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Distribution variation of heavy metals in maricultural sediments and their enrichment, ecological risk and possible source—A case study from Zhelin bay in Southern China

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ABSTRACT

The study characterized the enrichment, ecological risk and possible source of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in sediments from a typical mariculture bay. The concentrations of the metals were analyzed in sediments collected from Zhelin bay. The distribution variation was examined during the past decade, which had an increase tendency till 2011. The enrichment factor and geoaccumulation indices suggested Pb, As, Cu and Zn were minor enrichment and unpolluted to moderately polluted, and Ni at cage mariculture area was moderately-severe enrichment and strongly polluted. This area had medium to high ecological risk, especially at the northwest coastal area of semi-closed bay, with high-medium to high ecological risk. Correlation and principal component analyses indicated that most of heavy metals, especially for As, Pb and Ni, primarily resulted from the combustion of gasoline and diesel fuel and the ship protective layer.

1. Introduction

Mariculture is a developing industry that makes a significant contribution to the national economy, and is an important animal protein supplement for the people in the coastal area of China (Zheng et al., 2009). However, mariculture activities cause the deposition of nitrogen, phosphorus and organic wastes and contribute to water eutrophication (Cao et al., 2007; Wu et al., 1994), and then result in the anoxic status and the increase of sulfide in surficial sediment (Liang et al., 2011; Xia et al., 2016). Significant quantities of heavy metals are discharged into rivers, which strongly causes accumulation and biomagnification along water, sediment and aquatic food chain. Sublethal effects or death frequently occur in local fish populations (McGeer et al., 2000; Jones et al., 2001; Almeida et al., 2002; Xu et al., 2004). Heavy metal contamination in coastal marine environments is becoming an increasingly serious threat in Chinese coastal waters (Ip et al., 2007; Zhang et al., 2007, 2009; Shi et al., 2010).

The metal pollutants from various anthropogenic activities as well as natural source normally sink into the coast sediments (Zwolsman et al., 1997; Chaudhary et al., 2013; Hu et al., 2015). Suspended sediments adsorb pollutants from water, thus lowering their concentration. However, sediments are also a possible delayed source of metal contaminants into overlying water due to desorption, redox reactions and remobilization processes (Christophorids et al., 2009). The degree of mobility, activity and bio-availability is influenced by many factors, namely, pH, temperature, redox potential, organic matter, ion exchange processes and microbial activity (Filgueiras et al., 2002). Sediments provide habitats and a food source for benthic fauna, and it has been found that heavy metals can be directly or indirectly bio-accumulated in benthic invertebrates (Kalantzi et al., 2013).

Located in the northeast part of Guangdong Province, Zhelin Bay is one of the most developed areas in China and is a semi-closed estuarial bay, where Huanggang River flowing through the entire county enters into the bay. The mariculture is introduced in the mid-1980s and has dramatically increased in the late 1990s. Now Zhelin Bay is the largest cage mariculture base and an important culture fish zone in South China (Qiao et al., 2010). There are many seaport container terminals used for international seafood export transportation in the southern bay.

Qiao and co-workers investigated the total contents of heavy metals in the surficial sediments sampled in the Zhelin Bay (Qiao et al., 2004; Qiao and Huang, 2006; Qiao et al., 2009), indicated that mariculture activities raised the loading of heavy metals in surficial sediments (Qiao et al., 2010; Wang et al., 2010). The study of annual variation of heavy metals in sediment of Zhelin bay was barely summarized. Therefore, a comprehensive study on the annual distribution, enrichment, ecological risk and possible source of heavy metals in surficial sediment of Zhelin Bay was important for the sustainable development of mariculture and the long-term improvement of public health.

In our study, the concentrations of heavy metals from surface sediments of Zhelin Bay were measured; the history concentrations were

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compared in order to assess their distribution, enrichment and ecological risk; Correlation analysis (CA) and principal component analysis (PCA) were used to define the possible sources of the heavy metals. The purposes of the study were to understand the impact of mariculture on metal contamination and provide crucial information for monitoring, management and conservation of coastal environments.

2. Materials and methods

2.1. Study site and sampling method

Sediment sampling was carried out with two periods in September 2011 and August 2013 at 11 sampling locations (Fig. 1). The undisturbed surficial sediments (10 cm) were collected using a Petersen grab, and quickly placed in the polypropylene bags fulfilled with N_2. The sediments were manually sampled in triplicates, and immediately transported to laboratory with a sample box and then frozen at −18 °C. The pH, temperature, dissolved oxygen and salinity of bottom water were measured using YSI water quality sensors (600R mode, YSI Inc., USA) at each sampling site.

2.2. Chemical analysis

The samples were dried at 70 °C for >24 h and re-weighted to determine the moisture contents. Sediment organic matter (OM) contents were estimated by the wet oxidation method using $K_2Cr_2O_7$ - H_2SO_4 (Mingorance et al., 2007). Acid volatile sulfide (AVS) analyses were performed based on the procedure as described by Fang et al. (2005). Briefly, sulfides in 5.0 g wet sediment samples were volatilized under N_2 stream by addition of 20 ml of 6 M HCl and trapped in 15 ml of 3% alkaline zinc acetate solution (75 ml of 20% zinc acetate solution added to 425 ml of 2 M NaOH). The dissolved sulfide in the trapping solution was determined using the methylene blue method. Total digestion of the sediment samples was conducted following the EPA 3052 method. The samples were weighted accurately 0.2 g and placed into a PTFE digestion tank, then digested by a mixture of 5 ml HNO_3 and 1 ml HF solution using a CEM Mars microwave digestion system. The concentrations of Al, Fe, Mn, Si, Cu, Ni, Pb, Zn and Cd in the final solutions were measured by inductively coupled plasma - optical emission spectrometer (ICP-OES, Spectro Ciros Vision) and atomic absorption spectrometry (AAS, Hitachi Z-2000), respectively. The concentrations of As and Hg were analyzed by atomic fluorescence spectrometry (AFS, Beijing Rayleigh). Analytical accuracy was achieved by the use of blanks and certified reference material including GBW 07314 and GBW 07334, issued by the State Oceanographic Administration of China.

