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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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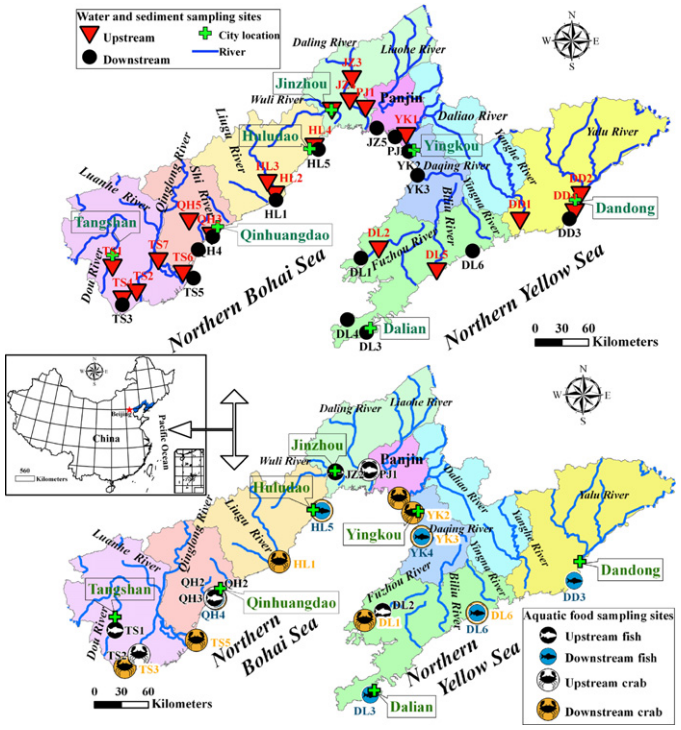


**Fig. 1.** Sampling sites for surface waters, sediments and biota samples in coastal watersheds (different color representing different administrative unit) of the CNBYS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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 $9 \pm 2$ cm with a wet weight of $180 \pm 30$ g (estimated average age 1–2 years) and Asia shore crabs with a carapace width of $3.2 \pm 0.4$ cm and a wet weight of $20 \pm 3$ 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

**Table 1**
Sample details and surrounding activities of sampling sites along the CNBYS.

| Sampling | | | | Samples | | | Land uses[b] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sea | Coastal region | River/sea | Sites | Water | Sediment | Biota | A | I | M | O |
| Northern Bohai Sea | Tangshan | Dou River | TS1 | *C*[a] | *C* | *C* | *C* | | | |
| | | Qionglong River | TS2 | *C* | *C* | *C* | *C* | | | |
| | | Bohai Sea | TS3 | *C* | *C* | *C* | *C* | | | |
| | | Shuanglong River | TS4 | *C* | *C* | *NC*[a] | *C* | | | |
| | | Bohai Sea | TS5 | *C* | *C* | *C* | | | | *C* |
| | | Luan River | TS6 | *C* | *C* | *NC* | *C* | | | |
| | | Luan River | TS7 | *C* | *C* | *NC* | *C* | | | |
| | Qinhuangdao | Bohai Sea | QH1 | *C* | *C* | *C* | | | | *C* |
| | | Xin River | QH2 | *C* | *C* | *C* | *C* | | | |
| | | Xin River | QH3 | *C* | *C* | *C* | *C* | | | *C* |
| | | Bohai Sea | QH4 | *C* | *C* | *C* | | | | *C* |
| | | Tianma River | QH5 | *C* | *C* | *C* | | | | |
| (Liaodong Bay) | Huludao | Bohai Sea | HL1 | *C* | *C* | *C* | | | | *C* |
| | | Liugu River | HL2 | *C* | *C* | *NC* | *C* | | | |
| | | Liugu River | HL3 | *C* | *C* | *C* | *C* | | | |
| | | Wuli River | HL4 | *C* | *C* | *NC* | | *C* | | |
| | | Bohai Sea | HL5 | *C* | *C* | *C* | | | | *C* |
| | Jinzhou | Xiaoling River | JZ1 | *NC* | *NC* | *NC* | | | *C* | |
| | | Daling River | JZ2 | *C* | *C* | *C* | | | *C* | |
| | | Daling River | JZ3 | *C* | *C* | *NC* | *C* | | | |
| | | Daling River | JZ4 | *C* | *C* | *NC* | | *C* | | |
| | | Bohai Sea | JZ5 | *C* | *C* | *NC* | *C* | | | |
| | Panjin | Shuangtaizi River | PJ1 | *C* | *C* | *C* | *C* | | | |
| | | Bohai Sea | PJ2 | *C* | *C* | *C* | | | | *C* |
| | Yingkou | Daliao River | YK1 | *C* | *C* | *NC* | | | *C* | |
| | | Bohai Sea | YK2 | *C* | *C* | *C* | | | *C* | |
| | | Bohai Sea | YK3 | *C* | *C* | *C* | | | | *C* |
| | Dalian | Bohai Sea | DL1 | *C* | *C* | *C* | *C* | | | |
| | | Fuzhou River | DL2 | *C* | *C* | *C* | | | | *C* |
| | | Bohai Sea | DL4 | *C* | *C* | *NC* | | | | *C* |
| | Total | | | 29 | 29 | 19 | 14 | 2 | 4 | 9 |
| Northern Yellow Sea | | Yellow Sea | DL3 | *C* | *NC* | *C* | | | *C* | |
| | | Biliu River | DL5 | *C* | *C* | *NC* | *C* | | | |
| | | Yellow Sea | DL6 | *C* | *C* | *C* | | | | *C* |
| | Dandong | Dayang River | DD1 | *C* | *C* | *NC* | *C* | | | |
| | | Yalu River | DD2 | *C* | *C* | *NC* | *C* | | | |
| | | Yellow Sea | DD3 | *C* | *C* | *C* | | *C* | | |
| | | Yalu River | DD4 | *C* | *C* | *NC* | | | | *C* |
| | Total | | | 7 | 6 | 3 | 3 | 1 | 1 | 3 |

