

The speciation and bioavailability of mercury in sediments of Haihe River, China

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Received 3 June 2004; accepted 24 August 2004

Available online 3 October 2004

Abstract

Twenty-one sediment samples in 11 sites along the Haihe River and Dagu Drainage River, Tianjin, China, were analyzed to investigate the pollution status and bioavailability of mercury (Hg). The results showed that the Haihe River was slightly polluted with Hg when flowing through Tianjin city. On the contrary, the sediments collected from Dagu Drainage River, an important drainage river in Tianjin, were found to have very high Hg concentrations and the highest concentration reached 8779.1 ng g⁻¹ (dry weight). The methylmercury (MeHg) concentrations accounted for 0.1–2.4% (average: 0.9%) of total mercury (HgT) and were strongly influenced by HgT ($r=0.91$, $p=0.99$, $n=20$) and total organic carbon (TOC; $r=0.76$, $p=0.99$, $n=20$) contents in sediments. Moreover, a five-step sequential selective extraction (SSE) procedure was used to study the bioavailability of Hg in sediments. The mercury in sediments existed mainly as element Hg and mercury sulfide, which accounted for 46.5% and 39.0% of HgT, respectively. The percentage of exchangeable Hg (defined as water soluble Hg plus ‘human stomach acid’ soluble Hg) was only 0.1–4.6%. The distribution of exchangeable Hg showed an obvious difference to that of HgT, indicating that the HgT concentrations were absolutely insufficient to evaluate the risk of Hg in sediments.

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Keywords: Speciation; Sequential extraction; Methylmercury; Mercury; Sediment

1. Introduction

In aquatic system, sediment is an important sink and source of mercury (Hg) and is also considered as the main production site of methylmercury (MeHg). Now, the concentration of total mercury (HgT) is not by far the most important because various chemical species of mercury behave distinctly, thereby affecting its biogeochemical behavior and toxicity to organisms (Cai et al., 1997). As the most toxic mercury species, MeHg is neurotoxic and can cause blockage of binding sites of enzymes, interfere protein synthesis and impede thymidine incorporation into DNA

(Thayer, 1984). Furthermore, MeHg could be accumulated in the animal and human food chain more easily than the inorganic forms; thus, it was given particular concern all the time.

On the other hand, the toxicity and bioavailability of mercury in sediment also depend on its interaction with the native matrix. As we know, Hg has an extremely high affinity for organic matter and S-containing ligands (Wall-schläger et al., 1996; Hintelmann et al., 1995). These complexes are often stable and thus this fraction of Hg has lower mobility and toxicity. On the other side, the water-soluble Hg has higher risk because it can easily enter the aquatic system and accumulate in organism. Moreover, changes in environmental conditions, such as acidification or redox potential, can cause Hg mobilization from the solid to the liquid phase and favour the contamination of

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surrounding waters. Therefore, it is indispensable to identify the main binding sites and phase associations of Hg when assessing its risk in sediment.

Tianjin city, with a population of 9.16 million, is an important industrial base in China. The total amounts of industrial and domestic effluents discharged in 1999 were 4.42×10^9 and 3.57×10^9 m³, respectively (Zhang, 2002). Haihe River is a central river flowing through the Tianjin city and gathering many other streams before entering Bohai Sea at last. It was polluted by the inpouring of industrial, domestic and agricultural effluents in recent years, which exerted a great disadvantageous effect to the ecosystem in it (Qin et al., 1998; Zhen et al., 1999). It was reported that the concentrations of biochemical oxygen demand (BOD; Liu et al., 2001), chemical oxygen demand (COD; Liu et al., 2001) and dissolved oxygen (DO; Zhao et al., 1996) were very high. Mercury as a very toxic element is still widely used in manufacture of chlorine, pesticides, fungicides and production of electrical goods, paper, batteries and so on. As many kinds of these factories have been built in Tianjin city, the discharge of industrial effluents might be a potential pollution source of Hg to Haihe River.

The aim of this work was to investigate the pollution status and bioavailability of Hg in Haihe River sediments. The HgT was determined by cold vapor atomic fluorescence spectrometry (CVAFS) and the MeHg in sediment was analyzed by HPLC-AFS. A five-step sequential selective extraction (SSE) method was used for studying the mobility and bioavailability of Hg in sediments. The distributions of HgT, MeHg and different fractions of Hg were investigated. Moreover, the relationships among

HgT, MeHg and total organic carbon (TOC) were also studied.

2. Materials and methods

2.1. Instrumentation

AF-610A atomic fluorescence spectrometer (Beijing Raleigh Analytical Instrument, China) was used for total mercury determination. The laboratory-established HPLC (P680 HPLC Pump, DIONEX, USA) and AFS (AF-610A, Beijing Raleigh Analytical Instrument) hyphenation system was as described previously (Liang et al., 2003a,b). A ZORBAX ODS column (4.6×150 mm, 5 μm, Agilent Technologies, USA) was utilized to separate MeHg in samples. Total organic carbon concentrations were determined using Apollo 9000 TOC analyzer (Tekmar-Dohrmann, USA). The stainless steel grab used for sampling was purchased from Wildlife Supply (Michigan, USA).

