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Particulate organic matter dynamics in coastal systems of the northern Beibu Gulf

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ABSTRACT

Estuarine particle fluxes are an integral part of land-ocean-connectivity and influence coastal environmental conditions. In areas with strong anthropogenic impact they may contribute to coastal eutrophication. To investigate the particulate biogeochemistry of a human affected estuary, we sampled suspended, sedimentary and plant particulate matter along the land-ocean continuum from Nanliu River to Lianzhou Bay in southern China. Riverine particle fluxes exceed inputs from land based pond aquaculture. Elemental (C/N) and isotopic composition of particulate organic carbon ($\delta^{13}C$) and total nitrogen ($\delta^{15}N$) showed that suspended and sedimentary organic matter (OM) mainly derive from freshwater and marine phytoplankton, with minor contributions from terrestrial and aquaculture derived particles. Amino acid composition indicates subseasonal variability of production and freshness of phytoplankton OM. Strongest compositional changes of suspended particles are associated with storm-related extreme precipitation events, which introduce soil derived OM. High concentrations of chlorophyll *a* reflect eutrophic conditions in riverine and coastal waters. Human impact results in high $\delta^{15}N$ signals in suspended, sedimentary and plant particulate matter. Using these in a comparison with two little affected sites shows that anthropogenic influence disperses from the Nanliu River to remote estuaries and mangrove areas. Our results suggest that autochthonous production binds anthropogenic nutrients in particles that are transported along the coast.

1. Introduction

Rivers and estuaries connect continents and oceans, and annually transport 150–205 × 10^6 t of particulate organic carbon (POC) (Beusen et al., 2005; Hedges et al., 1997; Meybeck and Vorosmarty, 1999; Seitzinger et al., 2005) and 21–23 × 10^6 t of particulate nitrogen (PN) (Meybeck, 1982; Seitzinger et al., 2002a) from land to sea. Contrary to the numerous investigations of carbon fluxes and dynamics, few studies have focused on particulate nitrogen (Seitzinger et al., 2002a), the most critical element in nutrient enrichment and eutrophication of coastal ecosystems (Seitzinger et al., 2002b).

Chinese rivers play a major role in global transport of particulate matter into the ocean (Milliman et al., 1984; Seitzinger et al., 2002a; Syvitski et al., 2005; Zhang et al., 1992), but data is mostly available for large rivers although small to medium sized rivers may contribute considerably to particle fluxes (e.g. Kao and Liu, 1997; Lyons et al., 2002; Milliman and Syvitski, 1992). Small rivers are also better suited for investigating processes and dynamics because they respond rapidly to seasonal and subseasonal natural or anthropogenic influences, while in major rivers short term regional changes may be masked by integration over the large catchments (Jennerjahn et al., 2008; Unger et al., 2013).

The particulate organic matter (POM) delivered by rivers is an important component in coastal biogeochemistry (Hedges et al., 1997; Raymond and Bauer, 2001; Wu et al., 2007). Investigations of coastal particle dynamics are challenging due to the large temporal and spatial variability in physical and chemical properties of rivers, estuaries and near shore waters (Raymond and Bauer, 2001). POC stable isotope composition ($\delta^{13}C$) is one tool to delineate organic matter (OM) sources in these systems (e.g. Bristow et al., 2012; Jennerjahn et al., 2008, 2004; Raymond and Bauer, 2001; Savoye et al., 2012). Variability in $\delta^{13}C$ within and

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between systems is to a large degree due to the relative contribution from different sources (Raymond and Bauer, 2001), because primary producers have $\delta^{13}C$ values according to their carbon source and assimilation pathway (see e.g. Hedges et al., 1997). These signals change only slightly during heterotrophic processing and degradation of POC and are therefore preserved in food webs and detritus (see Hedges et al., 1997; Middelburg and Herman, 2007; Raymond and Bauer, 2001). However, some POC sources in estuaries may have wide and overlapping ranges of $\delta^{13}C$. For instance, overlapping values of freshwater phytoplankton (-34 to -26‰; Bristow et al., 2012 and references therein), terrestrial C3 plants (-33 to -22‰; Bender, 1971) and sewage (-28 to -23‰; Andrews et al., 1998; Thornton and McManus, 1994) hamper the discrimination of autochthonous, terrestrial, or anthropogenic material in rivers. The elemental carbon to nitrogen ratio (C/N) differs between sources because high contents of nitrogen-free biomacromolecules cause high values in vascular plants (C/N 20–500) compared to phytoplankton (C/N ≈ 7), bacteria (C/N ≈ 4) and fungi (C/N ≈ 10) (Hedges et al., 1986). The use of C/N to identify organic matter sources is complicated because it changes during degradation. While terrestrial vascular plant C/N tends to decrease due to colonization with bacteria, algal detritus becomes nitrogen depleted due to preferential consumption of N-containing molecules (Middelburg and Herman, 2007). These restrictions may be overcome by combined use of both indicators (Bristow et al., 2012; Raymond and Bauer, 2001).

