

# **Spatial and temporal variations of mercury in sediments from Victoria Harbour, Hong Kong**

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Mercury (Hg) is listed as a priority pollutant by many international agencies because of its persistence, bioaccumulation, and toxicity (PBT) in the environment. With the development of agriculture and industry, Hg has been extensively used in the manufacture of pesticides, fungicides, electrical goods, paper, batteries and other items, which has caused large amounts of Hg to be emitted to the environment.

The ocean is an important sink in the global Hg cycling. In recent years, the biogeochemistry of Hg in coastal and estuarial environments has received particular attention (Mason et al., 1996; Horvat et al., 1999; Hines et al., 2000; Conaway et al., 2003). Mercury enters the marine environment through various pathways, including wastewater discharges and atmospheric deposition. Two important processes are involved in the cycling of Hg in coastal and ocean environments. The first is the methylation of inorganic Hg to organomercury in water and sediment systems. This

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will affect the toxicity and bioavailability of Hg. The second is the bioaccumulation of Hg in aquatic organisms through the food chain. This will result in higher methylmercury (MeHg) concentrations in seafood, and may ultimately threaten human health.

Hong Kong is located on the southern coast of China and is made up of Hong Kong Island, the Kowloon Peninsula, the New Territories, and surrounding islands. The population of Hong Kong, about half of whom live on Hong Kong Island and in the Kowloon Peninsula, exceeded 6.9 million in 2005 (HK CSD, 2006). Hong Kong is also one of the busiest port-cities in the world. In the past few decades until recently, it had a thriving manufacturing industry. Because of the uncontrolled disposal of domestic and industrial wastewater, especially from the 1960s to the 1980s, the coastal waters of Hong Kong have become seriously contaminated (Morton, 1989; Wong and Tanner, 1997; Blackmore, 1998).

Victoria Harbour is a major port of Hong Kong and lies between the highly urbanized and industrial areas of Hong Kong Island and the Kowloon Peninsula. The length and area of the harbour are 12 km and about 5000 ha, respectively (Morton, 1989). In the past, the wastewater from both sides was discharged directly into the harbour after simple screening (HK EPD, 2004). According to the government of Hong Kong, the harbour received an estimated 1.5 Mt of sewage and industrial wastewater per day in 1995 (Hong Kong Government, 1995). In 1997, about 340 t of total biochemical oxygen demand (BOD), 280 t of total suspended solids, and 3 t of toxic metals were discharged into the harbour every day (Yung et al., 1999). As a

result, the harbour is heavily contaminated with bacteria (Yung et al., 1999), heavy metals (Tanner et al., 2000), and organic pollutants (Connell et al., 1998). Although some efforts at controlling the pollution have been made and the water quality has improved in recent years, high concentrations of Hg (8  $\mu\text{g/g}$ ) were still found in sediment from Victoria Harbour in 2004 (HK EPD, 2004). In addition, the distribution, especially the historical changes and species, of Hg in Victoria Harbour has thus far received little research attention.

The aim of this work was to study the spatial distribution and historical changes of Hg in sediments from Victoria Harbour. The concentration of MeHg in selected sediment samples was also be investigated.

A map of the study area and the locations of the sampling sites are shown in Fig. 1. Five sampling sites from east (B1) to west (B5) of Victoria Harbour were selected to provide good coverage of the harbour area and avoid regions with known sediment disturbances (e.g., dredged areas and environments adjacent to intensive reclamation activities). The geographic positions and depths of water in the sampling sites are shown in Table 1. The grab sediment samples were collected every two months from August 2004 to October 2005 with a Van Veen Grab Sampler. A single set of sediment cores were collected in October 2004 using a Kajak gravity corer. The corer was driven into the sediment by gravity and the sediment core was retained in a 70 mm PVC tube. Each core was sliced into thin sections at 2 cm intervals using a plastic cutter. All samples were stored in polyethylene bags and frozen at  $-20^{\circ}\text{C}$  immediately

after collection. Before being analyzed, the sediments were freeze-dried at  $-45^{\circ}\text{C}$  for 3 days and then ground in an agate grinder until fine particles were obtained.