2.2. Reagents and standards

Stock solutions of standard mercury chloride (HgCl₂, Merck) and methylmercury chloride (CH₃HgCl, Merck; 1 mg mL⁻¹ as Hg) were prepared by dissolving appropriate amounts of which in 5% (v/v) HNO₃ and methanol, respectively. The mercury working solutions were obtained by dilution with 10% (v/v) HNO₃ or methanol and prepared daily before use. All solutions were stored at 4 °C.

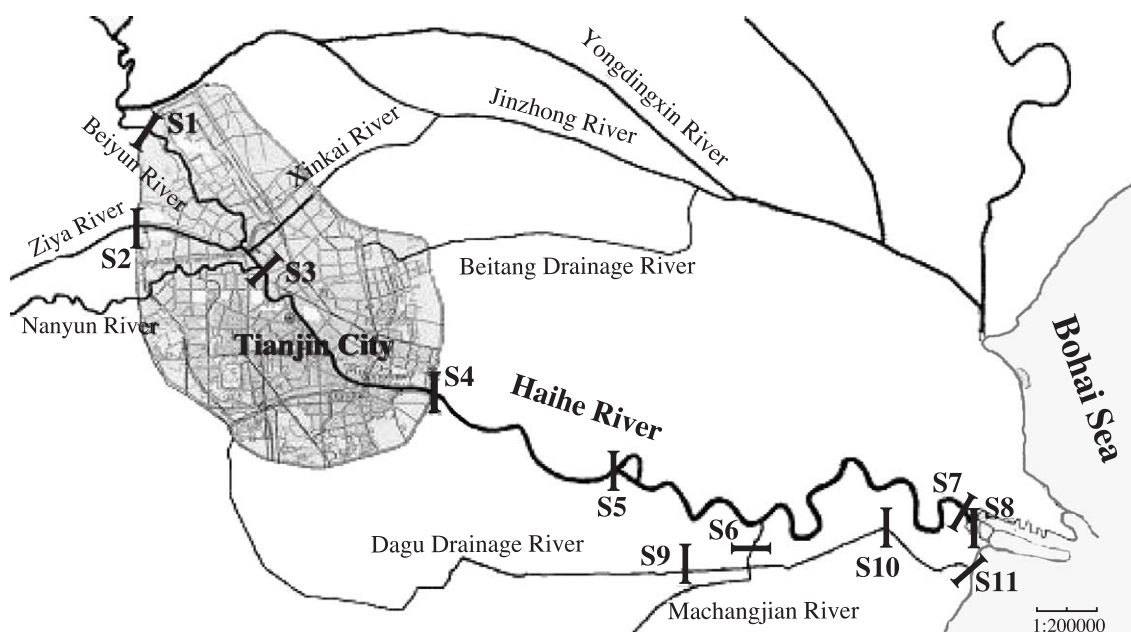


Fig. 1. The map of the study area.

The HPLC mobile phase was prepared by pipetting 10 mL CH₃CN, 25 µL 2-Mercaptoethanol (Merck) and 10 mL 3 mol L⁻¹ NH₄Ac solutions to Milli-Q water to 500 mL, then filtered through a 0.45-µm membrane filter before use.

Bromine monochloride (BrCl) should be prepared in a fume hood. Twenty-seven grams of KBr crystals were added to a 2.5-L bottle of low Hg concentrated HCl. Using a clean magnetic stir bar, the contents were stirred 1 h. Then, 38 g of KBrO₃ were added slowly to the acid mixture while stirring. When all of the KBrO₃ is added, the solution should change from yellow to red to orange. The bottle was loosely capped, and the solution was stirred for another hour before tightening the lid.

KBH₄ solutions (0.2%, m/v) were prepared before use by dissolving the required amount in 0.2% (m/v) KOH solution. An oxidant solution of 1% (m/v) K₂S₂O₈ solution was prepared in 10% (v/v) HCl. The mixture solution containing 0.1 mol L⁻¹ CH₃COOH and 0.01 mol L⁻¹ HCl was obtained by diluting 6 mL of glacial acetic acid and 0.8 mL of concentrated HCl to 1 L with Milli-Q water. KOH solution (1 mol L⁻¹) and HNO₃ solution (12 mol L⁻¹) were also used in this work.

2.3. Sample collection

A total of 21 sediment samples in 11 sites along the Haihe River and Dagu Drainage River was collected on July 12–13 and Sept. 6–7, 2003, respectively. The map of study area and the locations of sampling sites are shown in Fig. 1. S1 and S2 locate in two headstreams of Haihe River (Beiyun River and Ziya River) and upriver to Tianjin city. They were chosen to judge if the river has been polluted before flowing through Tianjin city. Xinkai River and Nanyun River are two streamlets outflowing from Haihe River and no sediments were sampled. S3, which lies in urban district, is an important intersection point of branches with Haihe River. However, the sediment was not obtained from there on July 12–13. S4 is the locus where Haihe River flows out to Tianjin city. S5 and S7 are two brakes in Haihe River and they control the flux of water in Haihe River. The water of Machangjian River inpour into Haihe River and S6 was selected there. As a contrast, three sites (S9, S10 and S11) in Dagu Drainage River were also sampled because this river is an important drainage river in Tianjin city and very near to Haihe River.

