizer, sewage, and atmospheric nitrogen deposition from fossil fuels. However, it is not easy to analyze the long-term changes of nutrient concentrations and loads in these rivers, as monitoring data for the Chinese rivers are not open to the public except the fact that some data were published for the Changjiang. It is thus difficult to evaluate how natural and anthropogenic activities have influenced the nutrient delivery on the national scale.

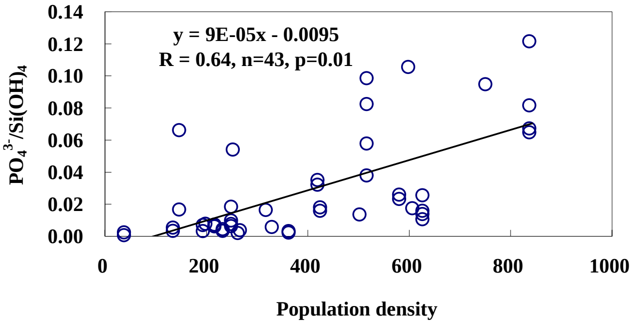

Fig. 3. Molar ratios of PO_4^{3-} to $Si(OH)_4$ versus population density (people/km^2) in the large Chinese and Korean rivers and embayments. Data sources for the rivers are shown in Table 2. Data sources for embayments are from investigations in 2006–2007 for Sanggou Bay (Unpublished data), 1997–1998 and 2001–2003 for Jiaozhou Bay (Liu et al., 2005a, 2007b), 1981–1982 and 1989–1990 for Hangzhou Bay (Gao et al., 1993), 2000 and 2002–2005 for Xiangshan Bay (Zhang et al., 2006; Zhang et al., 2003), 2005 for Sanmen Bay (Wang et al., 2007b), 1981–1982 and 1990 for Taizhou Bay (Chinese Compilation Committee of Embayments, 1993), 1997–2002 for Daya Bay (Qiu et al., 2005), and 1993–2003 for the summer and 1991–1992 for the winter for Dapeng Bay (Li et al., 2004; Chinese Compilation Committee of Embayments, 1998a).

The most frequently sampled Changjiang is given as an example. The DIN concentrations and load in the Changjiang increased about 6–10 times in the last thirty years. The increase was attributed to the intensification of agriculture and the use of mineral fertilizers. The amount of N fertilizer applied to the Changjiang drainage basin increased 15 times during that period (Li et al., 2007; Müller et al., 2008). The PO_4^{3-} levels showed negligible increases (Duan et al., 2007; Liu et al., 2003a; Müller et al., 2008), even though P fertilizer use in the Changjiang drainage basin has also increased substantially (Liu et al., 2003a). This is perhaps because phosphate was more likely to be adsorbed onto particles (Zhang, 2007). Phosphate concentrations are generally higher in the rivers flowing through urban areas due to domestic wastewater discharge. For example, the concentrations of PO_4^{3-} in wastewater from sewage treatment plants in Qingdao are more than 80 μM (Liu et al., 2005). Molar ratios of PO_4^{3-} to $Si(OH)_4$ can be used to infer the nutrient contributions from urban areas relative to rock weathering in the drainage basin. When nutrient data from the major Chinese and Korean rivers and embayments are put together, molar ratios of PO_4^{3-} to $Si(OH)_4$ increase linearly (R=0.64, n=43) with increase in population density at p=0.01 (Fig. 3). The scatter in Fig. 3 comes from uneven distribution of population, very low concentration of phosphate and low ratios of $PO_4^{3-}/Si(OH)_4$, and the different chemical reaction pathways for PO_4^{3-} and $Si(OH)_4$. DIN concentrations in the rivers are mainly correlated with fertilizer application (Liu et al., 2003a; Zhang, 1996). These compositional relationships among nutrient compounds in the river water indicate that ecosystem dynamics including primary production and phytoplankton species composition in coastal waters also have been altered as coastal zones become urbanized. The limiting nutrient may be changed from phosphorus to nitrogen with urbanization and in some areas silicon becomes limiting nutrient, such as Jiaozhou Bay (Liu et al., 2008a). More studies are needed to further investigate this phenomenon.