For total Hg (THg) analysis,  $\sim 0.25$  g of sediment was digested with 5 mL of aqua regia in a water bath at  $95^{\circ}\text{C}$  for 2 h and shaken frequently. After cooling, the solution was diluted to 25 mL with Milli-Q water and centrifuged at 3000 rpm for 15 min. The THg was determined by cold vapor atomic fluorescence spectrometry (CVAFS, AF-620, Beijing Raleigh Analytical Instrument, China) using  $\text{KBH}_4$  for the reduction step. The detection limit ( $3\sigma$ ) obtained for THg was 0.5 ng/g. The method was validated by analyzing the certified reference materials (CRMs). The results of the analysis are shown in Table 2.

For the MeHg analysis,  $\sim 4$  g sediment was weighed into a 40-mL glass centrifuge tube. About 5 mL Milli-Q water and 4 mL of acidic  $\text{KBr-CuSO}_4$  solution (3:1) were added. The tube was mechanically shaken overnight. Then, 6 mL of  $\text{CH}_2\text{Cl}_2$  was added and shaken for another 1h to extract organomercury compounds into the  $\text{CH}_2\text{Cl}_2$  phase. After centrifuging at 3000 rpm for 15 min, the  $\text{CH}_2\text{Cl}_2$  phase (4 mL) was transferred into a 10 mL glass tube and extracted with  $\text{Na}_2\text{S}_2\text{O}_3$  solution (0.01M, 1 mL). The solution was shaken for 45 min in order to hasten the extraction speed. After setting for a few minutes for phase separation, the aqueous phase was pipetted into a clean 1-mL vial. The MeHg was determined by a laboratory-established HPLC (P680 HPLC Pump, DIONEX, USA) and AFS (AF-610A, Beijing Raleigh Analytical Instrument, China) hyphenation system, which has been described previously (Liang et al., 2003). An Xterra MS  $\text{C}_{18}$  column

(3.9×150 mm, 5 µm, Waters Corporation, USA) was used to separate MeHg in solutions. The detection limit for MeHg was 0.1 ng Hg/g. The method was validated with NIST 2796 and the result was in good agreement with the certified value (see Table 2). Due to the lack of sediment CRMs for MeHg in our laboratory, two sediment samples were spiked with 10 ng of MeHg standard, and the recoveries of MeHg were between 85-110%.

The  $^{210}\text{Pb}$  radiometric technique was used to estimate the chronology of the sediment cores. The  $^{210}\text{Pb}$  activities of the samples were determined by measuring the alpha-radioactivity of its granddaughter nuclide  $^{210}\text{Po}$ . The  $^{210}\text{Po}$  was extracted, purified, and self-plated onto a silver disc at 70-80°C in 0.5 M HCl, and  $^{209}\text{Po}$  was used as the yield monitor and tracer in quantification. The alpha-activity was counted by computerized multi-channel alpha spectrometry with gold-silicon surface barrier detectors. The supported  $^{210}\text{Pb}$  was determined by the alpha activity of the supporting parent,  $^{226}\text{Ra}$ , via the co-precipitation of  $\text{BaSO}_4$ .

The THg concentrations in surface sediments of Victoria Harbour ranged from 0.047 to 0.855 µg/g (dry wt.) with an average concentration of 0.247 µg/g (Fig. 2). B1 is located at the junction of Victoria Harbour and the South China Sea, which is less effected by the discharge of waste from Hong Kong. The concentrations of THg in the sediments at this site were the lowest among all of the sampling stations, ranging from 0.047 to 0.127 µg/g (average: 0.07 µg/g). In contrast, because B2 and B3 are near industrial areas and urban zones, the concentrations of THg in sediments from B2 and

B3 were much higher than those from other sites. The concentrations of THg in sediments from B4 and B5 were lower than those from B2 and B3, but still higher than those from B1.

