Mercury profiles in sediments of the Pearl River Estuary and the surrounding coastal area of South China

Jian-bo Shi [1, 2], Carman C.M. Ip [2], Gan Zhang [3], Gui-bin Jiang[1], Xiang-dong Li [2 *]

[1]*State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China*

[2]*Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

[3]*State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

[*]Corresponding author (X. D. Li)

E-mail: cexdli@polyu.edu.hk

Fax: (852) 2334 6389

Tel.: (852) 2766 6041

Abstract

The spatial and temporal variations of mercury (Hg) in sediments of the Pearl River Estuary (PRE) and the surrounding coastal area (South China Sea) were studied. In surface sediments, the concentrations of Hg ranged from 1.5 to 201 ng/g, with an average of 54.4 ng/g, displaying a decreasing trend with the distance from the estuary to the open sea. This pattern indicates that the anthropogenic emissions from the Pearl River Delta (PRD) region are probably the main sources of Hg in this coastal region. Using the ^{210}Pb dating technique, the historical changes in the concentrations and influxes of Hg in the last 100 years were also investigated. The variations in Hg influxes in sediment cores obviously correlate with the economic development and urbanization that has occurred the PRD region, especially in the last three decades.

Keywords: Mercury; Sediment; Influx; ^{210}Pb; Pearl River Estuary; South China

Capsule: The spatial and historical changes of Hg in sediment reflect the industrial development and urbanization of the region in south China.

1. Introduction

The biogeochemistry of mercury (Hg) in coastal and estuarial environments has been widely studied because of the high toxicity and biomagnification of this chemical element in the aquatic system (Mason et al., 1996; Horvat et al., 1999; Hines et al., 2000; Conaway et al., 2003; García-Rico et al., 2006). However, the biogeochemical cycles of Hg in different estuaries are variable and complicated due to the diverse input, physical, chemical, and hydrological conditions of Hg. As a result, the behavior of Hg may differ from one estuary to another (Horvat et al., 1999; Conaway et al., 2003).

China plays an important role in global anthropogenic Hg emissions. Hg emissions in China were estimated to total approximately 696 tons in 2003, with an average rate of increase of 2.9% per year during the period 1995-2003 (Wu et al., 2006). A large amount of the Hg emissions obviously correlates with the rapid economic development that has taken place in the region during the last three decades. The increase in emissions of Hg has also caused the air, water, and soil in China to become seriously polluted (Feng, 2005; Jiang et al., 2006).

The Pearl River Estuary (PRE), located in south China, is created by the inflows of fresh water to the South China Sea. The estuary covers an area of 8000 km^2, with the distance from north to south averaging about 49 km, and from east to west varying from 4 to 58 km (Zhang et al., 2003; Ip et al., 2004). The PRE has been found to be contaminated by a number of metal and organic pollutants, a result of the rapid urbanization and industrialization that has been occurring in the Pearl River Delta

(PRD) region during the last a few decades (Hong et al., 1999; Fu et al., 2003; Ip et al., 2005; Liu et al., 2005; Mai et al., 2005; Chen et al., 2006). The PRD region, consisting of part of Guangdong Province as well as China's two special administrative regions of Hong Kong and Macao, is known as one of the most industrialized and urbanized regions in China. A large number of factories have been set up in the PRD region to produce a wide range of goods, including electronic products, medicines, cars, toys, clothing, and others. In 2002, exports from the PRD accounted for 35% of China's total exports (Streets et al., 2006). Without effective treatment, the pollutants from the PRD would enter the PRE through direct discharge or with the run-off of river water. Several studies have demonstrated that PRE is the main reservoir of persistent organic pollutants, such as OCPs, PAHs, PCBs, and PBDEs (Chen et al., 2006; Guan et al., 2007; Guan et al., 2009). An estimated 23 metric tons of PBDEs have been discharged into the PRE in the last 20 years (Guan et al., 2007). Meanwhile, high concentrations of trace metals have also been found in the sediments and aquatic organisms of the PRE (Ip et al., 2005; Ip et al., 2006). However, Hg has largely been ignored in most studies of pollutants in the region, and thus the extent to which the PRE is contaminated with Hg is still unknown. Our previous investigation in Victoria Harbour, a part of the PRE, showed that the total Hg concentrations in surface sediments ranged from 47 to 855 ng/g (dry wt.), indicating the possible contamination of Hg in this area (Shi et al., 2007).

