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Mercury in coastal watersheds along the Chinese Northern Bohai and Yellow Seas

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ABSTRACT

The concentration of total mercury [Hg] in waters, sediments and biota (carp and crabs) as well as the concentration of methyl mercury [MeHg] in biota from upstream (surface water systems) and downstream (coastal and estuarine systems) areas within coastal watersheds along the Chinese Northern Bohai and Yellow Seas were investigated. In most waters tested, the [Hg] could have adverse effects on coastal wildlife. Based on the Chinese water quality standards for mercury, 67% of upstream waters cannot be used for agriculture or recreation. Furthermore, 53% of downstream waters cannot be used as harbors or for industrial development. The [Hg] in 3% of sediments from the Wuli and Luanhe Rivers were sufficient to cause adverse effects on ecosystems. The [Hg] in 41% of downstream crabs and the [MeHg] in 29% of downstream crabs were higher than the limits for human consumption set by the Chinese government. In all abiotic and biotic samples, only the downstream carp from the Northern Yellow Sea had a [Hg] or [MeHg] higher than those from the Northern Bohai Sea. Industrialization and urbanization were the primary sources of mercury contamination in the aquatic ecosystems studied.

1. Introduction

Mercury (Hg) is one of the most hazardous, persistent and toxic contaminants that can be transported from an emission source and bioaccumulated in aquatic environments [1]. The ocean is a sink in the global Hg cycle [2]. Human activities, such as mining, industrial development and urban expansion in coastal environments, are the primary sources of terrestrial Hg. The Hg released from point sources and long-range air transport has contaminated the coastal environments in China and has been a concern due to Hg accumulation in aquatic food webs [3].

Contamination of the environment with Hg is recognized as one of the primary environmental problems in China [4–9], and China contributes approximately 28% of global Hg emissions to the atmosphere due to human activities [4]. As a result of China's rapid industrialization, urbanization and agro-livestock farming development in coastal areas, Hg pollution has received increased attention [10–12]. Some coastal watersheds along the Bohai and Yellow Seas have been polluted by industrial wastewater and sewage discharge as well as atmospheric deposition [7,10,13–15]. The primary area of Hg pollution along the Bohai and Yellow Seas is in the northern regions. This area is home to a dense human population as well as plentiful wildlife and marine life living along the coasts and the surrounding rivers and estuaries [10,14,16–19]. Because environmental processes and biological community structures change along fluvial gradients within coastal river basins, the bioavailability of Hg varies relative to the abiotic environmental factors that undergo transition from headwaters to downstream reaches and coastal habitats [20–22]. Consequently, the [Hg] and associated risks would also be expected to change along the course of river basins from the inland tributaries to the sea [3,23]. However, previous research has focused on downstream areas (coastal and estuarine systems, namely marine and saline water systems), such as estuaries, coasts and bays along the Chinese Northern Bohai and Yellow Seas (CNBYS). Thus, the status and distribution of Hg pollution in upstream areas (surface water systems, namely freshwater systems) within the coastal watersheds are still unclear. Furthermore, the differences in water, sediment and biota Hg content between upstream areas and downstream areas within coastal watersheds on a regional scale are largely unknown [10,19,24–30]. Although the risks of Hg contamination in different environments along the CNBYS have been studied previously, gaps in our understanding of riverine transport of Hg to estuaries, coasts and bays remain. To develop pollution control strategies and systematic approaches for better management of Hg from inland rivers to the sea, information on input, transport, accumulation and geochemical distribution of Hg within coastal watersheds along the CNBYS is needed. In aquatic systems, inorganic Hg is converted to MeHg,

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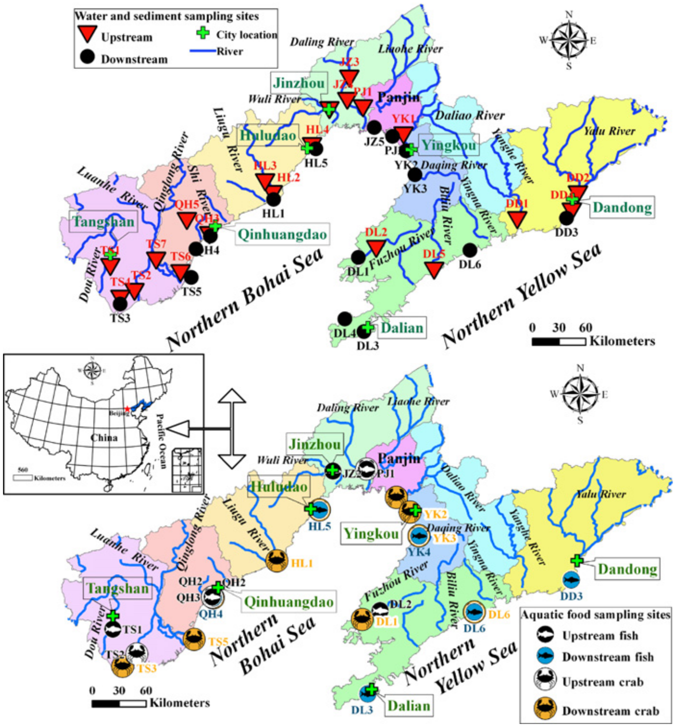

Fig. 1. Sampling sites for surface waters, sediments and biota samples in coastal watersheds (different color representing different administrative unit) of the CNBYS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

which is the form of Hg that accumulates in aquatic food webs [31]. To better assess the potential hazard of Hg in aquatic ecosystems, the [MeHg] in biota were analyzed; however, the [MeHg] in waters and sediments was not measured in this study.

