Estuarine, Coastal and Shelf Science 93 (2011) 431–437

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

# Particle dynamics of $^{7}$Be, $^{210}$Pb and the implications of sedimentation of heavy metals in the Wenjiao/Wenchang and Wanquan River estuaries, Hainan, China

Dekun Huang, Jinzhou Du*, Jing Zhang

*State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China*

ARTICLE INFO

*Article history:*
Received 28 January 2011
Accepted 12 May 2011
Available online 20 May 2011

*Keywords:*
suspended particles
$^{7}$Be
$^{210}$Pb
heavy metals
removal
Hainan Island

ABSTRACT

Radionuclides (i.e., $^{7}$Be and $^{210}$Pb) can be used to trace particle and sediment dynamics and to quantify coastal oceanic processes with time scales ranging from a few days to a hundred years. Here, we study the settling dynamics of suspended particles and the implication by sedimentary heavy metals in the Wenjiao/Wenchang River and Wanquan River estuaries through the measurement of the particulate $^{7}$Be and $^{210}$Pb nuclides. Activity in the particulate phase had a range of 2.1–54.5 and 4.6–67.9 Bq kg$^{-1}$ for $^{7}$Be and excess $^{210}$Pb ($^{210}$Pb$_{xs}$), respectively, in the Wenjiao/Wenchang River estuary. In the Wanquan River estuary, activity is in the range of 1.2–43.5 Bq kg$^{-1}$ for $^{7}$Be and 6.2–194.5 Bq kg$^{-1}$ for $^{210}$Pb$_{xs}$. At the same time, activity in the dissolved phase had a range of 0.46–1.26 and 0.30–1.17 Bq m$^{-3}$ for $^{7}$Be and $^{210}$Pb, respectively, in the Wenjiao/Wenchang River estuary; ranges of 0.10–2.31 and 0.09–1.87 Bq m$^{-3}$ for $^{7}$Be and $^{210}$Pb, respectively, were observed in the Wanquan River estuary. The distribution coefficients ($K_d$) for the two nuclides decreased within increased in suspended particle matters (SPM) concentration and/or salinity in Wanquan River estuary. The residence times of particulate $^{7}$Be and $^{210}$Pb$_{xs}$ had ranges of 0.4–1.6 and 1.65–5.15 days, respectively, in the Wenjiao/Wenchang River estuary; and ranges of 0.02–3.2 and 0.61–4.44 days, respectively in the Wanquan River estuary. All residence times for the two nuclides increased in the seaward direction. In the Wenjiao/Wenchang River estuary, we found that 11.8–21.0% of Cu, 3.0–9.0% of Zn and 43.2–69.9% for Cd is removed from the water column and deposited into the estuary, and 24.2–34.8% for Cu, 7.2–23.8% for Zn, and 70.0–82.5% for Cd in the Wanquan River estuary, respectively.



## 1. Introduction

Estuaries and coasts are commonly described as complex filters at the land–sea margin where both significant transformations of river and stream-borne suspended sediments and the biogeochemical cycling of key nutrients occur (Swarzenski et al., 2001, 2003; Rao et al., 2011). Rivers and estuaries can serve as important sources of metal and organic contaminants to coastal marine environments. Particle-reactive radionuclides (i.e., $^{7}$Be and $^{210}$Pb) serve as a set of powerful tracers that can be used to quantify sedimentary dynamics, including rates of suspended particulate matter removal (Ciffroy et al., 2003; Baskaran and Swarzenski, 2007; Jweda et al., 2008), sediment transport, sediment focusing/erosion, sediment resuspension and sediment accumulation and mixing (Dibb and Rice, 1989; Feng et al., 1999a, 1999b; Giffin and Corbett, 2003; Lima et al., 2005; Du et al., 2010). These nuclides can also serve as analogs for tracing the fate and transport of other particle-reactive contaminants in marine systems, such as polychlorinated biphenyls (PCBs) (Gustafsson et al., 1997a), polycyclic aromatic hydrocarbons (PAHs) (Gustafsson et al., 1997b; Fitzgerald et al., 2001) and heavy metals (Feng et al., 2002). Results from research on the transport and sources of metal contaminants (Ag, Cd, Cu, Pb and Zn) in the Hudson estuaries showed that metal contamination in the water column can come not only from local sediment resuspension but also from lateral advection (Feng et al., 2002).

The climate of Hainan is characterized by tropical monsoons and tropical oceans: offshore winds prevail during the winter monsoon season while landward winds prevail during the summer monsoon season. Tropical storms and typhoons frequently hit the island in August and September, bringing large amounts of rainfall (Mao et al., 2006). Wanquan River is the third largest river of Hainan Island, with a total length of about 163 km and drainage area of about $3.68 \times 10^{3}$ km$^{2}$. And its average annual runoff is $5.2 \times 10^{9}$ m$^{3}$ yr$^{-1}$(Zeng and Zeng, 1989; Wang et al., 2006). Wenjiao and Wenchang rivers, with a total length of 56 km and 37 km, directly inject into the Bamen Bay, with a total runoff about

* Corresponding author.
*E-mail address:* jzdu@sklec.ecnu.edu.cn (J. Du).

0272-7714/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ecss.2011.05.013

$6.52 \times 10^8$ $m^3$ $yr^{-1}$ (Wenjiao River: 11.6 $m^3$ $s^{-1}$; Wenchang River: 9.09 $m^3$ $s^{-1}$). Bamen Bay is a typical semi-enclosed water body, with a surface area of 40 $km^2$ historically and an average water depth of 1.0 m. The average tidal range is 0.75 m and the maximum tidal range is 2.06 m (Wang, 2002; Wang et al., 2006). Both estuaries have a micro-tidal, irregular diurnal tidal regime with mean range of about 0.7–0.8 m. The two estuaries are shallow lagoon region (<2 m) and the flow rate are low. This study focused on the distribution and dynamics of particulate radionuclides and the removal of heavy metal contaminants in the Wenjiao/Wenchang River and Wanquan River estuaries, both located on the northeastern coastline of Hainan, China. Coral reefs, mangroves and sea grass ecosystems all grow along this coastline. We seek to explain the distribution of these nuclides and to predict the removal rates of trace heavy metals in the estuaries. The removal behaviors of these heavy metals can provide a unique opportunity to understand the impacts of contamination on the river–estuarine ecosystem.