The aim of the present work was to study the spatial and temporal distribution of Hg in sediments of the PRE and its surrounding coastal area. Using the ^{210}Pb dating

technique, the historical changes in the concentrations and influxes of Hg in the last 100 years were also investigated.

2. Materials and methods

2.1 Sample collection

The map of the study area and the locations of the sampling sites are shown in Fig. 1. A total of 39 surface sediment samples were collected in September 2002. The sampling locations were distributed across the PRE and its surrounding coastal area. The surface sediments (top 10 cm) were taken with a stainless steel grab sampler. Three sediment cores were also collected in this area in June 2000. The core sediments were taken using a gravity corer with an automatic clutch and reverse catcher. The diameters of the outside steel corer and the inside sampling PVC coring tube were 56 and 46 mm, respectively. The sediment cores were sliced into 2 cm intervals from 0 to 50 cm and into 4 cm intervals from 50 cm to the end of the cores.

All of the samples were stored in polyethylene bags at 4-6℃ immediately after collection. In the laboratory, the sediments were freeze-dried at -45℃ for 3 days and then ground in an agate grinder until fine particles were obtained.

2.2 Determination of Hg in sediments

To analyze the total amount of Hg present in the samples, about 0.25 g of grounded sediment samples were digested with 5 mL of aqua regia in an AIM 500 Automated Block Digestion System (A.I. Scientific Pty Ltd, Australia) at 95℃ for 2 h

and shaken frequently. After cooling down, the solutions were diluted to 25 mL with Milli-Q water and then centrifuged at 3000 rpm for 15 min. The Hg concentrations were determined by the Flow Injection Mercury System (FIMS, Perkin Elmer) using $SnCl_2$ for the reduction step.

For the analytical quality control, reagent blanks, certified reference materials (CRMs), and sample replicates were randomly inserted in the analysis. The determined concentrations of Hg in two sediment CRMs (36±2 ng/g in NIST 1646a and 282±8 ng/g in GBW07310, n=4) were both in good agreement with their certified values (40 ng/g in NIST 1646a and 280±40 in GBW07310), indicating the method was accurate and reliable.

2.3 ^{210}Pb dating

The ^{210}Pb radiometric technique was used to estimate the chronology of the sediment cores. A constant rate of the ^{210}Pb supply (CRS) model was applied to date the sediment cores, to obtain sediment influxes over time (McCall et al., 1984). The detailed method and results of ^{210}Pb dating have been described elsewhere (Ip et al., 2004).

2.4 Geochemical mapping

The concentrations of Hg were used as the input data for grid-based contour mapping, to study the spatial distribution of Hg in the PRE and its surrounding coastal area. The software used was ArcGIS 8.2, and the Inverse Distance Weighted (IDW) method was adopted for the interpolation of the geochemical data.

3. Results and discussion

3.1 Spatial distribution

The concentrations of Hg in surface sediments ranged from 1.5 to 201 ng/g. The average and median concentrations were 54.4 and 36.2 ng/g, respectively. The geochemical map of Hg in the study area is shown in Fig. 2. The spatial distribution of Hg was similar with those of Cu, Zn, and Pb (Ip et al., 2006), displaying a decreasing pattern with increasing distance from the estuary to the open sea. This indicates that anthropogenic emissions from the PRD are probably the main sources of Hg in the sediments of the PRE and its surrounding coastal area. Although it had been thought that the outflow of the Pearl River is the most important source of Hg in the estuary, the concentrations of Hg in sediments near the end of the Pearl River were relatively low. By contrast, two hotspots were found at the mouth of the PRE and the northwest part of the coastal zone, a sign of the influence of the discharge of waste from the coastal cities, and the circulation currents in the estuary.