The stable isotope signature of PN ($\delta^{15}N$) may not be a suitable indicator for OM sources within one system because $\delta^{15}N$ of different sources can overlap (see e.g. Bristow et al., 2012; Maksymowska et al., 2000; Middelburg and Nieuwenhuize, 1998 and references therein) as it depends strongly on the $\delta^{15}N$ of the original dissolved nitrogen assimilated into OM (Cifuentes et al., 1988; Liu et al., 2007). Processes like nitrification, denitrification, assimilation, and ammonification (Cifuentes et al., 1989; Granger et al., 2010, 2008, 2004) as well as OM degradation (Lehmann et al., 2002) change a source's $\delta^{15}N$ due to isotope fractionation, i.e. the preferential uptake or removal of the lighter, more mobile ^{14}N isotope during thermodynamic and physiological processes. These changes can, thus, be used to assess nitrogen processing (e.g. Middelburg and Herman, 2007). Also, $\delta^{15}N$ can work as a footprint for nitrogen inputs, particularly when comparing variability between different systems (Robinson, 2001). Between-system variability mostly depends on $\delta^{15}N$ of original local nitrogen sources and effects of nitrogen conversion processes are less pronounced than within systems (Robinson, 2001). Thus, the $\delta^{15}N$ of suspended particles, sediments, micro and macro algae, and higher plants have been used successfully to trace nitrogen sources, including anthropogenic inputs, in different systems (e.g. Abreu et al., 2006; Bao et al., 2013; Costanzo et al., 2005, 2004, 2003, 2001; Harrington et al., 1998). Nitrogen transformations in human affected watersheds cause a depletion of ^{14}N (e.g. Anderson and Cabana, 2006). Thus, high anthropogenic influence resulting in strong nitrogen loading to aquatic systems is accompanied by elevated $\delta^{15}N$ (e.g. Middelburg and Herman, 2007). These high values can be traced from areas directly affected by aquaculture to remote systems (e.g. Costanzo et al., 2001; Herbeck and Unger, 2013).

The identification of OM sources may be further improved by using the composition of amino acids (AA), which account for $>30\%$ of organic carbon and about 60 to 80% of the nitrogen in marine particles and plankton (Cowie and Hedges, 1992; Dauwe and Middelburg, 1998; Van Mooy et al., 2002), rendering them representative for most OM. The reactivity of AA varies between monomers and the degree of OM degradation is mirrored in the Degradation Index (DI; Dauwe et al., 1999) and Reactivity Index (RI; ratio of proteinogenic to non-proteiongenic AA; Jennerjahn and Ittekkot, 1999). High values of DI and RI indicate high OM reactivity, and values decrease with progressing degradation. Amino sugars (AS) are less abundant and less reactive than AA, so that advanced degradation is reflected in decreasing AA/AS ratios (Benner and Kaiser, 2003; Gupta and Kawahata, 2000; Haake et al., 1992; Müller et al., 1986).

In this study, we use carbon and nitrogen ratios and isotopic composition as well as amino acid characteristics of suspended, sedimentary, and plant particulate matter to understand OM dynamics within the small Nanliu River estuary and between three different coastal sites along the coast of Guangxi province in southern China. Coastal China is among the most densely populated and rapidly developing regions on earth. Coastal development has caused the loss of $>60\%$ of Chinas mangrove systems (Li and Lee, 1997), mostly due to conversion to aquaculture facilities (Bao et al., 2013). The effects of human enhanced nutrient and organic matter fluxes on coastal productivity are still poorly understood in China (Wu et al., 2007), but there is evidence for increased coastal eutrophication (e.g. Cai et al., 2004; Chen and Hong, 2011; Herbeck et al., 2012; Hodgkiss and Ho, 1997; Kaiser et al., 2013; Yuan et al., 2012).

2. Material and methods

2.1. Study sites and sampling

Guangxi Province in southern China has a coastline of 1164 km (www.nanning.gov.cn, 2010) along the northern Beibu Gulf, the north-western part of the South China Sea (Fig. 1). This subtropical coast is influenced by the East Asian monsoon with dry boreal winter–spring and wet boreal summer–autumn seasons (Wu et al., 2008). Long term average annual precipitation is 179 cm yr^{-1} but was considerably lower at 152 cm yr^{-1} during the study period (Climate.usurf.usu.edu, Beihai meteorological station, 1954–2011). During the rainy season daily precipitation is highly variable with periods of no rainfall. Tropical cyclones occur up to 5 times a year between May and November and cause short term climatic and hydrographic extremes (Committee of Annals of Chinese Estuaries, 1998, p. 65). Coinciding with our fieldwork, a tropical storm originating from typhoon Nesat passed the coast on 1 October 2011 and caused extreme winds and precipitation (Fig. 2).

With a length of 287 km and average discharge of 5.313×10^9 m^3 yr^{-1} (Chen et al., 2007), the small Nanliu River is the longest river in Guangxi Province with the highest discharge. The catchment area of 9704 km² (Dai et al., 2011) is dominated by agriculture of mainly rice and sugar cane. Zonation based on salinity distribution and geography divides the macrotidal estuary into river, inner and outer estuary, and bay (Kaiser et al., 2013). In the estuary, the mangroves *Aegiceras corniculatum* and *Kandelia candel* cover intertidal islands and river banks. Deforestation has decreased the forest area from 1790 ha in the early 1990s (Li and Lee, 1997) to only approximately 515 ha in 2011, mainly due to conversion into aquaculture ponds. Approximately 6500 ha of brackish water shrimp culture cover the landward area of the inner estuary. They are mostly enclosed by flood protection dykes and connected to the estuary via drainage channels. With operations suspended during dry season, pond effluents are discharged only twice annually after harvest during the wet season. The semi-enclosed Lianzhou Bay covers an area of 237 km², 70% of which comprise the shallow subtidal sandbanks of the outer estuary (Jiang et al., 2008), and tidally exchanges water with the Beibu Gulf across a 24.4 km wide opening (Sun et al., 2014). Along the coast mixed diurnal–semidiurnal tides have a range of up to 5.36 m (Committee of Annals of Chinese Estuaries, 1998).