All the sediments were collected with a stainless steel grab from the surface sediment (0–5 cm), then placed into polytetrafluoroethylene (PTFE) bags, frozen at -20 °C immediately after the collection. Because vacuum drying was often suggested for drying of some certified reference materials (CRMs; such as DORM-2 and TORT-2) and freeze drying has been used in preparation of CRM IAEA-142 (Horvat et al., 1997), the sediments collected from Haihe River and Dagu Drainage River were freeze dried,

ground and passed through a 40-mesh sieve, then thoroughly homogenized and kept in a silica gel desiccator until analyzing.

2.4. Procedures

For total mercury (HgT) analysis, 0.25 g of sediment was weighed in a 25-mL graduated tube and 5 mL Milli-Q water and 5 mL aqua regia were added. The mixture in the tube was then heated 2 h with a water bath at 95 °C and shaken frequently. After cooling, the content was diluted to 25 mL with Milli-Q water. The HgT can be determined by CVAFS directly when the solution was limpid.

Table 1
Scheme for the sequence extraction of mercury in sediment

| Step | Extraction method | Fraction of Hg |
|------|--|-------------------------------------|
| 1 | Two grams of sediments were weighed into a 50-mL glass centrifuge tube and 20 mL of Milli-Q water was added. The tube was vibrated for 18 h at room temperature, and then centrifuged. An exactly known volume of the extraction (8 mL) was filtered and transferred into a 10-mL tube. One milliliter of concentrated HNO ₃ and 0.1 mL of BrCl were added. The volume was then made up to 10 mL by adding in Milli-Q water. The residue was washed with 20 mL water by shaking for 15 min, centrifuged, and the rinse was discarded. | Water soluble (Hg-w) |
| 2 | The residue was extracted with 20 mL of 0.1 mol L ⁻¹ CH ₃ COOH+0.01 mol L ⁻¹ HCl solution and then rinsed with another 20 mL solution. The detailed operation conditions were the same as those of step 1. | 'Human stomach acid' soluble (Hg-h) |
| 3 | The residue was extracted with 20 mL of 1 mol L ⁻¹ KOH solution and then rinsed with another 20 mL solution. The detailed operation conditions were the same as those of step 1. Because the solution has high acid neutralizing capacity, more concentrated HNO ₃ (1.5 mL) should be added. | Organo-chelated (Hg-o) |
| 4 | The residue was extracted with 20 mL of 12 mol L ⁻¹ HNO ₃ solution and then rinsed with another 20 mL solution. The detailed operation conditions were the same as those of step 1. When determining the total Hg in this fraction, a series of mercury standard solutions in 12 mol L ⁻¹ HNO ₃ were used. | Elemental Hg (Hg-e) |
| 5 | The residue was air dried at room temperature, and the total Hg was digested with aqua regia and determined by CVAFS. The procedure was the same as those of determination of total Hg in sediment. | Mercuric sulfide (Hg-s) |

The determination of methylmercury in sediments was based on acid extraction (Wilken and Hintelmann, 1991; Hintelmann et al., 1997) and HPLC-CVAFS technique published previously (Liang et al., 2003a) with the following modifications. Ten grams of sediment were weighed into a 250-mL flask and 50 mL of 6 mol L⁻¹ HCl solution was added. The flask was mechanically shaken overnight, and then 25 mL CH₂Cl₂ was added and shaken for another 2 h to extract organic mercury into the CH₂Cl₂ phase. After centrifugation, the CH₂Cl₂ phase was transferred into a 25-mL graduated tube and concentrated to 4 mL with a gentle stream of pure nitrogen. Then, the solution was extracted with 1 mL 0.01 mol L⁻¹ sodium thiosulfate. Shaking 45 min was needed to hasten the extraction speed. After setting for a few minutes for phase separation, the water phase was removed by micropipette and transferred into a clean 1-mL screw cap glass vial. The MeHg was determined by HPLC-CVAFS at optimized conditions.

The sequential extraction procedure was based on Bloom's five-step sequential extraction scheme (Bloom et al., 2003), which is summarized in Table 1. The total Hg in each fraction was determined by CVAFS after oxidation with BrCl, since BrCl has been found to be an excellent oxidant and preservative for total Hg in water samples (Bloom and Crecelius, 1983) and adopted in EPA method 1631.

3. Results and discussion

3.1. Evaluation of the methods

For HgT determination, the method was verified by analysis of two certified reference materials (sediment GBW07310 for HgT, 280±40 ng g⁻¹ and soil GBW08302 for HgT, 18 ng g⁻¹). Our results for HgT were 275±11 ng g⁻¹ (n=5) in GBW07310 and 22±4 ng g⁻¹ (n=5) in GBW08302, respectively. The HPLC-CVAFS system was validated with certified reference material DORM-2 (Dogfish muscle) and the result was in good agreement with the certified values (Liang et al., 2003a). Due to lack of sediment certified reference materials (CRMs) for MeHg in our laboratory, 10 and 100 µL of 1 µg mL⁻¹ MeHg standard solutions were respectively added into sediments of S5 and S11 collected on July 12–13. The spiked recoveries of MeHg were between 80% and 96%. For sequential selective extraction, sediment certified reference material GBW07310 was also determined and the recovery of Hg ($\sum\text{Hg}/\text{HgT}$) was 89%. The contents and percentages of Hg in each fraction were shown in Tables 2 and 3, respectively. For other samples, the ratios of $\sum\text{Hg}$ to HgT ranged from 76% to 117% (Table 2), which indicated that the method was reliable and repeatable.

