

**Nutrient dynamics in tropical rivers**

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# Nutrient dynamics in tropical rivers, estuarine-lagoons, and coastal ecosystems along the eastern Hainan Island

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## Abstract

Nutrient dynamics were studied along the eastern Hainan Island based on field observations during 2006–2009, to understand nutrient biogeochemical processes and to have an overview of human perturbations on coastal ecosystems in this tropical region. The concentrations of nutrients in the rivers had seasonal variations enriched with dissolved inorganic nitrogen (DIN). High riverine concentrations of nitrate were mainly originated from agricultural fertilizer input. The ratios of  $\text{DIN} : \text{PO}_4^{3-}$  ranged from 37 to 1063, suggesting preferential  $\text{PO}_4^{3-}$  relative to nitrogen in the rivers. The areal yields of dissolved silicate (DSi) varied from 76 to  $448 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$  due to erosion over the drainage area, inducing high levels of DSi among worldwide tropical systems. Aquaculture ponds contained high concentrations of  $\text{NH}_4^+$  (up to  $157 \mu\text{M}$ ) and DON (up to  $130 \mu\text{M}$ ). Particulate phosphorus concentrations ( $0.5 \sim 1.4 \mu\text{M}$ ) were in lower level compared with estuaries around the world. Particulate silicate levels in rivers and lagoons were lower than global average level. Nutrient biogeochemistry in coastal areas were affected by human activities (e.g. aquaculture, agriculture), as well as natural events such as typhoon. Nutrient concentrations were low because open sea water dispersed land-derived nutrients. Nutrient budgets were built based on a steady-state box model, which showed that riverine fluxes would be magnified by estuarine processes (e.g. regeneration, desorption) in the Wenchanghe/Wenjiaohe Estuary, Wanquan River estuary, and the Laoyehai Lagoon except in the Xiaohai Lagoon. Riverine and ground-water input were the major sources of nutrients to the Xiaohai Lagoon and the Laiyehai Lagoon, respectively. Riverine input and aquaculture effluent were the major sources of nutrients to the eastern coastal of Hainan Island. Nutrient inputs to the coastal ecosystem can be increased by typhoon-induced runoff of rainwater, and phytoplankton bloom in the sea would be caused.

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## 1 Introduction

Estuaries and coastal areas, which are regions of high population density and intense human activities, cover approximately 7% of the surface area of the world's ocean, while account for 30% of the total net oceanic primary production (Alongi, 1998; Gattuso et al., 1998; Dürr et al., 2011; Pan and Wang, 2012). The rapid increase of human activities induced more nutrients transport from land to sea in the past decades, resulted in environmental deterioration and biogeochemical processes modification (Seitzinger et al., 2005; Halpern et al., 2008; Martin et al., 2008; Qu and Kroeze, 2010). Tropical estuaries, which are the most biogeochemical active zones in the biosphere, are more easily affected by anthropogenic nutrient loading than higher latitude (Yule et al., 2010; Smith et al., 2012), especially in tropical South and Southeast Asia coastal regions, which are among the most heavily modified by human activities worldwide (Jennerjahn et al., 2008). These systems are highly sensitive to natural environmental changes and human activities, such as land use, geomorphologic evolution (Jia et al., 2012), and deforestation (Meunier et al., 2011). Asian rivers are severely affected by human activities and catchment degradation due to rapid economic development and population growth (Dudgeon, 2000; Yule et al., 2010). However, nutrient processing and characteristics of tropical rivers and estuaries are poorly studied relative to temperate zone (Thomas et al., 2004; Smith et al., 2012).

As an oligotrophic ocean, the South China Sea (SCS) is located in the tropical to subtropical in the western Pacific Ocean with a total area of about  $3.5 \times 10^6 \text{ km}^2$ , and is one of the largest marginal seas in the world (Xu et al., 2008; Ning et al., 2009). It is bounded by the China continent, Vietnam, Gulf of Thailand, Sunda Shelf, Borneo, Taiwan, and Philippine (Ning et al., 2004). The SCS is dominated by the East Asia Monsoon (Su, 2004), with southwesterly winds prevailing in summer and autumn and northeasterly winds in winter and spring (Chen and Chen, 2006). Summer upwelling and cyclonic eddy which driven by SW monsoon were one of the most important physical processes in the coastal waters of the northern SCS (Li et al., 2010). There are

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29 rivers that directly discharge into the northern SCS (Ning et al., 2009), and the Pearl River is the largest one with water discharge of  $482.1 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$  (Liu et al., 2009). The growing load of nutrients in the Pearl River has been caused by the excessive release of waste as a result of economic growth and urban development in recent decades (Huang et al., 2003; Chen and Chen, 2006; Ning et al., 2009). HABs which caused enormous economic losses in aquaculture (Wang et al., 2008) occurred frequently off the Pearl River due to excess N input (Yin et al., 2004). Many estuarine eutrophication studies have focused on this large estuary system (Yin, 2002; Yin et al., 2004; Xu et al., 2008; Qiu et al., 2010). Nutrient conditions in small well flushed estuaries are less known, such as estuaries along the eastern Hainan Island (Fig. 1).

In our study, we focused on the eastern coast of the Hainan Island, which is affected by natural processes (i.e. monsoon, upwelling, and rivers discharge) and human activities (i.e. agriculture, aquaculture, fishing, and tourism) (Chai et al., 2001; Jing et al., 2009; Su et al., 2011). Economic development which could increase nutrients load and influence nutrient cycling in the coastal region has caused environmental problems, resulted in accelerating coastal ecosystems degeneration and eutrophication occurring (Pan et al., 2007), i.e., more than 10 % coastal area off the Bamen Bay was heavily polluted in 2008 (Hainan Ocean State of the Environment, 2008) and red tide occurred in 2010 (Hainan Ocean State of the Environment, 2010). Compared with the Pearl River, rivers along the eastern Hainan Island discharging into the SCS are all small sized (Table 1), while, small sized rivers are more easily affected by human activities and environmental changes than large river systems (Jennerjahn et al., 2008). Additionally, tropical island rivers with in a rainy region have flashy hydrological regimen, resulting in short time response to heavy rainfall events (Gupta, 1995; Ramírez et al., 2012), such as typhoon. The island is frequently hit by tropical storms and typhoons in August and September (Zhang et al., 2010), bringing large amounts of rainfall (Mao et al., 2006). Typhoon plays an important role in enhancing oceanic primary productivity in oligotrophic ocean waters (Ning et al., 2004), especially in typhoon-dominated sea (Zheng and Tang, 2007; Zhao et al., 2009). Nutrient loads in rivers and phytoplankton

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biomass can be increased by typhoon-related flood. Furthermore, submarine ground-  
water is also a potential significant source of nutrient from land to ocean, and plays  
an important role in coastal nutrient cycling (Slomp and Van Cappellen, 2004; Moore  
et al., 2006; de Sieyes et al., 2011). Areal groundwater inputs may be similar in mag-  
nitude with riverine inputs in some coastal locations (Moore, 1996; Paerl, 1997). Un-  
der the combined effects of human activities and natural events, coastal ecosystem of  
the tropical region is vulnerable and undergoing accelerated decline. Hence, it is very  
necessary to understand nutrients biogeochemical cycles and sources in the tropical  
coastal ecosystem.

Six investigations were carried out along the eastern Hainan Island during the period  
2006–2009. Here, we present results from study on nutrient dynamics in water and sus-  
pended matter from tropical rivers, their associated estuaries, lagoons, and adjacent  
coast of the eastern Hainan Island. The aim of this study was to conduct the first com-  
prehensive spatial-temporal nutrients distribution in the tropical shallow coastal region,  
to delineate the effects of natural and anthropogenic factors of land-derived nutrients  
on the biogeochemistry of tropical streams, and to assess the human activities impact  
on water quality and ecosystem of the receiving coastal waters.

## 2 Materials and methods

### 2.1 Study area

Hainan Island is the largest island in the SCS, located at the southernmost tip of the  
country, with a coastline length of 1550 km, and is separated from the mainland of  
China by Qiongzhou Strait (Li et al., 2011a). It covers a land area of  $35.4 \times 10^3$  km<sup>2</sup>,  
with a population of nearly 9.08 million in 2011 (Hainan Statistical Yearbook, 2012). The  
area is characterized by a tropical monsoonal climate (Zeng and Zeng, 1989), with pre-  
vail northerly winds in winter; southerly winds in summer (Wang, 2002). About 80 % of  
annual precipitation occurs during the wet season from May to October with annual

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rainfall 1600–1800 mm (Mao et al., 2006). Four types of topographical coast were formed due to different construction factors and marine dynamics in this island (Wang et al., 2006). The coast is subject to mixed semidiurnal microtides with a tidal ranges of usually < 1 m and around 1.6 m at neap and spring tide, respectively (Krumme et al., 2012). A coastal upwelling exists in the eastern Hainan Island driven by strong southwest monsoon and topography (Jing et al., 2009; Su and Pohlmann, 2009). The upwelling starts in April and disappears in October with a width ranging from 30 m water depth to 10 km offshore (Li et al., 2011a).

The study area locates along the eastern Hainan Island from Tongguling to the Laoyehai Lagoon (LYH) (Fig. 1), has a narrow continental shelf with a depth ranging from 0 to 100 m (Tang et al., 2003) and opens to the sea. Four coastal estuarine–lagoons along the coastline were formed in a transgression process during the Quaternary (Wang et al., 2006). Coastal lagoons with shallow water environments are under the freshwater and marine interactions, connected with open sea via narrow channels, and semi-closed by sand barriers (Bruun et al., 1978; Jia et al., 2012). The Wenchanghe (WC; annual freshwater discharge  $9.09 \text{ m}^3 \text{ s}^{-1}$ ) and the Wenjiaohe (WJ; discharge  $11.6 \text{ m}^3 \text{ s}^{-1}$ ), which connected with the sea through a narrow natural channel (about 9.0 km long; Wang et al., 2006), empty into the kidney-shaped lagoon (Bamen Bay) (Zeng and Zeng, 1989). An outer semi-closed that named Gao-long bay was formed due to hydrodynamics and the sediment transport. The Wenchanghe/Wenjianhe Estuary (WWE) is characterized by mixed semi-diurnal microtides, with an average tidal amplitude of < 2 m (Unger et al., 2013). Comprehensive investigations revealed that nutrients show non-conservatively behavior. Riverine input, groundwater discharge and aquaculture effluents were the major source of nutrients in the estuary (Liu et al., 2011). The water residence time was estimated to be 7.8 days in the WWE based on the box model (Liu et al., 2011). Anchor stations observations indicated that nutrient concentrations varied with tide in the Bamen Bay, while it was not obvious in the Qinglan tidal inlet (Liu et al., 2011).

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As the third largest river in the Hainan Island, the Wanquan River (WQ) directly empties into the SCS, and a typical dynamic lagoon–tidal inlet–barrier system was formed (Zhu et al., 2005). The river is a mountainous river system with high elevation to length ratio ( $3.34 \times 10^{-3}$ , Zhang et al., 2013). Approximately  $3.9 \times 10^6 \text{ tyr}^{-1}$  sediment was loaded to the estuary (Wang et al., 2006). The Wanquan River estuary (WQE) is comprised two semi-closed parts, the Wanquan River tidal inlet and the Shamei Lagoon. The Tayang River (TYR) and the Lunyanghe (LY), which flow through cultivated land, enter the WQ from the north. The Jiuqujiang (JQJ) and the Longgunhe (LG) empty into the Shamei Lagoon from the west and south with freshwater discharge of  $10.2 \text{ m}^3 \text{ s}^{-1}$  and  $7.5 \text{ m}^3 \text{ s}^{-1}$ , respectively (Wang, 2002). The WQE has a micro and irregular diurnal tidal regime with a mean range of approximately 0.7–0.8 m (Zhu et al., 2005). The water residence time was estimated to be 0.2–4.7 days. Riverine input was the major source of nutrients to the estuary (Li et al., 2013). The salinity of the Shamei Lagoon has been reduced to  $< 1$  because of aquaculture activities which decreased the flushing efficiency of the tidal dynamics (Ge et al., 2004; Jia et al., 2012).

The Xiaohai Lagoon (XH) is a typically well–developed tidal inlet–lagoon system as the largest lagoon in the Hainan Island. Surface area of the gourd-shaped lagoon has decreased from about  $49 \text{ km}^2$  in 1960 to approximately  $44 \text{ km}^2$  with a mean water depth of 1.5 m in nowadays because of land reclamation and aquaculture activities (Wang et al., 2006; Tian and Li, 2007; Gong et al., 2008). Eight rivers empty into the XH with annual mean total discharge of  $26.5 \text{ m}^3 \text{ s}^{-1}$ . It connects the coastal region through a narrow tidal channel which had been installed about 5000 fishing cages since 1986 (Gong et al., 2009). It is a significant fishery port along the eastern Hainan Island. Aquaculture activities have been developed tremendously in recent decades, result in deterioration of flushing efficiency of the tidal dynamics. Water residence time has increased from 45 to 71 days in the lagoon (Gong et al., 2008).

