



## Estuarine modification of dissolved and particulate trace metals in major rivers of East-Hainan, 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  $Fe > Pb > Co > Ni > Cu \approx Cd$ . 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.

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### 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 (Chiffolleau 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.

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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 ( $\sim 20^\circ\text{N}$ ).

## 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<sup>2</sup>, a total length of 156.6 km and a mean annual discharge of 163.9 m<sup>3</sup>/s, is the third largest river in Hainan Island

(Chendong et al., 2003). The Wenchang River (drainage area 381 km<sup>2</sup>, total length 37 km, mean annual discharge 9.1 m<sup>3</sup>/s) and the Wenjiao River (drainage area 522 km<sup>2</sup>, total length 56 km, mean annual discharge 11.6 m<sup>3</sup>/s) empty into the Bamen Bay (Zeng and Zeng, 1989) and form the Wenchang/Wenjiao River estuary (areal extent:  $\sim 40$  km<sup>2</sup>; 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<sub>2</sub>O<sub>3</sub> (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

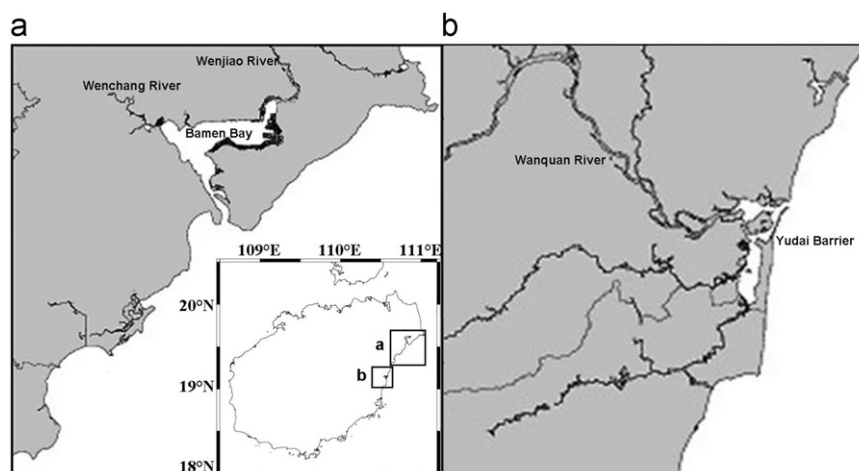


Fig. 1. Estuaries of East Hainan under investigation: (a) Wenchang/Wenjiao river estuary (WWR) and (b) Wanquan river estuary (WR).

with an estimated area of  $\sim 21.6 \text{ km}^2$  and estimated effluents of  $\sim 210 \cdot 10^6 \text{ m}^3/\text{yr}$  (Herbeck et al., this issue; Unger et al., this issue;). Minor contamination of both systems may also originate from municipal discharge of small towns. Hainan has a population density of 255 inhabitants/ $\text{km}^2$ .

## 2.2. Sampling

Surface water samples were collected during the dry season (Dec. 2006) and the wet seasons (Aug. 2007 and Jul./Aug. 2008) in the WR and the WWR (exact positions may be obtained from the corresponding author upon request). Upstream of the ship, low-density polyethylene bottles (LDPE, 1 L, Nalgene<sup>®</sup>) were filled by hand with surface water from a depth of about 0.3 m. Within 20 h the water samples were drawn through acid-cleaned  $0.4 \mu\text{m}$  polycarbonate filters (pre-weighed, Nuclepore, Whatman) into LDPE bottles (Nalgene<sup>®</sup>). A 10 mL aliquot of each sample was filled into a glass ampoule for the determination of the dissolved organic carbon (DOC) followed by the addition of phosphoric acid to remove the inorganic carbon and for sterilization. After acidification to pH 2 with sub-boiled concentrated nitric acid, sample bottles for trace elements were wrapped in polyethylene bags and stored at room temperature. The filter cakes were transferred to Petri dishes and stored at  $-10 \text{ }^\circ\text{C}$ .

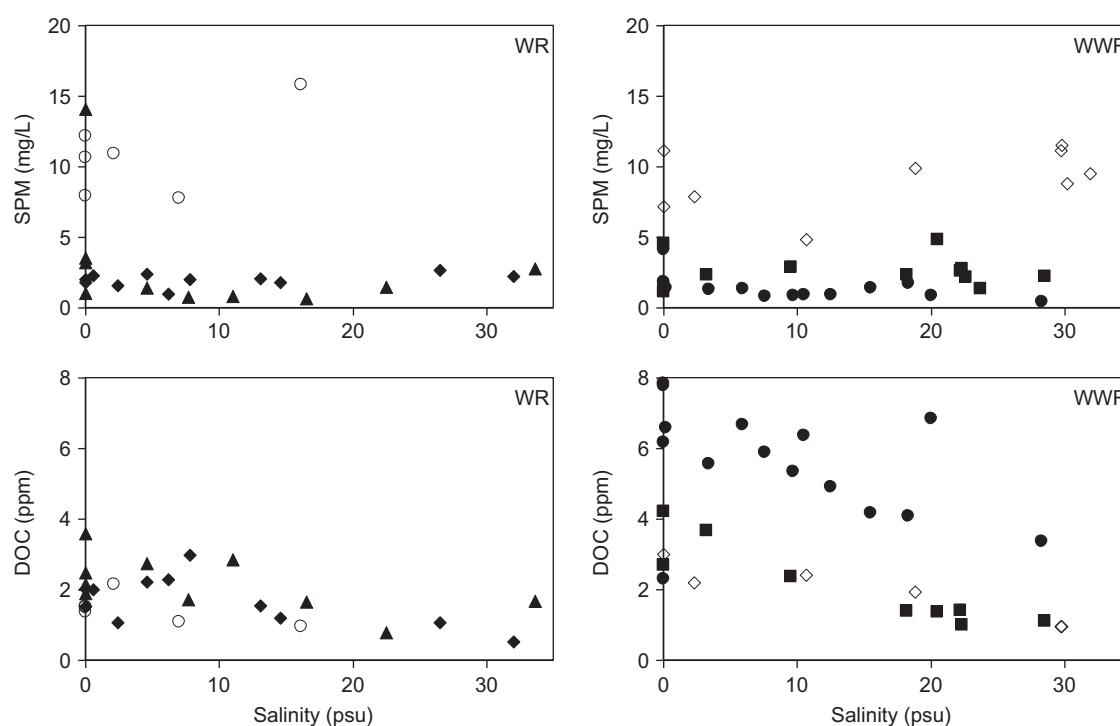
## 2.3. Pretreatment and measurement of dissolved metals

Sample work-up was performed in a clean-air room (class 1000) with additional clean benches of class 100. The filtrates were first irradiated in a UV-digester at  $90 \text{ }^\circ\text{C}$  for 2 h with addition of hydrogen peroxide in order to destroy the organic complexes. Then the trace metals were preconcentrated by an extraction/backextraction procedure developed by our workgroup based on the work of Danielsson et al. (1978). A 40–100 g sample (depending on the metal concentration) was weighed into a fluorinated ethylene propylene separatory funnel (FEP, Nalgene<sup>®</sup>) and after