Compared with the background level of THg in marine sediments (0.05-0.08 $\mu\text{g/g}$ , Fujii, 1976; 0.02-0.1 $\mu\text{g/g}$ , Lindqvist et al., 1984), the central part of the harbour was apparently contaminated with Hg, and it is speculated that industrial discharges from Hong Kong Island and the Kowloon Peninsula are the main source of Hg in Victoria Harbour. Table 3 shows the THg and MeHg in sediments from some estuaries and coasts. Although the THg concentrations in sediments from Victoria Harbour were lower than those from the Anadyr Estuary (Russia) and Seine Estuary (France), they exceeded those from other coastal areas, such as the South Florida Estuaries, San Francisco Bay, the Polish coast and the nearby East China Sea and Malaysian coast. However, according to the criteria for sediment quality in Hong Kong, the THg concentrations in all sediments were still under the Upper Chemical Exceedance Level (UCEL, 1  $\mu\text{g/g}$  for THg; HK ETWB, 2002).

The seasonal variations of THg concentrations in sediments are shown in Fig. 2. In B1, B4, and B5, the effects of seasonal changes on the THg contents are insignificant. The amounts of THg in the sediments collected from B2 and B3 in February 2005 were much higher than in the other sites. This was probably influenced by the discharge of waste and the low discharges of fresh water from the Pearl River.

Sediment cores collected in October 2004 and radiometrically dated revealed irregular unsupported  $^{210}\text{Pb}$  activities in samples from B2, B3 and B5 due to

physical/biological mixing processes. The unsupported  $^{210}\text{Pb}$  activities in cores B1 and B4 decreased linearly with depth, which allowed the CIC (constant initial concentration of unsupported  $^{210}\text{Pb}$ ) model to be used to calculate the average sedimentation rate (Robbins and Edgington, 1975). The CIC model assumes a constant initial concentration of unsupported  $^{210}\text{Pb}$  and a constant sedimentation rate over the period of time for which the unsupported  $^{210}\text{Pb}$  is measurable. The average sedimentation rates estimated by CIC model in B1 and B4 were 0.33 cm/y and 1.2 cm/y, respectively.

The vertical distribution of THg in the sediment cores is shown in Fig. 3. No significant changes in THg concentrations were found in the B1 core, corresponding to the period from 1840 to the present. This result demonstrated that B1 was less affected than the other areas from human activity in the past 160 years. In the B4 core, the changes in the amount of THg in the sediment were obviously correlated with the urbanization and industrialization of Hong Kong. The development of industry in Hong Kong started in the early 1960s and increased rapidly in the 1970s. During this period, a large number of factories were established that produced basic industrial chemicals, paints, electroplating, enamelware and batteries etc. As a result, the concentrations of THg in the sediment were low before 1972 (38 cm in depth), but increased significantly after 1972 and peaked in 1976. The amount of THg contained in the sediment declined after 1982 because many factories were moved to mainland China in the early 1980s, and industrial activities in the territory decreased accordingly. In the 1990s, the government made some effort to control pollution, and

the THg concentrations in sediment become lower than 0.2 µg/g. Although no dating information exists for B2, B3 and B5 sediment cores, the relatively high THg levels found in the deeper layers at all three sites likely reflect past industrial discharges. Cores from B4 and B5 contained relatively low concentrations of THg in the upper 18 cm sections suggesting recent mercury inputs were substantially diminished in these areas. In contrast, levels recorded in surface sediments from B2 and B3 were indicative of recent increase in mercury pollution. Such findings may be attributed to increase sewage discharges into the areas and/or the resuspension of older sediments.