The LYH with a surface area about  $26 \text{ km}^2$  (Ji et al., 2013) can be divided into two parts: the inner bay, where the fish ponds are concentrated and which is hardly affected by the tide; the tidal channel, which is approximately 8 km long with quite a number of

fishing cages for fish-farming connecting to the sea. The width of the tidal channel has been narrowed from 425 m in 1960s to 75 m in nowadays (Wang et al., 2006). Three rivers directly empty into the LYH with a very low river discharge (approximately  $0.4 \text{ m s}^{-1}$ ) (Ji et al., 2013).

The study tropical coastal environment represents a diverse range of geomorphological settings and biological habitat types. It has a number of small-sized mountainous rivers, dense mangrove vegetation and a mainly shallow shelf with coral reef and seagrass (Roder et al., 2013). Agriculture was the major land use in the island. Terrestrial materials were transported from fresh to brackish water mangrove ecotone through the shallow estuarine environment. Over the past decades, many coastal areas where were mangrove are being developed into aquaculture, residential and golf course communities. The area of mangrove forest in the Hainan Island was approximately 10 000 ha in 1972, but approximately 57 % of the mangrove had been lost for deforestation, reclamation, and aquaculture ponds in 2003 (Zhou, 2004). The environments have been affected by human activities, inducing significant changes in hydrology of the system, anthropogenic nutrient delivery, coral reef ecosystems and other coastal habitats (Roder et al., 2013; Zhang et al., 2013).

## 2.2 Sampling

Six cruises were carried out along the eastern Hainan Island during December 2006 (winter), August 2007 (summer), July–August 2008 (summer), August–September 2008 (summer), March–April 2009 (spring), and July–August 2009 (summer), covered a broad range of water bodies. The station locations are shown in Fig. 1. We considered the cruises in August 2007, July–August 2008, and July–August 2009 as in wet season, in December 2006 and March–April 2009 as in dry season. Anchor stations, which were set off the Bamen Bay, were observed over 25 h and carried out during August 2007, July 2008, and July 2009, respectively. During the July 2008 and April 2009 cruises, water samples were collected in Changqi Bay which is the second largest aquaculture production area to see the influence of aquaculture. Coastal water



samples, which were within coral reef region, were collected by small boat to know human activities impacts on coral reef. Moreover, water samples from shrimp ponds and groundwater which were obtained from wells located on around the study area were also collected.

Water samples from rivers and shrimp ponds were collected from river bank or by small boat and ponds edge with 1 L acid-cleaned polyethylene bottles attached to the end of a fiber-glass reinforced plastic pole. Water samples were collected based on salinity gradient in the estuaries and lagoons. Surface water samples from estuaries and lagoons were collected in acid-cleaned polyethylene bottles during spring tides. Adjacent sea water samples were collected with 10 L Niskin bottles from various depths chosen from CTD readings. A WTM MultiLine F/Set3 multi-parameter probe was used to measure water temperature and salinity both in rivers and estuaries. Coastal water temperature and salinity were measured by CTD (SBE<sup>®</sup> 25, USA). Samples for dissolved nutrients were filtered through acid precleaned 0.45  $\mu\text{m}$  pore-size acetate cellulose filters. The filtrates were poisoned by saturated  $\text{HgCl}_2$  solution immediately and took back to laboratory for analysis. The filters were dried at 45  $^{\circ}\text{C}$  and weighted to determine the mass of suspended particulate matter (SPM), particulate inorganic phosphorus (PIP), and particulate organic phosphorus (POP). Samples for particulate biogenic silicon (PBSi) and lithogenic silicon (LSi) were filtered through 47 mm polycarbonate membrane with 0.4  $\mu\text{m}$  pore size that had been dried at 45  $^{\circ}\text{C}$ .

### 2.3 Chemical analysis

Nutrient concentrations were determined using an Auto-Analyzer Skalar SAN<sup>plus</sup> in the laboratory (Liu et al., 2011). The total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) were measured according to the methods of Grasshoff et al. (1999). The analytical precision of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , DSi, TDN, and TDP were < 5%. The concentration of dissolved inorganic nitrogen (DIN) is the sum of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$ . The concentrations of dissolved organic nitrogen (DON) and dissolved organic

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phosphorus (DOP) are estimated by subtraction of DIN from TDN and  $\text{PO}_4^{3-}$  from TDP, respectively.

Particulate phosphorus in the SPM was measured using the methods of Aspila et al. (1976). The extracted  $\text{PO}_4^{3-}$  was measured by spectrophotometry. The analytical precision of total particulate phosphorus (TPP), PIP, and POP were < 5 % (Li et al., 2011b). The concentration of POP is estimated by subtraction of PIP from TPP. Particulate phosphorus (PP) concentration is the sum of PIP and POP. The PBSi and LSi in the SPM were measured based on the methods of Ragueneau et al. (2005). The extracted DSi was measured by spectrophotometry. The analytical precision of PBSi and LSi were 7 % ( $n = 7$ ) and 8 % ( $n = 7$ ), respectively (Li et al., 2011b).

## 2.4 Estuarine nutrient budgets

Nutrient budgets for the estuarine–lagoon systems along the eastern Hainan coast were estimated based on a box model designed by Land Ocean Interactions in the Coastal Zone (LOICZ) (Gordon et al., 1996; Liu et al., 2009). This box model was widely used for nutrient budgets in estuarine and coastal ecosystems to understand the internal biogeochemical processes and external nutrient inputs about the study system (Savchuk, 2005). In this model, we assumed that our study systems were in a steady state and we treated them as a single box which mixed well.

Briefly, the water mass balance (Eq. 1), salinity balance (Eq. 2), and non-conservative fluxes of nutrient elements (Eq. 3) that based on nutrient concentrations and water budgets were estimated as follows:

$$V_R = V_{in} - V_{out} = -V_Q - V_P - V_G - V_W + V_E \quad (1)$$

$$V_X(S_1 - S_2) = S_R V_R \quad (2)$$

$$\Delta Y = \sum \text{outflux} - \sum \text{influx} = V_R C_R + V_X C_X - V_Q C_Q - V_P C_P \quad (3)$$

where  $V_R$  is the residual flow,  $V_Q$ ,  $V_P$ ,  $V_G$ ,  $V_W$ ,  $V_E$ ,  $V_{in}$ ,  $V_{out}$ , and  $V_X$  are the river discharge, precipitation, groundwater, wastewater, evaporation, inflow, outflow of water

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from the system of interest, and the mixing flow between the two systems, respectively. We assumed that the salinity of fresh water was 0 ( $V_Q$ ,  $V_P$ , and  $V_E$ ). In addition,  $S_R = (S_1 + S_2)/2$ .  $S_1$  and  $S_2$  in Eq. (2) refer to the average salinity of the system of interest and the adjacent system, respectively. Hence, the total water exchange time ( $\tau$ ) of the system of interest was estimated from the ratio  $V_S$  to  $(V_R + V_X)$ .  $V_S$  is the volume of the system. In Eq. (3),  $C_R$  and  $C_X$  are the average element concentrations in the residual flow and mixing flow, and equating to  $(C_1 + C_2)/2$ ,  $(C_1 - C_2)$ , respectively;  $C_Q$  and  $C_P$  are the average element concentrations in the river discharge and the precipitation, respectively.  $C_1$  and  $C_2$  are the average element concentrations in the system of interest and the adjacent system, respectively. A negative or positive sign for  $\Delta Y$  indicates that the system of interest was a sink or a source, respectively. Furthermore, this model was used to construct particulate nutrient budgets, such as constructing phosphorus budget for the East China Sea (Fang, 2004). We used a 2-box model to estimate particulate nutrient budgets as dissolved nutrient budgets (Li et al., 2013) as a function of different water residence time between the Shamei Lagoon and the Wanquan River tidal inlet in the WQE.

### 3 Results

#### 3.1 Hydrographic conditions

The physico-chemical parameters in this study are listed in Table 2. Surface water temperature was lower in dry season than in wet season during the study periods (Table 2), reflecting the seasonality of this tropical system. On 4–8 August 2008, Typhoon Kammuri passed the study area in quite a distance large rainfall were induced (40–145 mm per day during the passage of Kammuri, Herbeck et al., 2011). A small temperature decrease of 3 °C was observed in the WC during post-typhoon.

Saline water could be found in the WC, WJ, and WQ rivers due to seawater intrusion in tidal estuaries with salinity of < 3.9 (Table 2). The salinity varied between 1.8–10.6

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for the XH during the study period. Aquaculture activities in the XH induced decreasing of the flushing efficiency of tidal dynamics and water exchange rate in recent decades (Wang et al., 2006; Liu et al., 2007), resulting in low and stable salinity. The salinity varied greatly in the LYH, which was 9.1–33.2 during the study periods under the interaction between freshwater and saltwater (Table 2). Salinity gradients were observed during our study periods in the LYH, with increasing salinity towards the mouth of the lagoon because of tide intrusion (Fig. 2b). The salinity in the inner lagoon of the LYH ranged from 9.1 to 16, reflecting the influences of fish farming.

SPM concentrations also had obviously seasonal variation. The concentrations of SPM ranged between  $7.85 \text{ mgL}^{-1}$  and  $46.3 \text{ mgL}^{-1}$  with means  $20.7 \text{ mgL}^{-1}$  in the WC (Table 2). A peak (to  $46.3 \text{ mgL}^{-1}$ ) was observed in the WC after the typhoon event. High SPM concentrations were measured in spring 2009 ( $35.1\text{--}85.6 \text{ mgL}^{-1}$ ) in the WJ where had wastewater input and shrimp ponds. The concentrations of SPM in the WQ were generally within the same range except 2009 spring cruise (Table 2). They ranged from  $7.47 \text{ mgL}^{-1}$  to  $71.1 \text{ mgL}^{-1}$  in the WQ in spring 2009 because of large river discharge (maximum  $278 \text{ m}^3 \text{ s}^{-1}$ ) which induced by first-rain event during the period. SPM concentrations in the WQ generally increased from upstream to downstream. SPM concentrations were higher during wet season than during dry season, with means of  $23.6 \pm 15.2 \text{ mgL}^{-1}$  and  $9.94 \pm 3.23 \text{ mgL}^{-1}$ . The concentrations of SPM ranged from 2.08 to  $20.6 \text{ mgL}^{-1}$  in the LYH (Table 2). Lower concentrations were recorded in the LYH than in the XH. Isotope analyses indicated that sedimentary rate after 1988 was about 2 times over the past decade because of anthropogenic activities which lead to authigenic organic matter significantly increased in the XH (Liu et al., 2007). The SPM levels in coastal region were obviously lower than in rivers and lagoons (Table 2) indicating effective removal in the estuarine–lagoons.

The surface water temperature in the coastal region increased from south to north both in August 2007 and 2008, and increased from north to south in April 2009 (Fig. 3). Recent research has shown that typhoons can cause cooling of the sea surface (Huang et al., 2010). The cruise in August 2007 took place after a typhoon event which might

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lead to lower temperature than in July–August 2008. The surface salinity gradually increased from onshore to offshore region and isohalines were parallel with the coastline (Fig. 3). Freshwater and sea water mix within a distance of about 10 km. Topographic effects would be another important reason for the different hydrodynamic conditions under different weather conditions in the study area (Su et al., 2011). Thermohaline stratification near the surface occurred at all stations both in 2007 and 2008 summer cruises. The isopleth of temperature gradually elevated from the bottom to the surface in summer (Figure S1 a, b) which was evident in the upper water column as a consequence of upwelling (Su et al., 2011) and the nutrients biogeochemistry would be affected.

Surface temperature increased from west to east and salinity had an opposite distribution in August 2008. A cyclonic eddy appeared at 18.5° N with a cold center that approached to the Bamen Bay (Su et al., 2011). The low salinity center with high temperature (Fig. 3d) in Aug/Sep 2008 cruise might be related to the eddy.