## 2. Sampling and methods

Approximately 200 L of surface water samples (0–1 m) was collected at the Wenjiao/Wenchang River and the Wanquan River in July and August of 2008 (Fig. 1). The water samples were passed through two consecutive 0.5-μm pre-cleaned polyethylene cartridge filters (Feng et al., 2002) to separate the particulate and dissolved phases of the radionuclides. The particulate samples were dried at 50 °C and ashed at 500 °C in the laboratory. The dissolved $^{7}Be$ and $^{210}Pb$ samples were co-precipitated with $Fe(OH)_3$, and the 200L dissolved sample was acidized with concentrated HCl. Following the addition of HCl, stable Pb (1 mg/100 L) and stable Be (1 mg/100 L) were added into the solution. After equilibrating for approximately 12 h, the $Fe(OH)_3$ precipitation was conducted using an ammonia solution with a pH of 7–8. After approximately 24 h, the precipitate and solution were separated by decanting the supernatant. The precipitate was then conducted by centrifugation and lyophilization in the laboratory (Kim et al., 1998; Baskaran and Swarzenski, 2007). Both the particulate and dissolved samples were transferred to the box for gamma analysis. The efficient of co-precipitation ((75 ± 7)%) of dissolved $^{210}Pb$ were obtained by analysis of stable Pb that we added quality amount using AAS. It is assumed that the efficient of co-precipitation of dissolved $^{7}Be$ are equaled to be those of $^{210}Pb$.

The radioactivity of $^{210}Pb$, $^{226}Ra$ and $^{7}Be$ was measured by a HPGe γ-ray detector (Canberra Be3830) with 35% counting efficiency and an energy resolution of 1.8 keV (at 1332 keV) using multi-layer shielding (ultra-low background system, 777 lead shield). The activities of $^{7}Be$ were determined from the γ-ray peak at 477.6 keV (10.5%). In this study, the activities of $^{210}Pb$ (i.e., supported and excess) were measured from its γ-radiation at 46.5 keV (4.25%). The activity of $^{226}Ra$ was determined at 295.2 keV (19.3%) and 351.9 keV (37.6%) for $^{214}Pb$ and at 609.3 keV (46.1%) and 1120.3 keV (15%) for $^{214}Bi$. The efficiency calibration of the detector systems was conducted by LabSOCS (Bronson, 2003). Excess $^{210}Pb$ ($^{210}Pb_{xs}$) activity was calculated by subtracting the estimated parent supported activity from the total activity in the suspended particles. Although we do not know the $^{222}Rn/^{226}Ra$ activity ratio in the SPM, a value of 0.5 has been reported in both lake and deep seas surface sediments and has been used to calculate $^{210}Pb_{xs}$ in the present work (Key et al., 1979; Imboden and Stiller, 1982; Baskaran and Santschi, 1993). Reported data for the short-lived nuclide $^{7}Be$ were corrected for the radioactive decay that had occurred between sample collection and analysis.

For metal analysis, the suspended particulate phase samples were digested by a combination of concentrated hydrofluoric acid

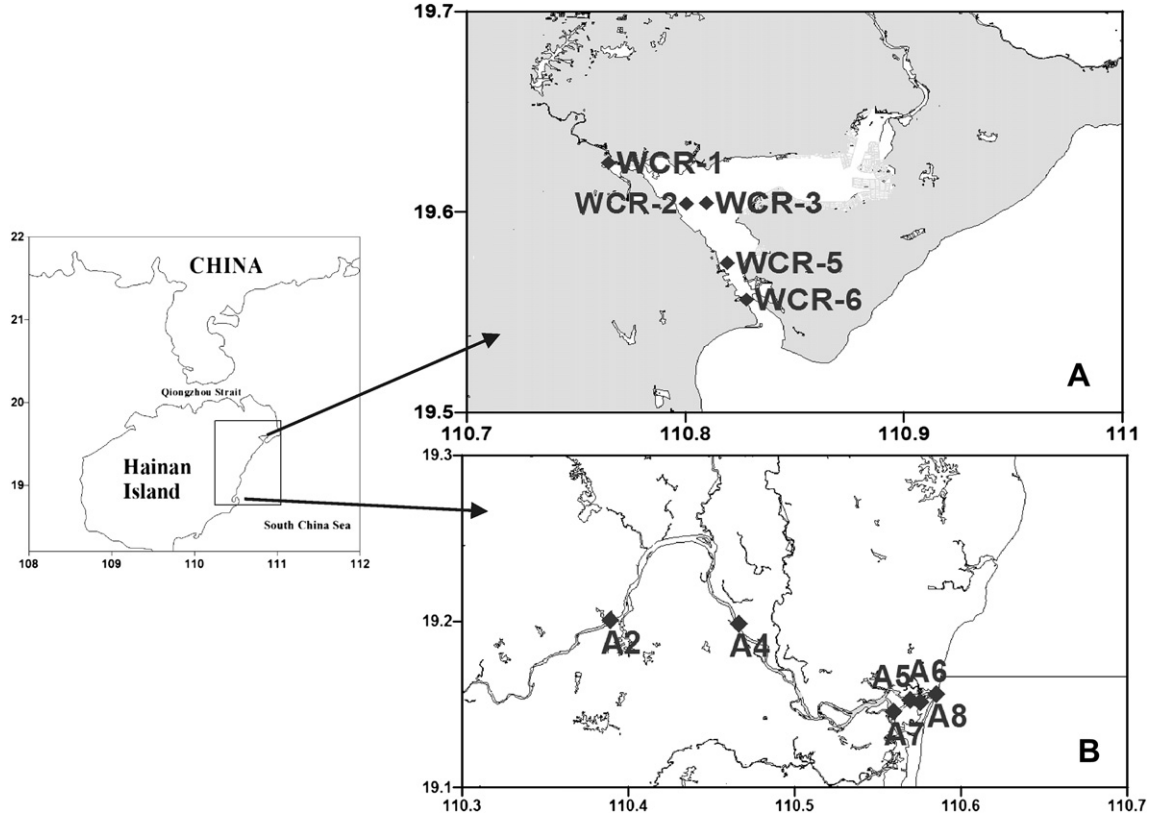


**Fig. 1.** Location maps of study area. Maps A and B show the station locations for surface water samples in the Wenjiao/Wenchang River and Wanquan River estuaries in detail.