MeHg is the most toxic and the most common species of organomercury in the environment. In an aquatic system, sediment is an important Hg sink and the main production site of MeHg as a result of biotic and abiotic methylation processes (Ullrich et al., 2001). The MeHg concentrations in sediments typically contain only about 1-1.5% of THg, and tend to be lower (<0.5%) in estuarine and marine environments (Gilmour and Bloom, 1995; Ullrich et al., 2001). Even so, MeHg is always of particular concern because of its high toxicity and tendency to accumulate in the food chain.

MeHg in surface sediments from B1, B4 and B5 were lower than the analytical detection limit (0.1 ng Hg/g, dry wt.). Detectable levels (0.2 to 1.5 ng Hg/g) were found in 70% of B2 and B3 samples (including sediment cores) and accounted for 0.03-0.4% (average: 0.14%) of the THg contents. The proportions of MeHg to THg agreed with the values reported in other works (Bloom et al., 1999; Sunderland et al., 2004; Canário et al., 2005). As shown in Table 3, the MeHg concentrations in



sediments from Victoria Harbour were comparable to those from the Polish coast and San Francisco Bay, but still higher than those from the South Florida Estuaries, the Malaysian coast and the Anadyr Estuary.

The variations in the amount of MeHg in sediment cores from B2 and B3 are shown in Fig. 4. In the sediment core from B2, the amount of MeHg declined with depth and was undetectable ( $<0.1$  ng Hg/g) under a depth of 18 cm. However, the variations in the concentrations of MeHg were irregular in the sediment core from B3. The concentrations of MeHg in surface sediments from both sites were generally higher than those in deeper layers. This reflects physical and chemical conditions that are more conducive to mercury methylation in the upper sediment zone (Stein et al., 1996).

The present study showed Hg contamination in sediments of Victoria Harbour, mainly attributed to past industrial development and urbanization in Hong Kong. The concentrations of MeHg in sediments were generally low, accounting for  $< 0.4\%$  of THg. Further studies on the uptake and transformation of Hg in benthic communities, particularly on the seasonal changes, will be of interest in the understanding of the geochemical cycling of Hg in subtropical coastal regions.

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

Sampling site	Latitude	Longitude	Depth of water (m)
B1	22°14.800' N	114°16.000' E	20
B2	22°17.500' N	114°13.500' E	19
B3	22°17.471' N	114°11.183' E	14
B4	22°18.400' N	114°06.500' E	11
B5	22°18.142' N	114°03.051' E	8

Table 2 Results of THg and MeHg in certified reference materials (CRMs)

CRMs	THg ( $\mu\text{g/g}$ )		MeHg ( $\text{ng/g}$ )	
	Certified	Determined *	Certified	Determined *
NIST 1646a (sediment)	0.04	$0.036 \pm 0.002$		
NIST 2709 (soil)	$1.40 \pm 0.08$	$1.425 \pm 0.016$		
GBW07310 (sediment)	$0.28 \pm 0.04$	$0.282 \pm 0.008$		
NIST 2976 (mussel tissue)			$27.8 \pm 1.1$	$29.7 \pm 3.5$

\* Mean  $\pm$  s, n = 4

Table 3 Comparison of THg and MeHg in sediments from different estuaries and coasts

Location	THg ( $\mu\text{g/g}$ )	MeHg ( $\text{ng/g}$ )	Reference
South Florida Estuaries, USA	0.02 (0.001-0.219)	0.078 (< 0.001-0.49)	(Kannan et al., 1998)
East China Sea, China	0.037 (<0.001-0.08)	2.7 (<0.2-5.5)	(Shi et al., 2005)
Malaysian coast, Malaysia	0.061 (0.02-0.127)	0.04 (0.01-0.05)	(Kannan and Falandysz, 1998)
Polish coast, Poland	0.164 (0.037-0.88)	0.64 (0.04-2.0)	(Kannan and Falandysz, 1998)
San Francisco Bay, USA	0.2 (0.02-0.7)	0.4 (0.1-1)	(Conaway et al., 2003)
Anadyr Estuary, Russia	0.339 (0.077-2.1)	0.24 (0.06-0.62)	(Kannan and Falandysz, 1998)
Seine Estuary, France	0.46 (0.3-1.0)	2.3 (0.1-6)	(Mikac et al., 1999)
Victoria Harbour, Hong Kong	0.247 (0.047-0.855)	<0.1-1.5	This work



## **Figure legends**

Fig. 1 The map of the study area

Fig. 2 The seasonal changes in the amounts of THg in surface sediments.