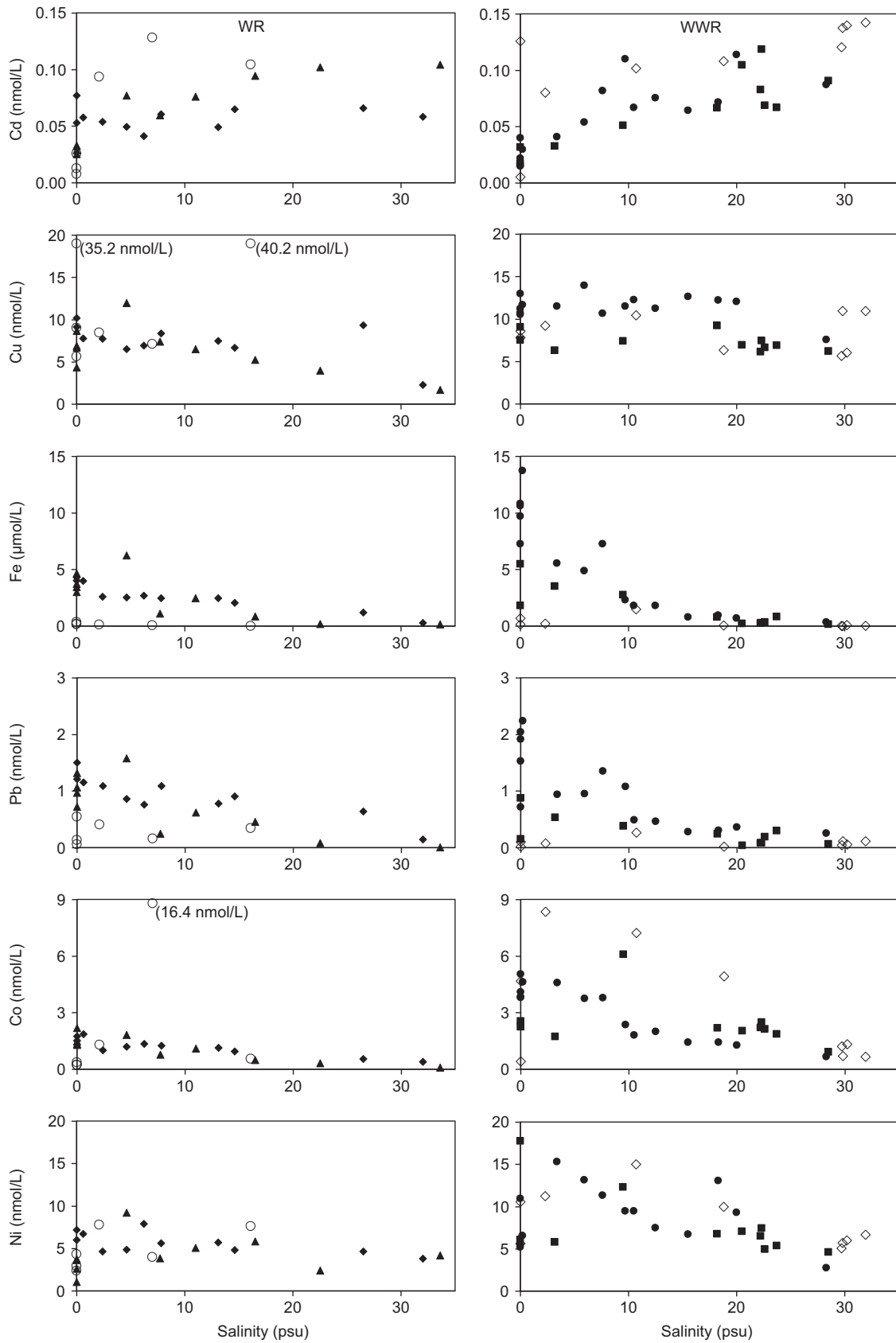
adding (i) ammonium acetate buffer to adjust the pH value of the sample to 4.0–4.5, (ii) 500  $\mu\text{L}$  APDC/NaDEDTC solution (0.06 M) and (iii) 10 mL Freon, the sample had been well shaken (15 min). After phase separation, the lower organic phase was drawn off into an acid-cleaned polypropylene tube and 100  $\mu\text{L}$  concentrated nitric acid were added, followed by a further addition of 1900  $\mu\text{L}$  Milli-Q water. After phase separation, the upper aqueous extract was removed into an acid-cleaned sample tube by using a pipette. The extract was analyzed by high-resolution inductively-coupled-plasma mass-spectrometry (HR-ICP-MS; Element 2, Thermo Scientific). Four certified reference materials from the National Research Council of Canada (NRCC) were investigated: SLRS-5 (river water), SLEW-3 (estuarine water), CASS-4 and NASS-5 (seawater); the results for all metals in all reference materials were inside the certified ranges. The detection limits ( $3\sigma$ ;  $n=13$ ) for Milli-Q water being subjected to UV-digestion and liquid/liquid-extraction were 0.004, 0.016, 2.63, 0.067, 0.004, 0.127 for Cd, Pb, Fe, Ni, Co, Cu, respectively. The mean precisions of replicates during the analysis of the certified reference materials were 0.7%, 2.6%, 10.2%, 5.7%, 2.6%, 5.3% for Cd, Pb, Fe, Ni, Co, Cu, respectively.

## 2.4. Pretreatment and analysis of particulate metals

The filter cakes were weighed and completely decomposed using a microwave-assisted pressure digestion technique after adding a mixture of concentrated nitric, hydrochloric and hydrofluoric acid (for details, see: Balzer et al., this issue). At regular intervals the certified reference material MESS-1 (marine sediment) from the NRCC was analyzed and all values were found to be in the certified ranges. The protocol implies a total destruction of the particles and includes trace metals in surface layers and in lattice positions. Therefore, results cannot be directly compared to many other studies of estuarine particles, during which the metals are leached from the surface layers by employing e.g.,



**Fig. 2.** Distribution of SPM and DOC vs. salinity (open symbols for the dry season and solid symbols for the wet seasons;  $\circ$ : WR 2006;  $\diamond$ : WWR 2006;  $\blacklozenge$ : WR 2007;  $\blacksquare$ : WWR 2007;  $\blacktriangle$ : WR 2008;  $\bullet$ : WWR 2008).



**Fig. 3.** Dissolved trace metals (left column: WR, right column: WWR) vs. salinity (open symbols: dry season, solid symbols: wet seasons; ○: WR 2006; ◇: WWR 2006; ◆: WR 2007; ■: WWR 2007; ▲: WR 2008; ●: WWR 2008); for further details: see text.

acetic acid or dilute hydrochloric acid. The metal concentrations were determined by HR-ICP-MS.

2.5. Other parameters

Environmental parameters such as salinity and pH were measured on the spot using a multi-sensor-device (MultiLine P3, WTW). Dissolved organic carbon (DOC) in the sealed glass ampoules was determined by high temperature catalytic oxidation (Total Carbon Analyzer, Apollo 9000; Tecmar) with a detection limit of 0.1 mg/L. Replicates from 19 samples gave an average relative standard deviations of 2.5% (n=5). Before use, the glass ampoules were pre-combusted at 450 °C for 4 h.

3. Results and discussion

3.1. Distribution of suspended particulate matter and environmental conditions

The distributions of the suspended particulate matter (SPM) and of the dissolved organic carbon (DOC), which were obtained during the three expeditions in the two estuaries, are shown in Fig. 2.

Except for a slight minimum at mid salinities, the SPM concentration was essentially constant in both estuaries during the wet seasons (Aug. 2007: on average 2.3 mg/L; Jul./Aug. 2008: on average 2.0 mg/L). The SPM values during the dry season (Dec. 2006: on average 9.8 mg/L) showed more variability and were distinctly higher than during both wet seasons, possibly originating from higher resuspension loadings at lower water levels. Also Li et al., this issue report higher SPM values for the dry seasons (Dec. 2006, Mar./Apr. 2009) in comparison to the wet seasons (Aug. 2007, Jul./Aug. 2008) for the Wanquan estuary (WR). The SPM concentrations were much lower than in other Chinese estuaries e.g., in the Daliao River (8–1001 mg/L; Guo et al., 2009), in the Changjiang estuary (70–350 mg/L; Koshikawa et al., 2007), or in the Zhujiang (Pearl River) Delta (70–247 mg/L; Ni et al., 2008). Summarizing the studies in several Chinese estuaries, Zhang and Liu (2002) reported a typical

SPM range from 10 mg/L to 20000 mg/L. The SPM content in both study areas is obviously at/below the lower limit of this range.

The DOC content generally decreased with increasing salinity with concentration ranges of 1–3 ppm during the dry season and 1–8 ppm during the two wet seasons. Comparable data was determined in the Amazon estuary (1–4 ppm; Sholkovitz et al., 1978) and in the Zhujiang estuary (1–4 ppm; Dai et al., 2000). The DOC content in the WWR was considerably higher than in the WR and its distribution showed much more scatter especially during the wet season of 2008. In accordance with the fact that the WWR is an aquacultural region with some biological activity, anthropogenic sources from the aquacultural activities and overflow during storms were suspected to be responsible for the higher DOC concentration in the WWR. In contrast to WR, both the river and the upper estuary (Bamen Bay) of the WWR system are surrounded by aquaculture ponds as shown in detail by Unger et al., this issue. Also the different DOC levels between the two wet seasons in WWR are probably related to different aquaculture inputs during the specific sampling campaigns.

The pH increased with increasing salinity (not shown). It ranged between 7.0 and 8.3 in the WR and between 6.8 and 8.5 in the WWR which is comparable with other Chinese estuaries: e.g., in the Zhujiang estuary (7.0–8.0; Dai et al., 2000) and in the Changjiang estuary (7.5–8.3; Zhang and Zhang, 2003).

3.2. Dissolved trace metals

The dissolved trace metal concentrations obtained during the three expeditions in the two estuaries are plotted as a function of salinity in Fig. 3. The dissolved metal concentrations depicted for salinity zero, which show considerable variability for most metals, are not always representative for the geographical freshwater entrance to the estuaries but also include samples which were taken upstream the rivers at different dates. The average concentrations for freshwater, in the estuarine mixing zone (0 < S < 28) and at high salinities of the WR and the WWR during the three expeditions are shown in Table 1.