Table 2
The Hg contents in each fraction of sediments (ng g⁻¹, dry weight)

| Sampling sites | Hg-w | Hg-h | Hg-o | Hg-e | Hg-s | $\sum\text{Hg}$ | $\sum\text{Hg}/\text{HgT}$ (%) |
|-------------------|------|-----------------|-------|--------|--------|-----------------|-----------------------------------|
| GBW07310 | 1.6 | 0.8 | 66.6 | 60.6 | 120.6 | 250.1 | 89 |
| <i>July 12–13</i> | | | | | | | |
| S1 | 0.8 | 0.5 | 22.9 | 37.8 | 54.2 | 116.2 | 102 |
| S2 | 0.3 | ND ^a | 10.1 | 31.7 | 19.1 | 61.1 | 101 |
| S4 | 2.4 | 0.6 | 29.3 | 67.6 | 76.5 | 176.4 | 101 |
| S5 | 0.8 | 0.6 | 11.2 | 63.1 | 50.6 | 126.3 | 89 |
| S6 | 0.8 | ND | 4.8 | 40.6 | 43.5 | 89.7 | 80 |
| S7 | 0.7 | ND | 14.6 | 53.9 | 34.8 | 104.0 | 104 |
| S8 | 0.6 | ND | 16.4 | 122.1 | 49.7 | 188.7 | 89 |
| S9 | 1.1 | 8.3 | 287.5 | 1425.7 | 552.7 | 2275.3 | 100 |
| S10 | 2.1 | 6.4 | 288.9 | 723.0 | 412.5 | 1432.9 | 82 |
| S11 | 1.2 | 2.5 | 59.2 | 422.3 | 308.6 | 793.8 | 79 |
| <i>Sept. 6–7</i> | | | | | | | |
| S1 | 1.2 | 1.3 | 13.0 | 21.7 | 32.4 | 69.6 | 117 |
| S2 | 0.3 | 1.8 | 14.1 | 19.1 | 29.5 | 64.9 | 117 |
| S3 | 0.1 | 1.5 | 33.0 | 431.8 | 1357.3 | 1823.6 | 84 |
| S4 | 0.6 | 0.1 | 27.8 | 48.1 | 57.9 | 134.5 | 103 |
| S5 | 1.3 | 1.7 | 17.0 | 58.2 | 54.6 | 132.8 | 103 |
| S6 | ND | 5.0 | 12.1 | 27.4 | 63.5 | 108.1 | 79 |
| S7 | 1.0 | 0.7 | 8.3 | 73.2 | 56.9 | 140.0 | 97 |
| S8 | 0.7 | 0.6 | 35.6 | 98.7 | 61.6 | 197.1 | 81 |
| S9 | 4.4 | 0.8 | 644.0 | 4370.2 | 1621.5 | 6640.9 | 76 |
| S10 | 2.0 | 4.6 | 467.0 | 1679.4 | 732.6 | 2885.6 | 85 |
| S11 | 1.2 | 0.1 | 60.2 | 272.7 | 116.5 | 450.6 | 77 |

^a Not detectable.

Table 3
Percentages of Hg in each fraction of sediments (%)

| Sampling sites | Hg-w | Hg-h | Hg-o | Hg-e | Hg-s |
|-------------------|------|-----------------|------|------|------|
| GBW07310 | 0.6 | 0.3 | 26.6 | 24.2 | 48.2 |
| <i>July 12–13</i> | | | | | |
| S1 | 0.7 | 0.4 | 19.7 | 32.5 | 46.6 |
| S2 | 0.5 | ND ^a | 16.5 | 51.9 | 31.3 |
| S4 | 1.4 | 0.3 | 16.6 | 38.3 | 43.4 |
| S5 | 0.6 | 0.5 | 8.9 | 50.0 | 40.1 |
| S6 | 0.9 | ND | 5.4 | 45.3 | 48.5 |
| S7 | 0.7 | ND | 14.0 | 51.8 | 33.5 |
| S8 | 0.3 | ND | 8.7 | 64.7 | 26.3 |
| S9 | ND | 0.4 | 12.6 | 62.7 | 24.3 |
| S10 | 0.1 | 0.4 | 20.2 | 50.5 | 28.8 |
| S11 | 0.2 | 0.3 | 7.5 | 53.2 | 38.9 |
| <i>Sept. 6–7</i> | | | | | |
| S1 | 1.7 | 1.9 | 18.7 | 31.2 | 46.6 |
| S2 | 0.5 | 2.8 | 21.7 | 29.4 | 45.5 |
| S3 | ND | 0.1 | 1.8 | 23.7 | 74.4 |
| S4 | 0.4 | 0.1 | 20.7 | 35.8 | 43.0 |
| S5 | 1.0 | 1.3 | 12.8 | 43.8 | 41.1 |
| S6 | ND | 4.6 | 11.2 | 25.3 | 58.7 |
| S7 | 0.7 | 0.5 | 5.9 | 52.3 | 40.6 |
| S8 | 0.4 | 0.3 | 18.1 | 50.1 | 31.3 |
| S9 | 0.1 | ND | 9.7 | 65.8 | 24.4 |
| S10 | 0.1 | 0.2 | 16.2 | 58.2 | 25.4 |
| S11 | 0.3 | ND | 13.4 | 60.5 | 25.9 |

^a Not detectable.