Fig. 3 The vertical distribution of THg in sediment cores

Fig. 4 The vertical distribution of MeHg in sediment cores from B2 and B3

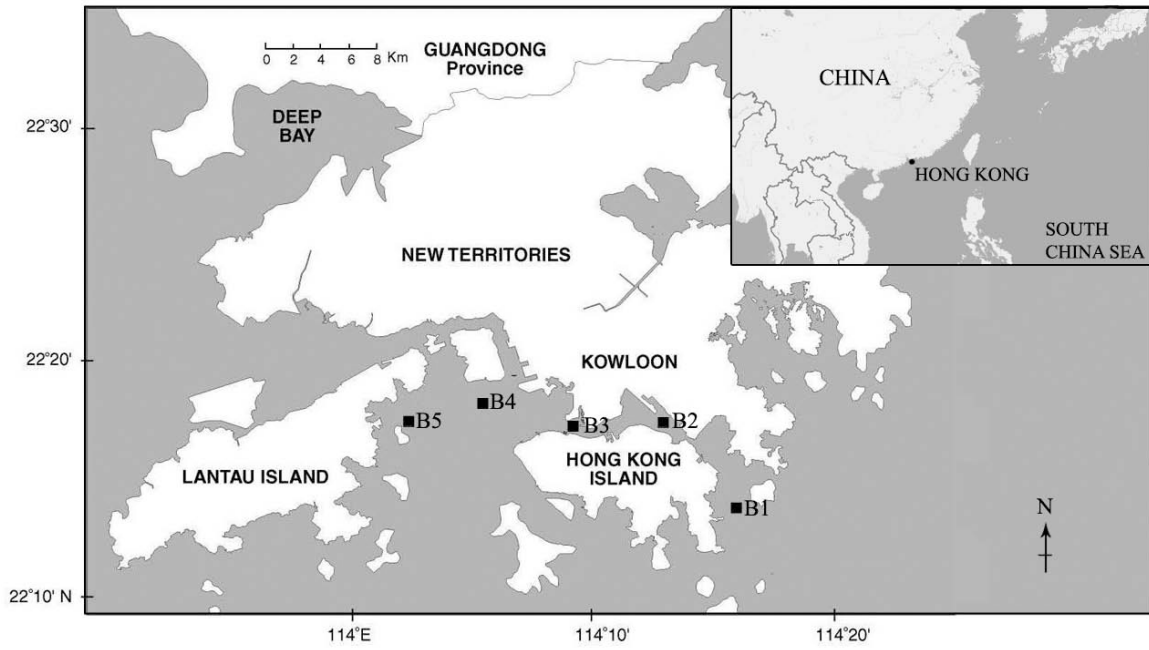


