Bull. Environ. Contam. Toxicol. (2005) 74:980–987

DOI: 10.1007/s00128-005-0676-1

Bulletin of Environmental Contamination and Toxicology

Methylmercury and Total Mercury in Sediments Collected from the East China Sea

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Received: 12 May 2004/Accepted: 16 February 2005

The extensive application of mercury compounds in agriculture and industry has resulted in serious mercury contaminations in the past years. Now mercury has become one of the global pollutants because higher concentrations have been detected in the deep ocean, the atmosphere, Antarctica and the Arctic (Fergusson 1990). As the most toxic and the most familiar organomercury compound in the environment, methylmercury (MeHg) has often been given particular concern. In aquatic system, sediment is an important sink and source of mercury. Mercury can be bound to organic carbon-containing particles and accumulated in sediment and it can also be released annually from sediments to surrounding media on the other hand (Stein et al. 1996). In addition, sediment, in which inorganic mercury can be converted to organic mercury by biomethylation or abiotic methylation, has also been considered as the main MeHg production site. Therefore, investigation of concentrations and species of mercury in sediments helps us to understand its transformation and distribution in the environment.

The East China Sea is the end-point of two famous rivers in China, Changjiang River and Qiantang River (Fig. 1). Along the coast there are many developed cities including Shanghai and Ningbo and a number of factories have also been set up there. The inpouring of Changjiang River, Qiantang River and the wastewater produced by factories has caused serious pollution in the East China Sea. As a result, several serious harmful algal blooms occurred in this area during 1990s (Ye and Huang 2003). Quantities of fish and shellfish died, which resulted in very large economic losses. On the other hand, Zhoushan Archipelago, a large fishery near to Hangzhou Bay, is one of main sources of fishes provided to markets all over the China. These situations urge the investigation of the mercury pollution in this area because mercury is easily accumulated in fish and affect human health ultimately. However, mercury contamination in this place was few studied and is still not very clear. The aim of this work is to investigate the concentrations and species of Hg in sediments of the East China Sea. The vertical and planar distributions of HgT and MeHg were both studied. The effects of some factors on the methylation of inorganic mercury in the East China Sea sediments were also investigated.

MATERIALS AND METHODS

Twenty-four sediment samples from eight sites in the East China Sea were collected

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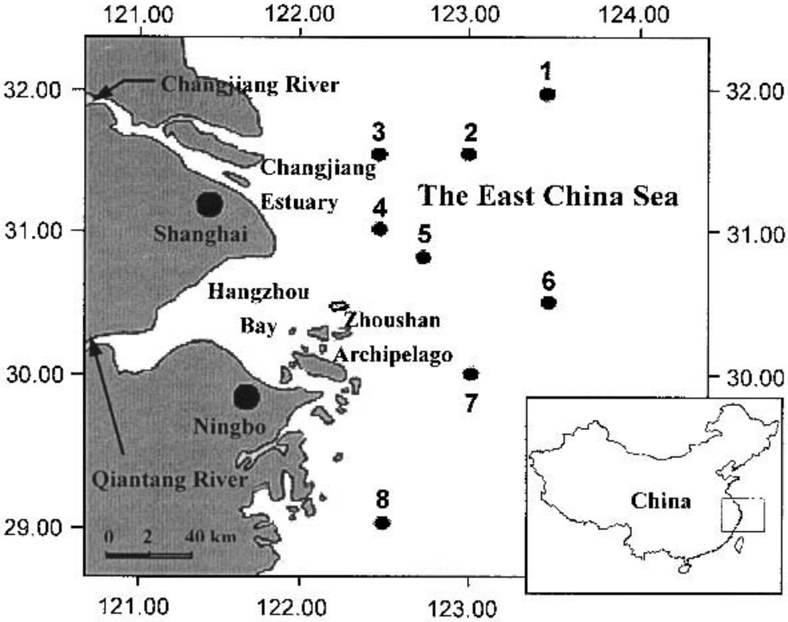

Figure 1. Map of study area.

Table 1. The geographic positions and depths of water in the sampling sites.

