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Low mercury levels in marine fish from estuarine and coastal environments in southern China

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ABSTRACT

This study is the first comprehensive evaluation of total Hg and methylmercury (MeHg) concentrations in wild marine fish from an estuarine and a coastal ecosystem in southern China. A total of 571 fish from 54 different species were examined. Our results showed that the Hg levels were generally low in the fish, and the Hg levels were below 30 ng g^{-1} (wet weight) for 82% of the samples, which may be related to the reduced size of the fish and altered food web structure due to overfishing. Decreased coastal wetland coverage and different carbon sources may be responsible for the habitat-specific Hg concentrations. The degree of biomagnification was relatively low in the two systems.

1. Introduction

Due to rapid economic development and the lack of stringent control over agricultural and industrial discharges, metal contamination is becoming an increasingly serious problem in China, especially mercury (Hg) contamination (Zhang and Wong, 2007; Feng and Qiu, 2008; Pan and Wang, 2012). The discharge of Hg has resulted in elevated Hg levels in air and various types of water bodies including rivers, lakes, and coastal waters, as well as in soils and sediments (Lin et al., 2012; Cheng and Hu, 2012). Assessing the consequences of the increasing Hg contamination is a pressing issue for government and scientific communities in China.

Hg is a global pollutant that can be easily transported over long distances. Its organic form methylmercury (MeHg) is extremely bioavailable to organisms and can be biomagnified along food chains to eventually pose a hazard to humans. The growing Hg contamination in China has led to public concern about inadvertently consuming Hg-contaminated food in recent years (Feng et al., 2008; Barrett, 2010). Of particular concern to public health is the Hg in fish which is considered the most important vector linking environmental Hg to humans. Despite reports of high Hg levels in environmental matrixes in China, interestingly, recent studies have indicated low Hg contamination in freshwater fish, even in those from contaminated sites (Liu et al., 2012). Possible explanations for this paradox include the rapid growth of low trophic level species and the time lag between contamination and bioaccumulation (Lin et al., 2012). Cheng and Hu (2012) suggested that the mercury levels in fish in China are generally low because the market is dominated by fast-growing farmed freshwater fish which generally have lower Hg concentrations than marine fish since the latter are primarily carnivores.

However, there is a paucity of information on the Hg levels in marine fish in China to date, especially the Hg levels in estuarine fish. It is possible that estuarine fish contain elevated levels of Hg as the Hg discharged into rivers may enter estuaries and be biotransformed and accumulated by the fish eventually. Estuaries are usually within the industrialized watersheds and are known to be repositories of contaminants including Hg. They are also considered as ‘critical areas’ of Hg methylation. High Hg concentrations in estuarine fish may be due to favorable geochemical conditions in sediments such as prevalence of wetlands, anoxia spots, and influence of tidal movement and flux which facilitate MeHg transport and production (Chen et al., 2009; Hammerschmidt and Fitzgerald, 2006; Fitzgerald et al., 2007; Bergamaschi et al., 2012). Severe Hg contamination has been observed in coastal waters in China (Wang et al., 2009), but there has not been any comprehensive evaluation of Hg levels in wild marine fish. Several studies have measured the concentrations of Hg in marine fish found in the coastal waters of China (Bohai Bay, Hong Kong, Chung et al., 2008; Li et al., 2013; Wang et al., 2013). But the actual sampled fish were taken from local fish markets, not directly from the coastal waters, and so the results may not reflect the Hg contamination in the local

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environments. An analysis of the Hg levels in wild marine fish taken directly from the coastal waters of China is necessary to provide insights into the Hg contamination situation in those waters.

This study was designed to investigate the Hg levels in wild marine fish found in the Pearl River Estuary (PRE) and the adjacent Dapeng Bay (DB) near Hong Kong. The two bodies of water were chosen for their contrasting geographical conditions. We hypothesize that (1) Hg concentrations are higher in the PRE fish since the PRE is more anthropogenically affected than DB; and (2) Hg concentrations in fish are closely related to their feeding habits and trophic levels.