Fig. 1 The map of the study area

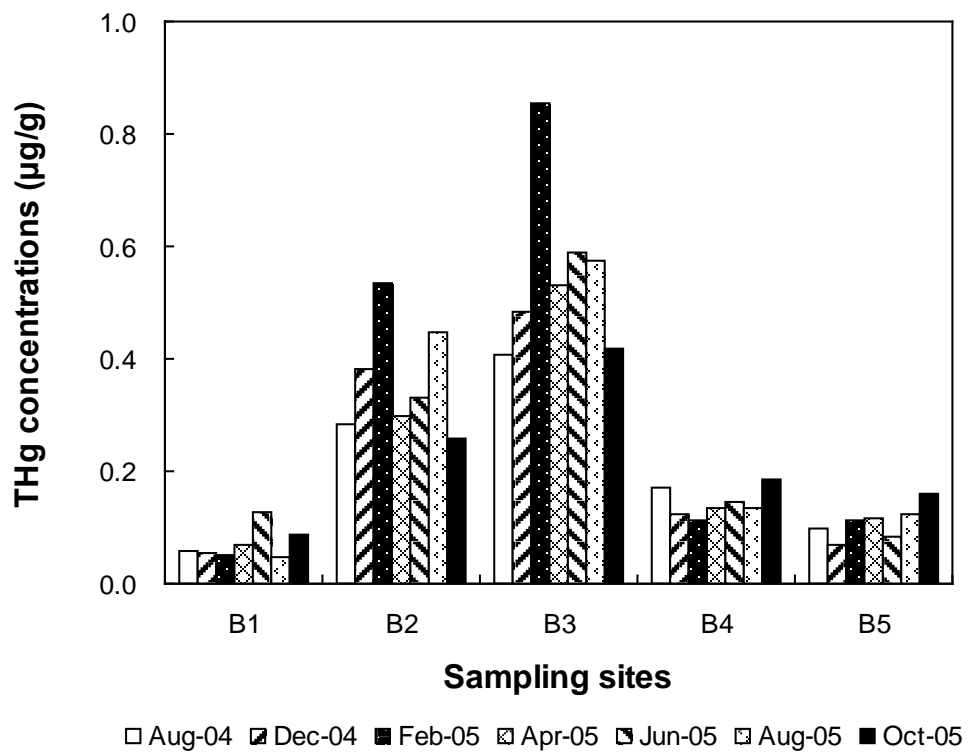


Fig. 2 The seasonal changes in the amounts of THg in surface sediments

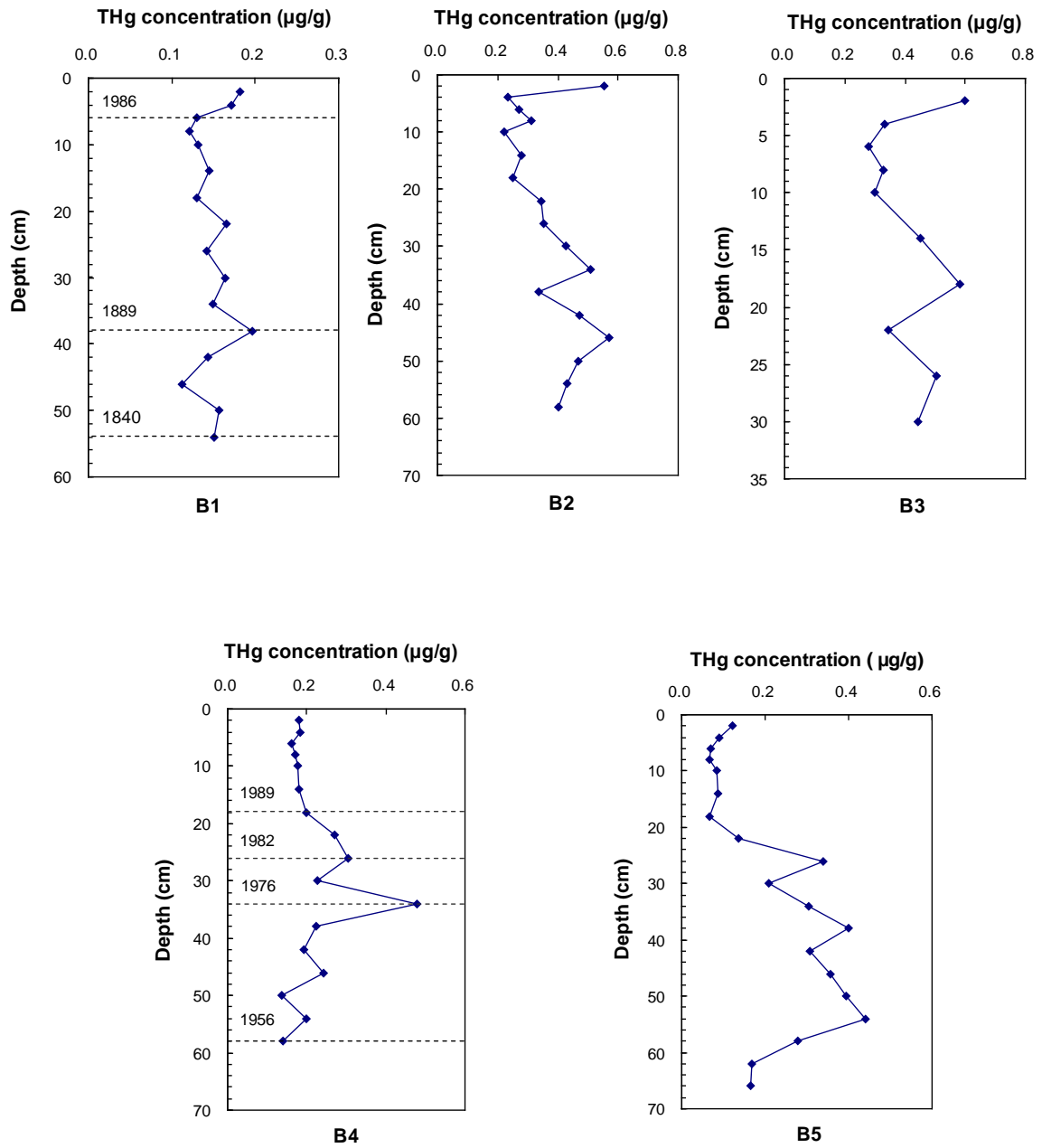