Sample site	Geographic position	Depth of water (m)
1	31° 59.893 ′ N; 123° 30.195 ′ E	39.8
2	31° 30.092 ′ N; 123° 00.272 ′ E	36.5
3	31° 30.061 ′ N; 122° 30.679 ′ E	28.5
4	31° 00.460 ′ N; 122° 29.870 ′ E	16.5
5	30° 41.866 ′ N; 122° 43.798 ′ E	65.8
6	30° 30.603 ′ N; 123° 29.623 ′ E	58.3
7	30° 00.220 ′ N; 123° 00.507 ′ E	51.0
8	29° 00.098 ′ N; 122° 30.665 ′ E	50.1

in November 4-15, 2002 and the map of study area is shown in Fig. 1. The geographic positions and depths of water in the sampling sites are shown in table 1. The site 1 is located in far north of the Changjiang Estuary, where is hardly affected by the water of the Changjiang river. The result of this site can act as background in this work. Sites 2 and 3 stand the same longitude as the Changjiang Estuary and are possibly polluted. In contrast to them, sites 4 and 5 have the most risk to be polluted because they are located in the junction of the Changjiang Estuary and Hangzhou Bay. Site 6 lies in line with sites 4 and 5, but far distance to them. Site 7 was selected in Zhoushan Archipelago. Site 8 is near to Ningbo city, and many other cities are also located there.

A research vessel, Science No. 1, was utilized during the voyage. The sediment cores were collected using a self-gravity sampling implement consisting of a 60cm plastic sampling tube. Upon retrieving the core in deck, different depth of sediments were subsampled with a plastic spatula. Due to little sediments were collected from sites 1 and 2, only top sediments (0-1cm) were sampled. All the sediments were placed into polytetrafluoroethylene (PTFE) bags, then frozen at –20℃ immediately after the collection. Before analyzing, the sediments were freezing dried, ground and passed through a 40-mesh sieve, then thoroughly homogenized and kept in a silicagel desiccator.

For total mercury (HgT) analysis, 0.25g of sediments were weighed and added 5mL of Milli-Q water and 5mL of aqua regia in a 25mL graduated tube. The mixture in the tube was then heated for 2hrs in a water bath at 95℃ and shaken frequently. After cooling, the contents were diluted to 25mL with Milli-Q water. When the solution was limpid, the HgT was then determined with a model AF-610A atomic fluorescence spectrometer (AFS, Beijing Raleigh Analytical Instrument Co., China). The method detection limit (3σ) obtained for sediments was approximately 0.5ng g^{-1}. In order to validate the method, the HgT in certified reference material (CRM) GBW07310 (sediment) was analyzed. The mean value and the deviation of five parallel determinations were shown in table 2.

The determination of methylmercury (MeHg) in sediments was based on acid extraction and HPLC-CVAFS detection with the following modifications. Five grams of sediment were weighed into a 50 mL centrifuge tube and 25mL of 6mol L^{-1} HCl solution was added. The tube was shaken overnight, and then 15mL of CH_2Cl_2 was added into the tube and shaking for another 2 hrs to extract organic mercury into the CH_2Cl_2 phase. After centrifuging at 2000rpm for 10min, the CH_2Cl_2 phase was transferred and concentrated on a rotary evaporator to about 1mL. Then the CH_2Cl_2 solution was transferred into a 10mL glass tube, diluting to 4mL with CH_2Cl_2 solution. At last, the solution was extracted with 1mL 0.01mol l^{-1} of sodium thiosulfate. Shaking 45 min was needed to hasten the extraction speed. Setting for a few minutes for phase separation, the water phase was removed by micropipette and transferred into a clean 1ml screw cap glass vial. The laboratory-established HPLC-CVAFS hyphenation system, including a P680 HPLC pump (DIONEX, USA), a homemade microwave digestion device and a model AF-610A AFS (Beijing Raleigh Analytical Instrument Co., China), has been described previously (Liang et al. 2003). The method detection limit obtained for MeHg in sediments was approximately 0.2ng g^{-1} as Hg. The HPLC-CVAFS system was validated with CRM DORM-2 (Dogfish muscle) and the result was in good agreement with the certified values (table 2). Due to lack of sediment certified reference materials for MeHg in our laboratory, 10μL of 2μg mL^{-1} MeHg standard solutions were added into two sediments collected from site 5 (surface and 20cm) and the recoveries of MeHg were between 90%-112%.

