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## Natural and human influences on nutrient transport through a small subtropical Chinese estuary

### David Kaiser<sup>a,\*</sup>, Daniela Unger<sup>a,1</sup>, Guanglong Qiu<sup>b,d</sup>, Haolang Zhou<sup>b</sup>, Huayang Gan<sup>c</sup>

<sup>a</sup> Leibniz Center for Tropical Marine Ecology, Wetland Dynamics Group, Biogeochemistry & Geology Department, D-28359 Bremen, Fahrenheitstr. 6–8, Germany

<sup>b</sup> Guangxi Mangrove Research Center, Guangxi Marine Environment & Coastal Wetland Research Center, Beihai 536000, 92 Chang Qing Dong Lu, Guangxi, China

<sup>c</sup> Institute of Maine Environmental & Engineering Geology, Guangzhou Marine Geological Survey, Guangzhou 520760, 188 Guanghai Rd., Guangdong, China

<sup>d</sup> State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, Beijing 100085, 18 Shuangqing Lu,

Haidian District, China

#### HIGHLIGHTS

- ▶ Small catchments supply high proportion of nutrients to north western South China Sea.
- ► Hinterland and offshore sources, not intensive aquaculture, dominate nitrogen input.
- Marcotides prevent near-shore eutrophication by dispersing human nutrient inputs.
- ► Long-term changes in nutrient delivery increased coastal productivity.

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#### ABSTRACT

Global understanding of land-ocean nutrient fluxes increasingly recognizes the disproportionate importance of small rivers. We studied nutrient fluxes from a small catchment in fast developing southern China to uncover effects of land-use. Water was sampled in the macro-tidal estuary of Nanliu River and adjacent Lianzhou Bay in spring and summer of investigate spatial and temporal variations of dissolved nutrients.

High riverine concentrations of nitrate (NO<sub>3</sub>; up to 220  $\mu$ M) and phosphate (PO<sub>4</sub>; up to 3.7  $\mu$ M) mainly originated from agricultural fertilizer input. Riverine dissolved silica (Si; up to 47  $\mu$ M) increased in the oligosaline part of the estuary through human disturbance of bottom sediments. Dissolved organic nitrogen (DON; up to 194  $\mu$ M) and ammonium (NH<sub>4</sub>; up to 40  $\mu$ M) concentrations increased within the estuary due to inputs from livestock and mussel beds, respectively. Aquaculture ponds contained high concentrations of NH<sub>4</sub> (up to 355  $\mu$ M) and DON (up to 151  $\mu$ M) but are not an important source to the estuary due to rare wastewater discharge and low absolute nutrient amounts relative to river export. Nutrient concentrations in Lianzhou Bay were low because tidal currents disperse land-derived nutrients offshore into the adjacent Beibu Gulf. A high proportion of regenerated nitrogen in the bay suggests that primary production is sustained by rapid in situ nutrient cycling between primary producers and benthic consumers. High nutrient export makes the Nanliu River an important nutrient source for the north-western South China Sea, despite its proportionately small size.

Macro-tide induced short-term concentration changes exceed variability on seasonal and sub-seasonal scales. All nutrients vary inter-annually and between seasons, depending on precipitation-driven river runoff. Total nutrient export to Beibu Gulf coastal waters is stronger during the high discharge period in summer and autumn. In recent years changing nitrogen to phosphorus ratios have alleviated phosphorus limitation in Lianzhou Bay, permitting increased primary productivity.

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#### 1. Introduction

Global anthropogenic development has dramatically increased nutrient loads to rivers (Caraco and Cole, 2001; Green et al., 2004; Seitzinger et al., 2005) with inorganic fertilizer being the most important source of inorganic nutrients (Seitzinger et al., 2005). Rivers integrate terrestrial signals along the watersheds and transfer them to estuaries (e.g. Green et al., 2006), the principal gateways from land

 <sup>\*</sup> Corresponding author. Tel.: +49 421 2380073; fax: +49 421 2380030.
*E-mail addresses*: david.kaiser@zmt-bremen.de, kaiser@uni-bremen.de (D. Kaiser), daniela.unger@desy.de (D. Unger), qalong@163.com (G. Qiu), zhouhaolang@sina.com (H. Zhou), ghuayang@126.com (H. Gan).

