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Speciation and risk of heavy metals in sediments and human health implications of heavy metals in edible nekton in Beibu Gulf, China: A case study of Qinzhou Bay

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ABSTRACT

We investigated the total concentrations of heavy metals in surface sediments and nekton, along with sediment metal chemical partitioning in Qinzhou Bay of the Beibu Gulf. Cd was preferentially associated with the acid-soluble fraction and Pb mainly with the reducible fraction, whereas a major portion of Cr, Ni, Cu, and Zn was strongly associated with the residual fractions. A principal component analysis (PCA) in sediment metal speciation revealed three groupings (Cd; Pb; Cr, Ni, Cu, and Zn) that mainly resulted from different distributions of the metals in the various fractions. The Cr concentrations in nekton species were higher than maximum Cr concentrations permitted by the Chinese National Standard (GB 2762-2012). Taking as a whole, surface sediments of Qinzhou Bay had a 21% incidence calculation of adverse biological effects, based on the mean probable-effects-levels quotient. A human health risk assessment indicated no significant adverse health effects from consumption of nekton.

Sediments effectively sinks for trace metals in marine and estuarine environments, but also act as a source of metals during changes in environmental conditions (such as redox potential, pH and others) (Chapman et al., 2013; Gu et al., 2014; Jonge et al., 2012; Nielsen et al., 2010). Heavy metal contamination in coastal marine environments is poses an increasingly serious threat in Chinese coastal waters (Ip et al., 2007; Pan and Wang, 2012; Z.H. Wang et al., 2013). Benthic flora and fauna constitute a crucial link for the coastal marine food web (Ribeiro et al., 2013). Metals, in the sediments, are absorbed by benthic organisms and bioaccumulate and biomagnify as they escalate in the food chain, resulting in fundamental alterations to ecosystems that may affect human health (Gu et al., 2012a; Malferrari et al., 2009; Plette et al., 1999; Ribeiro et al., 2013; Teuchies et al., 2012). Although the total metal concentrations in sediments can offer valuable information on overall pollution levels, many studies have concluded that total metal concentration is an insufficient measure of the environmental impact of contaminated sediments, since the environmental behavior of metals depends strongly upon their specific chemical forms and binding states (Gao and Chen, 2012; Gleyzes et al., 2002). Hence, it is crucial to distinguish and quantify metal species in sediments to predict their mobility, bioavailability, and potential environmental toxicity. Sequential extraction is an important and ubiquitous method that provides information about the strength of metal binding to particulates and the phase associations of metals in solid matrix (Hass and Fine, 2010; Sutherland, 2010; Tessier et al., 1979). Among such techniques, the BCR procedure is one of the most widely used in numerous types of solid samples, including freshwater sediments, salt water sediments, soil, sewage sludge, and particulate matter (Filgueiras et al., 2002; Gleyzes et al., 2002; Hass and Fine, 2010; Sutherland, 2010).

Marine nekton comprising fish, crustaceans, and cephalopods, is consumed by humans worldwide. It offers high protein and low saturated fat content and for omega fatty acids, which are known for their health benefits (Ip et al., 2005; Naylor et al., 2000; Sapkota et al., 2008; Wu et al., 2014). However, marine nekton may be contaminated by metals from various sources, including industrial and domestic wastewater, and water pollution in natural runoff and contributory rivers (Ip et al., 2005; S.-L. Wang et al., 2013; Wang, 2013). Investigations of heavy metal accumulation in nekton have largely been carried out in food safety studies. Heavy metals accumulate as they move up the food chain, and may threaten human health when they reach a threshold concentration (Gu et al., 2012a; Wang, 2013). Therefore, it is crucial to determine the heavy metal concentrations in widely consumed nekton species.

The Beibu Gulf (also known as the Gulf of Tonkin or Bac Bo Gulf), has become one of the most important areas of economic development in China because of its bountiful resources and strategic location to both China and other Southeast Asian countries (Yu and Mu, 2006; Zhang et al., 2014; Zheng et al., 2012). As a semi-enclosed bay surrounded by the land territories of Vietnam and China's

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Hainan, Guangxi and Guangdong provinces (Fig. 1), the Beibu Gulf has a weak self- purification capability (Yu and Mu, 2006; Zhang et al., 2014). Over the past decade, the nature ecosystem structure and environmental quality of three rivers that flow into the gulf—the Maoling, the Jingu, Qin estuaries—have been under stress because of rapid industrialization and urbanization (Xia et al., 2011; Zhang et al., 2014; Zheng et al., 2012).

Qinzhou Bay, covers an area of approximately 380 km^2 in the northeast part of the Beibu Gulf and is a busy region greatly affected by anthropogenic industrial activities. The surrounding area contains several important economic development districts in Guangxi Province, noted for petrochemical, plastic, and printing industries as well as the Hongsha nuclear power station. This land-based industrial output is supplemented by a well-developed fish, shrimp, and shellfish aquaculture in the Bay, and widespread cage-cultured fisheries in the inner waters. To date, few studies have measured the total heavy metal concentrations in surface sediments from Qinzhou Bay, reporting slight pollution (Shu et al., 2013; Zhang et al., 2010). To the best of our knowledge, investigations related to metal speciation in sediments and heavy metals in nekton are scarce in Qinzhou Bay. Therefore, this study aimed to (1) Survey total metal concentrations, explore the sources and behavior of the metals, and evaluate their ecological risks in sediments, and (2) determine the metals in the nekton and assess their human health risk.