Table 1 shows the content of Hg in different marine sediments. Compared with the reported background total Hg levels in marine sediments (50-80 ng/g, (Fujii, 1976); 20-100 ng/g, (Lindqvist et al., 1984)), the sediments collected from the PRE were significantly contaminated with Hg. However, the concentrations of Hg in most sediments from the coastal area were still within the background range (<80 ng/g, see Fig. 2). As a whole, the concentrations of Hg in the study area were higher than those in sediments from the Arctic Ocean Basin, South Florida Estuaries (USA), and the

East China Sea (China), but lower than those in the Malaysian coast (Malaysia), San Francisco Bay (USA), Anadyr Estuary (Russia), and Seine Estuary (France).

3.2 Temporal distribution

Three sediment cores were collected from the study area and dated using the ^{210}Pb technique. The vertical distributions of Hg in sediment cores and the year in which they are estimated to have become present are shown in Fig. 3. Cores 14 and 25 are located around the two zones with high concentrations of Hg. Core 30 is located in the South China Sea outside the PRE and close to Hong Kong. Therefore, the concentrations of Hg in cores 14 and 25 were significantly higher than those in core 30. In core 14, the concentrations of Hg were relatively higher in the upper 45 cm, corresponding to the period from 1972 to the present, and then decreased with the depth in the rest of the core. The concentrations of Hg in core 25 decreased slightly with depth in the profile, but were significantly high in the top 10 cm of sediments (after 1980). In these two cores, the concentrations of Hg in the sediments of the PRE increased during the last century, especially in the last 2-3 decades. However, in core 30, the change in Hg concentrations with depth was not significant, except that the concentrations of Hg in 5-7 cm (1990-1993) and 27-31 cm (1970-1974) were slightly higher than in other layers.

3.3 Influx of Hg

In order to identify the influence of anthropogenic inputs, the influxes of Hg in

the sediment cores were calculated. The influxes of Hg for decade *j* in sediment core *i* were calculated using the following equation (Yang et al., 2002):

$$Influx = \sum A_i \rho_{it} D_{it} C_{it}, \quad (1)$$

where A_i is the area of the sediment core (cm^2), ρ_{it} is the sediment dry density for interval *t* (e.g., decade) (g/cm^3), D_{it} is the thickness of the sediment for interval *t* within decade *j* in core *i* (cm), and C_{it} is the concentration of Hg for interval *t* (ng/g). The changes of Hg influxes in sediment cores in the last 100 years are shown in Fig. 4. The influxes of Hg in core 14 increased gradually in the last century, but rapidly after the 1970s, especially in the 1990s. The influx of Hg in the 1990s was approximately 9 times that in the 1900s and 3 times that in the 1950s. In core 25, high influxes of Hg were also found after the 1970s, despite a small reduction in the 1980s and 1990s. The increase in influxes of Hg in cores 14 and 25 obviously correlates with the economic development and urbanization of the PRD region, especially in the last three decades. In core 30, which is located outside of the PRE, the influx of Hg increased from the 1950s and peaked in the 1960s. The influx of Hg in the 1990s was only 45% of that in the 1960s and even less than that in the 1950s. This showed that the Hg in this core probably came from discharges related to Hong Kong, because the development of Hong Kong's industry started in the 1950s and rapidly increased in the 1960s and 1970s. During this period, a large number of factories were established, which produced basic industrial chemicals, paints, electroplating, enamelware, batteries, and so forth. In the early 1980s, many factories were moved to mainland China, and industrial activities in the territory declined significantly in the last few decades.

Meanwhile, since the 1980s, the Hong Kong government has made efforts to put in place some strict controls over the discharge of pollutants (Shi et al., 2007).

4. Conclusions

The concentrations of Hg in surface sediments of the PRE and the surrounding coastal area decreased with the increasing distance from the estuary to the open sea, indicating that the Hg contamination was mainly caused by anthropogenic emissions from the PRD region. By using the ^{210}Pb dating technique, the historical changes in the concentrations and influxes of Hg in sediment cores in the last 100 years were revealed. The influxes of Hg in sediments were found to significantly correlate with the economic development and urbanization that has taken place in the PRD region, especially in the last three decades.

Acknowledgments

The work described here was supported by the Research Grants Council of the Hong Kong SAR Government (PolyU 5212/05E and N_PolyU 535/05), the Area of Excellence Scheme under the University Grants Committee of the Hong Kong SAR Government (AoE/P04/2004), and the National Natural Science Foundation of China (20807047).