**Table 1**
Hydrological and particulate $^{7}$Be and $^{210}$Pb activity in both the suspended particle and dissolved phases of the Wenjiao/Wenchang River and Wanquan River estuaries.

| Location | | SPM | Water depth | Salinity | $^{7}$Be | | $^{210}$Pb | |
|---|---|---|---|---|---|---|---|---|
| | | g m$^{-3}$ | m | ‰ | $A_p$ (Bq kg$^{-1}$) | $A_d$ (Bq m$^{-3}$) | $A_p$ (Bq kg$^{-1}$) | $A_d$ (Bq m$^{-3}$) |
| Wenchang/Wenjiao | WCR-1 | 8.71 | 1.9 | 0.03 | 54.5 | 0.77 | 67.9 | 1.17 |
| | WCR-2 | 14.24 | 2.0 | 2.70 | 51.8 | 0.46 | 52.4 | 0.46 |
| | WCR-3 | 47.01 | 2.0 | 9.50 | 20.0 | 1.01 | 14.0 | 1.12 |
| | WCR-5 | 98.58 | 6.2 | 28.3 | 5.7 | 0.91 | 4.6 | 0.82 |
| | WCR-6 | 88.68 | 8.0 | 32.4 | 2.1 | 1.26 | 4.9 | 0.30 |
| Wanquan | WQ-A2 | 4.74 | 0.5 | 0.03 | 14.9 | 0.10 | 176.2 | 0.16 |
| | WQ-A4 | 11.47 | 0.5 | 0.03 | 43.5 | 1.60 | 194.5 | 1.87 |
| | WQ-A5 | 42.58 | 2.8 | 6.6 | 42.5 | 1.72 | 11.8 | 0.72 |
| | WQ-A6 | 65.71 | 4.1 | 23.0 | 25.0 | 0.78 | 7.6 | 0.21 |
| | WQ-A7 | 15.29 | 2.0 | 7.0 | 15.5 | 2.31 | 42.5 | 0.09 |
| | WQ-A8 | 81.04 | 6.0 | 34.0 | 1.2 | 0.63 | 6.2 | 0.12 |

(HF), perchloric acid ($HClO_4$) and nitric acid ($HNO_3$) in a closed Teflon system (Zhang, 1995, 1999). Metal concentrations were measured by flame or graphite furnace atomic absorption spectrophotometer (AAS) (PE-AA800). Cartridge filter blanks were also analyzed for trace metals. The dissolved nuclides were co-precipitated with $Fe(OH)_3$ using the procedure mentioned above and measured by AAS. The efficient of co-precipitation of dissolved Zn, Cu, and Cd were obtained by analysis of Pb that we added quality amount using AAS, and the average efficient is (75 ± 7)%.

## 3. Results

### 3.1. Total suspended particulate matter and salinity

The location, water depth, salinity and SPM of samples are listed Table 1. The salinity ranged from 0.03 to 32.4 while SPM concentrations ranged from 8.71 to 98.58 g m$^{-3}$ for the Wenjiao/Wenchang River estuary. For the Wanquan River estuary, the ranges of salinity and SPM concentrations were 0.03–34.0 and 4.74–81.04 g m$^{-3}$, respectively. SPM concentrations in the Wenjiao/Wenchang River estuary increased from the fresh water end to the seaward end. In comparison with reported SPM values in the Changjiang estuary, our measured values of SPM in the Wenjiao/Wenchang River and Wanquan River estuaries were high. However, the fresh water end-number of SPM in the Changjiang estuary is much higher (Zhang et al., 2007; Huang et al., 2010).

### 3.2. Activity of radionuclides of the dissolved and particulate phases

The activity values of particulate and dissolved nuclides $^{7}$Be and $^{210}Pb_{xs}$ are listed in Table 1. Activity of particulate $^{7}$Be and $^{210}Pb_{xs}$ had a range of 1.2–54.5 and 4.6–194.5 Bq kg$^{-3}$,respectively, with respective average values of 25.6 Bq kg$^{-3}$ and 52.4 Bq kg$^{-3}$. The activity of $^{7}$Be increased with both salinity and SPM in the Wenjiao/Wenchang River (Fig. 2).

In the dissolved phase, the activity of $^{7}$Be and $^{210}$Pb had a range of 0.10–2.31 and 0.09–1.87 Bq m$^{-3}$, respectively, with respective averages of 1.05 and 0.64 Bq m$^{-3}$. In most cases, maximum activity occurred in the mid-salinity regions of both river estuaries.

### 3.3. Concentration of heavy metals in the dissolved and particulate phases

Particulate Zn, Cu and Cd concentrations in the Wenjiao/Wenchang River estuary had ranged, of 8.3–398.1, 5.4–119.9 and 1.5–4.1 μg g$^{-1}$, respectively, with a corresponding salinity range of 0–32.4. Particulate concentrations of Zn, Cu and Cd in the Wanquan River estuary were similar: from 4.0 to 464.6 (Zn), 4.0–101.4 (Cu) and 0.4–3.7 (Cd) μg g$^{-1}$, with a salinity range of 0–34.0. Compared to concentrations in larger rivers, the concentrations of heavy metals in particle in both rivers are comparable, but the value of the fresh end-number was higher. Dissolved concentrations of Zn, Cu and Cd had ranges of 3.4–13.7 mg m$^{-3}$, 0.5–1.2 mg m$^{-3}$ and 2.4–24.0 μg m$^{-3}$, respectively, in both rivers.

## 4. Discussion

### 4.1. Distribution coefficients of nuclides in the water column

The partitioning of $^{7}$Be and $^{210}$Pb between the particulate and dissolved phases can be evaluated from the distribution coefficient, $K_d$ (cm$^3$ g$^{-1}$):

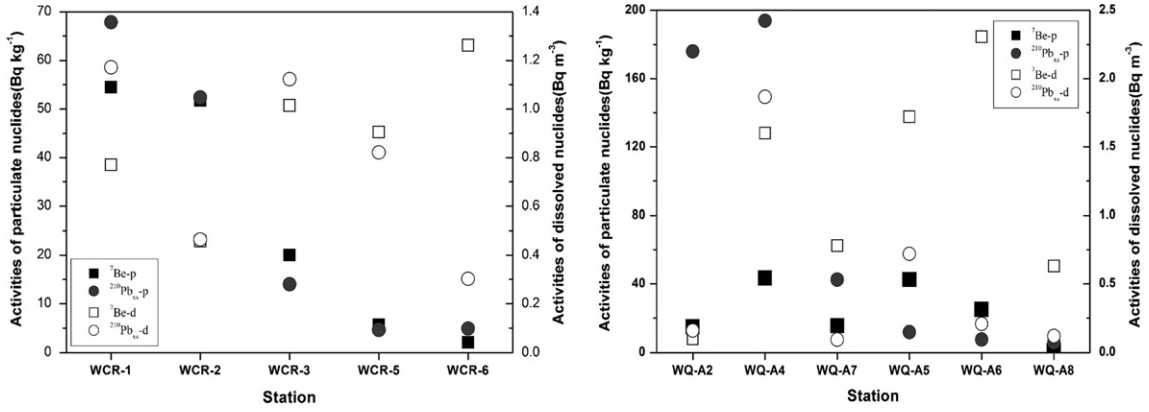


**Fig. 2.** Activity distribution of nuclides in both particulate (Bq kg$^{-1}$) and dissolved (Bq m$^{-3}$) phases in the Wenjiao/Wenchang River and Wanquan River estuaries.