Sediment samples were collected with a stainless steel Van Veen bottom grab sampler from 12 different sites distributed throughout Qinzhou Bay in March 2013 (Fig. 1). Samples aliquots were taken from the undisturbed top 3 cm of sediments with a polyethylene spatula and placed in self-sealing polyethylene bags. All samples were stored frozen at −4 °C until further analysis. One set of aliquots was used for grain size analysis; the other set was dried at 50 °C to constant weight, homogenized with an agate mortar and pestle, sieved with a 250 mesh sieve (<63 μm), and stored at −4 °C in self-sealing polyethylene bags until organic matter (OM), calcium carbonate ($CaCO_3$), and metal analysis.

Samples were pretreated for grain size in accordance with the Chinese National Standard (GB/T12763.8-2007). The sample granulometry was discriminated by laser diffractometer (Mastersizer 2000, Malvern, UK). The OM and $CaCO_3$ were estimated by the loss-on-ignition technique. Specifically, the sample was heated at 550 °C for 4 h to estimate OM and for a further 2 h at 1000 °C to estimate $CaCO_3$ content (Rabenhorst, 1988). Both OM and $CaCO_3$ were determined as a percentage of dry weight. Total metal microwave digestion protocols followed EPA Method 3050B and the digestion was performed on a microwave labstation (Ethos Plus, Milestone, Italy). A sequential extraction procedure following that described by Rauret et al. (1999) was conducted to elucidate the metal fractionation. This scheme classifies the metals into four operationally defined geochemical fractions: acid soluble,

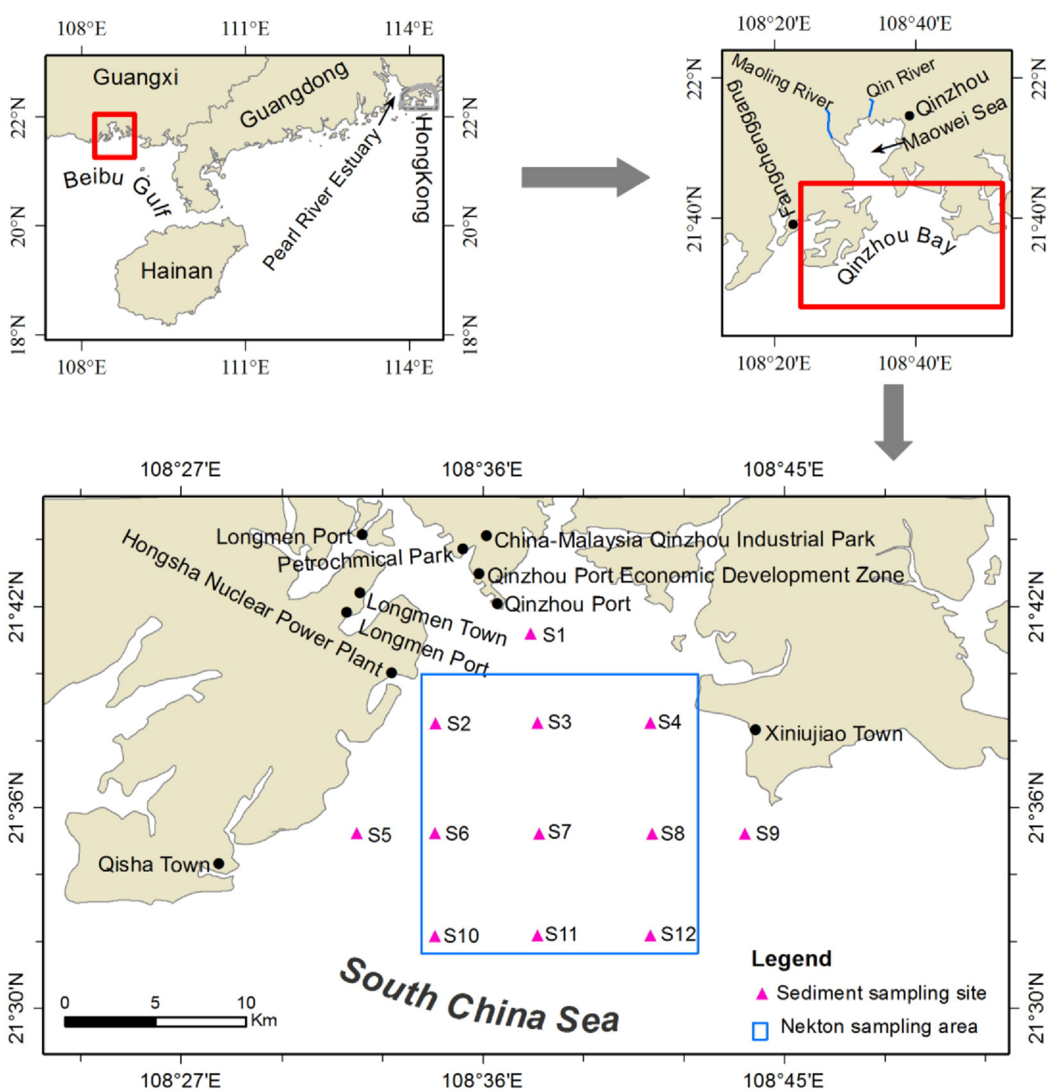

Fig. 1. Map of sampling sites in Qinzhou Bay, South China Sea.