References

Chen, S.J., Luo, X.J., Mai, B.X., Sheng, G.Y., Fu, J.M., Zeng, E.Y., 2006. Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine

pesticides in sediments of the Pearl River Estuary and the northern South China Sea. Environmental Science & Technology 40, 709-714.

Conaway, C.H., Squire, S., Mason, R.P., Flegal, A.R., 2003. Mercury speciation in the San Francisco Bay estuary. Marine Chemistry 80, 199-225.

Feng, X., 2005. Mercury pollution in China - an overview, in: Pirrone, N., Mahaffey, K. (Eds.), Dynamics of mercury pollution on regional and global scale: atmospheric process, human exposure around the world. Springer Publishers: Norwell, MA, pp. 657-678.

Fu, J.M., Mai, B.X., Sheng, G.Y., Zhang, G., Wang, X.M., Peng, P.A., Xiao, X.M., Ran, R., Cheng, F.Z., Peng, X.Z., Wang, Z.S., Tang, U.W., 2003. Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere 52, 1411-1422.

Fujii, M., 1976. Mercury distribution in lithosphere and atmosphere. Kodansha Scientific, Tokyo.

García-Rico, L., Rodríguez, M.V., Jara-Marini, M.E., 2006. Geochemistry of mercury in sediment of oyster areas in Sonora, Mexico. Marine Pollution Bulletin 52, 447-469.

Gobeil, C., Macdonald, R.W., Smith, J.N., 1999. Mercury profiles in sediments of the Artic Ocean Basins. Environmental Science & Technology 33, 4194-4198.

Guan, Y.F., Wang, J.Z., Ni, H.G., Luo, X.J., Mai, B.X., Zeng, E.Y., 2007. Riverine inputs of polybrominated diphenyl ethers from the Pearl River Delta (China) to the coastal ocean. Environmental Science & Technology 41, 6007-6013.

Guan, Y.F., Wang, J.Z., Ni, H.G., Zeng, E.Y., 2009. Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: Assessment of mass loading, input source and environmental fate. Environmental Pollution 157, 618-624.

Hines, M.E., Horvat, M., Faganeli, J., Bonzongo, J.-C.J., Barkay, T., Major, E.B., Scott, K.J., Bailey, E.A., Warwick, J.J., Lyons, W.B., 2000. Mercury biogeochemistry in the Idrija River, Slovenia, from above the mine into the Gulf of Trieste. Environmental Research Section A 83, 129-139.

248 Hong, H.S., Chen, W.Q., Xu, L., Wang, X.H., Zhang, L.P., 1999. Distribution and fate
249 of organochlorine pollutants in the Pearl River Estuary. Marine Pollution Bulletin
250 39, 376-382.
251 Horvat, M., Covelli, S., Faganeli, J., Logar, M., Mandić, V., Rajar, R., Širca, A., Žagar,
252 D., 1999. Mercury in contaminated coastal environments; a case study: the Gulf
253 of Trieste. The Science of the Total Environment 237/238, 43-56.
254 Ip, C.C.M., Li, X.D., Zhang, G., Farmer, J.G., Wai, O.W.H., LI, Y.S., 2004. Over one
255 hundred years of trace metal fluxes in the sediments of the Pearl River Estuary,
256 South China. Environmental Pollution 132, 157-172.
257 Ip, C.C.M., Li, X.D., Zhang, G., Wai, O.W.H., LI, Y.S., 2006. Trace metal distribution
258 in sediments of the Pearl River Estuary and the surrounding coastal area, South
259 China. Environmental Pollution 147, 311-323.
260 Ip, C.C.M., Li, X.D., Zhang, G., Wong, C.S.C., Zhang, W.L., 2005. Heavy metal and
261 Pb isotopic compositions of aquatic organisms in the Pearl River Estuary, South
262 China. Environmental Pollution 138, 494-504.
263 Jiang, G.B., Shi, J.B., Feng, X.B., 2006. Mercury pollution in China. Environmental
264 Science & Technology 40, 3673-3678.
265 Kannan, K., Falandysz, J., 1998. Speciation and concentrations of mercury in certain
266 coastal marine sediment. Water, Air, and Soil Pollution 103, 129-136.
267 Kannan, K., Smith, J.R.G., Lee, R.F., Windom, H.L., Heitmuller, P.T., Macauley, J.M.,
268 Summers, J.K., 1998. Distribution of total mercury and methyl mercury in water,
269 sediment and fish from South Florida Estuaries. Archives of Environmental
270 Contamination and Toxicology 34, 109-118.
271 Lindqvist, O., Jernelöv, A., Johansson, K., Rohde, H., 1984. Mercury in the Swedish
272 environment. Global and local sources. National Swedish Environmental
273 Protection Board.
274 Liu, G.Q., Zhang, G., Li, X.D., Li, J., Peng, X.Z., Qi, S.H., 2005. Sedimentary record
275 of polycyclic aromatic hydrocarbons in a sediment core from the Pearl River
276 Estuary, South China. Marine Pollution Bulletin 51, 912-921.
277 Mai, B.X., Zeng, E.Y., Luo, X.J., Yang, Q.S., Zhang, G., Li, X.D., Sheng, G.Y., Fu,