For Fe and Mn analysis, 0.1g of sediment was directly weighed into a PTFE digestion container. 2mL of HNO_3, 2mL of H_2O_2 and 0.5mL of HF were added in sequence. The container was sealed and placed in stainless steel bomb with a

Table 2. Analytical results of total mercury, manganese, iron and methylmercury contents in certified reference materials*.

Element	GBW07310 (sediment)		DORM-2 (Dogfish muscle)	
	Certified	Determined	Certified	Determined
HgT (ng g^{-1})	280 ± 40	275 ± 11		
Mn (μg g^{-1})	1013 ± 44	945 ± 9		
Fe (%)	0.19	0.19 ± 0.01		
MeHg (ng g^{-1})			4470 ± 320	4237 ± 143

*Mean ± s, n = 5

screwclosure to avoid any acid leakage and placed in an oven. The oven was heated and the temperature was kept at 180℃ for 8 hrs. After cooling to room temperature, the solution was completely transferred into a 100mL volumetric flask and diluted with Milli-Q water. Then Fe and Mn in solutions were determined by Agilent 7500i inductively coupled plasma-mass spectrometry (ICP-MS, Agilent Technologies Co. Ltd. USA) at recommendatory conditions. For accuracy, the Fe and Mn concentrations in CRM GBW07310 (sediment) were determined and the results are also shown in table 2.

RESULTS AND DISCUSSION

The concentrations of HgT, MeHg and the ratios of MeHg to HgT are shown in table 3. HgT concentrations in sediments ranged from <0.5 to 79.8ng g^{-1} (dry weight) and the average value was 37.0ng g^{-1}. The highest MeHg concentration was 5.5ng Hg g^{-1} (dry weight) and the average value was 2.7ng Hg g^{-1}. As shown in table 4, the concentrations of HgT are similar with those in South Florida Estuaries and Malaysian coast, and lower than those in other estuaries. On the other hand, the MeHg concentrations are similar with those in Scheldt Estuary and Seine Estuary (France), but higher than those in other locations. The background level of HgT in sea sediments was reported between 50ng g^{-1} and 80ng g^{-1} (Fujii 1976) and MeHg concentrations were typically lower than 10ng g^{-1} for estuarine sediments (Mikac et al. 1999). Therefore, we concluded that the sediments from the East China Sea were not contaminated with mercury. However, higher percentages of MeHg (average: 8.8%) were found in this work because 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). The exactly reason for this high percentage was not clear because the methylation and demethylation of Hg in sediment could be affected by lots of factors including total Hg level, organic matter content, oxygen, temperature, pH, salinity, chloride, sulphate and sulphide (Ullrich et al. 2001). The relationship between HgT and MeHg was also investigated. HgT was not correlated (r = 0.41, n = 20) with MeHg, suggesting that factors other than HgT loading control the MeHg contents in sediments of the East China Sea. Therefore, the HgT concentration was not always a good predictor of MeHg level in aquatic system (Craig and Moreton 1983; Kannan et al. 1998a).

Table 3. Concentrations of total and methyl mercury, total organic carbon, iron and manganese in sediments (dry weight).