Table 1

Dissolved trace metals (average values ± 1 standard deviation; n=number of values) in freshwater (S=0), in the estuarine mixing zone (0 < S < 28) and at high salinities (S > 28) of the WR and the WWR during the dry season (2006) and the wet seasons (2007 and 2008).

Expedition	Cd nmol/L	Cu nmol/L	Fe µmol/L	Pb nmol/L	Co nmol/L	Ni nmol/L
WR 2006						
S=0 (n=3)	0.02 ± 0.01	17 ± 16	0.23 ± 0.09	0.25 ± 0.26	0.27 ± 0.08	3.2 ± 1.0
0 < S < 28 (n=3)	0.11 ± 0.02	19 ± 19	0.06 ± 0.05	0.30 ± 0.13	6.1 ± 9.0	6.5 ± 2.2
S > 28 (n=0)	-	-	-	-	-	-
WWR 2006						
S=0 (n=2)	0.07 ± 0.09	8.2 ± 0.5	0.44 ± 0.39	0.06 ± 0.06	2.6 ± 3.0	8.1 ± 0.5
0 < S < 28 (n=3)	0.10 ± 0.01	8.7 ± 2.1	0.59 ± 0.79	0.12 ± 0.13	6.8 ± 1.7	12.1 ± 2.6
S > 28 (n=4)	0.14 ± 0.01	8.4 ± 2.9	0.04 ± 0.03	0.08 ± 0.04	0.98 ± 0.34	5.9 ± 0.7
WR 2007						
S=0 (n=2)	0.06 ± 0.02	9.7 ± 0.7	4.2 ± 0.2	1.4 ± 0.2	1.6 ± 0.2	6.6 ± 0.8
0 < S < 28 (n=8)	0.06 ± 0.01	7.6 ± 0.9	2.5 ± 0.8	0.81 ± 0.18	1.2 ± 0.4	5.6 ± 1.2
S > 28 (n=1)	0.06	2.3	0.28	0.15	0.41	3.8
WWR 2007						
S=0 (n=2)	0.02 ± 0.01	8.3 ± 1.1	3.7 ± 2.6	0.51 ± 0.51	2.4 ± 0.2	11.9 ± 8.3
0 < S < 28 (n=8)	0.07 ± 0.03	7.1 ± 1.0	1.1 ± 1.3	0.23 ± 0.17	2.6 ± 1.4	7.0 ± 2.3
S > 28 (n=1)	0.09	6.2	0.16	0.06	0.91	4.6
WR 2008						
S=0 (n=4)	0.03 ± 0.00	6.6 ± 1.8	3.7 ± 0.7	1.0 ± 0.2	1.6 ± 0.4	2.8 ± 1.3
0 < S < 28 (n=5)	0.08 ± 0.02	7.0 ± 3.0	2.2 ± 2.4	0.60 ± 0.58	0.90 ± 0.59	5.3 ± 2.6
S > 28 (n=1)	0.10	1.7	0.16	0.01	0.09	4.2
WWR 2008						
S=0 (n=4)	0.02 ± 0.01	11.4 ± 1.1	9.6 ± 1.6	1.6 ± 0.6	4.2 ± 0.6	6.8 ± 2.8
0 < S < 28 (n=10)	0.07 ± 0.03	12.0 ± 0.9	4.0 ± 4.1	0.85 ± 0.61	2.7 ± 1.3	10.2 ± 3.0
S > 28 (n=1)	0.09	7.6	0.35	0.25	0.67	2.8

**Cadmium:** Dissolved Cd concentrations generally increased with increasing salinity from 0.01 to 0.05 nmol/L in the freshwater to about 0.14 nmol/L in the saline waters during the dry season (only WWR) and to about 0.10 nmol/L at salinities above  $S=28$  during the wet seasons. During the dry season of 2006 and the wet season of Jul./Aug. 2008, the dissolved Cd showed a clear positive deviation from the theoretical dilution line in both estuaries. A similar non-conservative behaviour of Cd was also observed in many other studies, including the Changjiang estuary (Edmond et al., 1985; Elbaz-Poulichet et al., 1987), the Hudson River estuary (Yang and Sañudo-Wilhelmy, 1998), the Loire estuary (Waeles et al., 2004) and during laboratory experiments (e.g., Roux et al., 1998). This behaviour indicates a mobilization of dissolved Cd from the SPM into the solution phase due to the formation of highly stable Cd-chloro-complexes (Van der Weijden et al., 1977; Kraepiel, et al., 1997). Although showing some scatter, the dissolved Cd distribution during the wet season of August 2007 seems to be conservative. Such a behaviour, which was also observed e.g., in the outer Severn estuary (Harper, 1991) and in the Rhone estuary in July 1987 (Elbaz-Poulichet et al., 1996), might be related to low particulate Cd per volume and a short residence time of water and particles in the estuary as suggested by Kraepiel et al. (1997). While the residence times in the Hainan estuaries are indeed short (see above), the actual concentrations of particulate Cd per volume in 2007 and 2008 do not explain such a different behaviour between the two years. Thus, the exact reason for it remains open. Dilution by enhanced rainfall and the slightly lower pH during the dry season might have contributed to the seasonally lower concentrations of dissolved Cd during the wet seasons (Hatje et al., 2003). Because the dry season is also associated with comparably high levels of SPM, very low concentrations of dissolved Fe and Pb (see below), and essentially equal values for dissolved Cu and Ni, unknown properties of the additional particles might have played a role for the removal of dissolved Fe and Pb and the simultaneous release of Cd.

**Copper:** With increasing salinity dissolved Cu exhibited a slight but continuous and essentially conservative decline, which is clearly evident in the WR during all investigated seasons, but can be identified in the WWR estuary only as a tendency. Elevated Cu concentrations were observed during the wet season 2008 in WWR, coinciding with higher levels of DOC (Fig. 2). In combination with more scatter this may be explained by irregular inputs from adjacent aquaculture ponds (Balzer et al., this issue). Dissolved copper decreased from typically about 8–12 nmol/L in the freshwater to about 3–7 nmol/L at higher salinities. A similar conservative behaviour of dissolved Cu was also observed in the Amazon plume (Boyle et al., 1982), in the Changjiang estuary (Edmond et al., 1985), in the Mississippi River Delta (Shiller and Boyle, 1991) and in the tropical Bang Pakong estuary (Windom et al., 1988), and seems to be related to the Cu speciation in form of stable complexes with organic ligands (Shiller and Boyle, 1991; Roux et al., 1998). Strong positive deviations from simple dilution of dissolved Cu as observed e.g., in the Scheldt estuary were explained by sulfide precipitation under anoxic conditions at low salinities (Pauco and Wollast, 1997; Zwolsman et al., 1997); however, oxygen depletion was not likely to occur in the estuaries under investigation.

**Iron:** Dissolved Fe in both study areas and during both wet seasons decreased from typically 5–10  $\mu\text{mol/L}$  in the riverine water to 0.1–0.2  $\mu\text{mol/L}$  at higher salinities. Although the concentration of dissolved Fe in both estuaries during the dry season was about 10 times lower than during both wet seasons, there was also a slight decrease with salinity in both estuaries. Dissolved Fe showed a non-conservative behaviour and appeared to be removed from solution in both estuaries and during both

dry and wet seasons. Two elevated data points for Fe (and Pb) at low salinities are considered outliers being due to either contamination or irregular input from aquaculture ponds. Field and laboratory studies indicate that the main process affecting Fe during estuarine mixing is flocculation of colloidal Fe forms and subsequent sedimentation, globally resulting in a removal of more than 90% of the Fe river input during its way to the ocean (Boyle et al., 1977; Sholkovitz, 1978). In the wet season of 2008, the dissolved Fe of the freshwater and at low salinities in the WWR was two times higher than during all other expeditions and in the WR, suggesting lateral inputs from aquaculture ponds as discussed before. The relatively low concentrations of Fe (and Pb) in solution during the dry season 2006 coincide with similar particulate Fe levels and similar Fe/Al ratios but an about six times higher SPM concentration. This suggests enhanced adsorption onto unsaturated sites of the additional particle load during 2006. However, the suspended particles form only a fraction of the total particulate load with a major contribution from bed sediments in addition to riverine particles (Kraepiel et al., 1997). Thus, the striking difference between dissolved Fe and Pb during the dry and the wet seasons might also arise from different ratios of the two particle types

**Lead:** In the estuaries, dissolved Pb during both wet seasons exhibited (similar to Fe) a very strong decline from riverine waters (1–2 nmol/L) to marine waters (0.02–0.3 nmol/L). Such a