<sup>&</sup>lt;sup>1</sup> Present address: Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany.

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to ocean (e.g. Abril et al., 2002). Estuaries influence the delivery of terrestrially derived nutrients to coastal water through physical, chemical, and biological processes (Officer and Lynch, 1981; Kaul and Froelich, 1984; Flindt et al., 1999; Cai et al., 2012; Hartzell and Jordan, 2012). This influence varies on time scales of decades (land use change, Li et al., 2007), seasons (precipitation and temperature changes, Wen et al., 2008), sub-season (extreme events, Caffrey et al., 2007; Herbeck et al., 2011), and days (tidal variation, Tay et al., 2012). Consequently, estuaries are important factors in nutrient management and deserve particular scientific attention (Conley, 2000).

Coastal wetlands exert a complex influence on estuarine nutrient transport (Valiela and Cole, 2002; Sánchez-Carrillo et al., 2009). In the tropics and subtropics mangroves may act as filters for river derived nutrient pollution (Robertson and Phillips, 1995; Tam and Wong, 1995; Wong et al., 1997; Rivera-Monroy et al., 1999; Wösten et al., 2003; Tam et al., 2009; Kaiser et al., in press), or a source of nutrients through outwelling (Wattayakorn et al., 1990; Hemminga et al., 1994; Lee, 1995; Dittmar and Lara, 2001; Kristensen et al., 2008). Around the globe, these services decline due to an alarming loss of mangrove ecosystems (Robertson and Alongi, 1992; Alongi, 2002; Valiela and Cole, 2002) which is often related to the conversion to aquaculture facilities (Wolanski et al., 2000). In China, the province with the largest mangrove areas, Guangdong, suffered a 63% areal loss between the 1950s and 90s, while in neighboring Guangxi province the mangrove area decreased from >12,246 ha to 5654 ha within a decade between the early 1980s and the early 1990s (Li and Lee, 1997). China is now the fastest growing producer of cultured brackish water shrimp, releasing billions of tons of untreated waste water (Biao and Kaijin, 2007) adding to the eutrophication caused by anthropogenically altered river nutrient export (Herbeck et al., 2012; Biao et al., 2004).

Due to different impacts on nitrogen, phosphorus, and silicon loads, human activities may induce shifts from nitrogen to phosphorus or silicon limitation and trigger community shifts in phytoplankton (Conley et al., 1993; Justic et al., 1995; Turner et al., 1998, 2003; Humborg et al., 2002) eventually leading to hypoxia, loss of biodiversity, and increased occurrence of harmful algal blooms (Cloern, 2001). In China these phenomena have been linked to increased nitrogen and phosphorus levels (Qi et al., 1995), and dominance of nondiatom phytoplankton (Hodgkiss and Ho, 1997; Li et al., 2007).

Many estuarine studies have focused on large systems with long residence times, neglecting small, well-flushed estuaries (Caffrey et al., 2007; Tay et al., 2012). One such system is the estuary of the Nanliu River in Guangxi Province, southern China. Located in fast developing coastal China (Xiong et al., 2008), it is subject to a host of globally relevant anthropogenic impacts, which bear the potential of causing eutrophication by increasing dissolved inorganic nutrients in the river (Committee of Annals of Chinese Estuaries, 1998). Moreover, the coastal waters of the Beibu Gulf are an economically important and developing part of the South China Sea, and support important wild fisheries (Yu and Mu, 2006). The ecological importance has been acknowledged by the establishment of RAMSAR sites and national-level protected areas of seagrass and mangroves in the region.

