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## Baseline

## Trace metals in sediments and benthic animals from aquaculture ponds near a mangrove wetland in Southern China

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## ABSTRACT

In this study, we measured the concentrations of trace metals (Cr, Cu, Zn, As, Cd, Pb and Hg) in typical cultured animals (crabs, clams, and shrimps) and sediments from aquaculture ponds nearby mangrove wetlands in Zhangjiang estuary, China. The contents of Cr, Cu, Cd, and Pb in mangrove sediments were significantly higher than those in pond sediments, while an inverse distribution was observed for Zn, As, and Hg. Significantly higher concentrations of trace metals were found in clams from the mangrove mudflats compared to those from the aquaculture ponds. The sources of trace metals in the clams were primarily from organic fertilizer, whereas those in the shrimp were from contaminated sediment. The results of geo-accumulation index and the ecological risk assessment indicated that the aquaculture ponds near the mangrove wetlands in this subtropical estuary posed a special risk of endogenous and exogenous trace metal pollution to nearby systems.

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Concerns about trace metal pollution in aquaculture have been growing around the world, especially in China (Li et al., 2013). Trace metal pollution in China is aggravated by the nation's rapid economic, industrial, and population growth (Wang et al., 2013). Trace metals discharged into aquaculture ponds can damage the aquatic product's quality as well as the aquatic ecosystem due to their toxicity and accumulation. The health of water bodies, fishes, and other organisms were frequently monitored to evaluate the trace metal pollution levels (Qiu et al., 2011; Rimondi et al., 2012; Zhang et al., 2012), among which, the health of benthic animals was especially measured to understand metal pollution in aquaculture ponds. Benthic animals play critical roles (e.g. filtering out contaminants) in the stability and security of aquatic ecosystems. Moreover, some benthic animals, such as shrimps, crabs, and oysters, are primary food sources for people in coastal regions (SOA, 2006).

In Southern China, aquaculture ponds are distributed mainly near mangrove wetlands or salt marshes (Feng et al., 2004). At the end of each aquaculture rotation, the pond sediments are usually cleaned to remove nutrients and pathogenic bacteria in the sediments (Chávez-Crooker and Obreque-Contreras, 2010; Wu et al., 2014). Our previous study indicated that high loadings of nitrogen and phosphorus in sediment washed-out from aquaculture ponds had exerted a

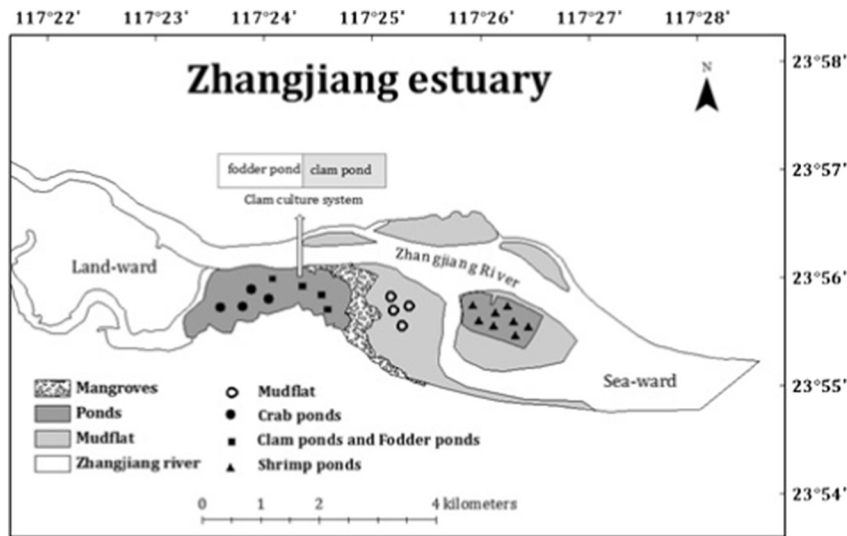
significant influence on mangrove wetlands in Southern China (Wu et al., 2014). However, trace metal pollution and sources in aquaculture ponds near mangrove wetlands have yet to be clearly understood. Given the potential negative influence of trace metals on aquatic ecosystems and mangrove wetlands, it is critical to examine both trace metal pollution and potential sources in aquaculture ponds near mangrove wetlands. In this study, we evaluated the degrees of trace metal pollution in the aquaculture ponds near mangrove forests in Zhangjiang estuary, a famous aquaculture base in Southern China.