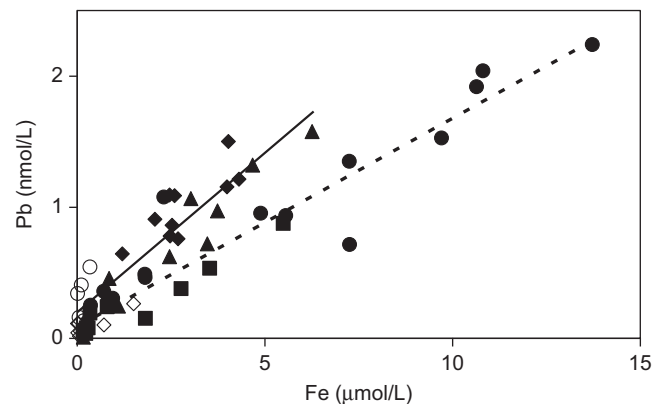


Fig. 4. Dissolved Pb vs. dissolved Fe (open symbols: dry season, solid symbols: wet seasons; ○: WR 2006; ◇: WWR 2006; ◆: WR 2007; ■: WWR 2007; ▲: WR 2008; ●: WWR 2008). Broken and solid line: correlation for all WWR data ( $r^2=0.849$ ) and for all WR data ( $r^2=0.923$ ), respectively.

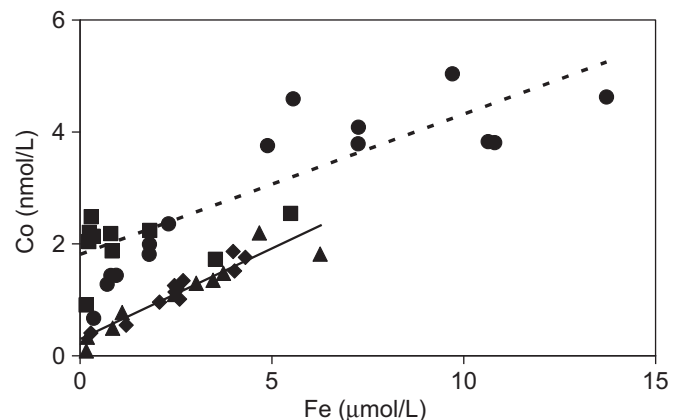
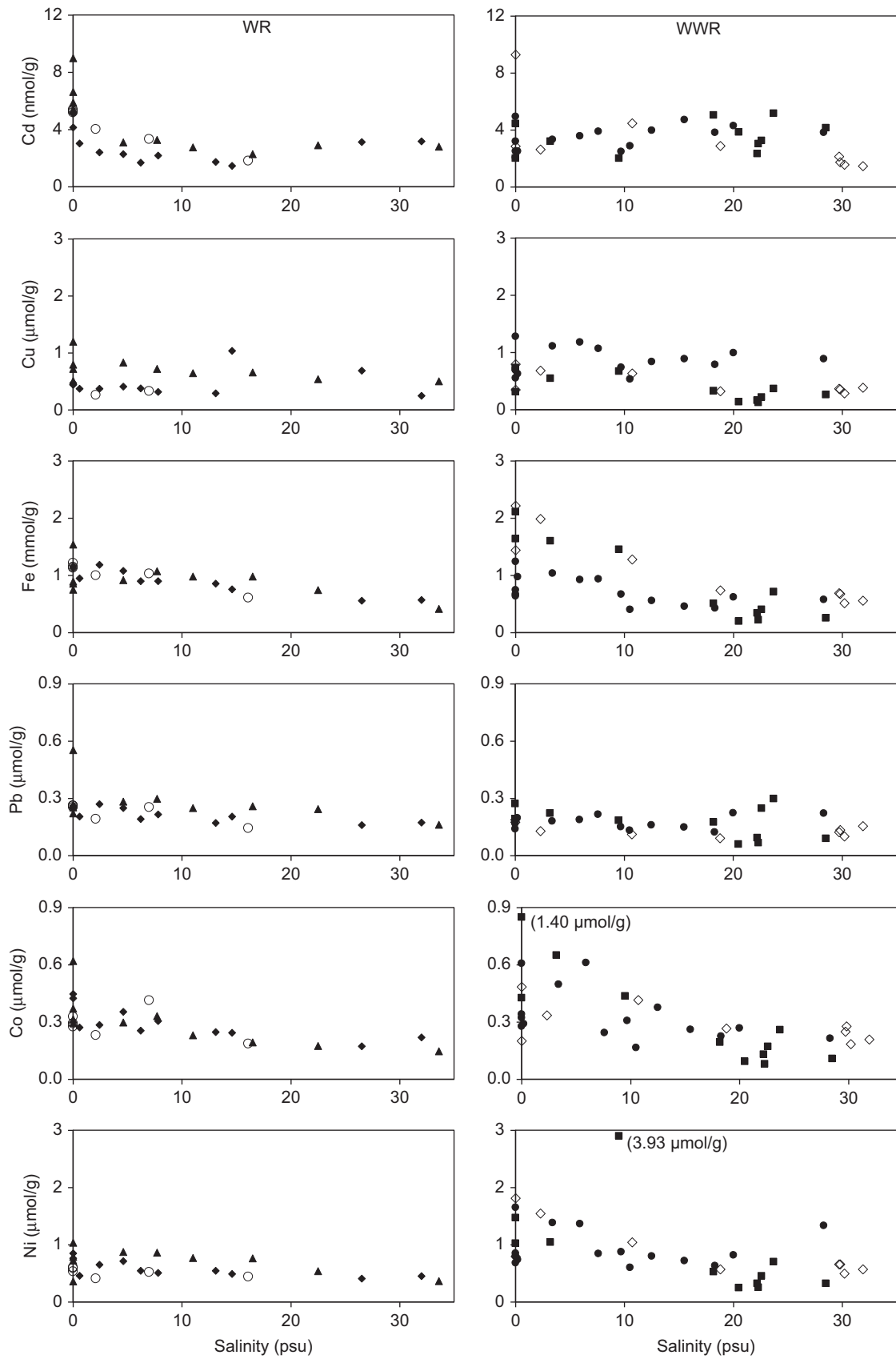


Fig. 5. Dissolved Co vs. dissolved Fe during the wet seasons (◆: WWR 2007; ■: WWR 2007; ▲: WR 2008; ●: WWR 2008). Broken and solid line: correlation for the WWR data ( $r^2=0.887$ ) and for the WR data ( $r^2=0.515$ ), respectively.



**Fig. 6.** Particulate trace metals (left column: WR, right column: WWR) vs. salinity (open symbols: dry season, solid symbols: wet seasons; ○: WR 2006; ◇: WWR 2006; ◆: WR 2007; ■: WWR 2007; ▲: WR 2008; ●: WWR 2008); for further details: see text.

distribution was also observed in the Gironde estuary (Elbaz-Poulichet et al., 1984), in the Bristol Channel (Harper, 1991), in the Bang Pakong (Windom et al., 1988) and in the Cochin estuary (Ouseph, 1992) and is often explained by rapid sorption of dissolved Pb onto re-suspended particles. In contrast, dissolved Pb during the dry season showed only a small decline with increasing salinity and was 40–80% lower than during the wet seasons. Considering the good correlation between dissolved Fe and dissolved Pb ( $r^2=0.849$  for all WR data,  $r^2=0.923$  for all WWR data; Fig. 4), a removal of dissolved Pb with freshly precipitated Fe-oxy-hydroxides may be suspected (e.g., Balls, 1990; Wen et al., 2008).

**Cobalt:** During both wet seasons, dissolved Co in WR decreased continuously with increasing salinity from 2 to 5 nmol/L to less than 1 nmol/L and behaved similar as Fe and Pb. Also the differences between WR and WWR were similar to Fe and suggest that the distribution of Co might also be controlled by co-precipitation with Fe-oxy-hydroxides (Fig. 5). The good correlation of dissolved Co vs Fe in WR ( $r^2=0.887$ ) during the wet seasons supports the predominance of Fe-related processes. On the other hand, the weak correlation for the WWR system ( $r^2=0.515$ ) provides evidence for contributions from other processes; most probable are lateral inputs from aquaculture ponds which girdle the WWR rivers and upper estuary in contrast to the WR estuary (Herbeck et al., this issue; Unger et al., this issue). This behaviour of Co during the wet seasons contrasts with reports of dissolved Co maxima at low or mid salinities (Windom et al., 1988; Martino et al., 2002; Takara et al., 2010). While the few observations during the dry season in WR and WWR might be interpreted as low salinity maxima or conservative behaviour (at  $S > 1$ ), it is clear that additional work is needed to understand the estuarine behaviour of cobalt.