[a] *C*: collected; *NC*: not collected.
[b] A: agricultural; I: industrial; M: municipal; and O: others.

readings). Calibration solutions were prepared daily in 1.2 mol/L HCl, 0.02 mol/L NaCl and acetate buffer (pH 5).

The limits of quantification (LOQs) of Hg in waters and sediments were 0.4 ng/L and 0.0090 mg/kg dry wt, respectively. The LOQs for Hg and MeHg in biota were 0.0018 and 0.00060 mg/kg wet wt, respectively. The [Hg] or [MeHg] in all method blanks were below the LOQs. Matrix spike duplicates were conducted for 3 samples of water, sediment and biota; actual field samples were spiked with 4 ng of Hg standard or 6 ng of MeHg standard. The recovery of Hg spiked into water, sediment and biota were 97–99%, 96–106% and 83–120%, respectively. The recovery of MeHg spiked into biota ranged from 91 to 107%. The found [Hg] and [MeHg] were in good agreement with the certified values (Table 2), suggesting the proposed methods were feasible in the determination of Hg in all samples. The relative percentage difference of sample duplicates was <10%.

### 2.4. Statistical analyses

Because of the limited sample sizes and non-normal distribution of concentrations, nonparametric statistical tests were applied. The differences in mean [Hg] between upstream and downstream abiotic and biological samples were evaluated using the Mann–Whitney *U* test with a significance level of $\alpha = 0.05$. Spearman rank correlations with a level of significance higher than 0.05 (Type I error) were reported. Statistical analyses were conducted using SPSS for Windows, version 16.0 (SPSS Inc, USA).

## 3. Results and discussion

### 3.1. Surface waters

The mean [Hg] in upstream waters of coastal rivers along the CNBYS was 1.1 μg/L, with a range of 0.87–1.5 μg/L. The [Hg] in downstream waters ranged from 0.92 to 1.2 μg/L, with a mean [Hg] of 1.0 μg/L (Table 3). The mean [Hg] was not significantly higher in the upstream waters than in the downstream waters (Mann–Whitney *U* test, $p > 0.05$). The mean [Hg] in upstream or downstream waters of coastal rivers along the NYS was not higher than that in the waters from the NBS ($p > 0.05$) (Table 3). The highest [Hg] (1.5 μg/L) was observed in upstream water from the Biliu River in Dalian (DL5). It has been reported that small-scale, primitive and even illegal gold mining activities are being conducted in the upstream area of the Biliu River watershed [37,38]. In addition, the largest discharge of sewage ($2.3 \times 10^8$ tons/a) and second largest discharge of industrial wastewater ($2.8 \times 10^8$ tons/a) in the Dalian could be responsible for the Hg contamination in the Biliu River. Upstream waters of the Yalu, Liugu and Dou Rivers

**Table 2**
Results of [Hg] and [MeHg] in certified reference materials (CRMs).

| Analyte | Reference material | *N* | Determination value (mean ± SD, ng/g dw) | Certified value (mean ± SD, ng/g dw) |
|---|---|---|---|---|
| [Hg] | GB ESS-1 | 3 | 16.2 ± 0.9 | 16 ± 3 |
| [Hg] | DORM-2 | 3 | 4500.8 ± 167.0 | 4640 ± 260 |
| [MeHg] | DORM-2 | 3 | 4246.5 ± 183.3 | 4470 ± 320 |

**Table 3**
Descriptive statistics for [Hg] in waters and sediments in coastal watersheds along the CNBYS.

| | | Water (μg/L) | | | Sediment (mg/kg dw) | | |
|---|---|---|---|---|---|---|---|
| | | Upstream | Downstream | Total | Upstream | Downstream | Total |
| Northern Bohai Sea | *N* | 17 | 12 | 29 | 17 | 12 | 29 |
| | Mean | 1.0 | 1.0 | 1.0 | 0.032 | 0.023 | 0.028 |
| | SD | 0.12 | 0.10 | 0.11 | 0.039 | 0.010 | 0.030 |
| | Min | 0.87 | 0.92 | 0.87 | 0.017 | 0.018 | 0.017 |
| | Max | 1.3 | 1.2 | 1.3 | 0.18 | 0.054 | 0.18 |
| Northern Yellow Sea | *N* | 4 | 3 | 7 | 4 | 2 | 6 |
| | Mean | 1.2 | 1.0 | 1.1 | 0.029 | 0.024 | 0.028 |
| | SD | 0.26 | 0.050 | 0.20 | 0.011 | 0.0017 | 0.0090 |
| | Min | 0.92 | 0.98 | 0.92 | 0.019 | 0.023 | 0.019 |
| | Max | 1.5 | 1.1 | 1.5 | 0.046 | 0.025 | 0.046 |
| Total | *N* | 21 | 15 | 36 | 21 | 14 | 35 |
| | Mean | 1.1 | 1.0 | 1.1 | 0.031 | 0.022 | 0.027 |
| | SD | 0.15 | 0.087 | 0.13 | 0.035 | 0.011 | 0.028 |
| | Min | 0.87 | 0.92 | 0.87 | 0.017 | 0.017 | 0.017 |
| | Max | 1.5 | 1.2 | 1.5 | 0.18 | 0.054 | 0.18 |