The aquaculture ponds and mudflats investigated in this study were located in Zhangjiang estuary, Yunxiao city, Fujian Province (23°55'47" N, 117°24'30"E) (Fig. 1). The estuary is semi-enclosed and faces the Taiwan Strait. It occupies 2360 ha and is fringed by an additional 117.9 ha of mangroves. The dominant mangrove species includes *Kandelia obovata*, *Aegiceras corniculatum*, and *Avicennia marina* (Wang et al., 2010). The main benthic animals includes crabs (*Scylla serrata*), clams (*Sinonovacula constricta*), and shrimps (*Litopenaeus vannamei*), which were cultured using different aquaculture systems at the study sites. The details of the culture process were described in the previous paper (Wu et al., 2014).

From 2010 to 2011, wild mature clams (WMC) with body length of 3–4 cm and wild immature clam (WIC) with body length of 1–2 cm were collected randomly from the mangrove wetland mudflat. Cultured mature clams (CMC) (body length: 4–5 cm) were collected from the aquaculture clam ponds, with five clams mixed to make a sub-sample.

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**Fig. 1.** Sampling sites in Zhangjiang estuary. The clam pond is for raising clams and the fodder pond is for cultivating diatom as the fodder of clams. The fodder pond and clam pond comprise the clam culture system (ccs).

Shrimp and crab samples were randomly collected from the aquaculture ponds. The surface sediments (0–5 cm) both in the ponds and mangrove mudflat were collected and four replicates for each site. Shrimp feed and organic fertilizers were also collected from the farmers with five repetitions for each sample.

In the lab, sediment samples were ground and sieved after freeze-drying. Tissue muscles of the animals were washed with deionized water and then freeze-dried, ground, and sieved. Fodders and organic fertilizers were dried at 60 °C, and then ground and sieved. Each sample was microwave-digested in Teflon vessels with nitric acid and hydrofluoric acid. The detailed procedures of sediment and animal samples treatment were described in Yi et al. (2011). The concentrations of Cu, Zn, Cr, Cd, and Pb were determined by an inductively coupled plasma mass spectrometry (ICP-MS) (NexION300X, PerkinElmer, USA). The concentrations of As and Hg in the sediment and organism samples were determined by atomic fluorescence spectrometry (AFS) (iCAP6000, Thermo Fisher, USA). Analytical quality control included analysis of reagent blank, sample blank, reference material, and duplicate samples. The certified reference material GSD1-3 (IGGEC, Institute of Geophysical and Geochemical Exploration, China) was used to for sediment samples while TORT-2 (NRC, Institute of National Measurement Standards, Canada) was used for organism samples.

The recoveries for metals in sediments ranged from 85% to 105% (Cu, Zn, Cr, Cd, Pb, As, and Hg), while the recoveries for metals in organism ranged from 88% to 110% (Cu, Zn, Cr, Cd, Pb, As, and Hg). Total organic carbon (TOC) and total nitrogen (TN) in the sediment samples were determined by an Elementar Analyzer Vario ELIII (Elementar GmbH, Germany). Sediment total phosphate (TP) was measured by molybdenum antimony resistance to colorimetric method after digestion by improved H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> (ISSCAS, 1978). Salinity and pH in sediment samples were measured with Orion 5 star multiple water quality meters (Orion 5 star, Thermo Fisher, USA). Unless otherwise stated, trace metal concentrations in sediment and benthic animal samples were expressed in mg/kg dry weight.