**Nickel:** During both wet seasons dissolved Ni concentration was essentially constant at about 5 nmol/L over the whole salinity profile in the WR, while in the WWR Ni decreased from 10 to 15 nmol/L to also about 5 nmol/L at higher salinities. When excluding two higher values, dissolved Ni might be considered conservative in both estuaries during the wet seasons, as also

observed e.g., in the Göta river estuary (Danielsson et al., 1983). A part of the Ni variability at low salinities may be explained by fluctuations in the incoming river water (Chaudry and Zwolsman, 2008) and (in the WWR) may also contain an anthropogenic contribution from the Wenchang town being located at the Wenchang tributary. In addition, at salinities of about  $S=20$  diffuse inputs in WWR from aquaculture may be suspected. During the dry season, dissolved Ni had a tendency for a positive deviation from conservative behaviour, which might also be attributed to anthropogenic discharges (e.g., Campbell et al., 1988; Martino et al., 2004).

### 3.3. Particulate trace metals

The concentrations of Cd, Cu, Fe, Pb, Co and Ni in the particles obtained during the three expeditions in the two estuaries are plotted as a function of salinity in Fig. 6. The average values are shown in Table 2. In the WR system, all particulate metals show a very homogeneous distribution with constant or slightly decreasing levels over the whole estuarine salinity profile. Except for some variability among the freshwater samples, no difference occurred between the seasons. In contrast, the salinity profiles of the particulate trace metals in the WWR system show much more scatter in the data, but mainly at the same concentration levels as in WR. Some slightly positive deviations from simple endmember mixing suggest that in WWR particles with different properties might have contributed to the composite signals. Likely candidates with slightly differing properties are riverine particles entering the estuary, resuspended bottom sediments and possibly also some aquacultural particles.

In order to identify particles of potentially differing origin among the expeditions and to obtain hints for biogenic and/or anthropogenic contributions (Zhang and Liu, 2002), the trace metal contents of all SPM samples were normalized to aluminium as a proxy for the mineral particle matrix (not shown). The particulate Al itself decreased linearly along the salinity profile from  $3.0 \pm 1$  mmol/g in the freshwaters and in the low salinity

**Table 2**  
Particulate trace metals (average values  $\pm 1$  standard deviation;  $n$ =number of values) in freshwater ( $S=0$ ), in the estuarine mixing zone ( $0 < S < 28$ ) and at high salinities ( $S > 28$ ) of the WR and the WWR during the dry season (2006) and the wet seasons (2007 and 2008).

Expedition	Cd nmol/g	Cu $\mu$ mol/g	Fe mmol/g	Pb $\mu$ mol/g	Co $\mu$ mol/g	Ni $\mu$ mol/g
WR 2006						
S=0 ( $n=3$ )	5.3 $\pm$ 0.1	0.33 $\pm$ 0.02	1.2 $\pm$ 0.0	0.26 $\pm$ 0.00	0.30 $\pm$ 0.03	0.57 $\pm$ 0.04
0 < S < 28 ( $n=3$ )	3.1 $\pm$ 1.1	0.28 $\pm$ 0.02	0.88 $\pm$ 0.24	0.20 $\pm$ 0.05	0.28 $\pm$ 0.12	0.46 $\pm$ 0.06
S > 28 ( $n=0$ )	–	–	–	–	–	–
WWR 2006						
S=0 ( $n=2$ )	6.1 $\pm$ 4.6	0.57 $\pm$ 0.32	1.8 $\pm$ 0.5	0.18 $\pm$ 0.01	0.34 $\pm$ 0.20	1.3 $\pm$ 0.7
0 < S < 28 ( $n=3$ )	3.3 $\pm$ 1.0	0.55 $\pm$ 0.20	1.3 $\pm$ 0.6	0.11 $\pm$ 0.02	0.34 $\pm$ 0.07	1.1 $\pm$ 0.5
S > 28 ( $n=4$ )	1.7 $\pm$ 0.3	0.35 $\pm$ 0.04	0.61 $\pm$ 0.09	0.13 $\pm$ 0.02	0.23 $\pm$ 0.04	0.60 $\pm$ 0.08
WR 2007						
S=0 ( $n=2$ )	4.6 $\pm$ 0.7	0.46 $\pm$ 0.02	1.1 $\pm$ 0.0	0.26 $\pm$ 0.01	0.44 $\pm$ 0.01	0.81 $\pm$ 0.06
0 < S < 28 ( $n=8$ )	2.2 $\pm$ 0.6	0.48 $\pm$ 0.25	0.91 $\pm$ 0.19	0.21 $\pm$ 0.04	0.27 $\pm$ 0.05	0.54 $\pm$ 0.10
S > 28 ( $n=1$ )	3.2	0.25	0.57	0.17	0.22	0.45
WWR 2007						
S=0 ( $n=2$ )	3.2 $\pm$ 1.7	0.52 $\pm$ 0.30	1.9 $\pm$ 0.3	0.23 $\pm$ 0.06	0.91 $\pm$ 0.69	1.2 $\pm$ 0.3
0 < S < 28 ( $n=8$ )	3.5 $\pm$ 1.1	0.32 $\pm$ 0.20	0.68 $\pm$ 0.55	0.17 $\pm$ 0.09	0.25 $\pm$ 0.20	0.9 $\pm$ 1.2
S > 28 ( $n=1$ )	4.2	0.26	0.26	0.09	0.11	0.32
WR 2008						
S=0 ( $n=4$ )	6.7 $\pm$ 1.6	0.81 $\pm$ 0.29	1.0 $\pm$ 0.4	0.32 $\pm$ 0.15	0.40 $\pm$ 0.15	0.73 $\pm$ 0.28
0 < S < 28 ( $n=5$ )	2.9 $\pm$ 0.4	0.68 $\pm$ 0.11	0.94 $\pm$ 0.12	0.27 $\pm$ 0.02	0.25 $\pm$ 0.07	0.76 $\pm$ 0.13
S > 28 ( $n=1$ )	2.8	0.50	0.42	0.16	0.15	0.37
WWR 2008						
S=0 ( $n=4$ )	3.2 $\pm$ 1.3	0.81 $\pm$ 0.32	0.82 $\pm$ 0.28	0.17 $\pm$ 0.02	0.39 $\pm$ 0.15	1.0 $\pm$ 0.4
0 < S < 28 ( $n=10$ )	3.5 $\pm$ 0.7	0.88 $\pm$ 0.21	0.70 $\pm$ 0.25	0.17 $\pm$ 0.03	0.32 $\pm$ 0.14	0.88 $\pm$ 0.28
S > 28 ( $n=1$ )	3.8	0.89	0.58	0.22	0.21	1.3



region to  $2.2 \pm 0.3$  mmol/g near the coastal endmember ( $S > 28$ ). The only exception were some low Al values during the wet season 2007 in WWR at  $S=20-22$ ; concomitant high ratios to Al for Cd and Pb but not for Cu, Co, Ni suggests an anthropogenic contribution; alternatively, it may originate from an unusually high fraction of biogenic particles with elevated contents of particulate carbonates and/or organic matter (e.g., Koshikawa et al., 2007).

From high riverine values in the WR particulate Cd rapidly decreased and remained constant over the whole salinity range during both wet seasons, which was also found in the Gironde estuary (Kraepiel et al., 1997). In the WWR system, the particulate Cd appeared to slightly increase, but at a similar level as in the WR. The Cd/Al ratio was constant along the salinity profile except for elevated ratios of Cd/Al (and also of Pb/Al) at  $S=20-28$  during the wet season 2007 in WWR. Exponential decreases of particulate Cd (and also Cu) over the whole salinity profile (i.e., negative deviations from simple dilution) being attributed to desorption into the dissolved phase (e.g., in the highly polluted Scheldt estuary; Zwolsman et al., 1997; Paucot and Wollast, 1997) cannot be detected in the Hainan estuaries. With few other exceptions (e.g., enrichment of particulate Cd at mid salinities in the Danshuei River estuary; Jiann et al., 2005), simple estuarine mixing seems to be the dominant feature of particulate Cd worldwide (e.g., Balls, 1990; Paalman and Van der Weijden, 1992; Wen et al., 2008; Zwolsman and van Eck, 1999).