3.2. Total mercury and methylmercury in sediments

The concentrations of HgT and MeHg in Haihe River and Dagu Drainage River sediments are presented in Table 4. Although the lowest HgT content in sediment was 55.4 ng g⁻¹ (dry weight), the average value reached 1036.5 ng g⁻¹ (dry weight). This was mainly because the sediments collected from four sites (S3, S9, S10 and S11) had unusually high HgT contents and the maximum value was 8779.1 ng g⁻¹ (dry weight). The distribution of HgT in Haihe River and Dagu Drainage River sediments is depicted in Fig. 2. Craig (1986) reported concentration ranges of 0.2 to 0.4 µg g⁻¹ total Hg for uncontaminated sediments, whereas sediments in urban, industrial or mineralized areas can contain up to 100 µg g⁻¹ total Hg. Fujii (1976) reported background levels of 0.05 µg g⁻¹ in river sediments, 0.1 to 0.3 µg g⁻¹ in lake sediments and 0.05 to 0.08 µg g⁻¹ in sea sediments. Therefore, the HgT contents in sediments collected from S1 and S2 (between 55.4 and 113.7 ng g⁻¹, dry weight) were only a little higher than the background values reported and within the ranges for uncontaminated sediments; thus, these two sites could be considered as uncontaminated. From S4 to S8, the HgT contents in sediments were slightly higher than those in sediments of S1 and S2, which ranged from 99.9 to 242.0 ng g⁻¹ (dry weight). In contrast to these, unexpected high mercury concentration (2172.6 ng g⁻¹ dry weight) was found in sediment collected from S3, which is located in urban district. Therefore, we can conclude that the Haihe

River was not polluted before entering into Tianjin city (S1 and S2). At the location of S3, the river was polluted seriously with Hg. We speculated that there were unknown pollution sources of Hg near to S3, which still need to be confirmed by further study in the future. However, the downstream areas (from S4 to S8) of S3 were just slightly polluted, probably because of the dilution of river water. Moreover, apart from these sites located in suburban areas of Tianjin city and a few factories built there, there were no other pollution sources of Hg in these areas (including S6). On the contrary, the sediments collected from Dagu Drainage River (S9–S11), an important drainage river in Tianjin city, were found to have very high Hg concentrations and the highest concentration reached 8779.1 ng g⁻¹ (dry weight). Hence, Dagu Drainage River has been polluted seriously with Hg, which also meant that the amount of Hg discharged from Tianjin industrial effluents was enormous. Because these effluents were poured into Bohai Sea directly, the Hg levels in fish and mollusk samples collected from this area of Bohai Sea are always high (Tan et al., 1982; Zhang and Chen, 1984; Liang et al., 2003b).

The MeHg contents in sediments account for normally 1% to 1.5% of HgT except for some lakes and wetlands where the percentage of MeHg can reach 10% (Gilmour et al., 1992; Ullrich et al., 2001). In Haihe River and Dagu Drainage River sediments, the MeHg concentrations ranged from 0.7 to 21.7 ng g⁻¹ (dry weight) and the average value was 2.9 ng g⁻¹ (dry weight). The percentages of MeHg in HgT were between 0.1% and 2.4% and the average was

Table 4
Concentrations of HgT, MeHg and TOC in Haihe River and Dagu Drainage River sediments (dry weight)

| Sampling sites | HgT (ng g ⁻¹) | MeHg (ng g ⁻¹) | MeHg/HgT (%) | TOC (mg g ⁻¹) |
|-------------------|---------------------------|----------------------------|--------------|---------------------------|
| <i>July 12–13</i> | | | | |
| S1 | 113.7 | 1.0 | 0.9 | 8.20 |
| S2 | 60.8 | 1.4 | 2.2 | 9.08 |
| S4 | 174.4 | 0.7 | 0.4 | 12.40 |
| S5 | 142.5 | 0.7 | 0.5 | 15.65 |
| S6 | 111.7 | 1.1 | 1.0 | 10.54 |
| S7 | 99.9 | 1.0 | 1.0 | 6.41 |
| S8 | 211.2 | 1.7 | 0.8 | 4.15 |
| S9 | 2279.5 | 1.2 | 0.1 | 58.63 |
| S10 | 1750.1 | 3.9 | 0.2 | 33.00 |
| S11 | 1001.0 | 21.7 | 2.2 | 5.47 |
| <i>Sept. 6–7</i> | | | | |
| S1 | 59.4 | 1.5 | 2.4 | 5.44 |
| S2 | 55.4 | 1.4 | 2.4 | 6.52 |
| S3 | 2172.6 | 3.4 | 0.2 | 22.40 |
| S4 | 131.2 | 0.8 | 0.6 | 7.30 |
| S5 | 128.5 | 1.4 | 1.1 | 33.16 |
| S6 | 137.6 | 0.9 | 0.7 | 8.54 |
| S7 | 144.4 | 0.9 | 0.6 | 4.18 |
| S8 | 242.0 | 1.3 | 0.5 | 4.66 |
| S9 | 8779.1 | 7.7 | 0.1 | 80.20 |
| S10 | 3389.6 | 5.2 | 0.2 | 45.66 |
| S11 | 582.4 | 2.3 | 0.4 | 4.58 |