To evaluate the degree of trace metal pollution in the sediments, geo-accumulation index ( $I_{geo}$ ) was calculated according to Müller's method (Müller, 1969) (Eq. (1)).

$$I_{geo} = \log_2([\text{sediment}]/1.5 * [\text{geochemical background}]) \quad (1)$$

where, the 1.5 factor is used to account for possible variations of the background data due to lithological variations. The soil background value in Southern China was used as the geochemical background (Table 1) (Li and Zheng, 1988).

**Table 1**  
Trace metal contents in mangrove and pond sediments. Lowercase represents deviation of trace metal contents in mangroves; capital letter represents the deviation of trace metal among different ponds (mean ± SE, mg/kg).

Type		Cr	Cu	Zn	As	Cd	Pb	Hg
Ponds	Crab	29.9 ± 4.06A	7.48 ± 0.51A	208 ± 93.6A	152 ± 43.2A	0.0900 ± 0.01A	30.5 ± 3.33A	0.450 ± 0.04A
	Clam	20.4 ± 1.3BC	9.83 ± 0.74B	357 ± 186A	440 ± 103BC	0.140 ± 0.02AB	38.3 ± 6.11AB	0.160 ± 0.02B
	Fodder	22.9 ± 1.98C	10.7 ± 0.54B	626 ± 219A	335 ± 65.3 AC	0.160 ± 0.02B	43.1 ± 3.46BC	0.260 ± 0.03C
	Shrimp average	14.3 ± 1.96D	5.62 ± 0.45C	283 ± 135A	145 ± 41.5A	0.120 ± 0.01AB	18.2 ± 2.56D	0.150 ± 0.02B
Mangroves	<i>Avicennia marina</i>	21.9 ± 6.47 <sup>a</sup>	8.41 ± 2.31 <sup>a</sup>	369 ± 182 <sup>a</sup>	268 ± 145 <sup>a</sup>	0.130 ± 0.03 <sup>a</sup>	32.5 ± 10.9 <sup>a</sup>	0.260 ± 0.14 <sup>a</sup>
	<i>Spartina alterniflora</i>	53.6 ± 2.33a	23.1 ± 0.59a	79.0 ± 2.25a	5.60 ± 0.69a	0.290 ± 0.1a	60.4 ± 2.61a	0.160 ± 0.03a
	<i>Kandelia candel</i>	63.9 ± 3.96a	26.3 ± 0.66a	87.0 ± 1.88a	9.43 ± 0.41b	0.210 ± 0.01b	67.3 ± 1.17a	0.110 ± 0.03a
	<i>Aegiceras corniculatum</i>	84.2 ± 20.7a	25.4 ± 0.72a	83.4 ± 2.31a	10.0 ± 0.38b	0.250 ± 0.02b	64.3 ± 1.74a	0.150 ± 0.06a
	Mudflat	78.3 ± 8.1a	26.1 ± 1.13a	85.3 ± 3.29a	11.6 ± 0.63c	0.390 ± 0.14c	70.9 ± 4.26a	0.160 ± 0.05a
	Average	57.7 ± 2.62a	23.5 ± 0.24a	80.1 ± 0.79a	7.18 ± 0.28d	0.270 ± 0.07d	63.5 ± 1.4a	0.150 ± 0.04a
BG		71.0 ± 12.31 <sup>a</sup>	25.3 ± 1.27 <sup>a</sup>	83.9 ± 2.96 <sup>a</sup>	9.56 ± 1.84 <sup>a</sup>	0.280 ± 0.08 <sup>a</sup>	66.5 ± 3.36 <sup>a</sup>	0.140 ± 0.02 <sup>a</sup>
		47.2	10.5	51.9	11.8	0.100	26.5	0.0400

BG: The soil background value of Southern China (Li and Zheng, 1988).

<sup>a</sup> Represents the deviation of average trace metal content between ponds and mangrove sediments.

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