In both estuaries and during dry and wet seasons the particulate Cu showed no considerable change except for a slight decrease towards the coast. Such distributions are often found in estuaries, e.g., in several Texas estuaries (Benoit et al., 1994) and in the Gironde estuary (Kraepiel et al., 1997). However, also a positive relation of particulate Cu (and Pb) to salinity as a result of pH dependent sorption to Fe–Mn-oxides has been reported (Hatje et al., 2001). In contrast to any other of the six particulate trace metals, elevated values of particulate Cu/Al were observed during the wet season 2008 in WWR over the whole salinity range. In accordance with comparatively high values for dissolved and particulate arsenic during the same season in WWR (Balzer et al., this issue), a relatively high contribution of copper-rich inputs from adjacent aquaculture ponds may be suspected. This presumption is corroborated by a few measurements of aquaculture effluents which showed some very high dissolved Cu values.

Particulate Fe, Ni and Co during all seasons decreased with increasing salinity, generally with a larger slope in the WWR than in the WR. Such a distribution pattern was often found, e.g., in the Clyde estuary (Balls, 1990), in the Rhine/Meuse estuary (Paalman and Van der Weijden, 1992) and in the Tanshui River estuary (Fang and Lin, 2002). Also particulate Pb showed a slight decrease with salinity but no temporal variability. This essentially conservative salinity profile agrees with observations in the Gironde estuary (Kraepiel et al., 1997) and – combined with a negative relation to salinity – it was also observed in the Weser estuary (Turner et al., 1992). The ratios to Al of particulate Fe, Pb, Co and Ni during all expeditions (and seasons) were rather constant over the whole salinity range except for some high values of Fe/Al in WWR at low to mid salinities in 2006 and 2007, and of Pb during the wet season 2008. It cannot be ruled out that the high Fe/Al during the dry season 2006 partly correspond to the extremely low dissolved Fe during that expedition.

A striking feature of the ratios to Al of all trace metals under investigation was their rather constant lower limit over the whole salinity range. The ratios (in: mol/mol) of  $Cd/Al=6.0 \cdot 10^{-7}$ ,  $Cu/Al=1.0 \cdot 10^{-4}$ ,  $Fe/Al=2.4 \cdot 10^{-1}$ ,  $Pb/Al=6.0 \cdot 10^{-5}$ ,  $Co/Al=8.0 \cdot 10^{-5}$  and  $Ni/Al=1.8 \cdot 10^{-4}$  might be representative for the lattice composition of the particles from the drainage area. However these ratios to Al for Cu, Fe, Co, Ni are lower by 18–70%

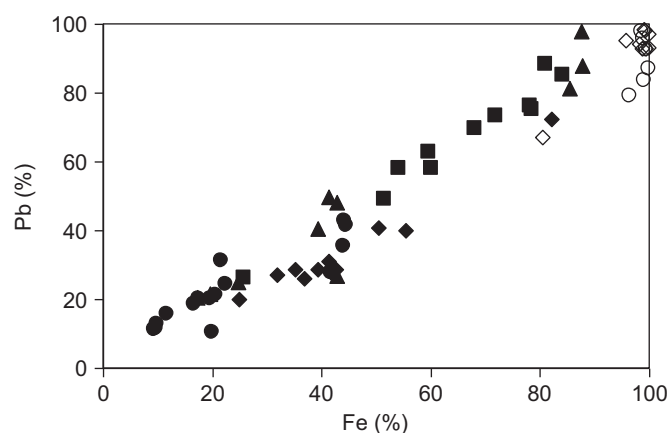


Fig. 7. Ratio of the percentages of the particulate metal on the sum of the dissolved and the particulate metal: Pb vs. Fe (open symbols: dry season, solid symbols: wet seasons; ○: WR 2006; ◇: WWR 2006; ◆: WR 2007; ■: WWR 2007; ▲: WR 2008; ●: WWR 2008).

than the top layer of the East-Hainan laterites which are the products of extreme tropical weathering (Ma et al., 2007; no data for Cd). In contrast, the Pb/Al of the estuarine particles was considerably higher than in the weathered laterites. If the above metal/Al ratios represent the lattice composition of the estuarine particles and if these particles are the weathering products of basalts from which the laterites formed, then the four metals Cu, Fe, Co and Ni were more refractory than Al in the parent material.

On a volume basis, the percentages of particulate metal on the total metal concentration (dissolved plus particulate) were essentially constant for Cd (~10%), Cu (~14%), Co (~30%) and Ni (~22%) in the estuarine waters ( $S > 0$ ), but with generally higher values during the dry season. In contrast to this behaviour of relatively constant particulate concentrations over the whole salinity range, the particulate concentrations per volume of Fe, Al, Cu, Ni, Pb, Cd in Galveston Bay all showed a general decrease (Wen et al., 2008).

The percentage of particulate Fe and Pb on the total concentration increased from about 10% to more than 80% along the salinity profile, which reflects the intense conversion of Fe and Pb from solution to particles in the estuaries and the strong preference of these two metals for particulate forms (Fig. 7). This also confirms the assessment made before, that flocculation of Fe colloids and co-precipitation of Pb were the dominant processes of particle-solution interaction for these metals in the two study areas.

The freshwater concentrations of particulate metals as one endmember for the mixing processes in the two estuaries were generally much lower than in typical European and North-American estuaries with a more industrialized character (Balls, 1989, 1990), but they agreed with other Chinese estuaries (Table 3). For the marine endmember with salinities  $S \approx 30$ , neither considerable temporal nor spatial variability was observed in the two estuaries and the concentrations were comparable with typical levels of particulate Fe, Cu, Co and Ni in the South China Sea (Ho et al., 2007).

### 3.4. Distribution coefficients

The use of partition coefficients  $K_D=C_p/C_s$  is a common approach for describing solid-solution interactions; the  $K_D$ , however, is not a true equilibrium coefficient, but an empirical term which depends on various factors such as solution and particle composition, speciation, analytical approach to particulate forms, ratio of colloidal forms to truly dissolved ions, DOC and SPM

**Table 3**  
Particulate trace metals and SPM of East-Hainan estuaries (average values  $\pm 1$  standard deviation) in comparison to selected Chinese rivers ( $S=0$ ) and estuaries ( $S>0$ ) (average or typical ranges; \*: estimated from the figures; \*\*: extract or leach).

Study area	SPM mg/L	Cd nmol/g	Cu $\mu\text{mol/g}$	Fe mmol/g	Pb $\mu\text{mol/g}$	Co $\mu\text{mol/g}$	Ni $\mu\text{mol/g}$	Refs.
East Hainan								
$S=0$	$5.3 \pm 4.4$	$4.9 \pm 2.1$	$0.62 \pm 0.29$	$1.21 \pm 0.46$	$0.24 \pm 0.09$	$0.44 \pm 0.27$	$0.90 \pm 0.40$	a
$0 < S < 28$	$3.0 \pm 3.3$	$3.1 \pm 0.9$	$0.57 \pm 0.29$	$0.85 \pm 0.38$	$0.19 \pm 0.06$	$0.29 \pm 0.12$	$0.79 \pm 0.61$	
$S > 28$	$6.1 \pm 4.6$	$2.7 \pm 1.0$	$0.44 \pm 0.21$	$0.54 \pm 0.14$	$0.15 \pm 0.04$	$0.20 \pm 0.05$	$0.59 \pm 0.3$	
Daliaohe ( $S=0$ )	851	–	0.80	0.93	0.69	1.42	2.91	b
Yalujiang ( $S=0$ )	127	5.6	0.62	0.69	0.27	0.23	0.63	c
Shuangtaizihe ( $S=0$ )	4651	6.9	0.60	0.78	0.40	0.35	0.86	c
Luanhe ( $S=0$ )	4633	7.4	0.86	0.90	0.33	0.29	0.88	c
Haihe ( $S=0$ )	3927	7.7	0.61	–	0.37	–	0.88	b
Huanghe ( $S=0$ )	25581	1.6	0.44	0.63	0.08	–	–	d
Huanghe ( $S=0$ )	2000–31500	1.5	0.42	0.67	0.08	0.24	0.69	e
Huanghe ( $S=0$ )	26829	1.5	0.42	0.67	0.08	0.24	0.69	b
Changjiang ( $S=0$ )	494	2.7	0.76	0.84	0.16	–	–	f
Changjiang ( $S=0$ )	539	2.6	0.98	0.93	0.24	0.32	2.11	b
Changjiang ( $S=0$ )	10–20000	3.6	0.98	0.93	0.19	0.32	1.09	c
Changjiang estuary ( $S > 0$ )	100–1000	4.1	0.7	0.94	0.15	0.52	0.95	g
Changjiang estuary ( $S > 0$ )**	70	2*	1.1*	0.5*	0.2*	0.4*	2.6*	h
Qiantangjiang ( $S=0$ )	187	2.5	1.41	–	0.37	–	1.58	b
Jiaojiang ( $S=0$ )	1254	6.7	0.57	0.65	0.26	0.29	0.79	c
Minjiang ( $S=0$ )	128	2.8	0.82	–	0.30	–	–	b
Jiulongjiang ( $S=0$ )	211	4.4	0.62	1.03	0.29	0.39	1.38	b
Zhujiang ( $S=0$ )	348	5.3	0.77	–	0.29	0.32	–	d
Zhujiang ( $S=0$ )	227	6.7	0.80	0.88	0.36	0.30	1.05	c
Tanshui River estuary ( $S > 0$ )**	15*	–	0.35–7.9	0.19–1.2	–	0.03–0.32	0.1–1.8	i
Tanshui River estuary ( $S > 0$ )	10*	2–20*	1–11*	–	0.2–0.7*	–	1–6*	j
Open South China Sea	0.4	–	0.68	0.40	–	0.25	0.46	k