J.M., 2005. Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta, China. Environmental Science & Technology 39, 49-56.

Mason, R.P., Reinfelder, J.R., Morel, F.M.M., 1996. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. Environmental Science & Technology 30, 1835-1845.

McCall, P.L., Robins, J.A., Matisoff, G., 1984. Cs-137 and Pb-210 transport and geochronologies in urbanized reservoirs with rapidly increasing sedimentation-rates. Chemical Geology 44, 33-65.

Mikac, N., Niessen, S., Ouddane, B., Wartel, M., 1999. Speciation of mercury in sediments of the Seine Estuary (France). Applied Organometallic Chemistry 13, 715-725.

Shi, J.B., Ip, C.C.M., Tang, C.W.Y., Zhang, G., Wu, R.S.S., Li, X.D., 2007. Spatial and temporal variations of mercury in sediments from Victoria Harbour, Hong Kong. Marine Pollution Bulletin 54, 480-485.

Shi, J.B., Liang, L.N., Yuan, C.G., He, B., Jiang, G.B., 2005. Methylmercury and total mercury in sediment collected from the East Chia Sea. Bulletin of Environmental Contamination and Toxicology 74, 980-987.

Streets, D.G., Yu, C., Bergin, M.H., Wang, X.M., Carmichael, G.R., 2006. Modeling study of air pollution due to the manufacture of export goods in China's Pearl River Delta. Environmental Science & Technology 40, 2099-2107.

Wu, Y., Wang, S.X., Streets, D.G., Hao, J.M., Chan, M., Jiang, J.K., 2006. Trends in anthropogenic mercury emissions in China from 1995 to 2003. Environmental Science & Technology 40, 5312-5318.

Yang, H., Rose, N.L., Battarbee, R.W., Boyle, J.F., 2002. Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment. Environmental Science & Technology 36, 1383-1388.

Zhang, G., Yan, J., Fu, J.M., Parker, A., Li, X.D., Wang, Z.S., 2003. Butyltins in sediments and biota from the Pearl River Delta, South China. Chemical Speciation and Bioavailability 14, 35-42.

Table 1 Comparison of the concentrations of Hg in different marine sediments

Location	Hg (ng/g)	Reference
The Arctic Ocean Basin	10-116	(Gobeil et al., 1999)
South Florida Estuaries, USA	20 (1-219)	(Kannan et al., 1998)
The East China Sea, China	37 (<0.5-80)	(Shi et al., 2005)
Malaysian coast, Malaysia	61 (20-127)	(Kannan and Falandysz, 1998)
San Francisco Bay, USA	201 (20-702)	(Conaway et al., 2003)
Anadyr Estuary, Russia	339 (77-2100)	(Kannan and Falandysz, 1998)
Seine Estuary, France	460 (300-1000)	(Mikac et al., 1999)
The PRE and coastal area, South China	54.4 (1.5-201.3)	This work

