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Estuarine modification of dissolved and particulate trace metals in major rivers of East-Hainan, China

Jun Fu [a], Xiao-Liang Tang [a], Jing Zhang [b], Wolfgang Balzer [a,*]

[a] University of Bremen, FB2, Marine Chemistry, PF 330440, D- 28334 Bremen, Germany
[b] State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 3663 Zhongshan Road North, Shanghai 200062, People's Republic of China

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ABSTRACT

Dissolved and particulate cadmium, copper, iron, lead, cobalt and nickel were analyzed in surface waters of the Wanquan River estuary and the Wenchang/Wenjiao River estuary in East-Hainan Island during the dry season (December 2006) and two wet seasons (August 2007 and July/August 2008). A major difference to other Chinese rivers was the very low concentration of suspended particles in these tropical Hainan estuaries. In the dissolved phase, a positive deviation from the theoretical dilution line was observed for Cd during different expeditions. Dissolved Cu and Ni essentially behaved conservatively, while Fe, Pb and partly also Co correlated in their negative deviation from simple mixing. Strong seasonal variability was observed only for dissolved Fe, Pb and Cd: sorption by the much higher loading with suspended particles during the dry season lead to a strong lowering of dissolved Fe and Pb, while the opposite was observed for dissolved Cd. In both estuaries all six metals in particulate form showed almost constant values with a tendency for slight decreases along the salinity profile. The normalization to particulate Al revealed some specific particle properties during the different expeditions. The dynamics of Fe chemistry dominated the distribution of Pb in all forms. The distribution coefficients K_D showed a general decrease in the order Fe > Pb > Co > Ni > Cu ≈ Cd. There was no "particle concentration effect"; rather the K_D's of Fe and Pb exhibited slightly positive correlations with the suspended particle loadings. Elevated concentrations levels in the Wenchang/Wenjiao river estuary, especially during the wet season 2008, were ascribed to diffuse inputs from aquaculture ponds which girdle the upper estuary. In comparison to major Chinese rivers, the tropical Hainan estuaries ($S > 0$) showed similar levels for Cd, Cu, Pb, Co and Ni in particles and solution, while Fe was enriched in both matrices. On a global scale, neither in the Wanquan river estuary nor in the Wenchang/Wenjiao river estuary significant trace metal contamination was observed.

1. Introduction

River-transported signals are subjected to a variety of physical, chemical and biological processes in the estuarine mixing zone, in which the boundary conditions are extremely variable in both space and time; estuaries can be thought of as acting as filters of the river-transported chemical signals, which can often emerge from the mixing zone in a form that is considerably modified with respect to that which entered the system (Chester, 1990). This concept of the estuarine filter is based on the fact that the mixing of the two very different end-member waters will result in the setting up of strong physico-chemical gradients in an environment. It is these gradients which are the driving force behind the filter. In addition, also organic matter production (Louis et al., 2009), the oxygenation state (Khalid et al., 1978; Zwolsman and van Eck, 1999), possible inputs from anoxic sediments (Salomons et al., 1987) and/or other processes may have influence.

Trace metals are a particularly interesting aspect of estuarine chemistry because their differing physical chemistries lead to a variety of geochemical behaviours (Shiller and Boyle, 1991). For example, previous studies have indicated an affinity of cobalt to manganese oxide phases and a removal of lead through adsorption onto the suspended particulate matter (Chiffoleau et al., 1994), the desorption of cadmium from suspended particles and the flocculation of iron colloids (Roux et al., 1998), the removal of copper from the dissolved phase at low salinities (Comber et al., 1995) and non-conservative behaviour of nickel (Wang and Liu, 2003). The trace metal behaviour in the large rivers and major estuaries of China at mid latitudes such as the Changjiang (Yangtze River) and the Huanghe (Yellow River) has been well studied (e.g., Zhang, 1995; Zhang and Liu, 2002; Wang et al., 2009; Tang et al., 2010), but about the trace metal chemistry in estuaries of tropical China, especially of Hainan Island, very little is known.

* Corresponding author. Tel.: +49 42121863070; fax: +49 42121863089.
E-mail address: balzer@mch.uni-bremen.de (W. Balzer).

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Adsorption/desorption is one of the most significant factors that affect the solid-solution interaction (O'Connor and Connolly, 1980). Under the assumption that equilibrium conditions prevail, the solid-solution-interaction can be described in terms of the conditional distribution coefficient (or partition coefficient) K_D, which is defined as the ratio of the adsorbed or the total particulate concentration (C_P, w/w) to the dissolved concentration (C_S, w/v) of a chemical constituent: $K_D = C_P/C_S$. K_D's are of fundamental significance to geochemical modelling and pollution impact assessment (e.g., Wood et al., 1995). The distribution coefficients provide empirical information on the combined effect of heterogeneous reactions of an element at the solid-solution interface. An elevated K_D value may indicate that an element is associated and transported with the solid phase, which eventually may become part of the sediment and may never reach the ocean. From the dependence of the distribution coefficients on salinity it is possible to identify whether or not there is a tendency for the release of the respective metal from the particulate matter, when proceeding from fresh water through brackish to seawater conditions. Estuarine cycling of trace metals covering all these aspects and including also changes over decades has been studied extensively in the Scheldt estuary; it is characterised as a system with strong physico-chemical gradients, large anthropogenic inputs, a very long mixing zone of fresh- and saltwater (up to 100 km) and a long residence time of about 3 months of water in the upper estuary (e.g., Paucot and Wollast, 1997; Zwolsman et al., 1997; Zwolsman and van Eck, 1999).