6.2 Water and nutrient budgets in estuaries

6.2.1 Estuarine nutrient budgets

Water and salt budgets for large Chinese estuaries are shown in Table 5. As freshwater discharge surpasses both precipitation and evaporation, the residual flow is off the estuaries and is similar to the river water discharge. Both the residual flow and water exchange flow or mixing flow in the summer are higher than those in the winter. The total water exchange time of the estuaries is less than 10 days, and it is 2–5 times longer in the winter than in the summer. Wastewater discharge to the estuaries is not included in the water budgets. The Zhujiang delta region has become one of the most densely populated and economically developed regions in China. The industrial wastewater and domestic sewage discharged from the Zhujiang delta, Hong Kong and Macau to the Zhujiang Estuary amounts to 3.02×10^6 m^3 day^{-1} and 3.35×10^6 m^3 day^{-1}, respectively, of which, more than 50% of domestic sewage is not treated and discharged into coastal water directly (Huang et al., 2003). These wastewater discharge accounts for less than 0.5% and 2% of the Zhujiang freshwater discharge in summer and winter, respectively. The proportion of wastewater to river freshwater discharge is less than 5% in the Huanghe (Tan, 2002), ∼1% in the Daliaohe and less than 1% in the Yalujiang (Zhang et al., 1997). The uncertainties can be up to 5% as we don not include wastewater in the water budgets.

The nutrient budgets for large Chinese estuaries are provided in Table 6. Atmospheric deposition of nutrients is very limited relative to riverine input owing to limited surface area. Both the residual and mixing flows transport nutrients off the estuaries. Table 6 reveals net source of NO_3^-, PO_4^{3-} and $Si(OH)_4$ in large Chinese estuaries except for PO_4^{3-} in the Huanghe in the summer. The model shows that the estuaries behave as a source of NH_4^+ except in the Changjiang and Daliaohe in both the winter and summer, in the Zhujiang in the summer, in the Huanghe and Jiulongjiang in the winter. Such budgets are a simple class of mathematical models that tend to provide robust estimates of integrated ecosystem performance. They provide neither direct experimental nor direct theoretical information about how the system works; the budgets can describe the system at space and time scales which may not be amenable to experimentation or detailed simulation modeling (Gordon et al., 1996).

Wastewater discharge was not considered for nutrient budgets as no data are available. However, the nutrient concentration in wastewater can play a considerable role in the nutrient budgets especially when considering estuaries in such a heavily populated area as the Chinese coast except for dissolved silicate. Potential consequences on nutrient budgets are estimated in case wastewater data are available. For the Zhujiang estuary, the water quality has been extensively examined, indicating that the estuary exhibits some symptoms of eutrophication and low dissolved oxygen due to anthropogenic activities, such as increased agricultural activities and sewage effluents (Dai et al., 2006; Huang et al., 2003; Yin et al., 2004). Model output indicated that in the Zhujiang estuary, the proportion of waste load to riverine flux was 0.1% in July 1999 and 1.0% in January 1999 for nitrate plus nitrite, 28.2% in July 1999 and 178% in January 1999 for ammonium, and 9.9% in July 1999 and 63.9% in January 1999 for phosphate (Hu and Li, 2009). Non-conservative fluxes should be 30.4×10^6 mol day^{-1} in the summer and 8.8×10^6 mol day^{-1} in the winter for nitrate, -1.18×10^6 mol day^{-1} in the summer and -7.5×10^6 mol day^{-1} in the winter for ammonium, and 0.044×10^6 mol day^{-1} in the summer and -0.098×10^6 mol day^{-1} in the winter for phosphate. This indicates that nitrate budget is similar when waste load is considered, while both ammonium and phosphate budgets are affected switching from a source to a sink when waste load is considered.