### 3.2 Nutrients in rivers and lagoons

Nutrient concentrations in rivers and lagoons along the eastern Hainan Island are shown in Tables 3 and 4. Nutrients varied greatly in difference water bodies during the study periods. Compared with other temperate and subtropical rivers of China (Liu et al., 2009), nutrients in rivers are enriched with DIN and DSi, and depleted with  $\text{PO}_4^{3-}$  (Tables 3, 4). The concentrations of DSi in rivers are high for tropical river systems (the average concentration for tropical rivers of 180–190  $\mu\text{M}$ , Jennerjahn, 2012) except the JQJ and LG rivers which empty into the Shamei Lagoon.  $\text{PO}_4^{3-}$  concentrations were always  $< 1.0 \mu\text{M}$  except for the JQJ in August 2009. The concentrations of DOP in rivers in wet season, which represented 52–97 % of TDP, were higher than in dry season. While, DON concentrations in dry season were higher than in wet season (Tables 3, 4). PIP and POP concentrations in the WC and WJ were 1.9–4.6 times higher than those in the WQ. The average concentrations of PBSi and LSi in the WJ were obviously higher than in other rivers (Table 3). This might be related to river discharge and

weathering rate. All PP and PBSi were well correlated with SPM both in the WWE and the WQE, suggesting influence of the fluvial input.

The areal yields of nutrients were estimated by the product of nutrient concentration with average freshwater discharge divided by the drainage area (Table 5). The areal yields of DIN in the study rivers were apparently higher than the average for large tropical and nontropical rivers. The  $\text{PO}_4^{3-}$  yields were lower than in tropical river systems (Table 5). The areal yields of DSi in the WQ with an average of  $448 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$  were greatly higher than in the tropical Citanduy, Indonesia, whose drainage area is comparable to the WQ. Both for DIN and  $\text{PO}_4^{3-}$  the yields in rivers were lower than the Brantas River (Table 5), which located in the most favorable region on the earth with regard to weathering and erosion conditions (Jennerjahn, 2012). The DSi yields for study rivers were also higher than in the Brantas River. Rock types might be responsible for the high chemical weathering.

Nutrients concentrations reflected linear dilution of freshwater by seawater in 2009 spring cruise except DON, DOP, and PBSi in the XH (Fig. 2a). Nonlinear correlations with salinity were observed in other two cruises. DON represented  $76 \pm 15\%$  of TDN in wet season, while it was  $36 \pm 15\%$  in April 2009. DOP represented  $50 \pm 20\%$  and  $47 \pm 20\%$  of TDP in wet and dry seasons, respectively. Low salinity (1.8) water with high nutrient concentrations ( $\text{NO}_3^-$ :  $45.0 \mu\text{M}$ ; DON:  $23.8 \mu\text{M}$ ) appeared in the west of the inner lagoon (station XH5) which might be related to terrigenous materials input via river runoff and weak hydrodynamics.

Nutrients were considerable scatter in the concentration vs. salinity (between 9 and 16, shaded part) relationship in the LYH due to aquaculture activities, and appeared to be subjected to seawater dilution when salinity  $> 16$  except LSi (Fig. 2b). The DIN composition was generally dominated by  $\text{NH}_4^+$  (accounted for 46–96%) in both seasons. DON accounted for  $\sim 58\%$  of TDN and was significantly low in April 2009. DOP represented 8–76% of TDP. DSi concentrations in the lagoon, which ranged from 6.02 to  $86.4 \mu\text{M}$ , were significantly lower than in other estuarine–lagoons in the study area. This might be related to low river discharge.

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### 3.3 Nutrients in shrimp ponds and groundwater

Nutrient concentrations in shrimp ponds varied considerably, as indicated by the large standard deviation (Table 3). Average nutrient concentrations were obviously higher in wet season than in dry season, especially for  $\text{NH}_4^+$  and DON (Table 3). The concentrations of  $\text{NO}_2^-$  in shrimp ponds ranged from 0.06 to 287  $\mu\text{M}$ , mostly were  $< 0.5 \mu\text{M}$  except one site which situates at Changqi Bay that reached 287  $\mu\text{M}$ . The concentrations of  $\text{PO}_4^{3-}$  in shrimp ponds ranged between 0.18 and 11.1  $\mu\text{M}$ .  $\text{PO}_4^{3-}$  concentrations were higher in wet season with an average of 6.17  $\mu\text{M}$  (Table 3). DIN :  $\text{PO}_4^{3-}$  ratios ranged between 0.6 and 216 in ponds water. Shrimp ponds held higher concentrations of DON in wet season than in rivers, but lower concentrations of  $\text{NO}_3^-$  than in rivers (Table 3). DON represented 21–98 % of TDN, and DOP was 8–69 % of TDP during the study periods.

The concentrations of nutrients in groundwater (GW) ranged over two orders of magnitude with very high DIN : DIP molar ratios (Table 3) during the investigation. Average concentrations were higher than other water bodies (rivers and shrimp water). Especially average  $\text{NO}_3^-$  concentrations, ranged from 446  $\mu\text{M}$  in wet season to 592  $\mu\text{M}$  in dry season, and accounted for 90 % of the DIN, this might be related to chemical fertilizer-N applied in the farmland and population density (Gu et al., 2011; Wang et al., 2012).

### 3.4 Nutrients distribution in coastal region

The horizontal and vertical distributions of nutrients in coastal waters are shown in Fig. 3 and Fig. 4, respectively. The horizontal distributions of nutrient decreased significantly from inshore areas to the direction of the open sea except DON (Fig. 3). Nutrient horizontal distributions were in general agreement with surface salinity distribution, had seasonal variations, and isopleth paralleled with coastline except in August 2008 cruise. High nutrient concentrations with low salinity mainly appeared off the WQE. The river discharge of the WQ was 278  $\text{m}^3 \text{s}^{-1}$  and 100  $\text{m}^3 \text{s}^{-1}$  when collected samples in spring 2009 and summer 2009, respectively. Under the combined actions of high runoff and prevailing southwesterly winds in summer, part of the WQ diluted water

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flows to northeast. Nutrients distributions were quite similar to the extending diluted water both in summer 2007 and summer 2009 (Fig. 3a, e). Nutrients distributions were extending southwest in spring 2009 (Fig. 3c). However, the freshwater discharge was just  $51.4 \text{ m}^3 \text{ s}^{-1}$  in July–August 2008. The influence of the freshwater was not so visible (Fig. 3b). The concentrations of nutrients decreased from south to north in August 2008 and terrigenous inputs were not observed (Fig. 3d). This distribution might be affected by the Hainan Coastal Current which travels from south to north (Chu et al., 1999). Figure 3e shows that high nutrients appeared in Qiongzhou Strait and east inshore waters of the Hainan Island. The isoplethes of nutrients in Qiongzhou Strait which can be affected by Nandu River were vertical with coastline and increased from the west to the east in summer 2009. The horizontal distribution of nutrients in summer 2009 also had a similar distribution with Chl *a* which was investigated in August 2008 (Li et al., 2011b). DON represented 47–97 %, 47–98 %, 14–97 % and 22–95 % of TDN in surface water in August 2007, July–August 2008, August 2008, and April 2009, respectively. DOP were 27–91 %, 32–95 %, 3.7–92 %, 27–87 % of TDP during the study period, respectively. DON and DOP were the main component of TDN and TDP in offshore surface waters in our study region. DON and DOP might be used by primary producers when phytoplankton growth was limited by nitrogen or phosphate (Engeland et al., 2010; Huang et al., 2005).

The vertical distributions of nutrients reflected the degree of water vertical mixing in each cruise. DIN, DIP, dissolved silicate, and TDP increased from surface to bottom both in summer 2007 and 2008 (Figure S1 a, b). DIN, DIP, and DSi were found to be evenly distributed in the onshore waters during spring 2009 (Figure S1 c). DIN, DIP, and DSi had similar vertical distribution and vertical distribution was impacted by the topography in Sect. 1#–6# and 9#–14# (Fig. 3e). DON and DOP gradually decreased from surface to bottom which had contrary vertical distribution with DIN.

Molar ratios in the shallow coastal region were obviously lower than in freshwater (Table 3, S1) and decreased from nearshore to offshore (Fig. 3). Molar ratios of  $\text{DIN} : \text{PO}_4^{3-}$  and  $\text{DSi} : \text{DIN}$  in August 2007, July–August 2008, and July–August 2009 were higher



than the Redfield ratio (Fig. 3a, b, e). DIN : PO<sub>4</sub><sup>3-</sup> molar ratios ranged from 1.0 to 25 in August 2008 with an average of 11 ±11 except one site with 51 (Fig. 3d). DSi to DIN molar ratios were higher than or comparable to Redfield ratio both in April 2009 and August 2008 (Fig. 3c, d). This indicated that the nitrogen would be the limited element for phytoplankton growth in shelf region. While P was the most limiting nutrient within the coral reef region for phytoplankton growth due to excess terrigenous N input. Diatom Si : C ratios, which had been used to estimate silica production in both global and local silicon budgets (Brzezinski, 1985), would be increased by a factor 2–3 due to the limitation by N, P or Fe in planktonic marine species (Ragueneau et al., 2000). PDSi to POC ratios were about 0.05 based on POC measured in neritic region in August 2007 (Tian, 2009). This value was within the range of 0.05–1 reported worldwide (Liu et al., 2007). However, the value was lower than Si to C ratio (0.13) that for diatom growth under nutrients sufficient conditions (Brzezinski, 1985).

### 3.5 Nutrients variability at anchor stations in coastal region

The concentrations of nutrients were obviously higher in near-bottom water than surface and sub-surface water in August 2007 except NH<sub>4</sub><sup>+</sup>, DON, and DOP (Fig. 4a). NO<sub>3</sub><sup>-</sup> was 0.01–0.37 μM in surface layer, and increased with depth, reaching 7.24 μM in near-bottom waters in August 2007. NO<sub>2</sub><sup>-</sup> was approximately 3-fold higher in near-bottom samples than in the surface (Fig. 4a). NH<sub>4</sub><sup>+</sup> was vertically well-mixed through the tidal cycle (Fig. 4a). PO<sub>4</sub><sup>3-</sup> in near-bottom water was 3–14-fold higher than in surface waters (0.04–0.17 μM) (Fig. 4a). Dissolved silicate concentrations increased steadily from 1.58–3.16 μM at the surface to 5.94–9.32 μM in near-bottom water (Fig. 4a). DIN/DIP ratio in August 2007 decreased from 12–61 in surface water to 14–20 in near-bottom water. DSi/DIN ratio ranged from 0.50 to 0.95 in surface water and 0.64–0.98 in near-bottom water. DON concentrations were higher in surface layer than in near-bottom, with means of 12.3 μM and 10.3 μM, respectively. TDN was dominated by DON (80–90%) in less than sub-surface layer.

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The concentrations of nutrients showed a well-mixed vertical profile throughout the water column in July–August 2008 (Fig. 4b). Nutrients concentrations changed 1– to 3–fold for  $\text{Si}(\text{OH})_4$ , TDN, DON, TDP and DOP, 5–6 times for  $\text{NO}_2^-$ , 3–7 times for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , and 3– to 11–fold for  $\text{NH}_4^+$ . The DIN/DIP ratio was 19–138 in surface water due to low concentrations of  $\text{PO}_4^{3-}$  (0.02–0.08  $\mu\text{M}$ ). High DON concentrations of 5.1–9.6  $\mu\text{M}$  comprised up to 60 % of the TDN through the water column. DOP was 0.09–0.24  $\mu\text{M}$ , represented 41–91 % of TDP, with a well-mixed vertical profile (Fig. 4b).

Nutrients concentrations in 30 m layer showed the influence of tidal effects, with low values during the flood tide and an increase during the ebb tide (Fig. 4c). Nutrients concentrations showed a strong vertical mixing in less than 30 m depth in August 2009 (Fig. 4c).  $\text{NH}_4^+$  concentrations (0.24–7.47  $\mu\text{M}$ ) were variable through the water column. DIN to DIP ratio was 3.6–21 in less than 30 m depth (average: 11) and 10–17 (average: 14) in bottom water. DSi/DIN ratio was 0.4–12 (average: 2.1) in surface water and 1.0–1.4 (average: 1.1) in bottom water. The freshwater and tidal effects were not significant during the spring and neap tides in the three investigations in the coast region.

### 3.6 Water and nutrient budgets

We just had annual discharge data about some streams, so we calculated annual nutrient fluxes from rivers to coastal region based on the nutrient budgets. Liu et al. (2011) and Li et al. (2013) had given a detailed description about dissolved nutrient budgets in the WWE and WQE along the eastern Hainan Island, respectively. Hence, we simply described dissolved nutrient budgets about the XH and LYH in Table 6.