contained relatively high [Hg] (Fig. 2a). One of the largest chemical fiber production bases in China (established in 1939) and paper making factories in Dandong are the likely sources of Hg in the Yalu River [24,39]. Furthermore, the large amount of runoff from the Yalu River ($2.4 \times 10^{10}$ $m^3$/a) would result in significant loading of Hg in the NYS. It is possible that townships and villages engaged in gold, manganese, molybdenum, iron, lead and zinc mining and processing might have contributed to the Hg in the Liugu River. The source of Hg in the Douhe River was attributed to the large amount of industrial wastewater ($2.9 \times 10^8$ tons/a) discharged from iron and steel smelting, coal mining, coal power generation, cement production and paper making in Tangshan [40]. Broadly speaking, 67% of upstream waters in the coastal rivers along the CNBYS had [Hg] above the maximum allowable limit for surface water quality-class V (1.0 μg/L), which is the limit for agriculture or recreation [41] (Table 4). Furthermore, based on standards for the ecological quality of surface water (Table 5), the [Hg] in upstream waters could adversely affect wildlife.

Relatively high [Hg] were found in downstream waters of the Shi, Liugu, Wuli and Daling Rivers along the west coast of Liaodong Bay (Fig. 2a). Based on an analysis of sources and trends of Hg emission [38], cement production, paper making, coal production and transportation and small-scale gold mining (accounting for 46% of all township and village industries) at downstream areas of the Shi and Liugu Rivers are most likely responsible for the Hg contamination [42]. Zinc smelting and chlor-alkali production resulted in higher [Hg] in the downstream waters of the Wuli and Daling Rivers [43]. Generally, 53% of the downstream water along the CNBYS had [Hg] that exceeded the Chinese sea water quality standard-class IV (0.5 μg/L), which is applicable to developed areas, such as harbors and industrial regions [44]. Furthermore, based on the ecological assessment and maximum/continuous concentration in sea water

**Table 4**
Descriptive statistics for [Hg] and [MeHg] in aquatic foods in coastal watersheds of the CNBYS.

| | | Carp (mg/kg ww) | | | | | | Crab (mg/kg ww) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Upstream | | Downstream | | Total | | Upstream | | Downstream | | Total | |
| | | [Hg] | [MeHg] | [Hg] | [MeHg] | [Hg] | [MeHg] | [Hg] | [MeHg] | [Hg] | [MeHg] | [Hg] | [MeHg] |
| Northern Bohai Sea | *N* | 6 | 6 | 4 | 4 | 10 | 10 | 3 | 3 | 17 | 17 | 20 | 20 |
| | Mean | 0.75 | 0.69 | 0.053 | 0.046 | 0.47 | 0.44 | 0.12 | 0.050 | 0.77 | 0.66 | 0.67 | 0.56 |
| | SD | 1.4 | 1.4 | 0.024 | 0.018 | 1.2 | 1.2 | 0.037 | 0.027 | 1.2 | 1.1 | 1.2 | 1.0 |
| | Minimum | 0.032 | 0.030 | 0.031 | 0.030 | 0.031 | 0.030 | 0.069 | 0.021 | 0.032 | 0.012 | 0.032 | 0.012 |
| | Maximum | 4.0 | 3.7 | 0.079 | 0.066 | 4.0 | 3.7 | 0.15 | 0.065 | 3.8 | 3.3 | 3.8 | 3.3 |
| Northern Yellow Sea | *N* | *NA*[a] | *NA* | 3 | 3 | 3 | 3 | *NA* | *NA* | 3 | 3 | 3 | 3 |
| | Mean | *NA* | *NA* | 0.19 | 0.16 | 0.19 | 0.16 | *NA* | *NA* | 0.68 | 0.55 | 0.68 | 0.55 |
| | SD | *NA* | *NA* | 0.16 | 0.14 | 0.16 | 0.14 | *NA* | *NA* | 0.99 | 0.78 | 0.99 | 0.78 |
| | Minimum | *NA* | *NA* | 0.087 | 0.072 | 0.087 | 0.072 | *NA* | *NA* | 0.051 | 0.031 | 0.051 | 0.031 |
| | Maximum | *NA* | *NA* | 0.37 | 0.32 | 0.37 | 0.32 | *NA* | *NA* | 1.8 | 1.5 | 1.8 | 1.5 |
| Total | *N* | 6 | 6 | 7 | 7 | 13 | 13 | 3 | 3 | 20 | 20 | 23 | 23 |
| | Mean | 0.75 | 0.69 | 0.11 | 0.090 | 0.40 | 0.37 | 0.12 | 0.050 | 0.76 | 0.64 | 0.67 | 0.56 |
| | SD | 1.4 | 1.4 | 0.11 | 0.10 | 1.1 | 1.0 | 0.037 | 0.027 | 1.1 | 1.1 | 1.1 | 1.0 |
| | Minimum | 0.032 | 0.030 | 0.031 | 0.031 | 0.031 | 0.031 | 0.069 | 0.021 | 0.032 | 0.012 | 0.032 | 0.012 |
| | Maximum | 4.0 | 3.7 | 0.37 | 0.32 | 4.0 | 3.7 | 0.15 | 0.065 | 3.8 | 3.3 | 3.8 | 3.3 |