For the Jiulongjiang estuary, model output indicated that the DIN load from domestic sewage and industrial wastewater was less than 1% of riverine input (Cao et al., 2005). Therefore, the budget results may not be affected when wastewater data are considered for the Jiulongjiang estuary. For the Yalujiang estuary, the proportion of waste load from urbanized region to seaward fluxes from the Yalujiang to the Yellow Sea was 32% in the flood season in 1994 and 4% in the dry season in 1996 for nitrate, 25% in the flood season in 1994 and 8% in the dry season in 1996 for ammonium, and 4% in the flood season in 1994 and 2% in the dry season in 1996 for phosphate (Liu and Zhang, 2004). Non-conservative fluxes should be -3.98×10^6 mol day^{-1} in the flood season and 0.17×10^6 mol day^{-1} in the dry season for nitrate, -0.061×10^6 mol day^{-1} in the flood season and 0.20×10^6 mol day^{-1} in the dry season for ammonium, and 0.028×10^6 mol day^{-1} in the flood season and 0.001×10^6 mol day^{-1} in the dry season for phosphate. This indicates that both nitrate and ammonium budgets in the flood season are affected switching from a source to a sink when waste load is considered, while phosphate budget is not affected when waste load is considered for the Yalujiang estuary. These results are different from those in the Zhujiang estuary; that is, both nitrate and ammonium budgets in the flood season in the Yalujiang estuary are affected when waste load is considered rather than in the dry season. In the Yalujiang, it seems that water flow in the dry season is supplied in a certain amount by ground water and tributaries in the upstream forest, which have a rather stable flow rate and chemical compositions. However, heavy rainfalls in the summer season could induce an intensive leaching of cultivated areas, the temporal transport of nutrients in the flood season could be nearly one order of magnitude higher than in the dry season in the Yalujiang (Zhang et al., 1998). For the other estuaries, both nitrogen and phosphorus budgets may be affected when waste load is considered to some extent depending on the system, element, and waste load. More studies are needed to investigate this phenomenon in detail.

6.2.2 Nutrient fluxes from estuaries to the Chinese Seas

Eutrophication has been a growing problem in many coastal and estuarine ecosystems around the world (Justić et al., 2003; Rabalais et al., 2002). The transformation of nutrients within estuaries affects the movement of nutrients from land to the ocean and eventually the sustainability of nearshore ecosystems (Nixon, 1995). Nutrient fluxes from estuaries to the Chinese Seas are estimated as sum of net residual flux ($C_R V_R$) and mixing flux ($C_X V_X$): $F_{\text{model}}=C_R V_R+C_X V_X$. Nutrient fluxes were higher in the summer than in the winter except for NH_4^+ in the Zhujiang (Table 7) due to wastewater discharge (Hu and Li, 2009). Total nutrient fluxes from major Chinese estuaries to the coastal region in the summer are 516×10^6 mol day^{-1} for NO_3^-, 24.8×10^6 mol day^{-1} for NH_4^+, 4.86×10^6 mol day^{-1} for PO_4^{3-} and 777×10^6 mol day^{-1} for $Si(OH)_4$, which are 3–4 times greater than those in the winter except for NH_4^+. These fluxes are 1.0–1.7 times of the riverine input ($F_{\text{river}}=CV_Q$), indicating that estuarine processes the most amplify the riverine flux by a factor of 1.7, and these estuarine processes may include scavenging, regeneration, and waste discharge. The nutrient load from major Chinese estuaries to the coastal seas represent 9% for DIN and 1.5% for PO_4^{3-} of the global load (DIN: 1350×10^9 mol yr^{-1}; PO_4^{3-}: 74×10^9 mol yr^{-1}) (Smith et al., 2003) with more nitrogen than phosphorus related to adsorption of phosphorus due to high total suspended matter load.