Site	Depth	HgT (ng g^{-1})	MeHg (ng Hg g^{-1})	MeHg / HgT (%)	TOC (mg g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})
1	0-1cm	4.2	<0.2		3.03	2.11	0.37
2	0-1 cm	<0.5	<0.2		1.42	1.75	0.57
3	0-1 cm	3.7	<0.2		3.76	1.98	0.50
	15 cm	<0.5	<0.2		3.17	2.00	0.38
	30 cm	23.7	2.0	8.4	5.84	2.16	0.39
4	0-1 cm	62.3	5.5	8.8	6.98	3.03	0.68
	10 cm	51.0	3.3	6.5	6.14	2.77	0.68
	20 cm	42.9	3.1	7.2	6.50	2.59	0.59
	30 cm	53.3	2.2	4.1	5.58	2.67	0.61
	40 cm	50.0	3.0	6.0	5.52	2.52	0.53
5	0 -1cm	27.5	2.2	8.0	9.26	2.96	0.56
	10 cm	44.4	1.9	4.3	9.29	2.55	0.52
	20 cm	25.0	1.9	7.6	8.31	2.76	0.48
	30 cm	66.7	2.2	3.3	8.44	2.75	0.49
6	0-1 cm	8.0	1.7	21.3	2.39	1.71	0.35
	15 cm	14.0	1.3	9.3	2.96	1.56	0.31
7	0-1 cm	12.3	1.4	11.4	6.55	1.83	0.38
	15 cm	6.1	1.6	26.2	6.34	2.09	0.38
8	0-1 cm	47.0	2.5	5.3	9.24	3.25	0.63
	10 cm	79.8	1.8	2.3	8.60	2.94	0.53
	20 cm	39.7	3.0	7.6	7.90	2.78	0.47
	30 cm	58.9	2.2	3.7	6.77	2.85	0.44
	40 cm	33.4	5.2	15.6	7.36	2.59	0.45
	50 cm	59.8	5.1	8.5	6.75	2.85	0.48

Table 4. Concentrations of total mercury and methylmercury in sediments from different estuaries and coasts.

Location	Total mercury (ng g^{-1})	Methylmercury (ng g^{-1})	Reference
South Florida Estuaries	20 (1-219)	0.078 (<0.001-0.49)	Kannan et al. 1998a
Malaysian coast	61 (20-127)	0.04 (0.01-0.05)	Kannan et al. 1998b
Polish coast	164 (37-880)	0.64 (0.04-2.0)	Kannan et al. 1998b
San Francisco Bay	200 (20-700)	0.4 (0.1-1)	Conaway et al. 2003
Anadyr Estuary, Russia	339 (77-2100)	0.24 (0.06-0.62)	Kannan et al. 1998b
Scheldt Estuary	(144-1890)	(0.8-6)	Baeyens et al. 1998
Seine Estuary, France	460 (300-1000)	2.3 (0.1-6)	Mikac et al. 1999

Because the concentrations of Hg in estuaries are directly related to the sources of contamination, mercury behavior often differs from one estuary to another (Horvat et al. 1999). As mentioned above, two famous rivers, Changjiang River and Qiantang River, enter into the East China Sea. As the largest one in China and the third largest in the world, the Changjiang River carries a total of ca. 470×10^6 tones of fine sediments to the East China Sea annually. Guo et al. (2000) has reported that the geochemical characters of surface sediments in the East China Sea have a very close correspondence to those of Changjiang River sediments. Therefore, Changjiang River might be the main source of mercury to the East China Sea. The planar distribution of HgT and MeHg contents in surface sediments were depicted in Fig. 2. The HgT was not detectable in site 2 and the MeHg was not detectable in sites 1, 2 and 3 too. The possible reason might be that these three sites are located in the north of the Changjiang Estuary and far from it thus are hardly influenced by it. In contrast to this, site 4, being located in the junction of Changjiang Estuary and Hangzhou Bay, had the highest HgT and MeHg. This was caused by the flow direction of water from Changjiang Estuary and Hangzhou Bay, which influenced the ultimate deposition of the pollutants. The HgT and MeHg contents in sediments of site 8 just took the second place because this site lies very close to the coast and many cities are located there. In addition, from HgT and MeHg contents in sites 4 to 7, a distinct conclusion can be made that the pollution status alleviated with the distance to the Changjiang Estuary thus sediment of site 6 had lower mercury contents than others. Although little reported, from above results we can speculate that the drainage of water from Changjiang Estuary and the effluents from those seaside cities are the main sources of mercury in the East China Sea.

Sediments cores were also collected in six sites except sites 1 and 2. The deepest sediment was collected from site 8 at 50cm. Xia et al. (1999) reported the sedimentation rate in the East China Sea was 2.5-3.0 cm/a. This showed the samples collected were all sedimentated during the past 20 years. The concentrations HgT and MeHg in sediments from different depth are shown in table 3. There was no significant relationship between the concentrations of HgT and depth, indicating that the changes of HgT concentrations in past 20 years were little. For MeHg, the concentrations in surface sediments were higher than those in deeper ones except site 7 and the highest MeHg concentration was found in surface sediment from site 4 (5.5ng g^{-1}). This is probably because temperatures and anoxic conditions are most conductive to methylation in the upper sediment zone and the methylation rates are greatest in the surface sediments (Stein et al. 1996). However, MeHg concentrations were unexpected increased in sediments from 30 cm and 40 cm from sites 4 and 8.