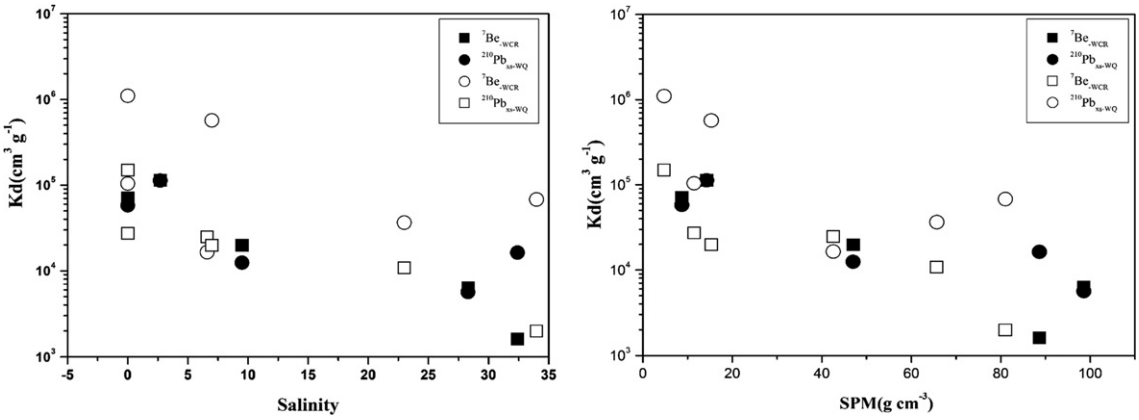


**Fig. 3.** Plots of distribution coefficients of nuclides ($K_d$, cm$^3$ g$^{-1}$) of $^7$Be and $^{210}$Pb$_{xs}$ vs. salinity and SPM in the Wenjiao/Wenchang River and Wanquan River estuaries.

$$K_d = \frac{A_p}{A_d \times SPM} \times 10^6 \quad (1)$$

where $A_p$ (Bq m$^{-3}$) and $A_d$ (Bq m$^{-3}$) are the activities of nuclide in the particulate and dissolved phases, and SPM is particle concentration (g cm$^{-3}$). The distribution coefficients for $^7$Be and $^{210}$Pb are plotted against SPM concentration in Fig. 3. $K_d$ values of $^7$Be and $^{210}$Pb calculated for the Wenjiao/Wenchang River estuary varied between $1.6 \times 10^3$ and $1.1 \times 10^5$ cm$^3$ g$^{-1}$ for $^7$Be, and from $5.6 \times 10^3$ to $1.1 \times 10^5$ cm$^3$ g$^{-1}$ for $^{210}$Pb. Values for the Wanquan River estuary were similar, with a range of $2.0 \times 10^3$–$1.5 \times 10^5$ cm$^3$ g$^{-1}$($^7$Be) and $1.6 \times 10^4$–$1.1 \times 10^6$ cm$^3$ g$^{-1}$($^{210}$Pb). There are several factors that can affect the partitioning of these radionuclides between the particulate and dissolved phases. First, increasing salinity may facilitate desorption of the particulate nuclide $^7$Be into the dissolved phase. As shown in Fig. 3, $K_d$ values of the nuclides are obviously decreasing with salinity in both the Wenjiao/Wenchang and the Wanquan River estuaries. As the concentration of SPM did not show large increases, the $K_d$ value was largely controlled by the salinity and not by the SPM Fig. 3 indicates that $K_d$ values also decreased with SPM concentration in both rivers.

In Sequim Bay, it was reported to be as high as ~50% of the $^7$Be that was found in the particulate phase, with SPM concentrations of ~20 mg L$^{-1}$ at salinity ca 30% (Bloom and Crecelius, 1983). In the Wenjiao/Wenchang and Wanquan River estuaries, the percent of particulate $^7$Be was also as high as ~50%, whereas the fraction of particulate phase $^{210}$Pb was typically much higher than 50%. This difference is likely due to the sizes of the particles, which affects the nuclides' behaviors differently. The resuspension of the upper layer surface sediment can occur in the estuary and the half-life of $^7$Be is much shorter than $^{210}$Pb, the percentage of surface sediments contributes to nuclide activity of $^7$Be and $^{210}$Pb in the water column can also differ greatly.

### 4.2. Residence times of $^{210}$Pb$_{xs}$ and $^7$Be in the water column

The residence times of $^7$Be and $^{210}$Pb$_{xs}$ in the water column can be evaluated using the measured activity of these radionuclides in the particles along with their calculated depositional fluxes.

Assuming that the nuclides in the water column were well mixed and that advection and diffusion is negligible (Baskaran and Santschi, 1993; Feng et al., 1998), the residence times ($\tau$) of $^7$Be and $^{210}$Pb$_{xs}$ in the water column can be calculated using the following equations (Baskaran and Santschi, 1993; Baskaran et al., 1997; Feng et al., 1999a; Baskaran and Swarzenski, 2007):

$$\tau_{Be,p} = \frac{A_{Be,p}}{\frac{I_{Be}}{h} - \lambda \times A_{Be}} \quad (2)$$

$$\tau_{Pb,p} = \frac{A_{Pb,p}}{\frac{I_{Pb}}{h} - \lambda \times A_{Pb}} \quad (3)$$

where $A_{Be,p}$ and $A_{Pb,p}$ are the respective activities of particulate $^7$Be and $^{210}$Pb in the whole water column, $A_{Be}$ and $A_{Pb}$ are the total activities of $^7$Be and $^{210}$Pb, $I_{Be}$ and $I_{Pb}$ are the atmospheric deposition fluxes of $^7$Be and $^{210}$Pb, $h$ is water column depth, and $\lambda_{Be}$ and

**Table 2**
Distribution coefficients (Kd) between the suspended particle and dissolved phases, percentage of nuclide activity in the particulate phase and residence times of particulate for $^7$Be and $^{210}$Pb along the Wenjiao/Wenchang River and Wanquan River estuaries.