6.3 The effect of increased riverine N and P fluxes on the ecosystems of the Chinese Seas

6.3.1 The contribution of N and P fluxes to the Chinese Seas

The coastal ocean is a highly dynamic and spatially heterogeneous compartment of the Earth system. Primary production in the Chinese Seas varies with season and region (Table 8). Given the surface area of 7.7×10^4 km^2, 38×10^4 km^2, 53×10^4 km^2 and 200×10^4 km^2 for the Bohai, Yellow Sea, and continental shelf region (<200 m) of the East China Sea and South China Sea, respectively, the total primary production would be 3.0, 12.6, 27.3 and

Table 7. Total nutrient fluxes (residual flux and mixing exchange flux) derived from steady state 1 box model. Please see the detailed model description in the text. Positive values indicate efflux from the studied system and negative sign indicates influx to the system.

Estuary	Season	Nutrient fluxes ($\times 10^6$ mol day^{-1}) NO_3^-	NH_4^+	PO_4^{3-}	$Si(OH)_4$
Yalujiang	Summer	39.6	0.33	0.063	14.9
Yalujiang	Winter	4.2	0.31	0.0073	8.1
Daliaohe	Summer	3.6	0.06	0.087	1.7
Daliaohe	Winter	2.3	0.10	0.017	0.9
Huanghe	Summer	4.8	0.078	−0.005	1.8
Huanghe	Winter	2.82	0.26	0.005	0.97
Changjiang	Summer	297	17.5	2.86	452
Changjiang	Winter	89.9	15.9	0.99	123
Minjiang	Summer	17.6	2.4	0.36	77.5
Minjiang	Winter	9.23	0.52	0.16	27.3
Jiulongjiang	Summer	5.58	1.4	0.060	46.1
Jiulongjiang	Winter	0.81	0.26	0.034	9.0
Zhujiang	Summer	148	3.1	1.44	182
Zhujiang	Winter	26.4	10.8	0.23	42.1

166.0×10^4 tonnes C day^{-1} in the Bohai, Yellow Sea, East China Sea shelf and South China Sea shelf in the summer, respectively; and 1.2, 2.9, 15.7, 164.0×10^4 tonnes C day^{-1} in the Bohai, Yellow Sea, East China Sea shelf and South China Sea shelf in the winter, respectively. Taking into account applying the Redfield stoichiometric ratio for phytoplankton nutrients (C:N:P=106:16:1), primary producers would assimilate 3.77–208.6×10^8 mol day^{-1} of nitrogen, and 0.24–13.0×10^8 mol day^{-1} of phosphorus in the summer, and 1.51–206.1×10^8 mol day^{-1} of nitrogen, and 0.09–12.9×10^8 mol day^{-1} of phosphorus in the winter. The estuarine contribution to the Chinese Seas can account for 4.1–15.1% of N and 1.6–5.7% of P in the Bohai, 6.7–12.3% of N and 0.6–2.1% of P in the Yellow Sea, 5.1–13.4% of N and 0.6–1.1% of P in the East China Sea shelf, and 0.1–1.0% of N and 0.02–0.17% of P in the South China Sea shelf required for phytoplankton growth. These results suggest that other nutrient sources, such as regenerated nutrients in water column and sediments and open ocean, play an important role for phytoplankton growth. Atmospheric deposition may be another important source of nutrients for the Chinese Seas. For example in the Yellow Sea, surrounded by the continuous land mass of China and Korea, atmospheric deposition represents 51% of the nitrogen load (Liu et al., 2003b).