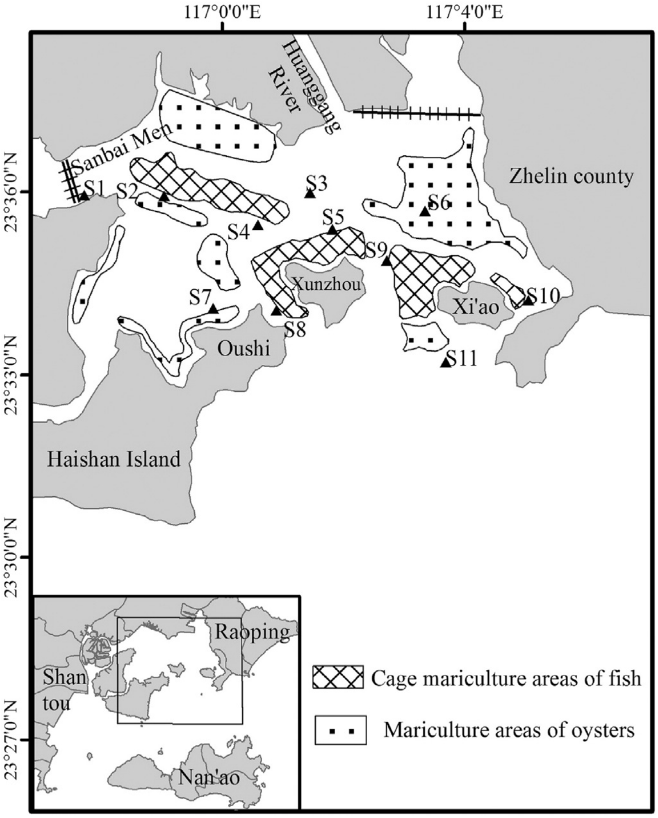

Fig. 1. The study area and sediment sampling sites in Zhelin Bay along the southern coast of China. Surface sediment samples were collected at sites 1–11.

Deionized water (Milli-Q) used throughout the experiments was boiled and purged with nitrogen to remove the dissolved oxygen. All glassware and plastic wares were soaked in 2.7 M HNO_3 for at least 24 h, and then rinsed with deionized water prior to use. Standard solutions of metals were prepared by diluting 1000 μg/ml stock standard solutions with deionized water. All of the chemicals used in the experiment were analytical-reagent grade or better.

2.3. Enrichment and pollution assessment

The enrichment factor (EF) was an effective tool for the regional comparison of trace metal concentration in sediments. It was defined as the concentration ratio of a considered element to a reference element in a given sample, divided by the same ratio of their background values, and calculated as: $EF = (C_i/C_{ref})_{sample}/(B_i/B_{ref})_{background}$ (Nolting et al., 1999). Where C_i was the measured concentration of i heavy metal, C_{ref} was the measured concentration of the reference element, B_i was the background value of the local region and B_{ref} was the background concentration of the reference element of the soil in the same region. Al was a commonly used reference element to compensate for fluctuations in both grain size and composition, since it represented the quantity of aluminosilicates, which was the predominant carrier phase for adsorbed elements in coastal sediments (Chatterjee et al., 2007). As we did not have the background value of Al for our study area, we adopted the Al concentration in crustal material (Martin and Whitfield, 1983).

The geoaccumulation indice (I_{geo}) was used to evaluate the levels of heavy metal contamination and possible sediment enrichment, and calculated as: $I_{geo} = \log_2[C_i/1.5B_i]$. According to Müller (1981), the I_{geo} can be classified into the following categories: unpolluted: $I_{geo} \le 0$; unpolluted to moderately: $0 < I_{geo} \le 1$; moderately polluted: $1 < I_{geo} \le 2$; moderately to strongly polluted: $2 < I_{geo} \le 3$; strongly polluted: $3 < I_{geo} \le 4$; strongly to extremely: $4 < I_{geo} \le 5$; extremely polluted: $I_{geo} > 5$.

2.4. Ecological risk assessment

2.4.1. Sediment quality guidelines (SQGs)

SQGs and different indexes were chosen to estimate the contamination extent of individual metals in the surface sediments of Zhelin Bay. The effects range low (ERL) and median (ERM) were the main parameters for estimating the adverse biological effects in marine and estuary sediments (Long et al., 1995). The ERL and ERM values, which depended on numerous toxicity tests, field studies, and altered benthic communities for sediment dwelling marine animals, were applied as guidelines for assessing the incidence of adverse biological effects of numerous pollutants, including metals in marine sediments (Long et al., 1995).

All the SQGs and index applied above took into account individual metals. Based on the fact that metals always occurred in sediments as complex mixtures, the mean ERL quotient method was conducted to determine the possible biological effect of combined toxicant groups by computing mean quotients for a large range of contaminants (Carr et al., 1996; Long et al., 2000). The mean ERL quotient was calculated

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