| Location | | $K_d$ (cm$^3$ g$^{-1}$) | | Percentages in particulate phase (%) | | Residence time (days) | |
|---|---|---|---|---|---|---|---|
| | | $^7$Be | $^{210}$Pb$_{xs}$ | $^7$Be | $^{210}$Pb$_{xs}$ | $^7$Be | $^{210}$Pb$_{xs}$ |
| Wenchang/Wenjiao | WCR-1 | $7.1 \times 10^4$ | $5.8 \times 10^4$ | 38.1 | 33.5 | 0.4 | 1.65 |
| | WCR-2 | $1.1 \times 10^5$ | $1.1 \times 10^5$ | 61.7 | 61.7 | 0.7 | 2.20 |
| | WCR-3 | $2.0 \times 10^4$ | $1.2 \times 10^4$ | 48.1 | 36.9 | 0.9 | 1.93 |
| | WCR-5 | $6.3 \times 10^3$ | $5.6 \times 10^3$ | 38.3 | 35.7 | 1.6 | 4.17 |
| | WCR-6 | $1.6 \times 10^3$ | $1.6 \times 10^4$ | 12.5 | 59.1 | 0.7 | 5.15 |
| Wanquan | WQ-A2 | $1.5 \times 10^5$ | $1.1 \times 10^6$ | 41.4 | 83.9 | 0.02 | 0.61 |
| | WQ-A4 | $2.7 \times 10^4$ | $1.0 \times 10^5$ | 23.8 | 54.4 | 0.1 | 1.64 |
| | WQ-A5 | $2.5 \times 10^4$ | $1.6 \times 10^4$ | 51.3 | 41.2 | 2.4 | 2.08 |
| | WQ-A6 | $1.1 \times 10^4$ | $3.6 \times 10^4$ | 41.6 | 70.5 | 3.2 | 3.00 |
| | WQ-A7 | $2.0 \times 10^4$ | $5.7 \times 10^5$ | 23.3 | 89.7 | 0.2 | 1.91 |
| | WQ-A8 | $2.0 \times 10^3$ | $6.8 \times 10^4$ | 13.8 | 87.6 | 0.3 | 4.44 |

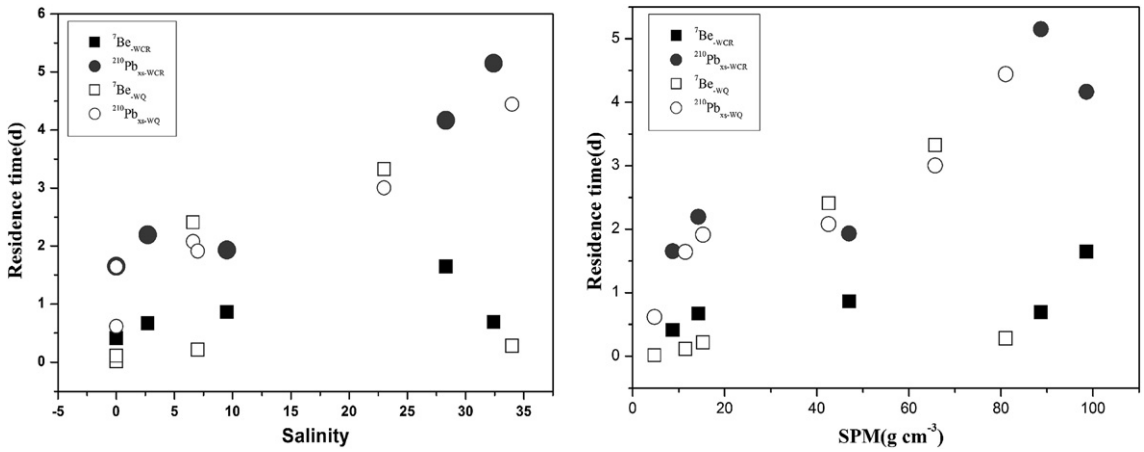


**Fig. 4.** Plots of residence times (in days) of particulate $^{7}$Be and $^{210}$Pb$_{xs}$ vs. salinity and SPM in the Wenjiao/Wenchang River and Wanquan River estuaries.

$\lambda_{Pb}$ are the decay constants of $^{7}$Be (0.0128 d$^{-1}$) and $^{210}$Pb ($8.53 \times 10^{-5}$ d$^{-1}$).

To estimate the atmospheric deposition fluxes of $^{7}$Be and $^{210}$Pb in the study regions, we collected rainfall from an event on August 6th, 2008. In this event, 10.5 mm of rain fell and deposition was estimated to be 4.05 ($^{7}$Be) and 1.02 Bq m$^{-2}$ ($^{210}$Pb) based on analysis of the collected samples. If we use the same formula to describe the relationship between rainfall and $^{7}$Be or $^{210}$Pb atmospheric deposition flux as has previously been used in Xiamen (Jia et al., 2003), then the atmospheric deposition fluxes in Hainan can be estimated as

$$I_{Be} = 0.0054P + 1.1313 \quad R^2 = 0.66 \tag{4}$$

$$I_{Pb} = 0.0015P + 0.3732 \quad R^2 = 0.63 \tag{5}$$

where $P$ represents precipitation (mm). Based on monthly (August) average 2008 precipitation of 203.4 mm (http://cdc.cma.gov.cn/index.jsp), the average atmospheric deposition fluxes of $^{7}$Be and $^{210}$Pb were calculated to be 2.23 and 0.68 Bq m$^{-2}$ day$^{-1}$, respectively.

The calculated residence times of particulate $^{7}$Be and $^{210}$Pb$_{xs}$ are shown in Table 2. The residence times of particulate $^{7}$Be in the Wenjiao/Wenchang River and Wanquan River were 0.4–1.6 and 0.02–3.2 days with an average of 0.86 and 1.06 days, respectively. The residence times of $^{210}$Pb$_{xs}$ were 1.65–5.15 days in the Wenjiao/Wenchang River and 0.61–4.44 days in the Wanquan River with average residence times of 3.02 and 2.28 days, respectively. The residence times of both estuaries were comparable.

The residence times of particulate $^{7}$Be and $^{210}$Pb$_{xs}$ are plotted against SPM concentrations and salinity in Fig. 4. As the plots in Fig. 4 show, the residence times of particulate $^{7}$Be and $^{210}$Pb$_{xs}$ each increased with salinity and SPM in the Wenjiao/Wenchang River and Wanquan River estuaries. It has been suggested that residence times are controlled by the amount of SPM (Baskaran and Swarzenski, 2007).

### 4.3. Removal behavior of trace metals in the Wenjiao/Wenchang River and Wanquan River estuaries

Plots of the distribution coefficient ($K_d$, cm$^3$ g$^{-1}$) of heavy trace metals in the Wenjiao/Wenchang River and Wanquan River estuaries are shown in Fig. 5.