2. Materials and methods

2.1. Study areas

Hong Kong's coastal waters can be divided into three longitudinal hydrographic zones: a western estuarine zone (PRE), an eastern oceanic zone (DB) and a central transition zone (Fig. 1). The western waters are greatly influenced by the riverine input of the Pearl River, the second largest river in China in terms of discharge with a watershed of 230,000 km^2. As the most economically developed and a densely populated area of South China, the PRE is very much affected by the uncontrolled release of wastes including metals (Zhang et al., 2009). The western waters are characterized by low salinity, high turbidity, high nutrients and mineral loads. By contrast, the eastern waters are unaffected by the drainage of the Pearl River and receive much less anthropogenic inputs than the western waters. These waters are mostly influenced by the oceanic current of the South China Sea and are high in salinity, rich in oxygen, and low in turbidity.

2.2. Fish sampling and processing

A variety of wild marine fish were caught with the help of local fishermen using gill nets or by trawling in the sampling areas from August to December, 2011 (Table 1 and Table 2). The number of fish species and the sample size for each species were dependent on the availability of fish during the sampling. Fish caught were placed in clean plastic bags and stored in an ice box, which was transported back to the laboratory immediately. The fish were frozen to −20 °C or below before further processing and analysis. In the laboratory the species of each thawed fish was identified and the total length (cm) and blotted total wet mass were recorded (g). The fish muscles were dissected from the dorsal areas using a stainless steel scalpel. Each muscle sample was subjected to a wet weight measurement before it was freeze-dried to obtain its wet-to-dry ratio (average 4.2). Dried samples were ground into a fine powder and stored in a clean polyethylene centrifuge vials before Hg and stable isotope analyses.

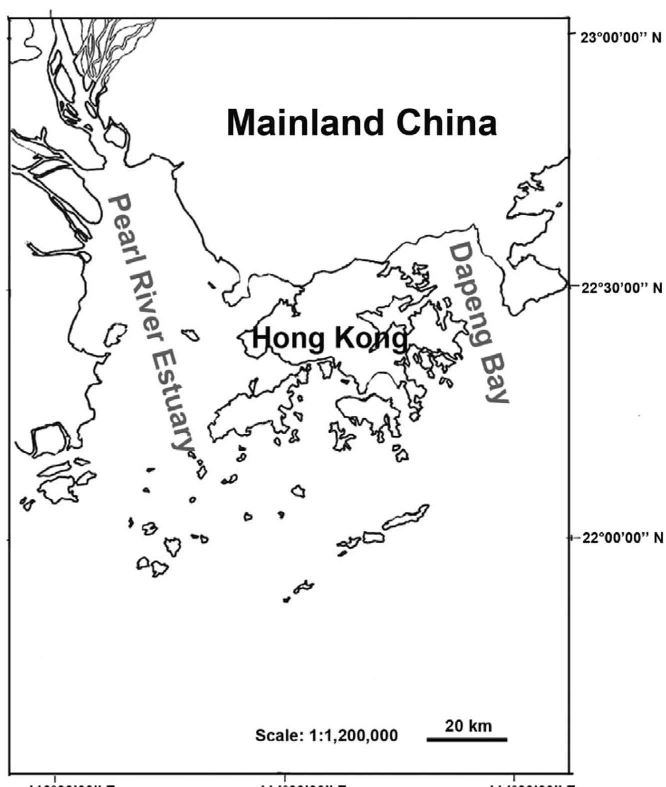

Fig. 1. Map showing the Pearl River Estuary and Dapeng Bay.

2.3. Measurements of THg and MeHg

For analysis of THg, approximately 0.2 g of powdered tissues (or 2 mL of supernatant, freeze-dried pellets) were digested at 190 °C with *aqua regia* (2 mL of HNO_3:6 mL of HCl) in a microwave digestion system. An aliquot of the digested sample was taken and diluted as appropriate. 0.5% (v/v) bromine monochloride was added to the diluted sample until a stable yellow color was obtained. The samples were reduced by addition of sodium chloride hydroxylamine hydrochloride immediately before analysis. THg was quantified by the single gold trap amalgamation technique using a cold-vapor atomic fluorescence spectrometer (QuickTrace® 8000, USA). Blanks were run for every batch of 20 samples.