#### 2. Material and methods

#### 2.1. Study site

Despite being the largest river in Guangxi, with its length of 287 km and a catchment area of 9704 km<sup>2</sup> (Dai et al., 2011), the Nanliu is a small river as compared to most other well-studied rivers in China and worldwide. Annual average discharge is  $5.313 \times 10^9$  m<sup>3</sup> at 168.3 m<sup>3</sup> s<sup>-1</sup> (Chen, 1997; Chen et al., 2007). The estuary is divided into three major branches debouching into Lianzhou Bay and the adjacent Gulf of Beibu, the north-western part of the South China

Sea (Fig. 1). Mostly diurnal macro tides have a tidal range of up to 5.36 m (Committee of Annals of Chinese Estuaries, 1998) and tidal excursion reaches at least 62 km upstream (Dai et al., 2011). Mangroves form islands within the estuary and fringe the river banks up to 7 km upstream. These forests are dominated by dwarf *Aegiceras corniculatum* intermixed with patches of *Kandelia candel*. Lianzhou Bay has an area of 237 km<sup>2</sup>, 70% of which are shallow subtidal sandbanks (Jiang et al., 2008).

The study region is influenced by the East Asian monsoon with a dry boreal winter–spring season and a wet boreal summer–autumn season (Wu et al., 2008). Daily average air temperatures range from 3.7 to 29.3 °C in early spring (Feb.–Apr.) and 13.2 to 33.2 °C in late summer (Aug.–Oct.). Monthly average precipitation is 49–81 mm and 82–385 mm, respectively (Fig. 2). Typhoons occur between May and November. During this study, the tropical storm Nesat caused extreme precipitation of 125 mm d<sup>-1</sup> as it passed the coast of Guangxi on 1 September 2011.

Human activities in the catchment area are dominated by agriculture. The main crops are rice and sugar cane, Guangxi being the largest producer of sugar cane in China (Lagos et al., 2011). Timber production from eucalyptus is a rapidly growing sector of agriculture (Bai and Gan, 1996). Pond aquaculture occupies the landward part of the estuary, with pond area exceeding 6500 ha (Zhou Haolang, pers. comm.). Ponds are in fallow during the winter season and discharge of pond water is restricted to the two short harvest periods in summer and autumn. This management differs from that in other regions of China (Herbeck et al., 2012; Biao and Kaijin, 2007) and South East Asia (Funge-Smith and Briggs, 1998), where cultivation is not interrupted in winter and water is repeatedly exchanged throughout the production cycle. Sand mining, dredging, and harvest of benthic infauna as well as husbandry of fowl and cattle are practiced along the river. Large mussel and oyster beds are situated in the shallow bay area off the river mouths (Fig. 1) from where over 70,000 t of clams and over 60,000 t of oysters were harvested in 2009 (Beihai Fishery Bureau; Zhou, pers. comm.). Additionally, municipal and industrial sewage are released from the coastal city of Beihai and its harbor.

#### 2.2. Sampling

Field work was carried out during early spring (Feb.-Apr.) and late summer (Aug.-Oct.) seasons of 2010 and 2011 (Fig. 2). Water was sampled during high tide at 5 to 10 stations along the salinity gradients of the western (NLW), middle (NLM), and eastern (NLE) branch of the Nanliu River. Ten stations were sampled in Lianzhou Bay. No samples could be obtained from the bay in spring 2010 due to logistical problems. At each station, one surface water sample was collected; bottom water was obtained using a Van Dorn water sampler if water was deeper than 1 m. In spring and summer 2011, sampling was carried out hourly over complete tidal cycles of 24 h during diurnal spring and semi-diurnal neap tides. The two tidal stations were set up in a mangrove fringed channel of the western river mouth and at the boundary between shallow and deep areas of the bay (Fig. 1). Additional samples were taken from mangrove channels during low tides as water flowed out of the forest as well as from several shrimp ponds, covering different stages of the production cycle. During the wet summer seasons rain samples were collected to assess the influence of wet atmospheric deposition.

All water samples were analyzed for temperature, salinity, and pH using a Hach-Lange HQ40D multisensor. Dissolved oxygen was measured directly in the surface waters using a Hach-Lange LD0101 optode. Water depth was measured using a handheld echo sounder (Echotest II). Water transparency was measured with a common Secchi disk. Water samples were immediately filtered through mixed ester-cellulose filters (nominal pore size of 0.45 µm) attached to sample-rinsed syringes. For analysis of inorganic nutrients samples

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