[a] Not available.

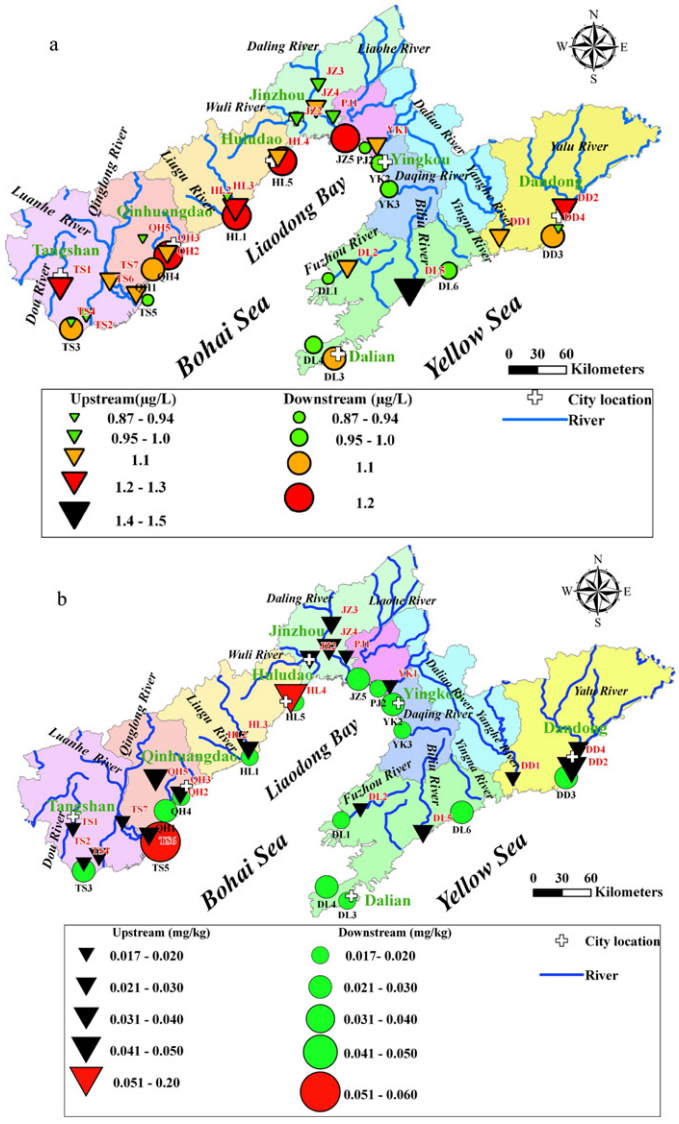


**Fig. 2.** Spatial distribution of [Hg] in surface waters (a) and sediments (b) of coastal watersheds of the CNBYS (legends were classified based on the guidelines in Table 5).

(Table 5), the observed [Hg] in downstream waters is sufficiently high to cause subtle and chronic adverse effects on coastal wildlife.

A large amount of coal is burned for domestic and industrial electricity in Northern China. Although no studies have linked Hg in water to direct atmospheric deposition, Hg originating from the combustion of coal was predicted to be a main source of Hg [15,23,45]. Both upstream and downstream waters near all cities except Yingkou and Jinzhou were contaminated with Hg. These results are consistent with increased atmospheric and/or wastewater discharges caused by recent industrialization and urbanization. However, some rivers, such as the Biliu, Liugu, Fuzhou and Luanhe, which are remote from large cities, also contained relatively high [Hg]. Because Hg can be transported via atmospheric circulation, these rivers are likely receiving atmospheric deposition of Hg in their watersheds [46].

### 3.2. Surface sediments

The [Hg] in sediments ranged from 0.017 to 0.18 mg/kg dw. The mean ± SD of [Hg] was 0.027 ± 0.028 mg/kg dw. The mean [Hg] was significantly higher in upstream sediments (0.031 mg/kg dw) than in downstream sediments (0.022 mg/kg dw) (Mann–Whitney