(a): This study, (b): Zhang (1995), (c): Zhang and Liu (2002), (d): Qu and Yan (1990), (e): Huang et al. (1992), (f): Martin and Meybeck (1979), (g): Zhang (1999), (h): Wang and Liu (2003), (i): Fang and Lin (2002), (j): Jiann et al. (2005), (k): Ho et al. (2007).

concentration, pH, temperature, and others (Bourg, 1987; Comans and van Dijk, 1988; Balls, 1989; Turner, 1996; Hatje et al., 2003). The situation is further complicated by the fact that suspended particles represent mixtures of particles originating from the rivers entering the estuary and from resuspended bottom sediments. For the samples of this study, the logarithms of the distribution coefficient were plotted versus salinity in Fig. 8.

Among the six elements under investigation, only the  $K_D$  value of Cd clearly decreased along the salinity profile in the estuary. This appears to result from complexation of dissolved Cd by seawater anions forming highly stable Cd-chloro-complexes and from successful competition of seawater cations for sorption sites on the SPM (e.g., Balls et al., 1994; Turner, 1996). In contrast, the  $K_D$ 's of Cu, Ni and Co showed neither temporal nor spatial variation nor any significant change with salinity.

Fe and Pb have the greatest affinity for the particulate phase with a  $\log_{10}K_D$  increase along the salinity profile from 5.4 to 8.0 L/kg for Fe and from 4.9 to 7.2 L/kg for Pb during the wet seasons. Such a positive correlation of  $K_D$ 's for Fe and Pb with salinity and no relation to salinity for Cu and Ni was often observed in estuaries (e.g., Balls et al., 1994). The higher  $K_D$ 's for Fe and Pb in both estuaries during the dry season were a consequence of its very low dissolved Fe and Pb and seemed to be related to the specific properties of its much higher SPM loading. Several processes may contribute to these peculiarities of the dry season, such as the additional input of particles with differing surface properties from the drainage basin and/or from bottom sediments, and the enhanced flocculation of colloidal Fe. An explanation is difficult, because the dissolved Fe during the dry season is – per volume – more than one order of magnitude lower than the Fe content in the particles which have a similar composition at all seasons (Fig. 6).

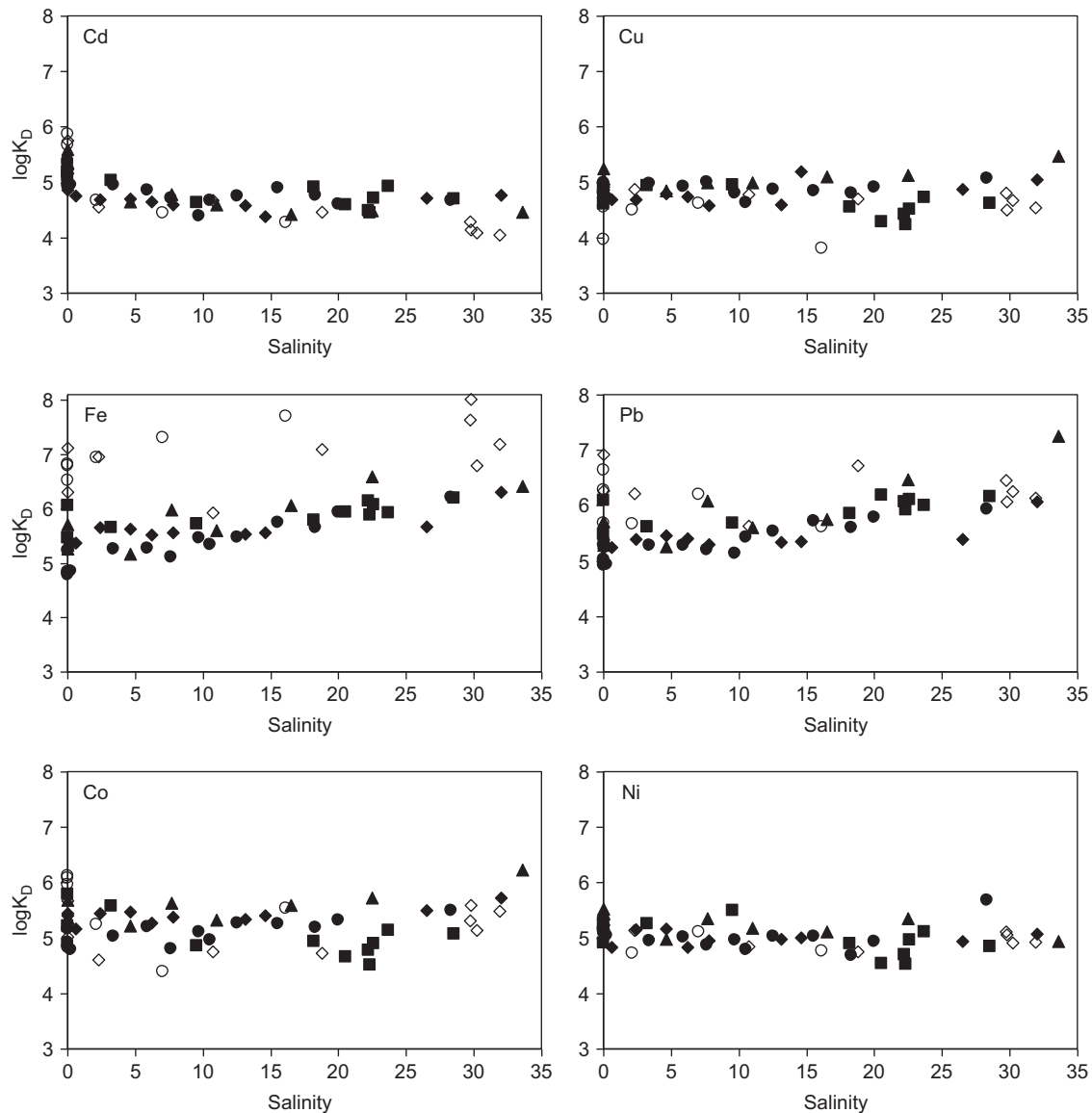
The general order of the  $\log_{10}K_D$  for all samples was on average: Fe (6.0) > Pb (5.7) > Co (5.3) > Ni (5.1) > Cu (4.8)  $\approx$  Cd (4.8), and essentially agreed with the results presented for the

Seine estuary (Pb > Co > Cu > Zn > Ni > Cd; total digestion; Chiffoleau et al., 1994) and for North Australian estuaries (Fe > Pb > Zn > Ni  $\approx$  Cd  $\approx$  Cu; extract at pH 2; Munksgaard and Parry, 2001). Although sorption processes of the trace metals are sensitive for the source and the composition of the particles, and although the  $K_D$  is influenced by the method adopted for the particulate metal determination (total destruction vs. partial extraction; Turner et al., 1992), the  $K_D$ 's obtained in this study differ from published data (e.g., Chiffoleau et al., 1994; Zhang, 1995; Kraepiel et al., 1997; Munksgaard and Parry, 2001; Tang et al., 2002) by less than one order of magnitude.

In estuarine studies a so-called “particle concentration effect” is often observed, which means that for a particular element the  $K_D$  decreases with increasing SPM loadings (e.g., Balls, 1989; Benoit et al., 1994; Jiann et al., 2005). When the  $K_D$ 's of this study are plotted vs. SPM (not shown), the values for all investigated metals form one cluster for the wet seasons at SPM loadings of 1–4 mg/L and a second cluster for the dry season at SPM loadings of 8–12 mg/L (cf. Fig. 2). Possibly owing to the overall relatively low SPM concentrations and the low particulate concentrations in WR and WWR, no relationship at all was found between  $K_D$ 's and SPM for Cd, Cu, Co and Ni, while Fe and Pb even showed a slight increase. Also in the Changjiang  $K_D$ 's of Cd, Cu and Ni did not change with increasing SPM concentration between 40 and 350 mg/L, while the  $K_D$ 's of Fe, Mn and Al showed drastic declines as a consequence of their high ratio of particulate metal to dissolved metal (Koshikawa et al., 2007). A stable concentration of particulate Cu, Ni and Pb in the Changjiang relative to the SPM, which varied over several orders of magnitude, was reported earlier by Zhang (1999).