For analysis of MeHg, approximately 40 mg of tissues were digested with 25% KOH in methanol at 60 °C for 3 h. MeHg in the extract was measured with an automated MeHg analytical system (MERX, Brooks Rand, USA). Briefly, 20–50 μL of the extract was buffered with sodium acetate at pH 4.9, and ethylated by sodium tetraethylborate in a 40 mL Teflon line borate glass bottle. The quantification of MeHg was automatically carried out by the MeHg analyzer with gas chromatographic separation and pyrolysis following atomic fluorescence detection. The method blanks were generally close to zero in our analysis. The analytical accuracy of THg and MeHg was validated by analyzing reference materials from the International Atomic Energy Agency (IAEA-436, tuna fish) between sample runs. The accepted recoveries ranged from 85 to 105%. Results are reported in ng g^{-1} on a wet weight (wet wt) basis.

2.4. Stable isotope analysis

Three composite samples were measured for stable isotopes of $\delta^{13}C$ and $\delta^{15}N$ for each species by Institute of Botany, Chinese Academy of Sciences, Beijing. Three individual samples (0.1 g each) were combined into one composite sample in order to obtain a representative sample for each species. Two or three randomly selected samples were used if sample size <8. Powdered samples were directly analyzed and lipid-extraction was not performed. Isotopic measurements were made using a Finnigan MAT Delta V advantage isotope ratio mass spectrometer. $\delta^{13}C$ and $\delta^{15}N$ are derived from the following equation:

$$\delta^{13}C \text{ or } \delta^{15}N_{\text{Sample}}\ (‰) = \left[\left(R_{\text{sample}}/R_{\text{standard}}\right) - 1\right] \times 1000$$

where R is the ratio of heavy to light isotope ($^{15}N/^{14}N$ or $^{13}C/^{12}C$) in the sample and standard. Vienna Pee Dee belemnite limestone for carbon and atmospheric N_2 for nitrogen were used as reference materials. Precision for $\delta^{15}N$ is ±0.3‰ and is ±0.4‰ for $\delta^{13}C$ based on the analysis of the standards.

2.5. Data treatment and statistical analysis

Comparisons of Hg concentrations among fish species were performed using one-way ANOVA followed by Tukey's multiple comparison test. To improve normality and homogeneity of variance, Hg concentrations were log_{10}-transformed. Hg levels in fish of the same species from western and eastern waters were compared using ANCOVA to compensate for size-related differences between regions. Prior to the ANCOVA test, Levene's test for equality of variances was performed. Linear regression analysis was performed to explore the relationship between Hg concentration and fish body size, $\delta^{13}C$, and $\delta^{15}N$. Comparisons and relationships were considered statistically significant at $p < 0.05$. All statistical analyses were performed in SPSS 16.0.

3. Results and discussion

3.1. Hg levels in wild fish from Hong Kong waters

A summary of fish species, size, MeHg, THg, and stable isotopic signatures is given in Table 1, Table 2 and Fig. 2. A total of 571 fish were collected, covering 9 orders, 23 families, and 54 species of fish, with 18 species collected from the western waters (PRE) and 45 species from the eastern waters (DB). Currently there are 25 orders, 124 families, and 390 genera of marine fish recorded in Hong Kong waters, and our samples have covered 7 of the 10 most abundant families: Gobiidae, Carangidae, Serranidae, Lutjanidae, Labridae, Scorpaenidae, Sciaenidae, Apogonidae, Clupeidae, and Tetraodontidae (Ni and Kwok, 1999). Our dataset is the most comprehensive one on Hg concentrations in coastal wild fish in China to date. Different types of fish were collected, including the