Wastewater from domestic and industrial and aquaculture effluents, which discharged directly into the lagoons, were ignored in the water budgets as no data available. Average submarine groundwater discharge (SGD) into the LYH was calculated to be  $4.11 \times 10^6 \text{ m}^3 \text{ day}^{-1}$  based on the excess radium isotopes and the water age of the LYH in April 2010 (Ji et al., 2013). Based on the water balance, the net water exchanges ( $V_R$ ) from the XH and the LYH to the SCS were  $864 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$  and

1519 × 10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup>, respectively. The water exchange flow from the SCS to the XH and the LYH were 717 × 10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup> and 2660 × 10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup>, respectively. The residual flow ( $V_R$ ) between the XH and the SCS was similar to the river discharge (834 × 10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup>). While the  $V_R$  between the LYH and the SCS was obviously higher than the river discharge (12.6 × 10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup>) and was similar to the SGD (1500 × 10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup>).

Nutrient transport fluxes from river, rainwater, and submarine groundwater into the study systems were based on the surveys undertaken in the period 2006–2009. Nutrients concentrations in rainwater were based on measurements during 2006–2009 at Wenchang City (Liu et al., 2011). SGD was ignored as no data available. The results of nutrient budgets showed that nutrient loads in the XH were mainly from riverine inputs, and the XH behaved as a sink of all nutrient elements except PO<sub>4</sub><sup>3-</sup> and DON. This indicated that nutrients were removed from the water bodies and buried into the sediments or transformed into other forms. This might be related to anthropogenic activities which lead to sedimentation rates increased rapidly and were about twice times as much as those before 1988 (Liu and Ge, 2012). The dissolved inorganic nutrient concentrations in submarine groundwater of the LYH were based on samples collected in April 2010 (Ji et al., 2013). The concentrations of dissolved organic nutrients in submarine groundwater were based on samples collected in April 2009 around the XH. As one nutrients source, rivers discharge into the LYH was very limited (0.4 ms<sup>-1</sup>, Ji et al., 2013). In addition, average concentrations of dissolved inorganic nutrients in those rivers (NO<sub>2</sub><sup>-</sup>: 0.67 μM, NO<sub>3</sub><sup>-</sup>: 1.63 μM, NH<sub>4</sub><sup>+</sup>: 3.40 μM, PO<sub>4</sub><sup>3-</sup>: 1.30 μM, DSi: 25.2 μM) were significantly lower than in other rivers along the eastern Hainan Island. Hence, dissolved organic and particulate nutrients were ignored as no data available. The results showed that the LYH behaved as a source of NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PIP, POP, PBSi, and LSi, and as a sink of NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, dissolved silicate, TDN, DON, TDP, and DOP. Groundwater was the major source of nutrients to the LYH.

Based on the water budgets, we knew that the WWE behaved as a sink of LSi, and as a source of PIP, POP, and PBSi. Both the Shamei Lagoon and the Wanquan River

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tidal inlet behaved as a source of particulate phosphorus and silicon without considered wastewater and aquaculture effluents.

## 4 Discussion

### 4.1 Biogeochemistry of nutrients in rivers and lagoons

#### 4.1.1 Nutrient dynamics in rivers and lagoons

The observed spatio-temporal variations of dissolved nutrients in rivers are probably the result of the systems and seasonally varying interaction of natural and anthropogenic factors. The DIN compositions in rivers were dominated by  $\text{NO}_3^-$  accounting for 56–98 % during both seasons (Tables 3, 4).  $\text{NO}_3^-$  concentrations in rivers were much higher than in other less-disturbed rivers in the world, such as the Amazon and Zaire (Cai et al., 2004), and lower than the tropical rivers like the Brantas River in Indonesia (141.5–169  $\mu\text{M}$ ), suggesting that inorganic nutrients might be derived from anthropogenic sources (Jänen et al., 2013), such as agriculture, aquaculture, and deforestation. Large amounts of  $\text{NO}_3^-$  can be released into nearby rivers where surface runoff in agricultural dominated regions (Jänen et al., 2013). The average concentrations of  $\text{PO}_4^{3-}$  in rivers were also between the pristine level (0.5  $\mu\text{M}$ ) and that for clean water (1.4  $\mu\text{M}$ ). The average DIN/DIP ratios (Tables 3, 4) were higher than the Redfield ratio indicating P limitation of primary production mainly due to high nitrate values. DON and DOP can account for large proportion of total dissolved N and P due to aquaculture activities, especially in shrimp ponds water. The concentrations of DSi were high in this tropical region, and maximum DSi concentrations were observed in the WQ with 327  $\mu\text{M}$ . DSi which is almost not affected by human activities is mainly derived from natural sources (Jennerjahn et al., 2009). The chemical weathering rate of the eastern Hainan Island, which is higher than the average global level (36  $\text{t km}^{-2} \text{yr}^{-1}$ ), is 42  $\text{t km}^{-2} \text{yr}^{-1}$  (Li, 2009). Tropical river basins play a major role in chemical weathering

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and transfer of DSi to rivers and oceans due to their geological and climatic settings (Jennerjahn et al., 2006; Bouwman et al., 2013).

Average concentrations of PP (0.5 ~ 1.4  $\mu\text{M}$ ) in the WWE, WQE, XH, and LYH were in lower level compared with estuaries around the world, such as Delaware estuary (PP 1 ~ 2  $\mu\text{M}$ , Lebo and Sharp, 1993), Humber estuary (PIP 14.3  $\mu\text{M}$ , POP 4.8  $\mu\text{M}$ , Prastka and Malcolm, 1994), Changjiang estuary (PIP 2.00  $\mu\text{M}$ , POP 1.02  $\mu\text{M}$ , Wang et al., 2009), this might be related to low SPM content in those estuarine-lagoons.

The PBSi levels in rivers and lagoons were lower than global average level (28  $\mu\text{M}$ ) (Conley, 1997), and also lower than other China rivers around Jiaozhou Bay (2.16 ~ 50.5  $\mu\text{M}$ ; Liu et al., 2008). However, the levels were higher than the Changjiang (2.0  $\pm$  1.6  $\mu\text{M}$ ; Liu et al., 2009). The contribution of PBSi to total silicon in these rivers was lower than the average global level (16%). The range of PBSi contents in the estuarine-lagoons (Table 3, Fig. 2) were comparable to that in Aulne estuary (5.6 ~ 52  $\mu\text{M}$ , Ragueneau et al., 2005) and Drake Passage estuary (4.24  $\mu\text{M}$ , Turner et al., 2003), while higher than Changjiang estuary (0.2 ~ 2.8  $\mu\text{M}$ , Liu et al., 2005) and Jiaozhou Bay (2.19  $\mu\text{M}$ , Luo et al., 2008). LSi levels along the eastern Hainan Island varied widely, and average concentrations were about 1.1–13 times in the Changjiang (21.1  $\pm$  12.1  $\mu\text{M}$ ; Liu et al., 2009). Both PBSi and LSi in the WWE and the WQE had positive correlation with SPM, hence, high concentrations of PBSi and LSi in these rivers and lagoons might be related to high weathering rate in tropical rivers.

Moreover, GW with high nutrients transports to the estuarine-lagoons (Table 3). Based on the naturally occurring Ra isotope distribution measured during the study periods, submarine groundwater discharge into the WWE, WQE, and LYH were calculated to be  $3.4 \pm 5.0 \text{ m}^3 \text{ s}^{-1}$  (Su et al., 2011),  $0.08 \pm 0.08 \text{ m}^3 \text{ s}^{-1}$  (Su et al., 2011),  $2.64\text{--}5.32 \times 10^6 \text{ m}^3 \text{ day}^{-1}$  (Ji et al., 2013), respectively. Large quantities of nutrients input into the small lagoon through SGD, eutrophication must be caused, especially in the LYH. Hypoxia conditions had been found in the inner bay of the LYH in August 2009 (Sun, 2011).

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5 Additionally, long-term alterations in nutrient fluxes can be caused by anthropogenic activities (Kaiser et al., 2013). Total organic carbon, total nitrogen, organic carbon and nitrogen isotope were analysed to reconstruct anthropogenic impacts on the Shamei Lagoon and the XH (Zhu et al., 2005; Jia et al., 2012; Liu and Ge, 2012). The results indicated that organic matter source and nitrate loading were increasingly affected by human activities in recent decades, and eutrophication was found (Jia et al., 2012; Liu and Ge, 2012). Population growth and economic development have been the main reason of increased terrestrial inputs. 80–100 % populations of 50 % of the coast countries which have higher population growth rate are concentrated within 100 km of the coast (Martínez et al., 2007). The annual population growth rate in the Hainan Island from 2000 to 2010 was 0.98 % and population has been growing in recent decades in Wenchang, Qionghai, and Wanning Cities (Fig. 5; Hainan Statistical Yearbook, 2010). Cultivated areas for crop production decreased in those cities in the past decades, while crop yield per unit area increased from 1095 kg ha<sup>-1</sup> in 1952 to 4083 kg ha<sup>-1</sup> in 1999. Hence, more fertilizers were used to increase crop production from 1987 to 15 2011, especially in Qionghai City. Furthermore, more than 50 % of the applied nitrogen could be transported to rivers due to low uptake efficiency of fertilizer (approximately 30–50 % in the tropical region, Han et al., 2010). Aquaculture areas increased, especially in Wenchang City with a factor of 8.8 (Fig. 5). Aquaculture can enhance N and P fluxes by recycling of the high organic matter load in their sediments. In addition, wastewater which directly emptied into ocean had been reduced for long-term development, however, 2.2 × 10<sup>7</sup> t wastewater still were discharged to the sea in 2010 in the island (Hainan Statistical Yearbook, 2010). Nutrient levels could be raised. Such as Danshuei River on Taiwan, the concentrations of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> were increased by an effluent input of 80 t yr<sup>-1</sup> into the upper of the river (Wen et al., 2008). Hence, the influence of human activities is very important for this tropical shallow coastal and must be considered. 25

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## 4.1.2 Areal yields of nutrients in rivers

The global scale DIN and DIP yields showed a significantly relationship between population density and runoff per unit area from the study by Smith et al. (2003). Smith et al. (2005) modified the regression analyses of data based on the hypothesis that small drainage basins differ significantly from larger basins. While, nutrients yields of rivers along the eastern Hainan Island show large deviations from the global scale predictions (Smith et al., 2003, 2005). The rivers catchments along the eastern Hainan Island fall in the size class  $10^2$ – $10^3$  km<sup>2</sup> of Smith et al. (2005), and the WQ catchment is in the size class  $10^3$ – $10^4$  km<sup>2</sup>. The observed areal yields of NO<sub>3</sub><sup>-</sup> in rivers were higher than from the tropical Kallada River, and comparable to the Citanduy River (Table 5) which is in the same size class with the WQ. DIN yields in the WJ, WQ, LG, LW, and TY rivers were much lower than the values predicted by Smith et al. (2003, 2005) models. The areal yields of DIN in the WC, JQJ, and LT rivers fell into the range predicted by the Smith et al. (2005) model. The areal yields of PO<sub>4</sub><sup>3-</sup> in rivers were significantly lower than those in the Kallada and Citanduy rivers. Population density was just 244 inhabitants km<sup>-2</sup> in 2010 (Hainan Statistical Yearbook, 2011) and major land use is agriculture in the study area. Hence, the excess nitrogen must be derived from fertilizer application was washed into the rivers. The use of fertilizer in Wenchang (2.6 tha<sup>-1</sup>), Qionghai (5.7 tha<sup>-1</sup>), and Wanning (2.1 tha<sup>-1</sup>) Cities in 2009 (Hainan Statistical Yearbook, 2010) were very higher than the global average (90 kg ha<sup>-1</sup>, Jennerjahn, 2012), and the uptake efficiency of nitrogen fertilizer were only 30–50 % in the tropical region (Han et al., 2010). Moreover, the use of pesticide in Wenchang (55 kg ha<sup>-1</sup>), Qionghai (60 kg ha<sup>-1</sup>), and Wanning (83 kg ha<sup>-1</sup>) Cities in 2009 (Hainan Statistical Yearbook, 2010) were higher than the China average (13 kg ha<sup>-1</sup>, Cui et al., 2006). Under such conditions nitrogen and phosphate could easily be washed into the river resulting in the high nitrogen and phosphate observed. Such as subtropical Nanliu River, Guangxi Province, PO<sub>4</sub><sup>3-</sup> was up to 3.7 μM that is consistent with high fertilizer application (Kaiser et al., 2013). While, P yields was low in our study tropical rivers

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systems, that might be related to adsorptions onto particulates as in the Chinese rivers (Liu et al., 2009). N and P omission were 42 % and 3–4 % from soils in Jakenan, respectively (Jennerjahn et al., 2009). P omission in our study area might be significantly lower than N and that might be the reason for the low P yield in those rivers.