### 3.5. Comparison of WR and WWR with other Chinese estuaries

This study asserted that all dissolved and particulate metals were similar or somewhat lower (Co, Ni) in the WR with its low



**Fig. 8.**  $\log_{10}K_D$  (L/kg) vs. salinity (open symbols: dry season, solid symbols: wet seasons; ○: WR 2006; ◇: WWR 2006; ◆: WR 2007; ■: WWR 2007; ▲: WR 2008; ●: WWR 2008).

industrial and agricultural run-off than in the WWR estuary, which probably is affected by aquacultural contamination plus some municipal sewage along the river (Tables 1 and 2). This is partly a consequence of the exceptional characteristics during the wet season of 2008 in the WWR, when not only DOC, but also dissolved Cu, Fe, Pb and Co at low salinities as well as the particulate Cu, Co and Ni were pronouncedly higher than during the other two expeditions. As also reported for dissolved arsenic (Balzer et al., this issue), this points to extraordinary lateral inputs probably originating from adjacent aquaculture ponds as shown for nutrients, dissolved organic matter and suspended particles by Herbeck et al., this issue.

A comparison of the particulate metal concentrations with large Chinese rivers demonstrates, that the two Hainan estuaries contained similar levels of Cd, Cu, Pb, Co and Ni (Table 3). The lower concentrations especially in the Huanghe and the Changjiang probably originate from lower trace metal contents in soils of the northern drainage areas (Zhang, 1995). It is noteworthy that the particulate and dissolved Fe concentrations in both study areas mostly exceeded those of the other estuaries listed in

Table 4. This is probably related to the generally high Fe content in the soils of Hainan Island, although a small contribution – via atmospheric transport – by the Shilu Iron Mine cannot be excluded.

The dissolved concentrations of the trace metals in the freshwater part of the WR and the WWR were similar (Cd, Ni, Cu) or higher (Fe, Pb, Co) than in the large Chinese rivers (Table 4). The most striking difference between the Hainan estuaries and the large rivers of mainland China is the orders of magnitude higher SPM loading of the latter (Zhang, 1995; Zhang and Liu, 2002). Higher SPM, however, possibly fostered by longer residence times only serve for a faster attainment of sorption equilibria, but gives no general direction for concentration changes in the solution phase.

With respect to the estuarine chemistry of the Chinese aquatic systems, detailed information is only available for the Changjiang with its rather stable estuarine trace metal distribution (Zhang, 1999; Wang and Liu, 2003) and about the subtropical Tanshui (Fang and Lin, 2002; Jiann et al., 2005). Compared to these estuarine systems, the tropical East-Hainan estuaries ( $S > 0$ ) generally contained similar or lower trace metal concentrations

**Table 4**  
Dissolved trace metals of East-Hainan estuaries (average values  $\pm 1$  standard deviation) in comparison to selected Chinese rivers ( $S=0$ ) and estuaries ( $S > 0$ ), (averages or typical ranges; \*: estimated from the figures).

Study area	SPM mg/L	Cd nmol/L	Cu nmol/L	Fe $\mu\text{mol/L}$	Pb nmol/L	Co nmol/L	Ni nmol/L	Refs.
East Hainan								
$S=0$	$5.3 \pm 4.4$	$0.03 \pm 0.03$	$10 \pm 6.8$	$4.1 \pm 3.6$	$0.88 \pm 0.65$	$2.2 \pm 1.6$	$5.9 \pm 4.0$	a
$0 < S < 28$	$3.0 \pm 3.3$	$0.07 \pm 0.03$	$9.6 \pm 5.7$	$2.2 \pm 2.7$	$0.59 \pm 0.49$	$2.7 \pm 3.0$	$7.7 \pm 3.2$	
$S > 28$	$6.1 \pm 4.6$	$0.11 \pm 0.03$	$6.4 \pm 3.4$	$0.14 \pm 0.13$	$0.10 \pm 0.08$	$0.75 \pm 0.40$	$4.9 \pm 1.3$	
Huanghe ( $S=0$ )	25600	0.02	22	0.35	0.14	0.21	6.9	b
Huanghe ( $S=0$ )	27000	0.03	20	0.24	0.13	0.30	7.5	c
Changjiang ( $S=0$ )	20–5000	0.03	26	0.55	0.26	–	2.5	d
Changjiang estuary ( $S > 0$ )	70	0.02–0.36	19–26	0.1–0.6	2.3–3.4	1.4–2.9	18–28	e
Minjiang ( $S=0$ )	128	0.04	14	–	0.63	–	–	c
Jiulongjiang ( $S=0$ )	211	0.03	13	16	0.07	0.14	1.4	c
Tanshui River estuary ( $S > 0$ )	15*	–	5–53	0.39–3.4	–	0.3–6.1	7–310	f
Tanshui River estuary ( $S > 0$ )	10*	0.20	60	–	0.88	–	138	g
Open South China Sea	–	0.01	0.8	0.19	–	–	2.3	h

(a): This study, (b): Zhang et al. (1994), (c): Zhang (1995), (d): Edmond et al. (1985), (e): Wang and Liu (2003), (f): Fang and Lin (2002), (g): Jiann et al. (2005), (h): Wen et al. (2006).

in the suspended particles (Table 3), and also similar or lower concentrations for Cd, Cu, Pb, Co and Ni, but higher levels of Fe the solution phase (Table 4). However, the concentration differences, the number of regions for comparison and the amount of necessary subsidiary data are not large enough to derive specific features for the estuarine chemistry of tropical East-Hainan.

The information compiled in Tables 3 and 4 demonstrate, that on a global scale the Chinese aquatic systems including the two Hainan estuaries have lower levels of dissolved and particulate metals than the estuaries of countries with a longer history of industrialization and with stronger signals of anthropogenic activities (Balls, 1989; Zhang, 1995). The concentrations of the investigated trace metals in solution and in the particles suggest a low level of contamination especially in these two Hainan estuaries.

#### 4. Conclusions

This study provides data for dissolved and particulate cadmium, copper, iron, lead, cobalt and nickel concentrations plus particulate aluminium along the salinity gradients of two estuaries of the tropical East-Hainan Island during both the wet and the dry season. The estuarine chemistry of the Wanquan River (WR) with its low industrial and agricultural run-off and of the Wenchang/Wenjiao River (WWR), which probably is affected by aquacultural contamination plus some municipal sewage, is similar but not identical.

It was found that the dissolved trace metals mostly behaved conservatively. A positive deviation from the theoretical dilution line was observed for dissolved cadmium, while the converse situation applied for iron and lead. Seasonal variability was observed during the dry season for dissolved iron and lead with a strong lowering and for dissolved Cd with higher values. 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, which itself decreased with salinity, revealed specific particle properties during the different expeditions, e.g., Cu-rich particles during the wet season 2008 in WWR, which coincided with very high DOC levels and generally low percentages of particulate metals on the total metal concentration (i.e., sum of dissolved and particulate) per unit volume. In general, the dynamics of Fe chemistry dominated the distribution of Pb in all forms and partly also of Co as revealed by correlations in the dissolved state and in their ratio of particulate metal to the total metal per unit volume.

The distribution coefficients of the trace metals  $K_D = C_P/C_S$  decreased in the order  $Fe > Pb > Co > Ni > Cu \approx Cd$ . Except for the expected  $K_D$  decrease of Cd with increasing salinity, the  $K_D$ 's of Cu, Co and Ni were constant, and Fe and Pb exhibited slightly positive correlations with salinity. There was no "particle concentration effect", i.e., a negative dependence of the  $K_D$  on the SPM level.

The most striking difference between the large Chinese rivers especially from temperate latitudes and the two Hainan water systems is the extremely low SPM in the latter ones. Together with its low levels of particulate trace metals, this entails the possibility that equilibrium desorption might be so small in absolute amounts that the transfer is hardly detectable in the solution phase.

One of the aims of this study was to use the distributions of environmentally relevant trace metals during estuarine mixing for assessing the pollution state of the East-Hainan estuaries. In most cases, both particulate and dissolved metal concentrations in the Wenchang/Wenjiao River estuary were higher than in the Wanquan River estuary, which is probably due to diffuse inputs from aquaculture ponds to the WWR system. The trace metal levels of these East-Hainan aquatic systems were similar to large rivers in mainland China and showed no significant contamination when compared to rivers and estuaries in Europe and North America. This is especially important with respect to the recently observed health decline of the coral reefs at the east coast of Hainan.

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