



# Influence of urbanization and industrialization on metal enrichment of sediment cores from Shantou Bay, South China



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## ABSTRACT

Four sediment cores were collected to investigate geochemical sources and to assess enrichment and pollution of metals in sediments from Shantou Bay, an area experiencing rapid economic development on the Southeastern Coast of China. The results indicated that the concentrations of the majority of metals showed a decrease with depth, with overall maximum values in the top layers, and that different sampling locations in the Bay received slightly different types of inputs. Three major sources were identified by correlation analysis and principal component analysis: river inputs, metropolitan, and port facilities discharge. Calculation of a pollution load index revealed overall low values, but the enrichment factor values for Pb and Cd were typically high for all cores. The mean concentrations of Cu, Pb, Zn and to some extent Cd exceeded the Effects-Range-Low values in the majority of the cases, indicating that there were possible ecotoxicological risks to organisms in Shantou Bay.

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## 1. Introduction

The south coast of China has experienced rapid urbanization and industrialization in recent decades. Increasing amounts of pollutants have been continuously discharging into the coastal system without proper treatment, which has had a significant environmental impact on the aquatic environment (Li et al., 2000; Ip et al., 2007). Coastal sediments are an important sink for a wide range of contaminants and have been considered as sensitive indicators for monitoring the marine environment (Chatterjee et al., 2007; Harikumar et al., 2009). Several studies have been performed in many rapid developing regions around Asia using core sediment profiles to investigate geochemical sources and the deposition environment to assess enrichment and pollution of metals, and to describe the contamination history of different environments; e.g. Manila Bay in the Philippines (Hosono et al., 2010); Hugli estuary in India (Chatterjee et al., 2007); Victoria Harbour in Hong Kong (Tanner et al., 2000); the Pearl River Estuary in China (Ip et al., 2004); Liaodong Bay in China (Xu et al., 2009); and the Nanliu River Estuary in China (Xia et al., 2011).

Shantou Bay, strategically located in the South China Coast and within the district of metropolitan Shantou City, was deeply modified by city expansion and port development, with the open

water area reduced from 126 km<sup>2</sup> to 72 km<sup>2</sup> (Li, 2004). Shantou City, one of the earliest state-level economic developments and reform zones in China with a population of over 5 million, has experienced rapid economic development and dramatic social transformation since 1980s. Currently, the shoreline of the Bay is densely populated, and is characterized by the presence of many industrial parks and port facilities (Li, 2004). To some degree, Shantou Bay provides a good example of a site where natural values and human pressures compete with each other, but where the degree of metal contamination has not been subject to any overall assessment. The present study focuses on the following objectives: (1) to observe the geochemical characteristics of metal contamination, including the potential contaminating sources and their interrelation in the sediment profiles; (2) to assess the contamination level and ecological environmental risk of metals in the sediments; and (3) to establish pollution trends in Shantou Bay, as a contribution to the fundamental knowledge for understanding environmental degradation problems and establishing strategic environmental control in coastal areas which are undergoing rapid development.

## 2. Materials and methods

### 2.1. Study area

Shantou Bay (116°30'–116°50' E, 23°20'–23°25' N) is created by unbalance extension of Rongjiang and Hanjiang River Mouths to South China Sea. Hanjiang River has annual transport capacity of suspended load of  $728 \times 10^4$  tonnes, being ten

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times than Rongjiang River (annual suspended load of  $27.3 \times 10^4$  tonnes), the river mouth of which extends faster to sea than that of Rongjiang River. As a result, a semi-closed embayment (Shantou Bay) formed between them with 22 km long, and a width varying from 0.7 km to 4 km, and a depth ranging from 4 m to 15 m. Shantou Bay can be divided two parts: (1) The inner bay, named Niutianyang (NTY), receiving freshwater from Rongjiang River and a tributary (Meixi River) of Hanjiang River, with an annual discharge of  $62.5 \times 10^8 \text{ m}^3$  and  $28 \times 10^8 \text{ m}^3$  respectively (Li, 2004). (2) The down stream of the bay is the location of Shantou Harbor with a narrow entrance to South China Sea. The principal energy input to the bay is derived from tidal waves, with an annual seawater input of  $720 \times 10^8 \text{ m}^3$ , being eight times than the freshwater input ( $90 \times 10^8 \text{ m}^3$ ) (Li, 2004). The hydraulic regime of the bay is subjected to the semi-diurnal tidal rhythm with a tidal range from 4.97 m (spring tide) to 0.3 m (neap tide).