#### 4.1.3 Estuarine-lagoons topography impacts

As one kind of wetlands, mangrove could offer a potential means to reduce the export of pollutants from aquaculture (nutrients, pesticides, organic matter). They receive nutrients to sustain the high productivity (Jennerjahn, 2012). Mangrove may act as filters for river derived nutrient pollution in the tropics and subtropics to protect seagrass and coral reefs ecosystems (Jennerjahn, 2012). Mangrove sediments are sinks of nitrogen and phosphorus in the WWE (Liu et al., 2011). However, aquaculture ponds can threaten mangrove ecosystems (Duke et al., 2007) through release large quantities of effluents enriched with nutrient elements (Molnar et al., 2013). 73 % of the fringing riverine mangrove has been lost since 1960s, replaced by aquaculture ponds in the WWE (Krumme et al., 2012), and cover approximately 750 ha in nowadays (Unger et al., 2013). Aquaculture ponds cover about 21.6 km<sup>2</sup> of the WWE (Herbeck et al., 2013). 6151 tyr<sup>-1</sup> total organic carbon, 1292 tyr<sup>-1</sup> total nitrogen, and 51 tyr<sup>-1</sup> dissolved phosphate from pond aquaculture are exported to coastal and back-reef waters of the northeast Hainan Island (Herbeck et al., 2013). Untreated municipal sewage from Wenchang City is another potential dissolved nutrients and particulate organic matter source for the estuary (Herbeck et al., 2011). Material temporarily trapped at low tides in the lagoon and the filter function of the Bamen Bay could reduce the nutrient export to coastal water considerably (Zhang et al., 2013). While, the estuary is a shallow water body and the water residence time in the estuary is short (about 7.8 days, Liu et al., 2011), large rainfall lead to high river discharge and the estuarine filter function was interrupted which lead to material released. High SPM (42 mgL<sup>-1</sup>) and nutrients were found at the reef flat of Dongjiao Yelin and Tanmen (Herbeck et al., 2013; Roder et al., 2013), resulting in reduction of light availability and stress caused by sedimentation in

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the reef flat (Roder et al., 2013). More anthropogenic organic matter in the WWE was transported to the coastal sea due to the degradation of mangrove forests and increase of aquaculture in past decades (Bao et al., 2013). More nutrients would be transported to the ocean in the meantime. This, in turn, will destruct the coastal ecosystems.

5 Similar to the WWE, the WQE is also a typical lagoon–tidal inlet–barrier system, freshwater with high nutrients directly empty into coastal region through the narrow tidal inlet (Fig. 1), especially when large river runoff which induced by heavy rain and freshwater could track up to 4.4 km off the estuary (Li et al., 2013). The WQE is much smaller than the WWE and there is no large mangrove area around the estuary. Additionally, the WQ runoff is larger than the WC and WJ, the interaction between estuary and sea is much stronger. Hence, estuarine filter function will be easily interrupted. The Shamei Lagoon, which is in the southern part of the estuary, approximately 60 % used for fish and shrimp ponds, connected with the sea through the tidal inlet. The JQJ and the LG with high nutrients empty into the lagoon from the west and south, respectively. 10 Nitrogen isotope also indicated that large inputs of nitrogen and phosphorus stimulated the growth of phytoplankton in the lagoon (Jia et al., 2012). This suggested that parts of nutrients accumulated in the lagoon, leading to eutrophication in the lagoon. While, nutrient enrichment often resulted in increasing algal biomass, reducing water clarity, and loss of submerged macrophytes in coastal waters (Spivak et al., 2009). Hence, 20 the ecology system in coastal zone off the WQE would be more easily affected by freshwater with high nutrients.

Terrestrial input, aquaculture activities, and phytoplankton should be important sources of nutrients in the XH. The LT and the LW with high nutrients (Table 4) directly empty into the northern lagoon that might be the reason of high nutrients in station XH2. The Taiyanghe (TY) was diverted directly empty into the SCS in 1972 (Wang et al., 2006), after that, river discharge was reduced by about 50 % and just 26.5 m<sup>3</sup> s<sup>-1</sup> in the lagoon (Gong et al., 2008). The morphology of the lagoon had been changed by human interventions since 1972, sand barrier continuous extended and the tidal inlet was narrowed, tidal current was difficult to reach the middle and southern 25

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lagoon. The northern part of the lagoon was easily affected by tidal current and river runoff compared with the inner lagoon. Hence, the southern part of the lagoon became a dead zone where residence time was longer than 150 days (Gong et al., 2008). Total organic carbon and total nitrogen in sediment analyses were used to reconstruct anthropogenic impacts on the lagoon (Liu and Ge, 2007). The results indicated that authigenic organic matter in the lagoon significantly increased since 1988 due to aquaculture activities, and large quantities of nutrients input induced deterioration of water quality of the XH (Liu and Ge, 2007). In addition, entrance mouth decreased from 140 m to less than 30 m in recently 30 yr because of reclamation and cage culture in the tidal inlet (Wang et al., 2003), causing serious inundation in October 2000 when a violent typhoon storm hit the island (Yu et al., 2002; Wang et al., 2003). Hence, high nutrients would be kept in the lagoon, resulting in algae or phytoplankton blooms and depleted oxygen of the Xiaohai Lagoon (Liu and Ge, 2012). Isotope compositions in sediment also indicated that eutrophication had been caused by anthropogenic activities in the southern and middle of the lagoon (Liu and Ge, 2012). Additionally,  $7.7 \times 10^4 \text{ mol day}^{-1}$  of DIN,  $0.2 \times 10^3 \text{ mol day}^{-1}$  of  $\text{PO}_4^{3-}$ , and  $31.5 \times 10^4 \text{ mol day}^{-1}$  of dissolved silicate were directly transported to the SCS through the TY in August 2008, coastal ecosystems would be affected.

Lots of fishing cages were also installed in the tidal channel in the LYH. Total organic carbon and polyunsaturated fatty acids (PUFAs) contents in sediments indicated that phytoplankton was the main source for organic matter (Sun, 2011). High nutrient concentrations which caused by aquaculture activities lead to high primary productivity in the lagoon. Eutrophication had appeared in the northwest of the inner lagoon (Sun, 2011). Oxygen might be depleted by algae or phytoplankton blooms in the inner lagoon.

The WQE, XH, and LYH were all separated with the ocean by a sand barrier. All the barriers continue to grow under the action of southeasterly winds that transported sediment from south to north (Wang and Li, 2006). Combined the effects of human activities and natural factors, the estuarine–lagoons may be changed to a closed water body and

eutrophication will occur due to high nutrients level. The relatively small, dynamic and fragile ecosystems must be altered. Such changes could result in changing input from the coastal system including riverine fluxes and activities such as mariculture, aeolian input (dust) or even changes in circulation patterns (Kress et al., 2005).

## 4.2 Biogeochemistry and sources of nutrients in the coastal region

Riverine nutrient input tends to be the dominant source in many coastal waters. River discharge is the main factor controlling matter transfer from land to sea, especially in small rivers (Ludwig et al., 2009; Han et al., 2012). Compare with other coastal region of China Sea which have large river input, the coast receives relatively little continental runoff. The influence of the Changjiang can be tracked up to 300–400 km over the shelf during high discharge (Zhang et al., 2007). The Pearl River plume can reach the Beibuwan through Qiongzhou Strait (Tang et al., 2003). High nutrient concentrations were only appeared in near shore region which can be easily affected by large runoff. Our results show that nutrient input to coastal waters is very low at low discharge, like July–August 2008 cruise, despite significant land use changes along the coast. In addition, the seasonal variation of salinity, temperature, and nutrients appeared to be closely coupled with monsoons. The WQ discharge was  $122 \text{ m}^3 \text{ s}^{-1}$  and  $278 \text{ m}^3 \text{ s}^{-1}$  in August 2007 and April 2009, respectively. Under the combine effects of large river discharge and winds direction, low salinity with high nutrient plume extended different pathway (Fig. 3). All estuarine–lagoons along the eastern Hainan Island connected with the ocean through a narrow tidal channel, large quantities of nutrients would be retained in the estuaries, especially particulate species.

SGD was a potentially important source of nutrients transport from land to sea off the Bamen Bay based on the naturally occurring  $^{226}\text{Ra}$  isotope measured during 2007 cruise (Su et al., 2010). Horizontal eddy diffusion flux of nutrients from coast to offshore area were estimated based on offshore nutrient gradients and horizontal eddy diffusion coefficient value which were estimated by  $^{226}\text{Ra}$  in August 2007 (Su et al., 2011).  $2.3 \times 10^8$  mol of N,  $1.5 \times 10^7$  mol of P, and  $5.1 \times 10^8$  mol of Si with a 100 km coastline within six

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months were transported from the study area to the SCS. Li et al. (2012) has reported that spatially discrete and temporally episodic nutrient fluxes which caused by physical phenomena such as eddy, fronts and filaments could play an important role in regions where phytoplankton growth is limited by nutrient. Compared with the estimates made  
 5 Chen et al. (2001), the horizontal transport of nutrients into the SCS supplied a small portion. Submarine groundwater enriched in nutrients with high N/P ratio may have an important impact on coastal ecosystems (Su et al., 2010). Its potential impact on the coastal environment of the eastern Hainan Island should be paying more attention and further investigation.

10 Furthermore, coastal erosion might be another significant source of materials to the coastal which transported by along shore drift and coastal currents. The trend of sea level rise of  $0.92 \text{ mm yr}^{-1}$  established for the east coast based on 1977–1978 and 1980–1993 could be responsible for the erosion (Wang, 2002). Additionally, the width of reef flat approximately 500–1000 m. Coral reef was subjected to serious break due to  
 15 human activities in recent twenty years, inducing shore erosion. The coastline receded  $\sim 10 \text{ m}$  per year (Wang, 1998).

### 4.3 Nutrient fluxes in estuarine-lagoons along the eastern Hainan Island

The volume ( $V_S$ ) of the XH and the LYH were  $6.6 \times 10^7 \text{ m}^3$  and  $5.0 \times 10^7 \text{ m}^3$ , respectively. The total water exchange time ( $\tau$ ) of the XH and the LYH can be estimated from the ratio  
 20  $V_S/(V_X + V_R)$ , were 15.2 days and 4.4 days, respectively. Nutrient fluxes from estuarine-lagoons to the SCS were estimated as the sum of the net residual flux ( $V_R C_R$ ) and the mixing flux ( $V_X C_X$ ). The dissolved inorganic nutrient fluxes were 392–1878 times the riverine input ( $F_{\text{model}} = V C_Q$ ) in the LYH. While, with the exception of  $\text{PO}_4^{3-}$  and DON, nutrient fluxes to the SCS were lower than riverine input in the XH. This might be related  
 25 to aquaculture activities which decreased flushing efficiency of the tidal dynamics, large quantities of nutrients were retained in the XH as a result.

Total nutrient fluxes from this four estuarine-lagoons to the coastal region are  $40.6 \times 10^7 \text{ mol yr}^{-1}$  for DIN,  $1.08 \times 10^7 \text{ mol yr}^{-1}$  for  $\text{PO}_4^{3-}$ ,  $128 \times 10^7 \text{ mol yr}^{-1}$  for  $\text{Si}(\text{OH})_4$ ,

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$16.4 \times 10^7 \text{ mol yr}^{-1}$  for DON,  $0.71 \times 10^7 \text{ mol yr}^{-1}$  for DOP,  $1.01 \times 10^7 \text{ mol yr}^{-1}$  for PIP,  $0.64 \times 10^7 \text{ mol yr}^{-1}$  for POP,  $8.50 \times 10^7 \text{ mol yr}^{-1}$  for PBSi, and  $131 \times 10^7 \text{ mol yr}^{-1}$  for LSi. DON represented 29 % of TDN, DOP was 40 % of TDP, and PP accounted for 48 % of TP. This indicated that fluxes of both dissolved organic and particulate P to the SCS, were important and might determine the impact on receiving coastal ecosystems, especially within the coral reef region. The flux ratio of  $\text{DIN} : \text{PO}_4^{3-}$  and  $\text{Si(OH)}_4 : \text{DIN}$  were approximately 40 and 3.0, respectively. The loading ratio derived by us exceeded the Redfield ratio, demonstrating that the ecosystem in the coastal zone of the SCS would be affected by the nutrient transport. Total nitrogen and dissolved phosphate transported to coastal region through effluent of shrimp ponds accounted for 22 % of nitrogen fluxes and 15 % of phosphorus fluxes, respectively. Primary production in continental shelf region ( $< 200 \text{ m}$ ) of the SCS would be  $602.3 \times 10^6 \text{ tC yr}^{-1}$  based on two seasons (summer and winter) data (Ning et al., 2004). We apply the Redfield stoichiometric ratio ( $\text{C} : \text{N} : \text{P} = 106 : 16 : 1$ ) for phytoplankton growth to estimate,  $10.7 \times 10^7 \text{ tyr}^{-1}$  of nitrogen and  $6.6 \times 10^6 \text{ tyr}^{-1}$  of phosphate would be assimilated by primary producers. The estuarine–lagoons contribution to the SCS could account for 0.005 % of nitrogen and 0.005 % of phosphate, respectively. The contribution of terrigenous nutrient input in this tropical shallow coastal region to primary production of the SCS is limited.