Different distribution patterns of trace metal fractions for each element were observed, as a result of different residence times in the estuaries and specific elemental reactivity. The values of $K_d$ in both estuaries are comparable, as shown in Table 3. Quantities of metal that can be deposited in the estuary are $6.2 \times 10^2$–$1.1 \times 10^4$ cm$^3$ g$^{-1}$ for Cu, $1.3 \times 10^2$–$3.9 \times 10^3$ cm$^3$ g$^{-1}$ for Zn, and $9.6 \times 10^3$–$3.8 \times 10^4$ cm$^3$ g$^{-1}$ for Cd in the Wenjiao/Wenchang River estuary and $8.6 \times 10^2$–$8.6 \times 10^3$ cm$^3$ g$^{-1}$ for Cu, $1.2 \times 10^2$–$8.4 \times 10^3$ cm$^3$ g$^{-1}$ for Zn, and $9.4 \times 10^3$–$8.6 \times 10^4$ cm$^3$ g$^{-1}$ for Cd in the Wanquan River estuary. As Fig. 5 shows, the distribution coefficients of Cd were higher than those of Zn and Cu in both estuaries. This result indicates that Cd has high particle reactivity. Particulate heavy metal behavior in the estuary might be associated with dissolved concentrations via processes (e.g. adsorption and desorption), which induces change of metal partitioning between the solid and solution. The variation between the metals may also concerned with the distribution characteristics between different fractions, such as Fe–Mn oxides and lattice-bound.

Many research findings have shown that particle-active nuclides can be good tracers of particle dynamics in the water column and act as analogs for "particle-reactive" pollutants (Baskaran and Santschi, 1993; Feng et al., 1999c). If the scavenging and removal processes of pollutants can be described through order kinetics, the removal constant ($\kappa_{sed}$, day$^{-1}$) (Chen and Huang, 1998) can be calculated as:

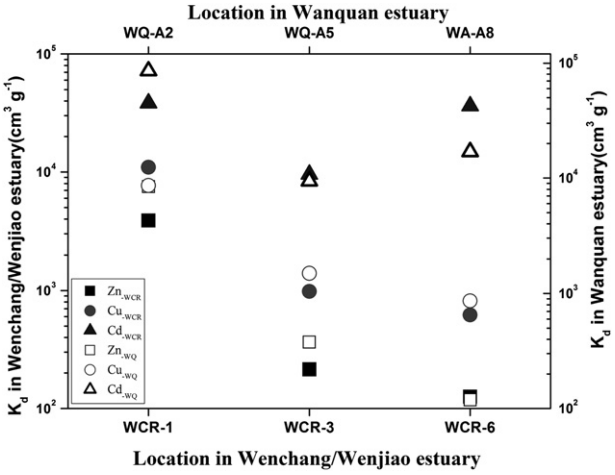


**Fig. 5.** Plots of distribution coefficients ($K_d$, cm$^3$ g$^{-1}$) of heavy trace metals in the Wenjiao/Wenchang River and Wanquan River estuaries.

**Table 3**
Heavy metal concentrations and their fractions of removal into sediments along the Wenjiao/Wenchang River and Wanquan River estuaries.

| | Particulate concentration | | | Dissolved concentration | | | $K_d$ | | | $F^{sed}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Zn ($\mu g\ g^{-3}$) | Cu ($\mu g\ g^{-3}$) | Cd ($\mu g\ g^{-3}$) | Zn ($mg\ m^{-3}$) | Cu ($mg\ m^{-3}$) | Cd ($\mu g\ m^{-3}$) | Zn ($cm^3\ g^{-1}$) | Cu ($cm^3\ g^{-1}$) | Cd ($cm^3\ g^{-1}$) | Zn | Cu | Cd |
| WCR-1 | 398.1 | 119.9 | 4.1 | 10.3 | 1.1 | 10.8 | $3.9 \times 10^3$ | $1.1 \times 10^4$ | $3.8 \times 10^4$ | 9.0% | 21.0% | 43.2% |
| WCR-3 | 29.4 | 10.6 | 2.3 | 13.7 | 1.1 | 24.0 | $2.2 \times 10^2$ | $9.8 \times 10^2$ | $9.6 \times 10^3$ | 3.0% | 11.8% | 48.5% |
| WCR-6 | 8.3 | 5.4 | 1.5 | 6.6 | 0.9 | 4.1 | $1.3 \times 10^2$ | $6.2 \times 10^2$ | $3.6 \times 10^4$ | 3.2% | 13.7% | 69.9% |
| WQ-A2 | 464.6 | 101.4 | 3.7 | 5.5 | 1.2 | 4.3 | $8.4 \times 10^3$ | $8.6 \times 10^3$ | $8.6 \times 10^4$ | 23.8% | 24.2% | 70.1% |
| WQ-A5 | 34.5 | 8.9 | 1.2 | 9.1 | 0.6 | 13.1 | $3.8 \times 10^2$ | $1.5 \times 10^3$ | $9.4 \times 10^3$ | 11.4% | 32.8% | 70.0% |
| WA-A8 | 4.0 | 4.0 | 0.4 | 3.4 | 0.5 | 2.4 | $1.2 \times 10^2$ | $8.6 \times 10^2$ | $1.7 \times 10^4$ | 7.2% | 34.8% | 82.5% |

$$\kappa_{sed} = F_M^P \varphi_{RI}^P = (K_d \times SPM)/\left(K_d \times SPM + 10^6\right) \times \varphi_{RI}^P \quad (6)$$

where $F_M^P$, SPM ($g\ m^{-3}$) and $\varphi_{RI}^P$ ($day^{-1}$) represent the fraction of particulate metals in the whole water column, concentration of suspended particulate matter and the removal constants of suspended particle in the water column, respectively. $K_d$ is the distribution coefficient ($cm^3\ g^{-1}$) for the pollutant.

There are two cases of pollutant transport into the estuary, a plug-flow case and a well mixed case. For first case, when a parcel of water with pollutants enters into estuary, it will lose pollutants to benthic sediment at a rate:

$$dc/dt = -\kappa_{sed}\, C \quad (7)$$

where $C$ is the total concentration in whole water column. The concentrations of pollutant remaining at the time at which that water exists in the system is:

$$C_{out} = C_{in} \cdot \exp(-\kappa_{sed}\, \tau_w) \quad (8)$$

where $C_{out}$ and $C_{in}$ are the concentrations of the pollutant in waters exiting and entering the estuary. $\tau_w$ is the time allowed for the reaction of the pollutant in the estuary.