6.3.2 Changing nutrient composition in the Chinese Seas

It is well known that N and P enrichment may lead to deficiency of dissolved silicate, hence, limit diatom growth, and result in food web changes in aquatic system (Conley et al., 1993). As discussed above, the riverine nutrient fluxes with more nitrogen than phosphorus may lead to potential phosphorus limitation for phytoplankton production in the Chinese Seas. It has been reported that when P was deficient and N was sufficient, the dominant species of phytoplankton communities readily changed from diatoms to dinoflagellates (Richardson, 1997). Therefore we suggest that riverine nutrient input may have an important impact on the coastal ecosystem of the Chinese Seas. Molar ratios of DIN/P decreased from 120–160 in the Huanghe estuary and Laizhou Bay to 5–10 in the Central Bohai and the Bohai Strait with phosphorus as a limiting element for phytoplankton production in the Huanghe estuary and Laizhou Bay (Turner et al., 1990; Zhang et al., 2004). In the whole Bohai, nitrate concentrations increased, but phosphate and silicate levels decreased with DIN/P ratios increasing four times from 3.3 to 14 and Si/DIN ratios decreasing about ten times from 10 to 1.0 in the last forty years (Liu et al., 2008b). This resulted in dramatic decrease in the ratio of diatoms to dinoflagellates. The dominant taxa of diatoms had been replaced by dinoflagellates in recent decades (Wang and Kang, 1998; Kang, 1991) and the big cell diatoms replaced by small cell diatoms between 1958 and 1999 (Sun et al., 2002). In the Yellow Sea, the DIN/P ratios decreased from 24–32 in the western part to 6–8 near the Korea peninsula, and molar ratios of Si/DIN in the upper layers increased from 1.0 off the Jiangsu coast to 4 to the south of Shandong Peninsula, and ca. 7 in the northern part of the research areas (Liu et al., 2003b). In the Yellow Sea, there is a trend of dominant phytoplankton species composition shifting from diatoms to non-diatoms, such as dinoflagellates and cyanophytes, thus increasing the proportion of the small-sized phytoplankton in the size structure of phytoplankton communities but more work are needed as no long-term data are available (Lin et al., 2005; Wang, 2001). In the East China Sea, the DIN/P ratios decreased from 30–134 in the inner shelf to 5–18 in the outer shelf region, while the Si/DIN ratios varied from 0.8–1.1 in the inner shelf to 0.5–2.0 in the outer shelf (Zhang et al., 2007b). Frequent harmful algal blooms (*Prorocentrum dentatum* and *Karenia mikimokoi)* have occurred in coastal waters of the East China Sea (Zhu et al., 1997; Li et al., 2007). Blooms dominated by diatoms have decreased, but non-diatom species dominated blooms increased (Li et al., 2007). Hypoxia has been reported off the Changjiang Estuary (Li et al., 2002) extending from the Changjiang plume ∼400 km offshore and ∼300 km southward along the coast of the East China Sea (Chen et al., 2007). Off the Zhujiang estuary, molar ratios of DIN/P were 33–89 and Si/DIN ratios were 0.7–3.4 (unpublished data; Peng et al., 2006). Harmful algal blooms, such as *Cryptomonas* sp. (Cryptophyceae), also occurred very frequently in the Pearl River Estuary (Weng et al., 2007). Changes of phytoplankton composition affected the fishery resources in the Chinese Seas. For example, in the Bohai, not only has the fishery biomass decreased, but also the fish community has changed from bottom fish to pelagic fish as the abundant species due to overfishing and environmental degradation (Jin, 2004).

Table 8. Seasonal primary production (mg C m^{-2} day^{-1}) in the Chinese Seas.

Region	Spring	Summer	Fall	Winter	Reference
Bohai	300±73	390±201	232±72	161±33	Fei et al. (1991); Lü et al. (1999); Sun et al. (2003)
Yellow Sea	2066 (66–5303)	331 (67–1020)	702 (281–1341)	75 (15–221)	Yang et al. (1999b)
East China Sea	307±156	515±315	371±154	297±121	Gong et al. (2003)
Northern South China Sea					
Shelf (<200 m)	620±220	830±420	450±240	820±40	Chen and Chen (2006)
Basin (>2000 m)	440±300	310±140	320±140	530±190	