## 2.2. Sediment sampling and preparation

Four sampling stations were chosen along a seaward direction (Fig. 1). During winter months (October–December 2010), four core sediments were taken using a gravity-type sediment corer (100 cm length and 5 cm diameter). Descriptions of the sediment cores are provided in Table 1. Cores STB1 and STB2 were collected at the extension of the Rongjiang and Meixi River mouths respectively. Core STB3 was collected in the mudflat of Shantou Harbor, where the aquatic environment suffers municipal and port sewage discharge. Core STB4 was collected at the bay mouth area which continuously receiving discharge waters from the Shantou Wastewater Treatment Plant (SWTP) with a daily capacity of  $2 \times 10^5$  tonnes. In the laboratory, the core sediments were sliced into 2 cm intervals from 0 to 10 cm and into 5 cm intervals from 10 cm to the end of the cores with a PVC spatula. After slicing, the subsamples were dried in a ventilated oven at  $60^\circ\text{C}$  to constant weight, and then were grounded to powder using an agate mortar and pestle. The powder was divided into two aliquots; one was sieved through a  $63 \mu\text{m}$  sieve for elemental analysis and the second kept in a sealed plastic vessel for sediment quality parameters (organic matter, % of silt, clay and sand).

## 2.3. Analysis of sediment

In all sections of the cores, grain size distribution was measured by wet sieving following the procedure described by Loring and Rantala (1992). Total organic matter (TOM) concentrations in the core sediments were determined using the loss on ignition method ( $550^\circ\text{C}$  overnight) (Chen et al., 2007). Calcium carbonate was analyzed by adopting the procedure of Loring and Rantala (1992).

For metal measurements, 0.5 g of dried and grounded sediment was accurately weighted and digested with a mixture of concentrated acids ( $\text{HNO}_3:\text{HCl} = 1:3$ ) following procedures described by Sin et al. (2001). Sample solutions and reagent blanks were analyzed for Cd, Cr, Co, Ni, Mn, Pb, Zn, Fe and Al using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer Inc. Optima 2000DV, USA). All sediment samples were analyzed in duplicate with analytical precisions better than 10%. A marine sediment reference material (GBW 07314, China) was used to test the analytical and instrumental accuracy of the method. The recovery rates for studied metals in GBW 07314 were higher than 82%.

**Table 1**

Location and description of core sediment depth and obtained subsamples.

| Core | Latitude (N) | Longitude (E) | Water depth (m) | Core depth (cm) | Salinity (ppt) | Number of subsamples |
|------|--------------|---------------|-----------------|-----------------|----------------|----------------------|
| STB1 | 23°21'16.33  | 116°35'25.68  | 5.6             | 90              | 2.0            | 21                   |
| STB2 | 23°20'32.65  | 116°38'42.24  | 4.2             | 75              | 4.5            | 18                   |
| STB3 | 23°20'16.24  | 116°42'39.51  | 4.8             | 80              | 19.2           | 19                   |
| STB4 | 23°19'58.92  | 116°45'14.05  | 6.0             | 90              | 25.7           | 21                   |

## 2.4. Assessment of sediment contamination

Various methods have been suggested for assessing metal contamination in sediments. In present study, pollutant indicators were calculated based on the average shale content to assess the degree of heavy metal contamination in sediments of Shantou Bay.

### 2.4.1. Enrichment factors (EF)

To differentiate elemental origins from anthropogenic sources and those from natural weathering, an enrichment factor (EF) was calculated based on aluminum normalization. The EF can be defined as follows:

$$EF = \frac{(\text{Me}/\text{Al})_{\text{sediment}}}{(\text{Me}/\text{Al})_{\text{shale}}} \quad (1)$$

where Me/Al is the ratio of the metal to Al. The assessment criteria for EFs were suggested by Birch (2003) for the metals studied with respected to shale average. An  $EF < 1$  indicates no enrichment,  $EF < 3$  is minor enrichment,  $EF = 3-5$  is moderate enrichment,  $EF = 5-10$  is moderately severe enrichment,  $EF = 10-25$  is severe enrichment,  $EF = 25-50$  is very severe enrichment and  $EF > 50$  is extremely severe enrichment.

### 2.4.2. Pollution load index (PLI)

The pollution load index for a given core was calculated from the contamination factors ( $CF = \text{Metal}_{\text{sediment}}/\text{Metal}_{\text{shale}}$ ) of each of its constituent samples (Huerta-Diaz et al., 2008), according to the following equation:

$$PLI = (\text{CFCd} \times \text{CFMn} \times \text{CFCu} \times \text{CFNi} \times \text{CFPb} \times \text{CFZn})/6 \quad (2)$$

where  $\text{Metal}_{\text{shale}}$  is the average concentration of metals in shale,  $\text{Metal}_{\text{sediment}}$  is the concentration of metals in sediment. According to Huerta-Diaz et al. (2008), PLI values of zero, one, or larger than one suggest absence of baseline pollutants, presence of them, or progressive deterioration of sediment quality, respectively.

### 2.4.3. Application of sediment quality guidelines (SQGs)

SQGs were used to estimate possible adverse biological effects of sedimentary contaminants in Shantou Bay, including sets of effect-range guidelines derived from



**Fig. 1.** The sampling stations in Shantou Bay, South China.

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