**Table 5**
Guidelines for Hg in water, sediment and biota.

| | [Hg]/[MeHg] | Reference |
|---|---|---|
| **Guidelines for mercury in water (μg/L)** | | |
| Chinese Hg standard for surface water, class V | 1 | [41] |
| Chinese sea water quality standard, class IV | 0.5 | [44] |
| Ecotoxicological Assessment Criteria | 0.005–0.05 | [71] |
| Criterion Maximum Concentration (acute effects) in saltwater | 1.8 | [72] |
| Criterion Continuous Concentration (chronic effects) in saltwater | 0.94 | [72] |
| Annual average value – Ecological Quality Status in surface water | 0.05 | [73] |
| Maximum allowable concentration – Ecological Quality Status in surface water | 0.07 | [73] |
| **Guidelines for mercury in sediment (mg/kg dw)** | | |
| Background concentrations | 0.05 | [48] |
| Sediment primary standard | 0.2 | [74] |
| Sediment quality guidelines (SQGs) | 1 | [49] |
| Threshold effect level (TEL) | 0.174 | [75] |
| Probable effect level (PEL) | 0.486 | [75] |
| Effect range low (ERL) | 0.15 | [75] |
| Effect range median (ERM) | 0.71 | [75] |
| **Guidelines for Hg in biota (mg/kg ww)** | | |
| Maximum limit permissible level of Hg for sea food | 0.5 | [76,77] |
| Maximum limit permissible level of Hg for fish | 0.3 | [61,78] |
| Maximum limit permissible level of MeHg for fish | 0.25 | [61,78] |
| Food and Drug Administration action level of Hg for commercial fish | 1 | [79] |
| Chronic mercury toxicity level of Hg for fish | 1–5 | [80] |
| Maximum limit permissible level of Hg for commercial fish | 0.2 | [81] |
| The Category I of Hg of Marine biological quality for crustacea | 0.05 | [60] |
| The Category II of Hg of Marine biological quality for crustacea | 0.1 | [60] |
| The Category III of Hg of Marine biological quality for crustacea | 0.3 | [60] |

*U* test, $p < 0.05$). In watersheds along the NBS, the mean [Hg] was significantly higher in upstream sediments (0.032 mg/kg dw) than in downstream sediments (0.023 mg/kg dw) ($p < 0.05$) (Table 3). In watersheds along the NYS, the mean [Hg] in upstream sediments was not different from that in downstream sediments ($p > 0.05$). However, there was no difference in the mean [Hg] in upstream/downstream sediments between the NBS and the NYS ($p > 0.05$) (Table 3). The highest [Hg] (0.18 mg/kg) in upstream sediments was observed at the Wuli River in Huludao (HL4) (Fig. 2b). However, this concentration was less than the value (8.7 mg/kg dw) published previously [14]. Because some industrial complexes were established along the Wuli River a long time ago, such as the Huludao Zinc Plant (the largest zinc smelting plant in Asia, established in 1935), and Jinzhou Chemical Refinery Plant (established in 1937), pyro-metallurgical treatment in the zinc smelting plant and chlor-alkali production in Huludao resulted in relatively large Hg emissions [10,19,43]. It was estimated that the total discharge of Hg into the Wuli River from 1952 to 1980 was 265 tons [45]. In addition, the [Hg] in the air at upstream areas of the Wuli River in 1991–1992 had reached 0.005 mg/m$^3$, which was 16.7 times higher than the Chinese maximum permissible limit of 0.0003 mg/m$^3$. The average [Hg] in the rain and dust from July to September 1991 were 2.14 mg/m$^2$ and 4.08 mg/kg dw, respectively [45]. It was determined that long-term deposition caused by these industries would be the most important determinant of [Hg] in upstream sediment of the Wuli River. The highest [Hg] in downstream sediments was found in the Luanhe River at Tangshan (Fig. 2b). The [Hg] in the sediments is likely indicative of the long-term effects of industrial activities within watersheds in Tangshan [47].

Only two of 35 sediments contained [Hg] that were higher than the background value of 0.05 mg/kg dw [48]. The [Hg] in upstream sediment of the Wuli River (HL4) exceeded the limits for potential adverse effects on benthic invertebrates such as the "Threshold Effect Level" (TEL) and the "Effect Range Low" (ERL) concentrations (Fig. 2 and Table 5). The [Hg] in other sediments were less than the threshold associated with adverse effects on invertebrates. According to the sediment quality guidelines (SQGs) established by the US EPA, the [Hg] observed in all sediments during this study would not classify them as "polluted", which is defined as [Hg] > 1 mg/kg dw [49]. Three percent of the sediments had [Hg] exceeding the limits associated with adverse effects on benthic invertebrates (Table 5).

Based on the spatial distribution of Hg in surface waters and sediments (Fig. 2), it was found that if an upstream site within a watershed had a high [Hg] in sediment, then the corresponding downstream site within the watershed would have a relatively high [Hg] in the water. This finding indicates that upstream sediment may be a source of Hg in the downstream water because of suspension and transportation of Hg by high flows of runoff and surface water. However, in general, the [Hg] in waters was not significantly correlated to the [Hg] in sediments ($p > 0.05$) (Table 6). The limited sample size, without considering the seasonal variations in Hg deposition and water and sediment chemistry, may account for the poor correlation [50].