Submarine groundwater discharge (SGD), which is the major source of nutrients in the LYH, was not included in the water budgets for the XH. If SGD in the XH was estimated based on SGD observations in the WWE ( $3.4 \pm 5.0 \text{ ms}^{-1}$ , Su et al., 2011) that all collected from wells, SGD accounted for  $\sim 13 \%$  of freshwater discharge in the XH. Hence, the XH would behave as a sink of all nutrient elements when SGD is considered. While, if it was estimated based on observations in the LYH ( $4.11 \times 10^6 \text{ m}^3 \text{ day}^{-1}$ , Ji et al., 2013), SGD were approximately 1.8 times the freshwater discharge in the XH. In addition, the average concentrations of nutrients in groundwater around the XH in April 2009 were  $1142 \pm 105 \mu\text{M}$  for DIN,  $51.9 \pm 56.9 \mu\text{M}$  for  $\text{PO}_4^{3-}$ , and  $548 \pm 182 \mu\text{M}$  for DSi,  $117 \pm 125 \mu\text{M}$  for DON, and  $8.19 \pm 9.14 \mu\text{M}$  for DOP. SGD would be the major source of nutrients in the XH. Furthermore, as an important lagoon for aquatic products

and fishery port in Wanning City (Gong et al., 2008), aquaculture effluents were not included in the water budgets for the XH, and also not included in the LYH. The area for marine aquaculture in Wanning City rose from 233 ha in 1989 to 1495 ha in 2008 (Hainan Statistical Yearbook, 1992, 2009). The uncertainties can be up to 25 % if we applied aquaculture effluents in the WWE ( $210 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ , Liu et al., 2011) to estimate the water budgets in the XH. It can be up to 14 % in the LYH. Hence,  $\text{PO}_4^{3-}$  and DON budgets in the XH are affected reversing a source to a sink when SGD and aquaculture effluents are considered, while,  $\text{NO}_2^-$  budget is affected switching from a source to a sink when aquaculture effluents is considered in the LYH. More nutrients would be storage in the XH and the LYH when SGD and aquaculture effluents were taken into account. Additionally, domestic sewage and agriculture pollutants (e.g., pesticides and fertilizers) were not included in the water budgets. Sewage emissions are an important source of nutrients for freshwater and coastal marine ecosystems (Bouwman et al., 2013). Therefore, more investigations on submarine groundwater, wastewater and aquaculture transports are needed.

#### 4.4 The typhoon impacts on nutrient dynamics

The eastern Hainan Island is the high precipitation region of the whole island with increasing rate at  $2.228 \text{ mm yr}^{-1}$  (Wang et al., 2006), and that typhoon-induced rainfall can account for 36 % of total annual rainfall (Wang, 1985). Nutrient loads in rivers and phytoplankton biomass can be increased by typhoon-related flood. Increasing N and P loading of rivers can enhance rates of photosynthetic and heterotrophic productivity, resulting in fundamental changes to aquatic food webs (Bouwman et al., 2013). Typhoon Kammuri made landfall along the south coast of China in the western Guangdong Province on 6 August 2008. On 7 August 2008 it passed the study area in a distance of approximately 200 km (Herbeck et al., 2011). The daily water discharge of Nandu River which empties into Qiongzhou Strait increased from  $249 \text{ m}^3 \text{ s}^{-1}$  on 6 August 2008 to  $1615 \text{ m}^3 \text{ s}^{-1}$  on 7 August. As the typhoon passed at some distance from the WQ, the freshwater discharge exhibited a peak ( $220 \text{ m}^3 \text{ s}^{-1}$ ) 5 days after the typhoon.



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The salinity varied between 0–31.2 before the typhoon and changed to 0–1.0 after the typhoon in the WQE. Freshwater could reach the estuary mouth after the typhoon where salinity was approximately 31 before the typhoon. The concentrations of SPM increased from 3.05–21.5 mgL<sup>-1</sup> to 12.0–23.3 mgL<sup>-1</sup> in the estuary. Typhoon-related rainfall could reinforce the effect of land-derived anthropogenic nutrients (Jennerjahn, 2012). Nutrient fluxes from the WQE to the SCS after the typhoon in August 2008 were 2.6–4.7 times pre-typhoon. River discharge, SPM and nutrients which derived from agriculture, aquaculture and urban effluents exported into coastal were also increased in the WQE after the typhoon (Herbeck et al., 2011; Liu et al., 2011). Furthermore, coral reef was affected by large nutrients and SPM loads (Roder et al., 2013).

A violent typhoon event made landfall in Wanning City with rainfall of 355 mm per day on October 2000, some towns around the lagoon, cultivated area, and fish ponds were submerged (Tian and Li, 2007). Typhoon Damrey made landfall on the eastern Hainan Island on 25 September 2005 with rainfall > 300 mm on 26 September (Zheng and Tang, 2007). The daily water discharge of the WQ increased from 64.4 m<sup>3</sup> s<sup>-1</sup> to 278 m<sup>3</sup> s<sup>-1</sup> after the first-rain (~ 118 mm) event in April 2009. If typhoons, which are often accompanied by heavy rainfall like Damrey, directly made landfall in the study area, large fluvial discharge of the WQ must be caused. Large quantities of dissolved and particulate materials must be exported to coastal waters as a result. The section observations in August 2007 took place following a typhoon event, low salinity (22.0) with high nutrients (NO<sub>3</sub><sup>-</sup>: 25.0 μM) appeared in coastal region off the WQE (Fig. 3a). In addition, atmospheric deposition during normal typhoon events (rainfall 300 mm, Liu et al., 2011) can approximately represent 11 %, 17 %, and 10 % of DIN, PO<sub>4</sub><sup>3-</sup>, and DSi of the study coastal region for annual atmospheric deposition, respectively. Offshore water is more easily affected by typhoon rain than normal rain discharge which tends to be confined to the coastal shelf.

Upwelling is a significant source of nutrients entering the shelf ecosystem, in particular phosphate, affecting the succession of phytoplankton populations (Liu et al., 2000; Dafner et al., 2007; Ou et al., 2008). Upwelling events occur frequently during summer

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monsoon along the eastern Hainan shelf (Su et al., 2011). Additionally, typhoons mainly occur from May to November which can affect Hainan Island (Ren et al., 2002; Liu et al., 2011). Offshore upwelling and coastal currents appear to be the dominant factors controlling the transport and source of the surficial sediments off the eastern Hainan Island (Huang et al., 2013). Typhoon with upwelling would nourish phytoplankton biomass by inducing transport of nutrient-rich water from both estuaries to offshore and sublayer to surface water in the eastern Hainan coast. Zheng and Tang (2007) reported that two phytoplankton blooms were triggered by Typhoon Damrey which passed through the Hainan Island during September 2005, nutrients were transported from land and below to the surface water via upwelling.

Typhoon frequency of 2.5 per year directly made landfall on the Hainan Island (Liu et al., 2011). Tropical storms are likely to increase in strength, duration, destructivity, and frequency in response to global climate change (Knutson et al., 2010; Kaiser et al., 2013). For coastal waters this will result in more frequent short-term changes of fresh-water and nutrient inputs, especially in the study area where water residence time was so short and easily interrupted. Increased hurricane/typhoon activity may enhance silicate weathering rates and exacerbate current sediment delivery loads, thereby increasing POC delivery and burial (Goldsmith et al., 2008). Hence, more attention should be paid for the influence of typhoon.

## 5 Conclusions

This study provides data for dissolved and particulate nutrients concentrations along the eastern Hainan Island during both wet and dry seasons. Under the combine effects of natural process and human activities, large quantities of nutrients transport from agriculture, aquaculture, and urban wastewater to the coastal region. Coastal ecosystems would be affected.

All nutrients had seasonal variation and decreased from rivers toward the coast. Nutrient levels in rivers were mainly affected by agriculture. Rivers are enriched with



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DIN and DSi, and depleted with  $\text{PO}_4^{3-}$ . The  $\text{PO}_4^{3-}$  concentrations and areal yields in rivers are lower than in other tropical rivers. The dissolved silicate levels and areal yields are higher for world tropical river systems due to rock type and high chemical weathering.

Nutrient processes in estuarine–lagoons were mainly affected by aquaculture activities. The flushing efficiency of the tidal dynamics was decreased. While the water residence time of estuarine–lagoons was short. Hence, estuarine–lagoons had a short response time to flood events and large quantities of nutrients were transported to coastal region accompanied with freshwater.

Nutrients were mainly affected by natural process in the shelf and still kept oligotrophic. Nutrient ratios show that the potential limiting nutrient phytoplankton biomass within the coral reef region was P due to terrestrial input, while N was the limited element for phytoplankton growth in the eastern shelf region of the Hainan Island. A simple steady-state box model was used to construct nutrient budgets to investigate nutrient biogeochemical process along eastern coast of the Hainan Island. The model results indicate that riverine input was the major source of nutrients to the WWE, WQE, and the XH, and it was GW in the LYH. Particularly riverine nitrogen and phosphorus exports into coastal stem from anthropogenic land-based sources. Most nutrients would be buried in the sediment or transformed to other forms in the estuarine–lagoons. The estuarine–lagoons exported approximately 0.005 % of nitrogen and 0.005 % of phosphorus for phytoplankton production in the SCS shelf (< 200 m).

**Supplementary material related to this article is available online at:**

**<http://www.biogeosciences-discuss.net/10/9091/2013/>**

**[bgd-10-9091-2013-supplement.pdf](#)**

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**Table 1.** Hydrographic characteristics of rivers along the eastern Hainan Island. (WC: Wenchanghe; WJ: Wenjiaohe; WQ: Wanquan River; JQJ: Jiuqujiang; LG: Longgunhe; LT: Longtouhe; LW: Longweihe; TY: Taiyanghe) (Wang, 2002; Zhang et al., 2006).

Source	Length (km)	Drainage Area (km <sup>2</sup> )	Discharge (m <sup>3</sup> s <sup>-1</sup> )	Rainfall (mm)				Evaporation (mm)			
				spring	summer	autumn	winter	spring	summer	autumn	winter
WC Douniu town	37.1	380.9	9.1	332.2	680.7	549.8	89.4	473.4	570.3	420.7	269.9
WJ Pokou village	56.0	522.0	11.6								
WQ Wuzhi mountain	163.0	3693.0	163.9	388.3	655.7	872.9	143.1	538.8	620.4	412.5	289.6
JQJ Wangtian lang	50.0	279.8	10.2								
LG Xianggen ridge	38.6	145.7	6.0								
LT Huangzhu ridge	42.2	140.1	6.1	429.1	775.3	1102	132.3	524.7	545.4	339.9	265.4
LW Liulian ridge	61.6	197.0	7.5								
TY Changsha ridge	82.5	576.3	23.8								

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**Table 2.** Temperature, salinity, and SPM in surface water of rivers, lagoons, and coastal region during the investigation periods. The average values are shown in parentheses.