Fig. 3 The vertical distribution of THg in sediment cores

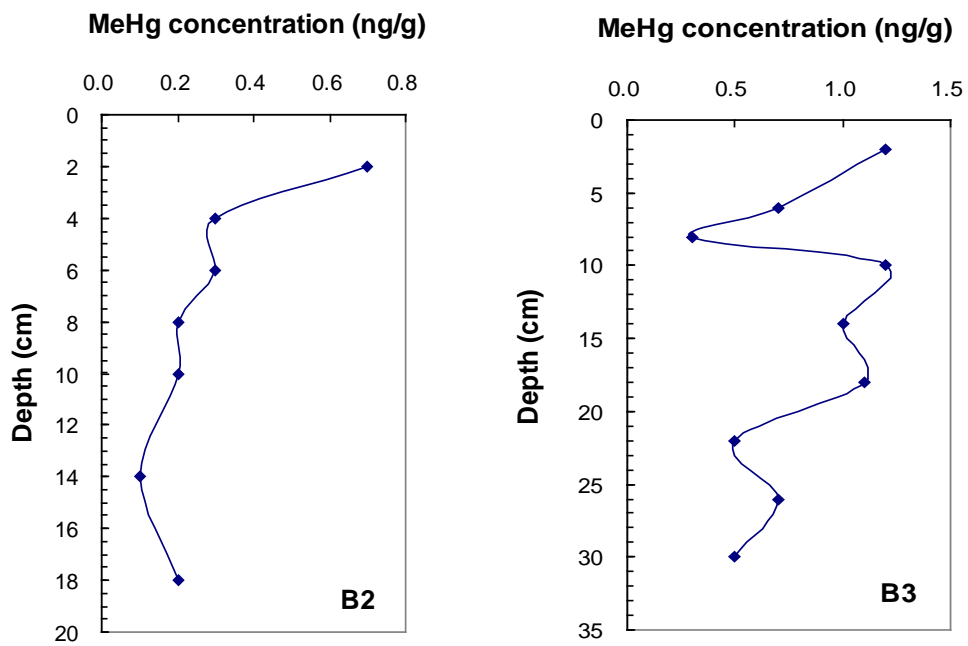


Fig. 4 The vertical distribution of MeHg in sediment cores from B2 and B3