### 3.3. Biota

The [Hg] and [MeHg] in carp and crabs are summarized in Table 4. The [Hg] in carp ranged from 0.031 to 4.0 mg/kg ww, with a mean ± SD of 0.40 ± 1.1 mg/kg ww. The [MeHg] in carp ranged from 0.031 to 3.7 mg/kg ww, with a mean ± SD of 0.37 ± 1.0 mg/kg ww. The mean [Hg] and [MeHg] in carp from upstream areas (0.75 and 0.69 mg/kg ww, respectively) were significantly higher than those from the downstream areas (0.11 and 0.090 mg/kg ww, respectively) (Mann–Whitney $U$ test, $p < 0.05$). The mean percentage of [MeHg] to [Hg] for all carp was 87 ± 6% with a range of 77–97%, indicating that organic Hg was the predominant form of Hg in the carp [51]. This pattern was also observed in previous studies worldwide [52,53]. The predominance of dietary exposure and ingestion of food resulted in a greater ratio of [MeHg] to [Hg] in carp [54,55]. Generally, the [Hg] and [MeHg] in 92% of carp (Figs. 3 and 4) were not only less than the maximum permissible concentration of 0.5 mg/kg ww allowed in edible parts of marine organisms traded internationally but also less than the maximum permissible [Hg] (0.3 mg/kg ww) and [MeHg] (0.25 mg/kg ww) regulated by the Ministry of Health of China (Table 5). Although Crucian carp is known to accumulate relatively small [Hg] in muscle, because this is one of the most consumed aquatic species in China, the greater ratio of [MeHg] to [Hg] could still pose potential risk to human health. In addition, predators that eat Crucian carp, such as the northern pike, largemouth bass, birds and mammals would be at high risk.

In watersheds along the NBS, upstream carp had a higher mean [Hg] and [MeHg] than downstream carp ($p < 0.05$). Unfortunately, we did not capture any carp or crab at upstream areas of these rivers. The mean [Hg] and [MeHg] in downstream carp captured along the NYS were higher than those collected along the NBS ($p < 0.05$) (Table 4). The highest [Hg] (4.0 mg/kg ww) and [MeHg] (3.7 mg/kg ww) in upstream carp were found in the Dou River at Tangshan (TS1), while the highest [Hg] (0.37 mg/kg ww) and [MeHg] (0.32 mg/kg ww) observed in downstream carp were at the coastal site in Dalian (DL3) (Figs. 3 and 4). The higher [Hg] in carp could be the result of dietary (organic detritus, filamentous algae, small benthic animals, and pieces and seeds of aquatic weeds) and habitat (bottom layer of the water column) exposure [54,55].

The [Hg] in crabs was in the range of 0.032–3.8 mg/kg ww (mean ± SD: 0.67 ± 1.1 mg/kg ww), while the [MeHg] was in the range of 0.012–3.3 mg/kg ww (mean ± SD: 0.56 ± 1.0 mg/kg ww). The mean [Hg] and [MeHg] were significantly higher in downstream crabs (0.76 and 0.64 mg/kg ww, respectively) than in upstream crabs (0.12 and 0.050 mg/kg ww, respectively) ($p < 0.05$). The mean percentage of [MeHg] to [Hg] for all crabs was 67 ± 5% with a range of 25–100%. The ratio of [MeHg] to [Hg] for crabs was significantly less than that for carp ($p < 0.05$). This difference was caused by differences between the bio-dynamics of Hg (II) and MeHg in each species [51,55–57]. The lower ratio of MeHg to Hg in crabs suggests decreased bioaccumulation of MeHg and less toxicity for higher trophic levels [58]. Factors, such as habitat type (shallow hard-bottom intertidal or sometimes subtidal habitats) or differences in prey availability, such as macroalgae, salt marsh grasses and small invertebrates between upstream and downstream areas, could explain the difference in the [Hg] and [MeHg] in crab samples [51,55–59].