Cruise	Temperature (°C)	Salinity	SPM (mgL <sup>-1</sup> )
<b>WC</b>			
Dec 2006	24.1	0	7.85
Aug 2007	27.0	0	12.7
Jul–Aug 2008 ( <i>n</i> = 2)	28.1–30.6 (29.4)	0.1–0.9	14.8–46.3 (30.5)
Mar–Apr 2009	27.1–27.9 (27.5)	0–3.9	11.1–19.8 (15.4)
Aug 2009	31.5	0	19.7
<b>WJ</b>			
Dec 2006	23.3	0	10.2
Aug 2007	–	0	8.31
Jul–Aug 2008 ( <i>n</i> = 3)	32.0–33.0 (32.7)	0	15.6–27.3 (19.6)
Mar–Apr 2009	25.7–27.2 (26.4)	0.1–0.4	35.1–85.1 (51.5)
<b>WQ</b>			
Dec 2006	–	0–0.1	11.9–12.6 (12.4)
Aug 2007	–	0	6.50–15.7 (9.73)
Jul–Aug 2008 ( <i>n</i> = 8)	29.3–32.5 (31.5)	0	4.91–18.0 (9.88)
Mar–Apr 2009	25.0–28.7 (27.0)	0	7.47–71.1 (26.3)
Aug 2009	–	–	8.92–15.9 (12.5)
JQJ (Mar–Apr 2009)	26.8	0	26.7
<b>XH</b>			
Jul–Aug 2008 ( <i>n</i> = 6)	27.1–27.7 (27.4)	5.8–10.4	13.9–25.6 (18.5)
Mar–Apr 2009	24.6–25.3 (25.0)	1.8–7.8	7.2–16.2 (9.94)
Aug 2009	28.2–30.9 (29.7)	9.2–16.5	11.8–55.7 (29.6)
<b>LYH</b>			
Jul–Aug 2008 ( <i>n</i> = 6)	27.7–29.1 (28.5)	9.1–18.1	3.93–13.1 (7.64)
Mar–Apr 2009	24.7–30.4 (27.2)	10.1–33.2	4.68–11.6 (9.21)
Aug 2009	–	13.4–32.2	2.08–20.6 (9.08)
<b>Coastal region</b>			
Aug 2007	27.1–31.1 (28.2)	22.0–34.2	0.56–8.44 (3.34)
Jul–Aug 2008 ( <i>n</i> = 39)	27.6–32.0 (29.5)	24.4–33.9	0.32–6.29 (2.16)
Aug–Sep 2008	26.3–33.6 (29.6)	29.7–33.7	–
Mar–Apr 2009	25.3–25.9 (24.5)	29.7–32.9	2.01–11.0 (4.90)

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**Table 3.** Mean  $\pm$  SD of nutrients concentrations ( $\mu\text{mol L}^{-1}$ ) and molar ratios in surface water of the Wenchanghe (WC), Wenjiaohe (WJ), Wanquan River (WQ), shrimp ponds, and groundwater (GW) during the investigation periods. (wet season: May to October; dry season: November to April).

	season	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{NH}_4^+$	TDN	DON	$\text{PO}_4^{3-}$	TDP	DOP
WC	dry	69.5 $\pm$ 29.4	2.22 $\pm$ 0.93	10.4 $\pm$ 5.79	123 $\pm$ 63.2	40.9 $\pm$ 29.1	0.55 $\pm$ 0.48	0.89 $\pm$ 0.36	0.34 $\pm$ 0.20
WC	wet	65.4 $\pm$ 2.61	2.79 $\pm$ 1.25	31.9 $\pm$ 22.3	119 $\pm$ 20.6	18.7 $\pm$ 5.56	0.66 $\pm$ 0.36	2.80 $\pm$ 2.74	2.14 $\pm$ 2.39
WJ	dry	90.2 $\pm$ 1.53	2.86 $\pm$ 0.10	3.92 $\pm$ 0.77	156 $\pm$ 3.85	59.3 $\pm$ 1.78	1.00 $\pm$ 0.09	1.51 $\pm$ 0.34	0.50 $\pm$ 0.26
WJ	wet	23.8 $\pm$ 3.10	2.18 $\pm$ 0.13	7.72 $\pm$ 0.56	79.9 $\pm$ 25.9	52.9 $\pm$ 14.5	0.35 $\pm$ 0.13	2.78 $\pm$ 1.19	2.42 $\pm$ 1.23
WQ	dry	52.4 $\pm$ 16.5	1.02 $\pm$ 0.42	4.80 $\pm$ 2.22	71.8 $\pm$ 18.8	13.5 $\pm$ 11.6	0.80 $\pm$ 0.21	1.57 $\pm$ 0.45	0.77 $\pm$ 0.41
WQ	wet	39.3 $\pm$ 13.7	0.91 $\pm$ 0.64	5.81 $\pm$ 3.97	57.9 $\pm$ 17.0	11.9 $\pm$ 5.34	0.57 $\pm$ 0.34	2.98 $\pm$ 1.66	2.41 $\pm$ 1.75
Shrimp	dry	6.85 $\pm$ 11.1	32.2 $\pm$ 95.4	4.84 $\pm$ 6.84	83.3 $\pm$ 126	39.4 $\pm$ 21.7	1.18 $\pm$ 1.56	1.79 $\pm$ 1.89	0.61 $\pm$ 0.40
Shrimp	wet	9.67 $\pm$ 4.91	103 $\pm$ 92.7	93.7 $\pm$ 77.6	309 $\pm$ 211	103 $\pm$ 39.0	6.17 $\pm$ 5.43	6.87 $\pm$ 5.89	0.70 $\pm$ 0.49
GW	dry	592 $\pm$ 434	0.57 $\pm$ 1.06	3.63 $\pm$ 4.42	725 $\pm$ 555	75.5 $\pm$ 81.3	13.1 $\pm$ 31.4	15.3 $\pm$ 34.5	2.22 $\pm$ 4.95
GW	wet	446 $\pm$ 490	1.02 $\pm$ 1.87	7.07 $\pm$ 13.4	492 $\pm$ 512	37.3 $\pm$ 38.0	2.09 $\pm$ 5.84	2.43 $\pm$ 6.25	0.34 $\pm$ 0.47

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Table 3. Continued.

	season	PIP	POP	Si(OH) <sub>4</sub>	PBSi	LSi	DIN/DIP	Si/DIN
WC	dry	1.22 ± 0.37	0.99 ± 0.53	167 ± 18.4	4.28 ± 3.77	69.8 ± 44.4	232 ± 160	2.3 ± 0.9
WC	wet	1.34 ± 0.21	0.93 ± 0.17	151 ± 25.6	3.28 ± 3.03	159 ± 178	171 ± 67	1.6 ± 0.3
WJ	dry	2.31 ± 0.81	1.38 ± 0.21	97.8 ± 1.92	20.4 ± 4.52	269 ± 50.0	97 ± 7.9	1.01 ± 0.04
WJ	wet	1.25 ± 0.10	1.60 ± 0.87	118 ± 6.43	6.20 ± 3.66	89.3 ± 37.9	99.2 ± 26.9	4.69 ± 2.20
WQ	dry	0.51 ± 0.27	0.54 ± 0.26	327 ± 69.1	7.64 ± 3.16	156 ± 155	78.9 ± 29.5	6.01 ± 1.67
WQ	wet	0.47 ± 0.29	0.45 ± 0.15	317 ± 29.0	4.88 ± 1.61	61.7 ± 30.1	95.1 ± 41.3	7.85 ± 3.14
Shrimp	dry	–	–	48.1 ± 56.5	–	–	40 ± 70	45 ± 86
Shrimp	wet	–	–	54.6 ± 29.4	–	–	36 ± 14	2.2 ± 3.6
GW	dry	–	–	330 ± 157	–	–	8430 ± 15767	6.6 ± 19
GW	wet	–	–	333 ± 164	–	–	3277 ± 8736	9.03 ± 19

"–" means no data

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**Table 4.** Nutrients ( $\mu\text{molL}^{-1}$ ) concentrations in surface water of other small rivers along the eastern Hainan Island in different season. (LY: Lunyanghe; YD: Yandunhe; SL: Shanlonghe; TYR: Tayang River; TY: Taiyanghe).

	date	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{NH}_4^+$	TDN	DON	$\text{PO}_4^{3-}$	TDP	DOP	$\text{Si}(\text{OH})_4$	PBSi	LSi	DIN/DIP	Si/DIN
SL	Mar, 2009	97.2	5.39	4.14	140	33.3	0.28	0.54	0.26	237	–	–	381	2.2
YD	Mar, 2009	144	2.63	2.28	180	30.9	0.14	0.52	0.38	210	–	–	1063	1.4
LY	Mar, 2009	122	5.42	5.55	169	35.6	0.60	0.93	0.33	214	–	–	218	1.6
TYR	Aug, 2009	57.3	1.20	9.77	123	54.6	0.75	1.56	0.81	195	16.8	23.6	91	2.9
JQJ	Aug, 2008	35.6	0.95	7.44	64.9	20.9	0.55	2.21	1.67	101	–	–	143	1.3
JQJ	Mar, 2009	96.6	1.71	5.09	142	38.7	0.10	0.78	0.68	101	10.5	70.5	1034	1.0
JQJ	Aug, 2009	70.2	2.89	6.89	130	50.4	2.16	–	–	148	11.7	98.9	37	1.9
LG	Aug, 2009	35.5	0.18	4.76	75.4	40.5	0.18	0.70	0.52	133	1.86	33.4	225	3.3
LT	Aug, 2008	55.7	0.62	8.30	91.1	20.3	0.38	3.04	2.66	195	–	–	170	3.0
LW	Aug, 2008	32.9	0.62	9.16	53.5	10.8	0.24	3.00	2.76	246	–	–	178	5.8
TY	Aug, 2008	35.1	0.98	8.01	50.3	6.25	0.11	2.44	2.34	180	–	–	401	4.1

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**Table 5.** Observed nutrient yields (Obs.) ( $\times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ ) (A) in rivers along the eastern Hainan Island. Predicted yields are calculated based on the formulas of (a) Smith et al. (2003) and (b) Smith et al. (2005). Nutrients areal yields ( $\times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ ) (B) of tropical and nontropical rivers (data are taken from Jennerjahn, 2012).

Panel A: Observed nutrient yields ( $\times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ ) of rivers along the eastern Hainan Island							
	DIN			$\text{PO}_4^{3-}$			DSi
	a	b	Obs.	a	b	Obs.	
WC	42	69	51	2.4	1.4	0.5	120
WJ	40	66	37	2.2	1.3	0.4	76
WQ	67	76	62	3.8	2.3	0.9	448
JQJ	58	89	78	3.3	1.8	1.1	134
LG	64	96	43	3.6	1.9	0.2	160
LT	67	99	77	3.8	2.0	0.5	268
LW	60	91	43	3.4	1.8	0.3	319
TY	64	96	46	3.6	1.9	0.1	234

Panel B: The areal yields ( $\times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$ ) of nutrients in the tropical and nontropical rivers			
	DIN	DSi	phosphate
Large tropical rivers	13	81	0.9
Large nontropical rivers	23	36	1.6
Kallada, India	10	81	6.0
Brantas, Indonesia	91	149	2.9
Citanduy, Indonesia	51	284	2.0

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**Table 6.** Nutrient budgets ( $10^6 \text{ molyr}^{-1}$ ) in the Xiaohai Lagoon (XH) and the Laoyehai Lagoon (LYH)  $C_1$  and  $C_2$  are the average nutrient concentrations in the system of interest and the adjacent system, respectively.  $V_R C_R$ ,  $V_X C_X$ , and  $\Delta$  are the residual nutrient transport out of the system of interest, the mixing exchange flux of nutrients, and the non-conservative flux of nutrients, respectively. Negative and positive signs of  $\Delta$  indicate that the system is a sink or a source, respectively.

	NO <sub>3</sub>	NO <sub>2</sub>	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	Si(OH) <sub>4</sub>	TDN	DON	TDP	DOP	PIP	POP	PBSi	LSi
Freshwater discharge (= $V_Q C_Q$ )													
XH	40.0	0.52	7.28	0.26	184	60.3	13.0	2.52	2.26	2.15	1.56	18.6	163
LYH	0.03	0.007	0.04	0.02	0.32	–	–	–	–	–	–	–	–
Atmospheric deposition (= $V_P C_P$ )													
XH	1.10	0.01	1.40	0.02	0.07	3.37	0.85	0.04	0.02	–	–	–	–
LYH	0.24	0.003	0.31	0.004	0.01	0.74	0.17	0.009	0.005	–	–	–	–
Groundwater discharge (= $V_G C_G$ )													
LYH	318	1.11	8.04	18.2	256	510	176	30.5	12.3	–	–	–	–
Residual flow (= $V_R C_R$ , $C_R = (C_1 + C_2)/2$ )													
XH	-4.85	-0.42	-3.35	-0.32	-62.5	-22.3	-13.7	-0.62	-0.29	-0.48	-0.61	-6.01	-45.4
LYH	-5.22	-1.57	-19.8	-1.56	-37.8	-63.6	-37.1	-2.19	-0.64	-0.60	-0.69	-5.52	-26.0
Mixing exchange (= $V_X C_X$ , $C_X = (C_1 - C_2)$ )													
XH	-5.24	0.012	-3.30	-0.35	-91.6	-18.8	-10.2	-0.52	-0.16	-0.75	-0.87	-6.58	-74.0
LYH	-7.85	-2.85	-60.8	-4.79	-87.2	-155	-83.8	-5.78	-1.01	-1.94	-1.91	-6.70	-85.6
Sink/Source ( $\Delta Y = \Sigma \text{outflux} - \Sigma \text{influx}$ )													
XH	-28.0	-0.12	-2.04	0.40	-30.0	-22.6	10.1	-1.42	-1.83	-0.92	-0.078	-5.96	-43.8
LYH	-306	3.30	72.1	-11.8	-131	-292	-55.3	-22.4	-10.6	2.54	2.59	12.2	112