Figure legends

Fig. 1 Map of the study area

Fig. 2 The spatial distribution of Hg in surface sediments

Fig. 3 The vertical distribution of Hg in sediment cores

Fig. 4 The influxes of Hg in sediment profiles

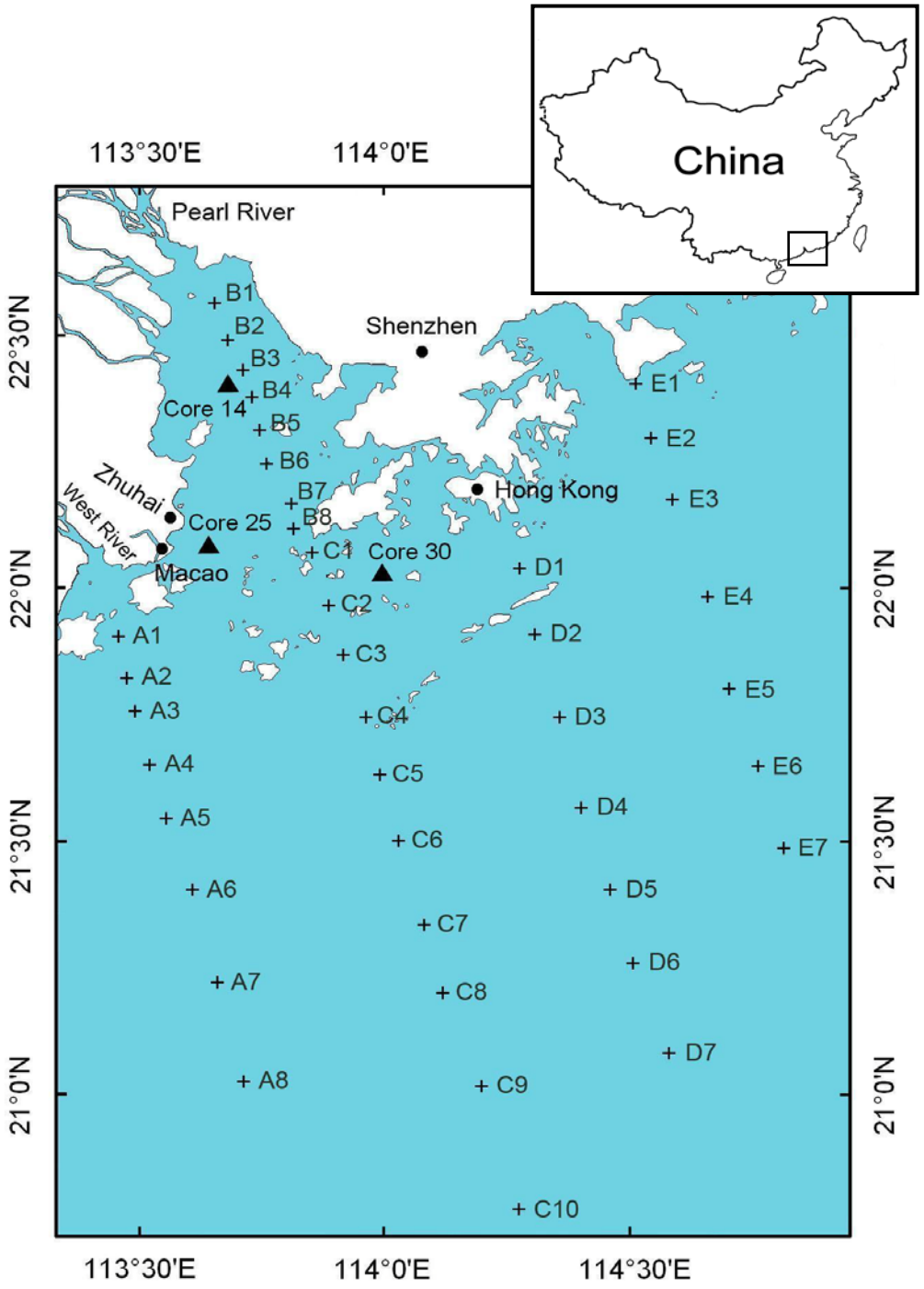
China
113°30'E
114°0'E
114°30'E
22°30'N
22°0'N
21°30'N
21°0'N
Pearl River
Shenzhen
Hong Kong
Zhuhai
West River
Macao
Core 14
Core 25
Core 30
B1
B2
B3
B4
B5
B6
B7
B8
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
A1
A2
A3
A4
A5
A6
A7
A8
D1
D2
D3
D4
D5
D6
D7
E1
E2
E3
E4
E5
E6
E7