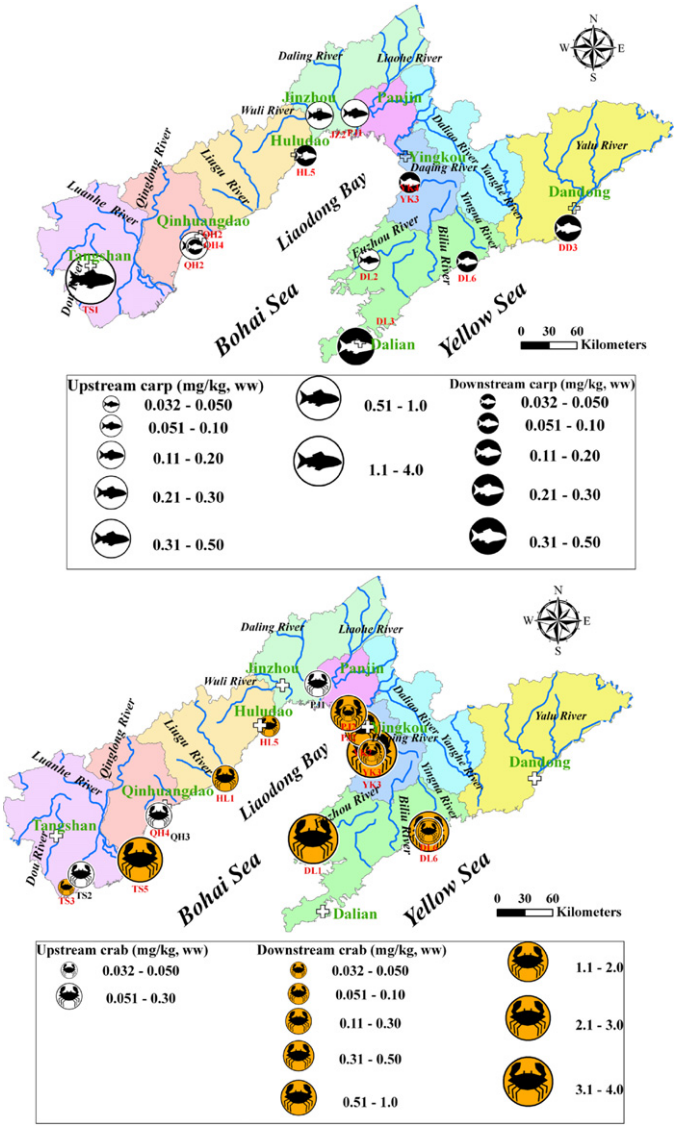


**Fig. 3.** Spatial distribution of [Hg] in biota samples in coastal watersheds of the CNBYS (legends were classified based on the guidelines in Table 5).

Based on the standards of marine biological quality suggested by the State Oceanic Administration of China, the environmental quality of marine areas can be categorized into the following three functional categories; Category I applies to marine fishing, aquaculture and natural reserve; Category II applies to water supply

**Table 6**
Correlation coefficients between [Hg] and [MeHg] in biota, surface water, and sediment.[a]

| | [Hg] in water | [Hg] in sediment | [Hg] in biota | [MeHg] in biota |
|---|---|---|---|---|
| [Hg] in water | 1 | −0.32 (23) | −0.28 (23) | −0.34 (23) |
| [Hg] in sediment | −0.19 (13) | 1 | 0.011 (23) | 0.021 (23) |
| [Hg] in biota | 0.039 (13) | 0.019 (13) | 1 | 0.96** (23) |
| [MeHg] in biota | −0.014 (13) | 0.011 (13) | 0.99** (13) | 1 |

[a] Spearman coefficients are shown above and below the diagonal line for and crab carp, respectively. The number of samples used is given in parentheses.
** Correlation is significant at the 0.01 level (2-tailed).

for general industry and scenic areas; and Category III applies to harbors and industrial areas (Table 5) [60]. Therefore, all upstream crabs and 82% of downstream crabs had a [Hg] that exceeded the Category I standard of 0.05 mg/kg. Furthermore, 33% of upstream crabs and 53% of downstream crabs exceeded the Category II standard of 0.1 mg/kg. None of the upstream crab but 41% of downstream crabs exceeded both the Category III standard of 0.3 mg/kg and the regulatory limit for human consumption of 0.5 mg/kg. Finally, 29% of downstream crabs contained [MeHg] that exceeded the standard for human consumption (0.5 mg/kg) [61]. Although some downstream crabs contained [Hg] and [MeHg] that were higher than limits for human consumption (0.5 mg/kg), crab is not highly consumed in China. Furthermore, the ratio of [MeHg] to [Hg] for crabs was low. Therefore, the risk to human health is likely small.

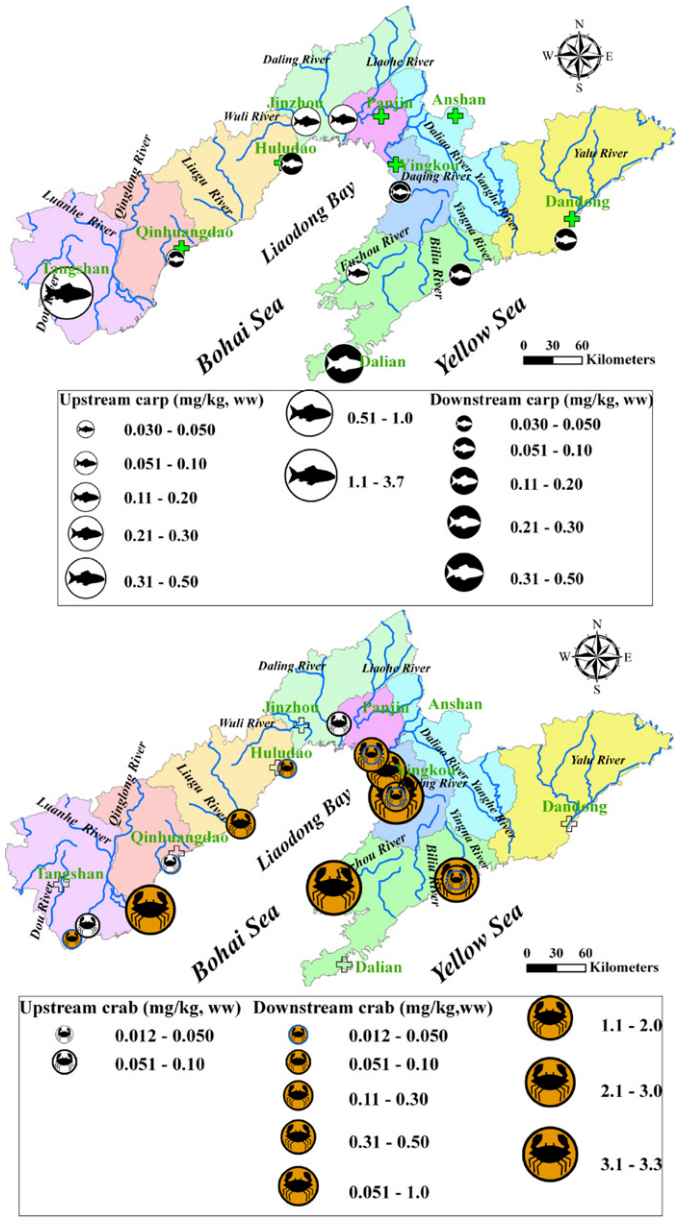


**Fig. 4.** Spatial distribution of [MeHg] in biota samples in coastal watersheds of the CNBYS (legends were classified based on the guidelines in Table 5).