The objectives of the present study were the following: (1) to determine the [Hg] in waters and sediments as well as the [Hg] and [MeHg] in biota collected from upstream areas of coastal rivers and downstream receiving waters on a watershed-level along the CNBYS; (2) to characterize the spatial distribution of [Hg] in waters, sediments and biota as well as the bioaccumulation of Hg and MeHg; and (3) to evaluate potential sources of Hg and determine the potential effects on the environment and human health.

2. Materials and methods

2.1. Study area

A map and detailed description of the study area along the CNBYS are shown in Fig. 1 and Table 1, respectively. There are two catchments for coastal rivers along the CNBYS. One is the Northern Bohai Sea (NBS), which collects water from the rivers in the west of Dalian. The second is the Northern Yellow Sea (NYS), which collects water from the rivers in the east of Dalian. The Liugu, Wuli, Daling, Liaohe, Daliao, Daqing and Fuzhou Rivers flow north to south into the NBS, while the other rivers flow north to south into the NYS (Fig. 1). There are 28 million people living in the coastal watersheds along the CNBYS, among which the watersheds in Tangshan have the greatest population. Coastal watersheds in Jinzhou and Panjin contain the largest proportion of farm land. The greatest proportions of rural and industrialized areas are found in the watersheds of Tangshan and Dalian, where the largest amounts of industrial waste and sewage are discharged.

2.2. Sampling

A total of 36 water samples were collected from 36 surface-water sites covering coastal rivers along the CNBYS (Fig. 1). Twenty-one water samples were obtained from upstream areas of coastal rivers and 15 from downstream areas. Clean sampling techniques were used during sample collection, preservation and storage [32]. Samples were collected in October 2008. Each water sample consisted of 5 homogenized sub-samples (1 L) taken from 0 to 10 cm depths in an area of approximately 25 m^2 into pre-cleaned and marked Teflon bottles. To keep dissolved metals in solution, water samples were acidified with HNO_3 to a pH of 2 or less at the time of collection, placed in a cool-box and delivered to the laboratory immediately.

Surface sediments were collected synoptically (except one site) where waters were collected. A total of 35 sediment samples were collected, among which, 21 were from the upstream areas and 14 from the downstream areas (Fig. 1). Each sample of sediment was composed of 5 homogenized sub-samples taken from the top 10-cm within a 5 m^2 area. Composite samples of sediment were placed in dark-colored Teflon bottles, refrigerated and returned immediately to the laboratory where they were dried at 4 °C, crushed, mixed thoroughly and passed through a 100-mesh nylon sieve and stored at 4 °C in the dark until analysis.

Crucian carp (*Carassius carassius*) and Asia shore crabs (*Hemigrapsus sanguineus*) were selected as representative biota because their habitats were evenly distributed throughout coastal areas along the CNBYS. Crucian carp of 9 ± 2 cm with a wet weight of 180 ± 30 g (estimated average age 1–2 years) and Asia shore crabs with a carapace width of 3.2 ± 0.4 cm and a wet weight of 20 ± 3 g (estimated average age 1–2 years) were collected. Composite samples of carp or crab comprised three individuals pooled to form a representative sample for each sampling site. A total of 36 composite samples were taken from 24 locations. Seven of the 13 pooled samples of carp were from the upstream areas, and 6 were from the downstream areas. Five of the 23 pooled samples of crab were from the upstream areas, and 18 were from the downstream areas (Fig. 1, Table 1). Biota samples were placed in water-tight polyethylene bags and frozen at −20 °C. In the laboratory, the samples were dissected and equal weights of muscle from replicates of the same species were combined. Aliquot of muscle were dried in an oven at 45 °C for 24 h and then analyzed for [Hg] and [MeHg].

2.3. Quantification of Hg

Surface waters were filtered through 0.45 μm PVDF membranes (Millipore) and analyzed directly for [Hg] using US EPA Method 1631E, which is based on cold vapor atomic fluorescence spectrometry (CVAFS) [33]. The [Hg] in sediments and biota was determined using a modified version of US EPA method 7474 [34,35]. The [MeHg] in samples of biota was measured using acid (3 N HNO_3) or hot alkali (25% NaOH) digestion, solvent (CH_2Cl_2) extraction and reverse extraction by water, ethylation and gas chromatography–cold vapor atomic fluorescence spectrometry (GC–CVAFS), which was developed by Liang et al. [36]. The [Hg] and [MeHg] in biota were expressed on a wet weight basis, while those in sediments were expressed on a dry weight basis.

Quality assurance and quality control procedures included the use of duplicates, method blanks, liquid standard solutions for instrument calibration, matrix spikes and certified reference materials (GB ESS1 and DORM-2 for sediment and biota samples, respectively). Instrument performance was calibrated using standard solutions containing different concentrations of each mercury species every 10 samples, and all were within the acceptable range (85–115% for Hg and 90–120% for MeHg compared to the initial