When the pollutant is introduced into the estuary system at the same time as the water, the time available for the reaction is the same as the residence time of the water. When water flows through the study area, the fraction of pollutant retained in sediment ($F_M^{sed}$) can be expressed by

$$F_1^{SED} = (C_{in} - C_{out})/C_{in} = 1 - \exp(-\kappa_{sed}\, \tau_w) \quad (9)$$

In the second case (the well mixed estuary), there is no pollutant gradient within the estuary and $C_{out}$ can be expressed as a one order process, while $\kappa_{out}$ can be expressed as a reciprocal of water residence time. Therefore, the ratio of mass of a pollutant removed into the sediments to the mass of pollutant exported out of the estuary will be a function of the ratio of the first rate constants: $\kappa_{sed}/\kappa_{out}$. Using the mass balance in the estuary, $C_{in} = C_{out} + C_{sed}$, one can obtain

$$\begin{aligned} F_2^{SED} &= (C_{in} - C_{out})/C_{in} = (\kappa_{sed}/\kappa_{out})/(\kappa_{sed}/\kappa_{out} + 1) \\ &= (\kappa_{sed} \times \tau_W)/(\kappa_{sed} \times \tau_W + 1) \end{aligned} \quad (10)$$

Using Eqs. (6) and (10), we can calculate the form of heavy metal removal into the sediment while both of the two estuaries can be considered as well mixed estuary. For this analysis, the water residence time ($\tau_w$) was obtained by Su et al.(personal communication), and is assumed to be 5.9 days in the Wenjiao/Wenchang River estuary and 13.6 days in the Wanquan River estuary. The residence time of suspended particle was obtained from the average residence times of both $^7$Be and $^{210}$Pb, 1.94 and 1.67 days for the Wenjiao/Wenchang River and Wanquan River estuaries. The calculated fractions of heavy metals removed into the sediment are summarized in Table 3. Table 3 shows that the percent of metals removed into the bottom sediments is larger in the Wanquan River estuary than in the Wenjiao/Wenchang River estuary. In the Wenjiao/Wenchang River estuary, removal percentages are 11.8–21.0% for Cu, 3.0–9.0% for Zn, and 43.2–69.9% for Cd, whereas removal percentages in the Wanquan River estuary are 24.2–34.8% for Cu, 7.2–23.8% for Zn, and 70.0–82.5% for Cd. Results indicate that most of the Cd was deposited in the estuary in both the Wenjiao/Wenchang and Wanquan River estuaries, whereas much of the Cu and Zn were transported to the coast. The higher percentage of Cd deposited into the sediment is due to the higher $K_d$ values. As expected, the fraction of heavy metals in sediment was strongly dependent on both SPM and $K_d$. In the present study, SPM showed a variation by a factor of 10, but the change in $K_d$ was greater than three orders of magnitude. Higher values of $K_d$ result in a greater percentage removal of heavy metals from the water column to the bottom sediments (Chen and Huang, 1998). This approach to evaluating the removal of heavy metals in the water column can be extended to the particle-reactive contaminant species that have similar $K_d$ values to those of PCBs and PAHs, for example (Gustafsson et al., 1997b; Feng et al., 1998).

## 5. Conclusions

The northeastern coastline of Hainan Island, China, is home to several ecosystems typical to this tropical region, such as coral reefs, mangroves, and sea grass beds. With an annual average rainfall of c.a. 1500 mm, heavy metal inputs from waste water, agriculture, and aquacultures into the coastal region can lead to significant impacts on the coastal ecosystems. The conclusions from our study can be drawn as follows:

Radionuclide activity in both the particulate and dissolved phases is comparable in both river estuaries. Activity in the Wanquan River estuary is $26.8 \pm 15.7$ ($n = 5$) and $28.8 \pm 12.5$($n = 5$) Bq $kg^{-1}$ for $^7$Be and $^{210}Pb_{xs}$, respectively, in the Wenjiao/Wenchang River estuary; activity is found to be $25.6 \pm 21.2$ ($n = 6$) and $52.4 \pm 13.9$($n = 6$) Bq $kg^{-1}$ for $^7$Be and $^{210}Pb_{xs}$, respectively in the Wanquan River estuary.

All residence times of SPM for the two nuclides increased in the seaward direction. It was found that most of the Cd was deposited in the estuary in both the Wenjiao/Wenchang and Wanquan River estuaries, while much of the Cu and Zn were transported to the coast. The approach in the present work for evaluating the removal of heavy metals in the water column uses powerful tools to evaluate the particle-reactive contaminant species and can be used to evaluate the removal of contaminants with $K_d$ values similar to those of heavy metals, such as PCBs, and PAHs.

## Acknowledgments

This research was supported by the Natural Science foundation of China (41021064, 40976054, 40830850) and the Ministry of Science and Technology of PR China (2007DFB20380).

## References


Baskaran, M., Santschi, P.H., 1993. The role of particles and colloids in the transport of radionuclides in coastal environments of Texas. Marine Chemistry 43 (1–4), 95–114.

Baskaran, M., Swarzenski, P.W., 2007. Seasonal variations on the residence times and partitioning of short-lived radionuclides ($^{234}$Th, $^{7}$Be and $^{210}$Pb) and depositional fluxes of $^{7}$Be and $^{210}$Pb in Tampa Bay, Florida. Marine Chemistry 104, 27–42.

Baskaran, M., Ravichandran, M., Bianchi, T.S., 1997. Cycling of $^{7}$Be and $^{210}$Pb in a high DOC, shallow, turbid estuary of southeast Texas. Estuarine, Coastal and Shelf Science 45, 165–176.

Bloom, N., Crecelius, E.A., 1983. Solubility behavior of atmospheric $^{7}$Be in the marine environment. Marine Chemistry 12 (4), 323–331.

Bronson, F.L., 2003. Validation of the accuracy of the LabSOCS software for mathematical efficiency calibration of Ge detectors for typical laboratory samples. Journal of Radioanalytical and Nuclear Chemistry 255 (1), 137–141.

Chen, M., Huang, Y.P., 1998. Fate of particle-reactive pollutant in Xiamen Bay. Acta Oceanologica Sinica 17, 503–508.

Ciffroy, P., Reyss, J.L., Siclet, F., 2003. Determination of the residence time of suspended particles in the turbidity maximum of the Loire estuary by Be-7 analysis. Estuarine Coastal and Shelf Science 57 (4), 553–568.

Dibb, J.E., Rice, D.L., 1989. The geochemistry of beryllium-7 in Chesapeake Bay. Estuarine, Coastal and Shelf Science 28 (4), 379–394.