In coastal watersheds along the NBS, downstream crabs had mean [Hg] and [MeHg] that were significantly higher than upstream crabs ($p < 0.05$). However, there was no statistically significant difference in the [Hg] or [MeHg] in downstream crabs between the NBS and the NYS ($p > 0.05$). Among the upstream crabs, the crab from upstream areas of the Qinglong River in Tangshan (TS2) contained the highest [Hg] (0.15 mg/kg ww) and [MeHg] (0.074 mg/kg ww). Among the downstream crabs, the crab from the downstream area of the Daliao River in Yinkou (YK3) contained the highest [Hg] (3.8 mg/kg ww) and [MeHg] (3.2 mg/kg ww) (Figs. 3 and 4). Thus, the crabs from the upstream area of the Qinglong River and the downstream area of the Daliao River pose the highest health risk to humans and predators.

The Spearman's correlation matrix showed that the [Hg] and [MeHg] in all carp and crabs were not significantly correlated with the [Hg] in waters or sediments (Table 6). These results were in agreement with those reported in previous studies [62–65]. Based on the spatial distribution of Hg and MeHg in waters, sediments and biota (Figs. 2–4), areas where a higher [Hg] was observed in waters and sediments were not correlated with the areas where the highest [Hg] and [MeHg] were observed in carp and crabs. While the processes responsible for the observed spatial variations in the [Hg] and [MeHg] are difficult to quantify and typically vary greatly with each watershed ecosystem [66,67], there are two possible explanations for the lack of correlation. First, Hg in carp and crabs is primarily bioaccumulated through diet, rather than directly taken up from the waters and sediments [68]. The [Hg] in waters and sediments is most likely unable to represent the bioavailable fraction of Hg for uptake. Differences in bioaccumulation of Hg could be due to species-specific biodynamics [55]. Second, at larger scales, the relationship of Hg in water, sediment and biota samples are complex due to the large number of watershed characteristics. For example, land use, vegetation cover, and soil type can have a strong influence on Hg speciation, partition, and biological availability, and particularly on MeHg production and exportation in these environments [69,70]. Furthermore, the bioaccumulation of Hg represents a complex interaction of biotic and abiotic variables (including trophic position, water chemistry and food chain length) [62,69] that were not accounted for in this study. To gain insight into the origin of Hg in aquatic biological populations, both environmental and biological factors should be taken into account in future studies. Long-term investigation is needed to understand the biogeochemistry of Hg in the environmental matrix of coastal watersheds as well as the bioavailability of Hg and its ecological risks.

## 4. Conclusions

An overview of Hg in different matrices within coastal watersheds along the CNBYS has been provided. The [Hg] was 0.87–1.5 μg/L in waters, 0.017–0.18 mg/kg dw in sediments, 0.031–4.0 mg/kg ww in carp and 0.032–3.8 mg/kg ww in crabs. The [MeHg] was 0.031–3.7 mg/kg ww in carp and 0.012–3.3 mg/kg ww in crabs. There was no difference in the [Hg] in waters in the upstream and downstream areas. Sixty-seven percent of upstream waters cannot be used for agriculture or recreation and could have adverse effects on wildlife, while 53% of downstream waters cannot be used for harbors or industry development and could cause some adverse effects on coastal wildlife. The upstream waters at the Dou, Liugu, Biliu and Yalu Rivers and the downstream waters at the Shi, Liugu, Wuli and Daling Rivers had relatively high [Hg]. The mean [Hg] in upstream sediments was remarkably high relative to downstream sediments, especially for the watersheds along the NBS. The highest [Hg] in sediments were found upstream of the Wuli River and downstream of the Luanhe River. However, only 3% of sediments had a [Hg] that could have adverse effects on aquatic ecosystems. The downstream carp captured along the NYS had a higher [Hg] and [MeHg] than those collected along the NBS. There was no significant difference in the [Hg] and [MeHg] in downstream crabs between the NBS and the NYS. Forty-one percent of the downstream crabs had a [Hg] exceeding the regulatory limit for human consumption (0.5 mg/kg ww), but only 29% of them had a [MeHg] above this limit. Ninety-two percent of carp had a [Hg] and [MeHg] less than the standards set by China and other countries. The potential hazard of carp and crabs with high [Hg] and [MeHg] should be of concern due to human and predator consumption. The release of Hg into the atmosphere, runoff, and surface water discharges caused by industrialization and urbanization were the most likely sources of Hg in coastal watersheds and risks to the aquatic food security in the CNBYS.

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