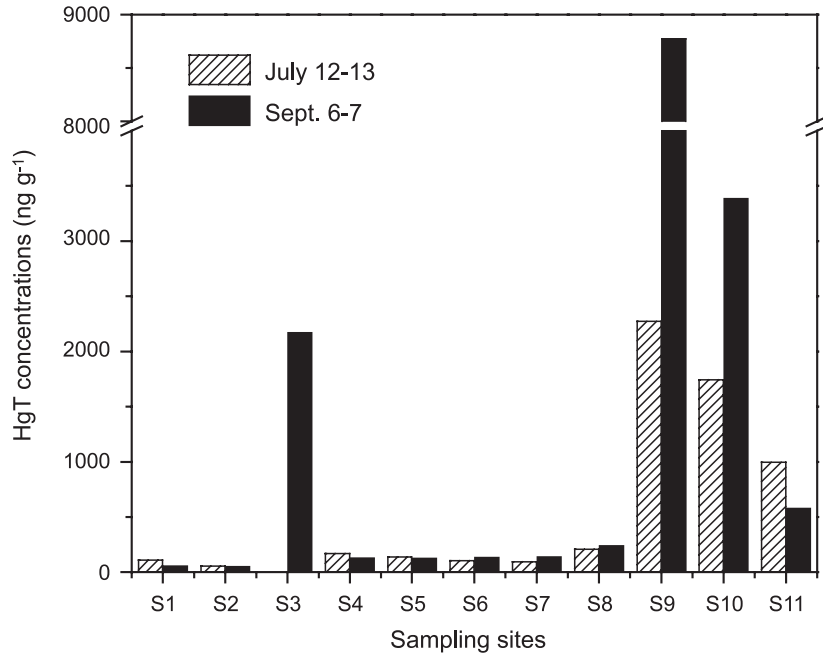


Fig. 2. The distribution of total Hg in Haihe River and Dagu Drainage River sediments.

0.9%. The distribution of MeHg in sediments is shown in Fig. 3. The concentration of MeHg (21.7 ng g⁻¹, dry weight) in sediment of S11 collected on July 12–13 was much higher than that in other sediments, although its percentage was only 2.2%. Except for this abnormally high MeHg concentration, the distribution of MeHg in Haihe River and Dagu Drainage River sediments was similar to that of HgT. The relationship between MeHg and HgT was then studied and MeHg showed a significant correlation

($r=0.91$, $p=0.99$, $n=20$; Fig. 4) with HgT when MeHg in sediment of S11 was excluded. This suggested that MeHg contents were partly controlled by the HgT in sediments.

Organic carbon plays an important role in the bioavailability and methylation of inorganic mercury, although its role has not been well understood (Andersson et al., 1990). Ullrich et al. (2001) argued that, on the one hand, organic carbon can enhance methylation by stimulating the activity of heterotrophic microorganisms, or through direct abiotic

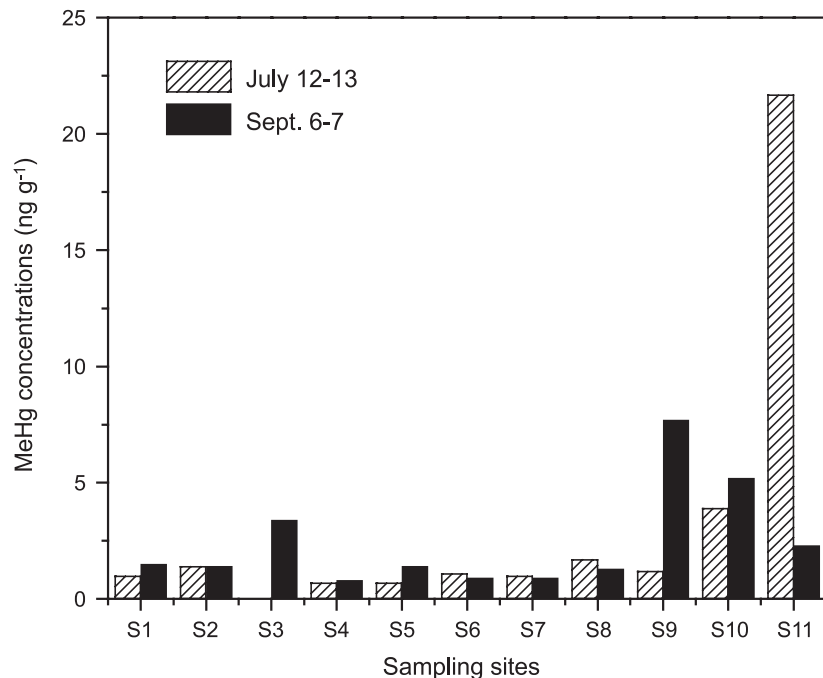


Fig. 3. The distribution of MeHg in Haihe River and Dagu Drainage River sediments.