6.4 Riverine inputs of silicon to the Chinese Seas

For biogenic silica, there are limited data from these estuaries. In May 2003, dissolved silicate, biogenic silica (BSi) and lithogenic silica (LSi) were measured in the mainstream and major tributaries of the Changjiang when the river discharge was approaching the annual average. The average concentrations were of 88.1±28.4 μM of $Si(OH)_4$, 2.0±1.6 μM of BSi and 21.1±12.1 μM of LSi (unpublished data). With respect to total silicon, $Si(OH)_4$ represented 79%, BSi accounted for 1.8% and LSi was 19%, of which BSi accounted for 2% of BSi plus $Si(OH)_4$. It was also reported that BSi concentrations in the Yongjiang were 1.7±0.36 μM, representing ∼1% of silicic acid plus BSi (Liu et al., 2005b). While BSi concentrations in the rivers of the Jiaozhou Bay (such as the Daguhe and Yanghe) accounted for 12% of BSi plus $Si(OH)_4$ (Liu et al., 2008a). BSi percent in the Changjiang and Yongjiang is lower than the global average values (Conley, 1997) due to high sediment load. The BSi percent in the rivers around the Jiaozhou Bay is similar to the value of 16% found for other world rivers (Conley, 1997). As most of the Chinese rivers are characterized by high contents of suspended particulate matter, we suppose that the contribution of BSi in the Changjiang is similar to the other major Chinese large rivers, and BSi fluxes from large Chinese estuaries to the Chinese Seas would be 15.8×10^6 mol day^{-1}. Therefore, the total $Si(OH)_4$ and BSi fluxes from large Chinese estuaries would be 691×10^6 mol day^{-1}. In the Bohai, the proportion of diatoms in the total phytoplankton population decreased from 98% in 1959–1960 to 90% in 1982–1993 and 87% in 1998–1999 (Wang and Kang, 1998; Kang, 1991; Sun et al., 2002). In the Yellow Sea, the proportion of diatoms decreased from 89% in the spring 1986 to 70% in the spring 1998 (Wang, 2001), but it was 97–99% in the autumn 2001 and the winter 2002 (Wang, 2003). In the inner shelf of the East China Sea, the proportion of diatoms showed a decreasing trend from about 85% in 1984 to about 60% in 2000 (Zhou et al., 2008). In the Zhujiang Estuary, diatom accounted for 86.8% of all phytoplankton in the wet season and 70% in the dry season (Huang et al., 2004). We assume that diatoms account for ca. 75% of the primary production in coastal areas of the Chinese Seas as the lower limit and taking into account applying the Redfield stoichiometric ratio for phytoplankton nutrients (C:N:Si=106:16:16), diatom primary producers would assimilate 185×10^8 mol day^{-1} of silicon. Thus, both riverine $Si(OH)_4$ and BSi fluxes may contribute 3.7% of silicon required for diatom growth in the Chinese Seas.