Organic carbon plays an important role in the bioavailability and methylation of inorganic mercury although its role has not been well understood. Ullrich et al. (2001) argued that, on the one hand, organic carbon could enhance methylation by stimulating the activity of heterotrophic microorganisms, or through direct abiotic 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 bacterias, particularly in the neutral pH range. Total organic carbon (TOC) concentrations in sediments were determined (table 3), which ranged from 1.42 mg g^{-1} to 9.29 mg g^{-1} and the average value was 6.17 mg g^{-1}. The TOC contents showed a significant correlation (r = 0.57,

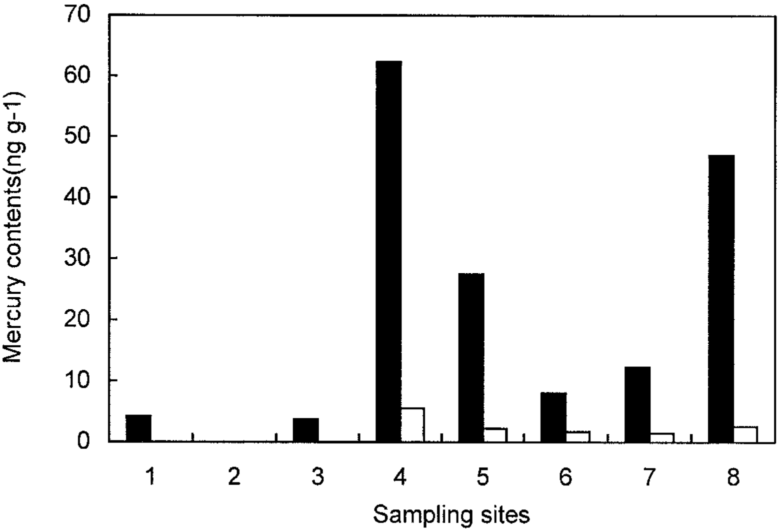

Figure 2. Distribution of HgT and MeHg in surface sediments.
(■) Total mercury, (□) Methylmercury

p = 0.99; n = 22) with HgT contents but not correlated (r = 0.13; n = 20) with MeHg contents. This indicates that TOC contents partially control the level of HgT in sediments of the East China Sea but don't affect the distribution of MeHg contents.

The redox cycling of Fe and Mn oxides can also influence the MeHg in sediments by partly controlling the dissolved mercury concentrations in sediment porewaters (Gagnon et al. 1997). In the oxidized surface layers of marine sediments, Hg was found to be primarily associated with fresh particulate organic matter and Fe and/or Mn oxyhydroxides, which limited dissolved Hg concentrations. Gobeil and Cossa (1993) have also found that dissolved Hg and Fe concentrations increased below 2cm from the sediment/water interface. The concentrations of Fe and Mn in sediments were investigated (shown in table 3). The mean content of Fe was 2.46 mg g^{-1} (between 1.56 and 3.25 mg g^{-1}) and the mean concentration of Mn was 0.49 mg g^{-1} (from 0.31 to 0.68 mg g^{-1}). The study of correlations indicated that Fe concentrations were significant correlated (r = 0.78, p= 0.99; n = 22) with HgT contents and weak correlated (r = 0.47, p = 0.95; n = 20) with MeHg contents. Similarly, the Mn concentrations in sediments were also correlated (r = 0.63, p= 0.99; n = 22) with HgT contents and weak correlated (r = 0.45, p = 0.95; n = 20) with MeHg contents. The above results just illustrated that Fe and Mn played equal role in the methylation of mercury in the sediments. And this might be explained that Fe and Mn usually formed Fe/Mn oxide and affected the available Hg and Eh in the sediment thereby influenced the methylation of mercury.

Acknowledgments. This work was jointly supported by the National Natural Science Foundation of China (20137010, 20205008) and the Chinese Academy of Science (KZCX2-414).

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