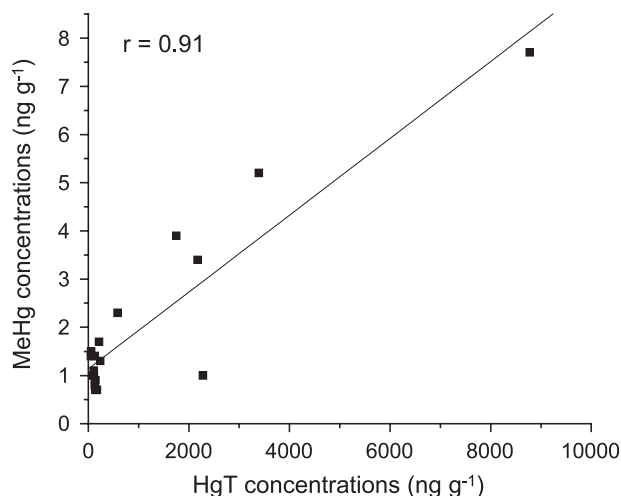


Fig. 4. The relationship between HgT and MeHg concentrations.

methylation of Hg by humic or fulvic substances. On the other hand, Hg methylation may be inhibited at high DOC concentrations due to increased complexation of Hg with organic ligands, reducing Hg bioavailability to bacteria, particularly in the neutral pH range. The TOC concentrations in Haihe River and Dagu Drainage River sediments were also investigated. The contents of TOC in sediments varied from 4.15 to 80.20 mg g⁻¹ (average: 18.39 mg g⁻¹). The HgT concentrations ($r=0.87$, $p=0.99$, $n=21$; Fig. 5a) and MeHg concentrations ($r=0.76$, $p=0.99$, $n=20$; Fig. 5b) were significantly correlated with TOC contents except the very high MeHg content, which indicates that the concentrations of HgT and MeHg in sediments of Haihe River and Dagu Drainage River were partly influenced by TOC contents in them. This result was in agreement with other studies (Conaway et al., 2003; Furutani and Rudd, 1980; Olson and Cooper, 1976).

3.3. The mobility and bioavailability of Hg in sediments

Sequential selective extractions (SSEs) method has been used widely for understanding element distribution in the solid phase. However, the traditional sequential extraction procedures are commonly used to study relatively “typical” transition metals (such as Cu, Ni, Co and Zn) and are not appropriate for mercury study (Wallschläger et al., 1998). Although some mercury-specific methods have been developed (Wallschläger et al., 1998; Revis et al., 1989a,b), the results on ambient samples are often contradictory. Recently, Bloom et al. (2003) developed and validated a new solid phase analytical scheme based upon selective extractions. Instead of species-specific information, this method provides differentiation of Hg compounds into behavioral classes. Hence, some traditional extractants used in SSEs, such as CH₃COOH, NH₂OH · HCl and H₂O₂, etc., were not adopted. In this new procedure, water, 0.1 mol L⁻¹ CH₃COOH+0.01 mol L⁻¹ HCl solution, 1 mol L⁻¹ KOH, 12 mol L⁻¹ HNO₃ and aqua regia were sequentially used to

extract Hg in sediment and the extracted Hg were defined as water soluble Hg (Hg-w), ‘human stomach acid’ soluble Hg (Hg-h), organo-chelated Hg (Hg-o), elemental Hg (Hg-e) and mercuric sulfide (Hg-s), respectively.

The above mentioned sequential extraction method was applied to analyze the Hg species in Haihe River and Dagu Drainage River sediments. Tables 2 and 3 give the concentrations and percentages of Hg in each fraction. Although these data are limited to describe the exactly binding states of Hg in sediments, they can provide some useful information about the mobility and bioavailability of Hg in sediments. As shown in Fig. 6, the Hg in Haihe River and Dagu Drainage River sediments exists mainly as Hg-e and Hg-s, which account for 46.5% and 39.0% of HgT, respectively. These two fractions of Hg have very low mobility and therefore can be thought of as unavailable species. Hg-o, accounting for 13.3% of HgT, has the moderate mobility. On the contrary, Hg-w and Hg-h account for only 0.6% and 0.9% of HgT in sediments. However, they have the highest risk since they can easily enter the aquatic system and accumulate in organism. Therefore, Hg-

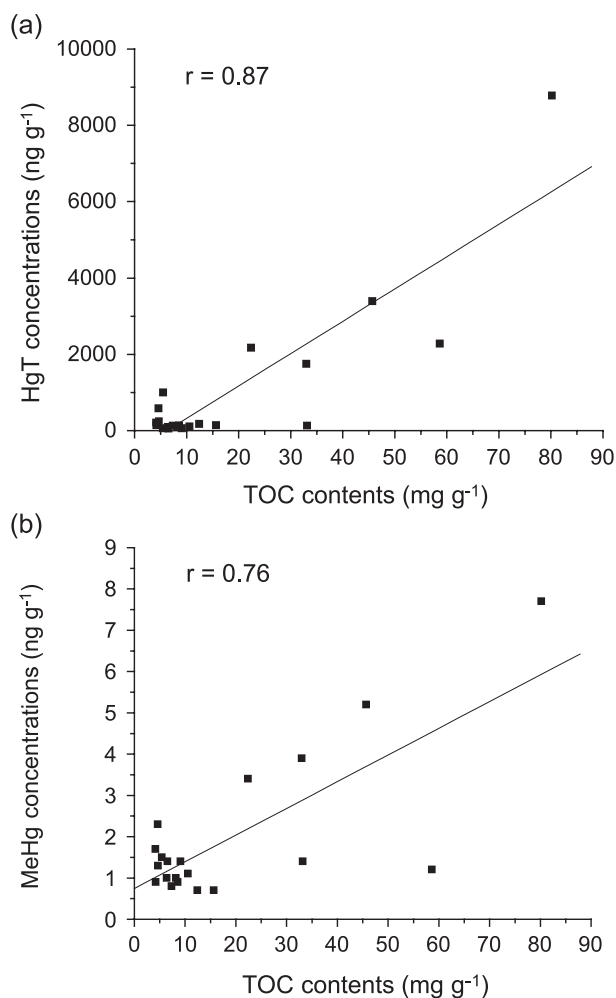


Fig. 5. The relationships between (a) TOC and HgT, and between (b) TOC and MeHg.