6.5 Particulate and organic P and N fluxes to the Chinese Seas

It is known that riverine transport of phosphorus mainly exists in the solid phase (Martin and Meybeck, 1979), which increases PO_4^{3-} load by as much as five times due to release of phosphate from particles entering the sea (Froelich, 1988). Although particulate and dissolved organic nutrients tend to be less bio-available than dissolved inorganic forms, the form of nutrient may determine the impact on receiving coastal marine ecosystems including loss of habitat and biodiversity, low dissolved oxygen conditions, and an increase in frequency and severity of harmful algae blooms (Cotner and Wetzel, 1992; Seitzinger et al., 2005). For dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), particulate nitrogen (PN) and particulate P (PP), there are limited data for these estuaries. The monthly average concentrations of element forms were 40.2 μM for DON, 0.29 μM for DOP, 39.6 μM for PN, and 16.2 μM for PP during 2001–2002 in the Huanghe (Tan, 2002). The transport fluxes from the Huanghe to the coastal region were 1.71×10^9 mol yr^{-1} for DON, 0.012×10^9 mol yr^{-1} for DOP, 1.69×10^9 mol yr^{-1} for PN, and 0.69×10^9 mol yr^{-1} for PP, with DON representing 13% of TDN, DOP accounting for 41% of TDP, PN being 11% of total N, and PP being 96% of total P. The average concentrations in the Changjiang were 18.3 μM for DON, 0.45 μM for DOP, 17.4 μM for PN, and 2.87 μM for PP based on investigations in April–May 1997, June 1998–March 1999, and July 2001 (Duan et al., 2008; Liu et al., 2003a, unpublished data). The concentrations of DOP and PP were 0.60 μM and 2.47 μM in the Jiulongjiang (Chen et al., 1998b; Yang and Hu, 1996) and 0.60 μM and 2.86 μM in the Daguhe (unpublished data). The transports from the other rivers except the Huanghe estimated using average values in the Changjiang, Jiulongjiang and Daguhe and total water discharge ($1607.6\times10^9\,m^3\,yr^{-1}$) were $29.4\times10^9\,mol\,yr^{-1}$ for DON, $0.88\times10^9\,mol\,yr^{-1}$ for DOP, $28.0\times10^9\,mol\,yr^{-1}$ for PN, and $4.39\times10^9\,mol\,yr^{-1}$ for PP. Therefore, the total fluxes from the Chinese rivers were $31.1\times10^9\,mol\,yr^{-1}$ for DON, $0.89\times10^9\,mol\,yr^{-1}$ for DOP, $29.7\times10^9\,mol\,yr^{-1}$ for PN, and $5.08\times10^9\,mol\,yr^{-1}$ for PP. While these extrapolations are inevitably rough, they indicate that DON represents 18% of TDN, DOP is 47% of TDP, PN is 15% of total N, and PP accounts for 73% of total P. This indicates that fluxes of both dissolved organic and particulate N and P, especially P, to the Chinese Seas are important and may determine the impact on receiving coastal marine ecosystems. There is growing evidence that phytoplankton can use both phosphate and DOP (Cotner and Wetzel, 1992; Huang et al., 2005) and DON is implicated in the formation of some coastal harmful algal blooms (Berg et al., 1997; Seitzinger et al., 2002).

7 Conclusions

The present work summarizes data from biogeochemical surveys of the major Chinese estuaries including the Changjiang and Zhujiang. The longer residence time in the estuaries allows greater utilization of nutrients by phytoplankton than in the rivers. The Chinese rivers are characterized by high DIN and low PO_4^{3-} concentrations. DIN: PO_4^{3-} ratios varied widely and were higher (up to 2000) than other rivers in the world. The dissolved silicate levels and areal yields in general are higher in the warm and wet South China rivers than those in the cold and dry North China rivers, due to differences in climate, rock type and physical and chemical weathering. Silica leaching from drainage areas is greater in subtropical zones relative to temperate zones.

Nutrient levels in the Chinese rivers are higher than those from the large and less-disturbed rivers in the world such as the Amazon and the Zaire, but comparable to the values for the European and North American polluted and eutrophic rivers such as the Loire, Po, Rhine, and Seine. Both nitrogen and phosphorus originate from agricultural and domestic wastes, and nitrogen is preferentially leached from the drainage basin compared to reactive phosphorus. With urbanization, the change in nutrient composition in the Chinese and Korean rivers may result in a change of limiting nutrient from phosphorus to nitrogen for phytoplankton production, and silicon for diatom productivity, and thereby modifying coastal ocean ecosystem.

For the large Chinese estuaries, atmospheric deposition of nutrients is limited relative to riverine inputs. Both the residual and mixing flow transport nutrients off the estuaries. Nutrient fluxes from major Chinese estuaries to coastal areas in the summer are 3–4 times higher than those in the winter except for NH_4^+. Taking into account considering the Redfield stoichiometric ratio for phytoplankton nutrients (C:N:P=106:16:1), the major Chinese estuaries transport 0.1–15.1% of nitrogen, 0.02–5.7% of phosphorus for phytoplankton production and 3.7% of silicon required for diatom growth in the continental shelf of the Chinese Seas. This demonstrates that other sources, such as regenerated nutrients in water column and sediments, exchange between the Chinese Seas and open Pacific Ocean and atmospheric deposition, play major role for phytoplankton growth.

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