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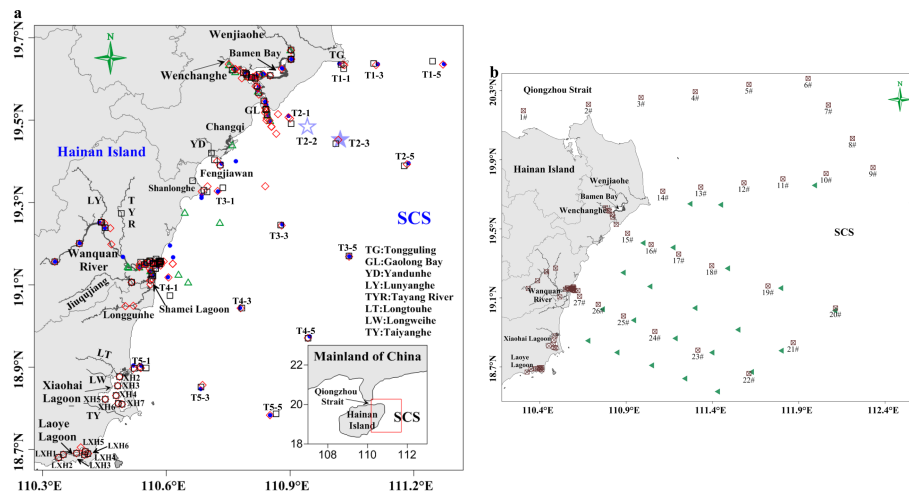
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**Fig. 1.** Locations map of the study area and sampling stations for the cruises along the eastern Hainan Island during 2006–2009. **(a)** Sampling stations for the cruises in rivers, estuaries, lagoons, and coastal region of the South China Sea in December 2006 ( $\Delta$ ), August 2007 ( $\bullet$ ), June–August 2008 ( $\diamond$ ), and March–April 2009 ( $\square$ ). Anchor stations carried out in August 2007 ( $\ast$ ), June 2008 ( $\star$ ). The red square in the map **(a)** shows the location of eastern Hainan Island in the South China Sea. **(b)** The sampling stations in the offshore of eastern Hainan Island in August 2008 ( $\blacktriangleleft$ ); sampling stations in rivers, estuaries, lagoons and offshore region in June–August 2009 ( $\boxtimes$ ) from Qiongzhou Strait to eastern Hainan Island (15#: anchor station).

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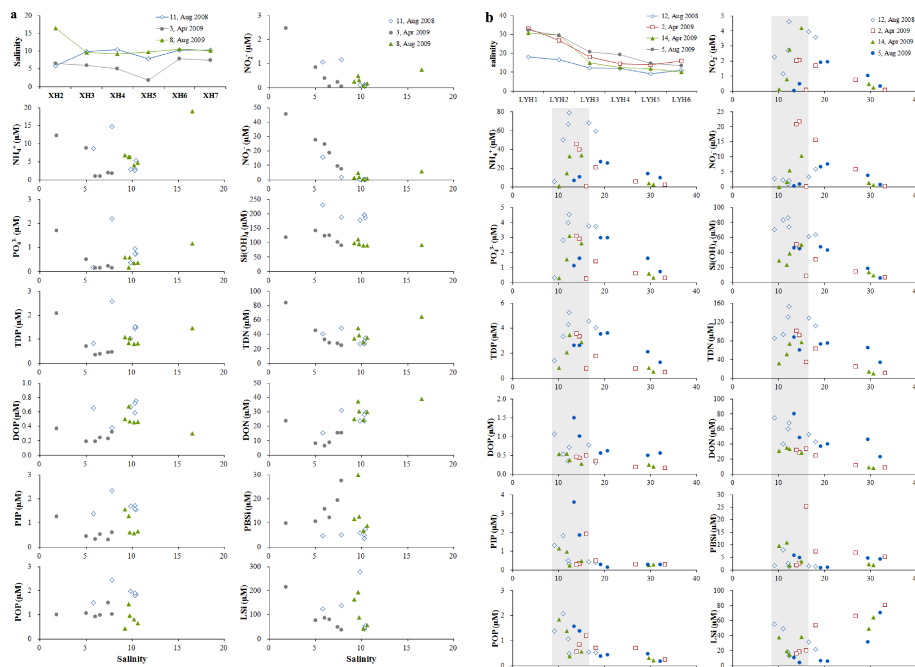


Fig. 2. Spatial distributions of salinity and nutrients ( $\mu\text{M}$ ) vs. salinity in surface waters of the Xiaohai Lagoon (a) and Laoyehai Lagoon (b) during the study periods.

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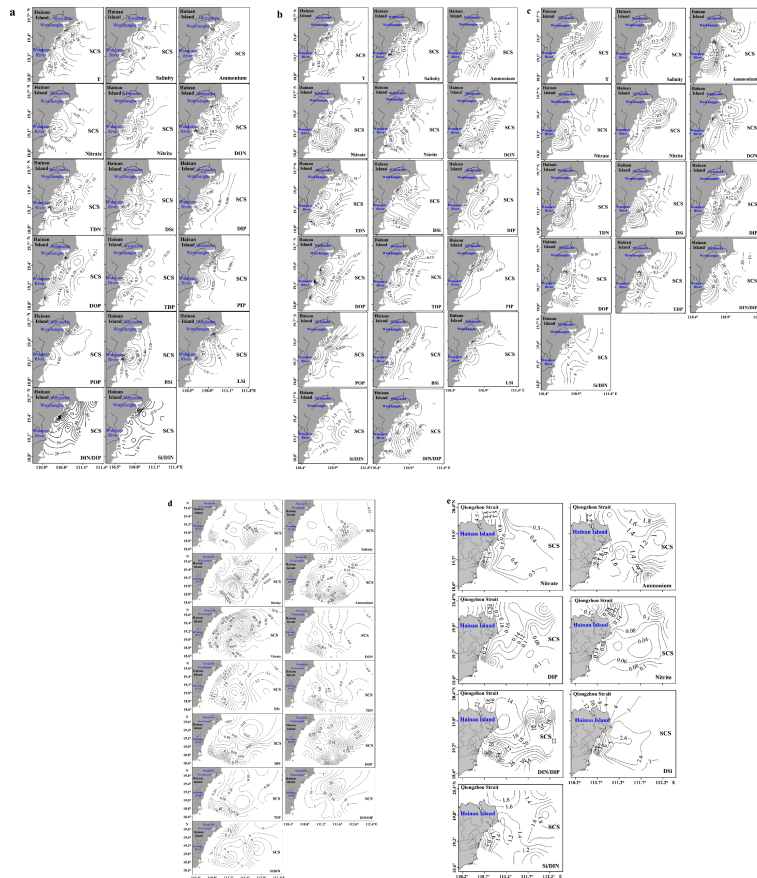
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**Fig. 3.** Horizontal distributions of surface Temperature ( $^{\circ}\text{C}$ ), salinity, nutrients ( $\mu\text{M}$ ), and molar ratios during 2007–2009. **(a)** 18–22 August 2007; **(b)** 27 July–2 August 2008; **(c)** 6–12 April 2009; **(d)** 29 August–1 September 2008; **(e)** 29 July–3 August 2009.

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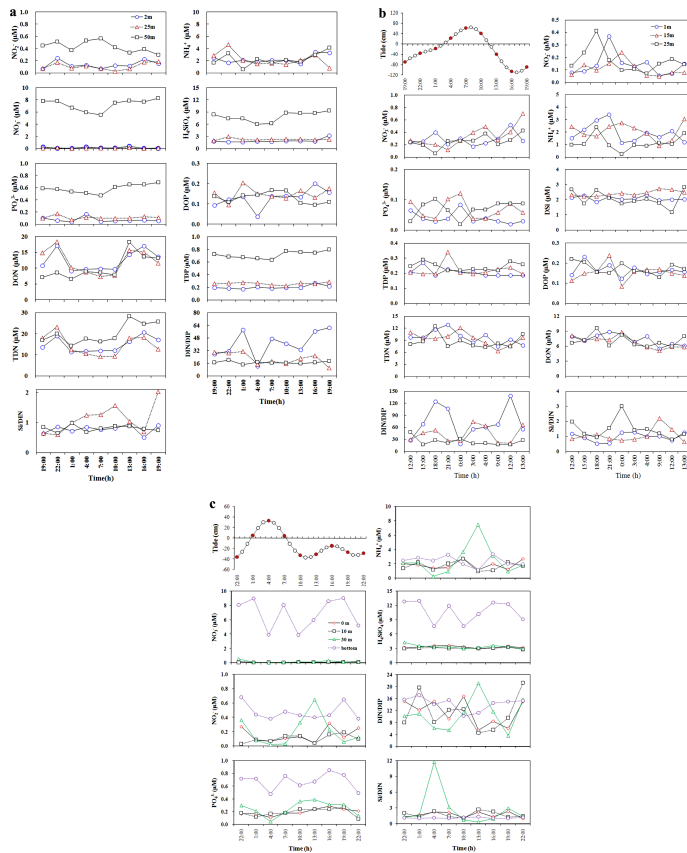
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**Fig. 4.** Concentrations of nutrients ( $\mu\text{M}$ ) at anchor station T2-3 in August 2007 (**a**), station T2-2 in July 2008 (**b**), and station 15# in July 2009 (**c**); the tide height (cm) during July 2008 and July 2009 were provided and the red circle represents sampling time.

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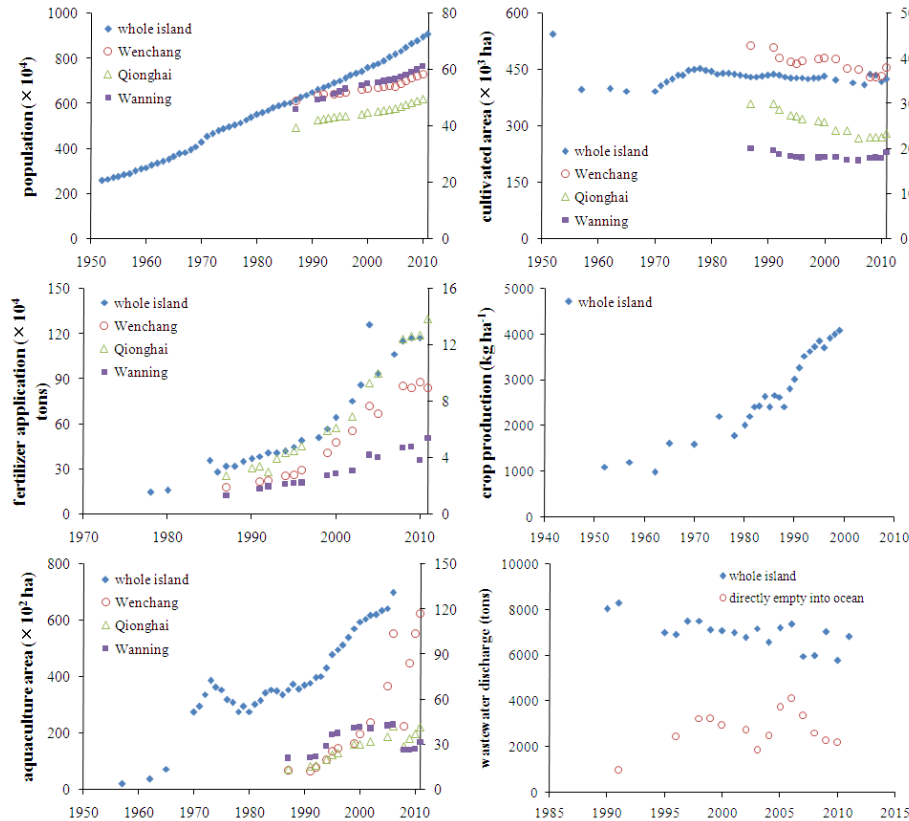
Interactive Discussion





## Nutrient dynamics in tropical rivers

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**Fig. 5.** Changes in population ( $\times 10^4$ ), cultivated area ( $\times 10^3$  ha), fertilizer application ( $\times 10^4$  tons), crop production ( $\text{kg ha}^{-1}$ ), aquaculture area ( $\times 10^2$  ha), and wastewater discharge (tons) of the Hainan Island from 1952 to 2011, Wenchang, Qionghai, and Wanning Cities from 1987 to 2011. The left side ordinate represents changes of the whole island, the right side ordinate represents changes in each city. The data are from the Hainan Statistical Yearbook (1988, 1992, 1997, 2000, 2005, 2009, 2010, and 2011).