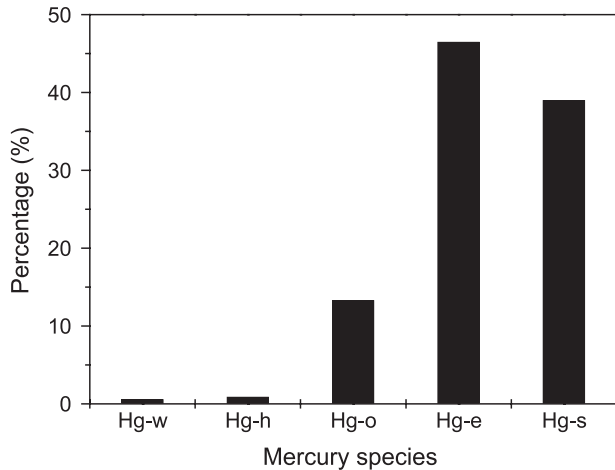


Fig. 6. The average percentages of Hg in each fraction.

w plus Hg-h was defined as exchangeable Hg in our work. The exchangeable Hg concentrations in Haihe River and Dagu Drainage River sediments ranged from 0.3 to 9.4 ng g⁻¹ (average: 2.9 ng g⁻¹, dry weight), accounting for 0.1–4.6% (average: 1.1%) of HgT in sediments. The distribution of exchangeable Hg in sediments was also studied (Fig. 7) and showed an obvious difference to that of HgT (Fig. 2). In sites 9, 10 and 11, the exchangeable Hg contents in sediments collected on July 12–13 were much higher than that in sediments collected on Sept. 6–7, which was opposite to the distribution of HgT in them. Furthermore, the exchangeable Hg in sediment of S6 collected on Sept. 6–7 reached 5.0 ng g⁻¹ (dry weight), although the total Hg for which was only 137.6 ng g⁻¹ (dry weight). Thus, the percentage of exchangeable Hg in this sediment was the maximum. All of these results confirmed that the total Hg concentrations were absolutely insufficient and it is indis-

pensable to identify the main binding sites and phase associations of Hg when assessing its risk in sediment.

4. Conclusions

The pollution status and bioavailability of mercury in Haihe River and Dagu Drainage River sediments were studied. Although the Haihe River was just slightly polluted with Hg after flowing through Tianjin city, the HgT concentrations in Dagu Drainage River sediments were extraordinarily high, indicating that the amount of Hg discharged from Tianjin industrial effluents was still enormous. MeHg contents in sediments showed similar trend with HgT and were partly influenced by HgT and TOC contents. The sequential selective extraction method has proved to be a powerful technique to provide much useful information about the mobility and bioavailability of Hg in sediments. Although the exchangeable Hg accounted a low percent of HgT, it ran the highest risk because it could easily enter into the aquatic system and accumulate in organism. Furthermore, the exchangeable Hg has a different variation with that of HgT contents in sediments, indicating that it is indispensable to identify the main binding sites and phase associations of Hg when assessing its risk in sediments.

Acknowledgements

This work was jointly supported by the National Basic Research Program of China (2003CB415001) and the National Natural Science Foundation of China (20137010 and 20205008).

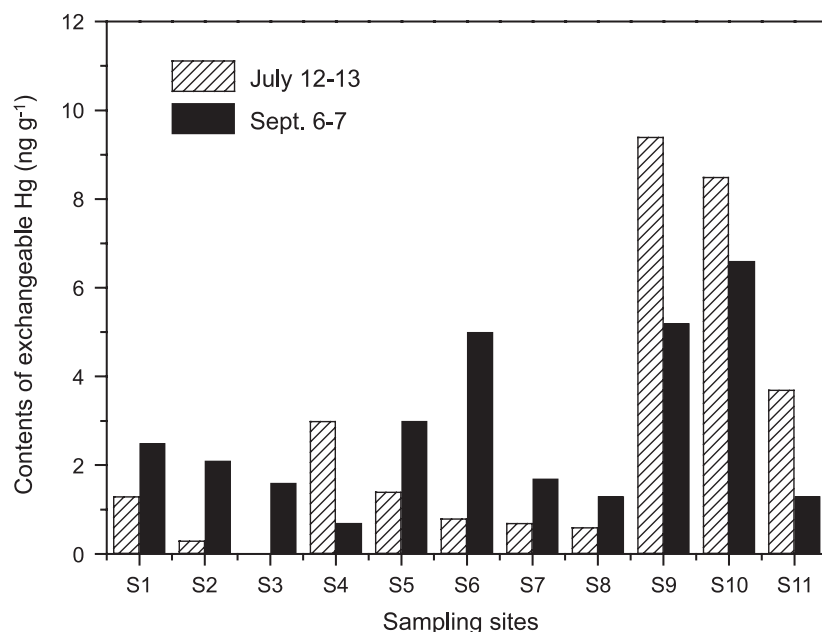


Fig. 7. The distribution of exchangeable Hg in Haihe River and Dagu Drainage River sediments.

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