In this paper we investigate the environmentally relevant trace metals cadmium, copper, iron, lead, cobalt and nickel in dissolved and particulate form. In addition to contributing to the general knowledge about the trace metal behaviour in tropical estuaries, a specific objective was to estimate the contamination state of the Wanquan River and the Wenchang/Wenjiao River estuaries of Hainan Island (~20°N).

2. Materials and methods

2.1. Study area

The Wanquan River (in the following: WR) and the Wenchang/Wenjiao River system (in the following: WWR) in East-Hainan are both located at the northern part of the tropical zone with a humid warm climate (Fig. 1). The Wanquan River, with a drainage area of 3693 km^2, a total length of 156.6 km and a mean annual discharge of 163.9 m^3/s, is the third largest river in Hainan Island (Chendong et al., 2003). The Wenchang River (drainage area 381 km^2, total length 37 km, mean annual discharge 9.1 m^3/s) and the Wenjiao River (drainage area 522 km^2, total length 56 km, mean annual discharge 11.6 m^3/s) empty into the Bamen Bay (Zeng and Zeng, 1989) and form the Wenchang/Wenjiao River estuary (areal extent: ~40 km^2; Herbeck et al., this issue). Both estuaries have a micro-tidal, irregular diurnal tidal regime with a mean range of about 0.7–0.8 m (Zhu et al., 2005). The salinity intrusion may extend 5 km from the Yudai Sand Barrier into the WR and from the Bamen Bay end into the WWR, respectively. The WWR is a shallow estuary (< 3 m; except for the shipping channel) with a low flow rate, while in the WR the position of the mixing zone is highly variable due to changes of the river discharge rate, tides and winds. About 80% of the annual rainfall (1740 mm/yr; Liu et al., 2011) and of the water flow in this region occurs in the wet period from May to November (Ma et al., 2007). Typhoons with heavy rainfall and elevated input of soil erosion products, nutrients and suspended particles (Herbeck et al., 2011) did not occur during the sampling for this study. The water residence time in the estuaries was estimated to be 7.8 day in WWR (Liu et al., 2011) and 0.2–4.7 day in WR (Li et al., this issue). Comprehensive nutrient investigations of the WWR system (Liu et al., 2011) revealed that the tributaries are enriched in dissolved inorganic nitrogen and depleted in dissolved inorganic phosphorus and have major contributions of dissolved organic forms to the total N and P dissolved concentrations; these elements – in contrast to Si – show non-conservative behaviour. The WWR system is characterized by lower silicate than average in tropical systems (Liu et al., 2011), while the Wanquan River estuary (WR) is enriched in silicate (Li et al., this issue). Because of the generally very low depths of about 3 m except for a few more meters in the shipping channels, oxygen depletion or anoxic conditions with their far reaching effects on redox-dependent trace metals (e.g., Balzer, 1982) were not observed and could not be expected. Ma et al. (2007) investigated major and trace elements in laterites of Northern Hainan which are in-situ weathering products developed from basalts. Typical soils of the study area are Oxisols which are especially rich in Fe_2O_3 (Li et al., 2012) which explains the comparatively high Fe values in the estuary found during the present study. The Shilu Iron Mine as China's largest iron mine is located in the western part of the Hainan Island (Hsieh and Zhong, 1990), but is outside the drainage area of either estuary studied. Nevertheless, the high Fe content of the soil and possibly also some atmospheric transport from this mine might affect aquatic processes of East-Hainan. In contrast to the WR, the upper WWR estuarine system is girdled by shrimp and fish ponds

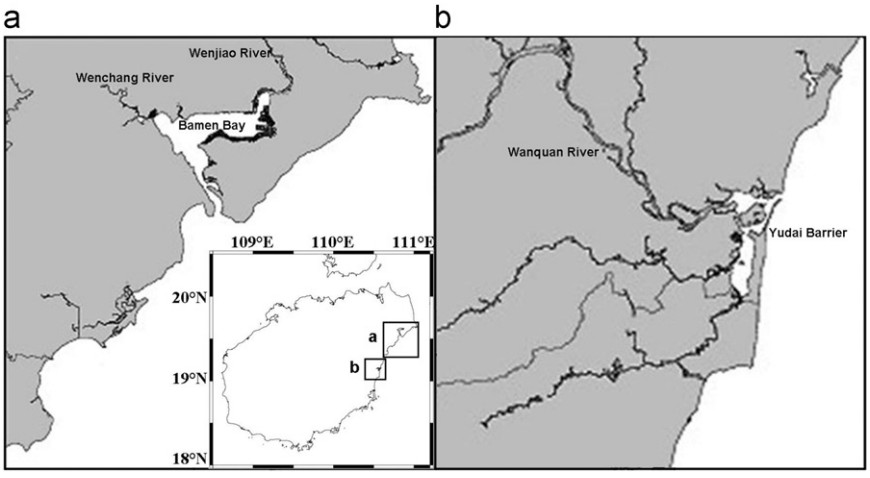

Fig 1. Estuaries of East Hainan under investigation: (a) Wenchang/Wenjiao river estuary (WWR) and (b) Wanquan river estuary (WR).