Du, J.Z., Wu, Y.F., Huang, D.K., Zhang, J., 2010. The use of $^{7}$Be, $^{210}$Pb and $^{137}$Cs tracers to the transport of surface sediment of the Changjiang estuary, China. Journal of Marine Systems 82, 286–294.

Feng, H., Cochran, J.K., Lwiza, H., Brownawell, B.J., Hirschberg, D.J., 1998. Distribution of heavy metal and PCB contaminants in the sediments of an urban estuary: the Hudson River. Marine Environmental Research 45 (1), 69–88.

Feng, H., Cochran, J.K., Hirschberg, D.J., 1999a. $^{234}$Th and $^{7}$Be as tracers for the transport and dynamics of suspended particles in a partially mixed estuary. Geochimica Cosmochimica Acta 23, 2487–2505.

Feng, H., Cochran, J.K., Hirschberg, D.J., 1999b. $^{234}$Th and $^{7}$Be as tracers for the sources of particles to the turbidity maximum of the Hudson River. Estuarine, Coastal and Shelf Science 49, 629–645.

Feng, H., Cochran, J.K., Hirschberg, D.J., 1999c. $^{234}$Th and $^{7}$Be as tracers for transport and sources of particle-associated contaminants in the Hudson River estuary. The Science of the Total Environment 237–238, 401–418.

Feng, H., Cochran, J. Kirk, Hirschberg, David J., 2002. Transport and sources of metal contaminants over the course of tidal cycle in the turbidity maximum zone of the Hudson River estuary. Water Research 36, 733–743.

Fitzgerald, S.A., Klump, J.V., Swarzenski, P.W., Mackenzie, R.A., Richards, K.D., 2001. Beryllium-7 as a tracer of short-term sediment deposition and resuspension in the Fox River, Wisconsin. Environmental Science and Technology 35, 300–305.

Giffin, D., Corbett, R., 2003. Evaluation of sediment dynamics in coastal systems via short-lived radioisotopes. Journal of Marine Systems 42, 83–96.

Gustafsson, Ö, Gschwend, P.M., Buesseler, K.O., 1997a. Settling removal rates of PCBs into the Northwestern Atlantic derived from $^{238}$U–$^{234}$Th disequilibria. Environmental Science and Technology 31 (12), 3544–3550.

Gustafsson, Ö, Gschwend, P.M., Buesseler, K.O., 1997b. Using Th-234 disequilibria to estimate the vertical removal rates of polycyclic aromatic hydrocarbons from the surface ocean. Marine Chemistry 57 (1–2), 11–23.

Huang, D., Du, J., Wu, Y., Li, D., Zhang, J., 2010. Sinking of particulate $^{234}Th_{xs}$, $^{7}$Be and $^{210}Pb_{xs}$ in the Changjiang estuary, China. Chinese Journal of Oceanology and Limnology 28 (6), 1152–1159.

Imboden, D.M., Stiller, M., 1982. The influence of radon diffusion on the $^{210}$Pb distribution in sediments. Journal of Geophysical Research 87, 557–565.

Jia, Cheng-xia, Liu, Guang-shan, Yang, Wei-feng, Zhang, Lei, Huang, Yi-pu, 2003. Atmospheric depositional fluxes of $^{7}$Be and $^{210}$Pb at Xiamen. Journal of Xiamen University (Natural Science) 42 (3), 352–357.

Jweda, J., Baskaran, M., van Hees, E., Schweitzer, L., 2008. Short-lived radionuclides ($^{7}$Be and $^{210}$Pb) as tracers of particle dynamics in a river system in southeast Michigan. Limnology and Oceanography 53, 1934–1944.

Key, R.M., Guinasso, N.L., Schink, D.R., 1979. Emanation of radon-222 from marine sediments. Marine Chemistry 7 (3), 221–250.

Kim, S.H., Hong, G.H., Baskaran, M., Park, K.M., Chung, C.S., Kim, K.H., 1998. Wet removal of atmospheric $^{7}$Be and $^{210}$Pb at the Korean Yellow Sea coast. The Yellow Sea 4, 58–68.

Lima, A.L., Hubeny, J.B., Reddy, C.M., King, J.W., Hughen, K.A., Eglinton, T.I., 2005. High-resolution historical records from Pettaquamscutt River basin sediments: 1. $^{210}$Pb and varve chronologies validate record of $^{137}$Cs released by the Chernobyl accident. Geochim Cosmochim Acta 69, 1803–1812.

Mao, L.M., Zhang, Y.L., Bi, H., 2006. Modern pollen deposits in coastal mangrove swamps from northern Hainan Island, China. Journal of Coastal Research 22 (6), 1423–1436.

Rao, V.P., Shynu, R., Kessarkar, P.M., Sundar, D., Michael, G.S., Narvekar, T., Blossom, V., Mehra, P., 2011. Suspended sediment dynamics on a seasonal scale in the Mandovi and Zuari estuaries, central west coast of India. Estuarine, Coastal and Shelf Science 91 (1), 78–86.

Swarzenski, P.W., Reich, C.D., Spechler, R.M., Kindinger, J.L., Moore, W.S., 2001. Using multiple geochemical tracers to characterize the hydrogeology of the submarine spring off Crescent Beach, Florida. Chemical Geology 179, 187–202.

Swarzenski, P.W., Porcelli, D., Andersson, P.S., Smoak, J.M., 2003. The behavior of U- and Th-series nuclides in the estuarine environment. Reviews in Mineralogy and Geochemistry 52, 577–606.

Wang, B.C., Chen, S.L., Gong, W.P., Ling, W.Q., Xu, Y., 2006. Development and Evolution of Estuarine Coast in Hainan Island. Ocean Press, Beijing (in Chinese).

Wang, Y., 2002. Features of Hainan Island coastal environment. Marine Geology Letters 18 (3), 1–9 (in Chinese).

Zeng, Z.X., Zeng, X.Z., 1989. Physicogeography of Hainan Island. Science Press, Beijing (in Chinese).

Zhang, J., 1995. Geochemistry of trace metals from Chinese river/estuary systems: an overview. Estuarine, Coastal and Shelf Science 41 (6), 631–658.

Zhang, J., 1999. Heavy metal compositions of suspended sediments in the Changjiang (Yangtze River) estuary: significance of riverine transport to the ocean. Continental Shelf Research 19 (12), 1521–1543.

Zhang, J., Wu, Y., Jennerjahn, T.C., Ittekkot, V., He, Q., 2007. Distribution of organic matter in the Changjiang (Yangtze River) Estuary and their stable carbon and nitrogen isotopic ratios: implications for source discrimination and sedimentary dynamics. Marine Chemistry 106 (1–2), 111–126.