Fig. 1

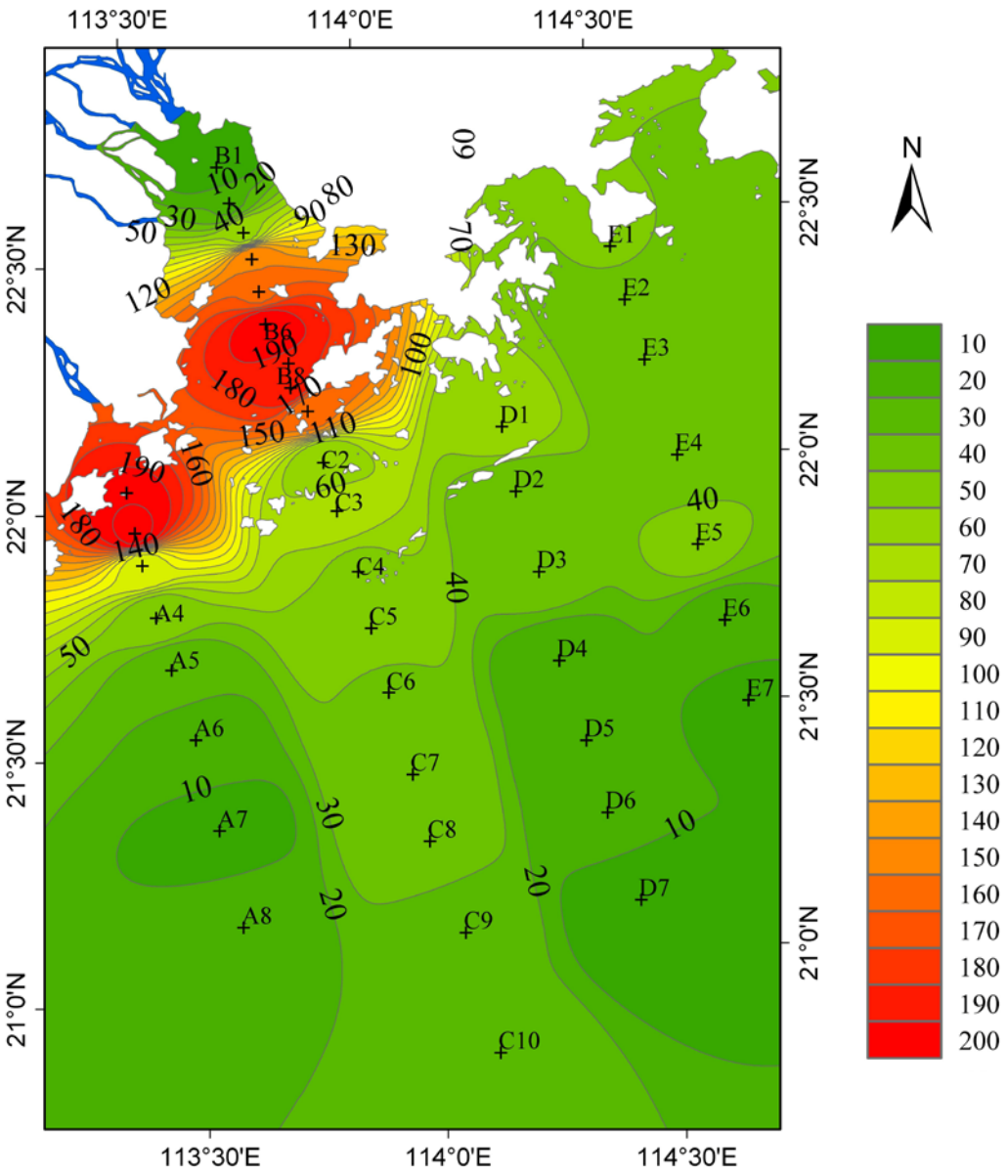
113°30'E
114°0'E
114°30'E
22°30'N
22°0'N
21°30'N
21°0'N
N
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

Fig. 2

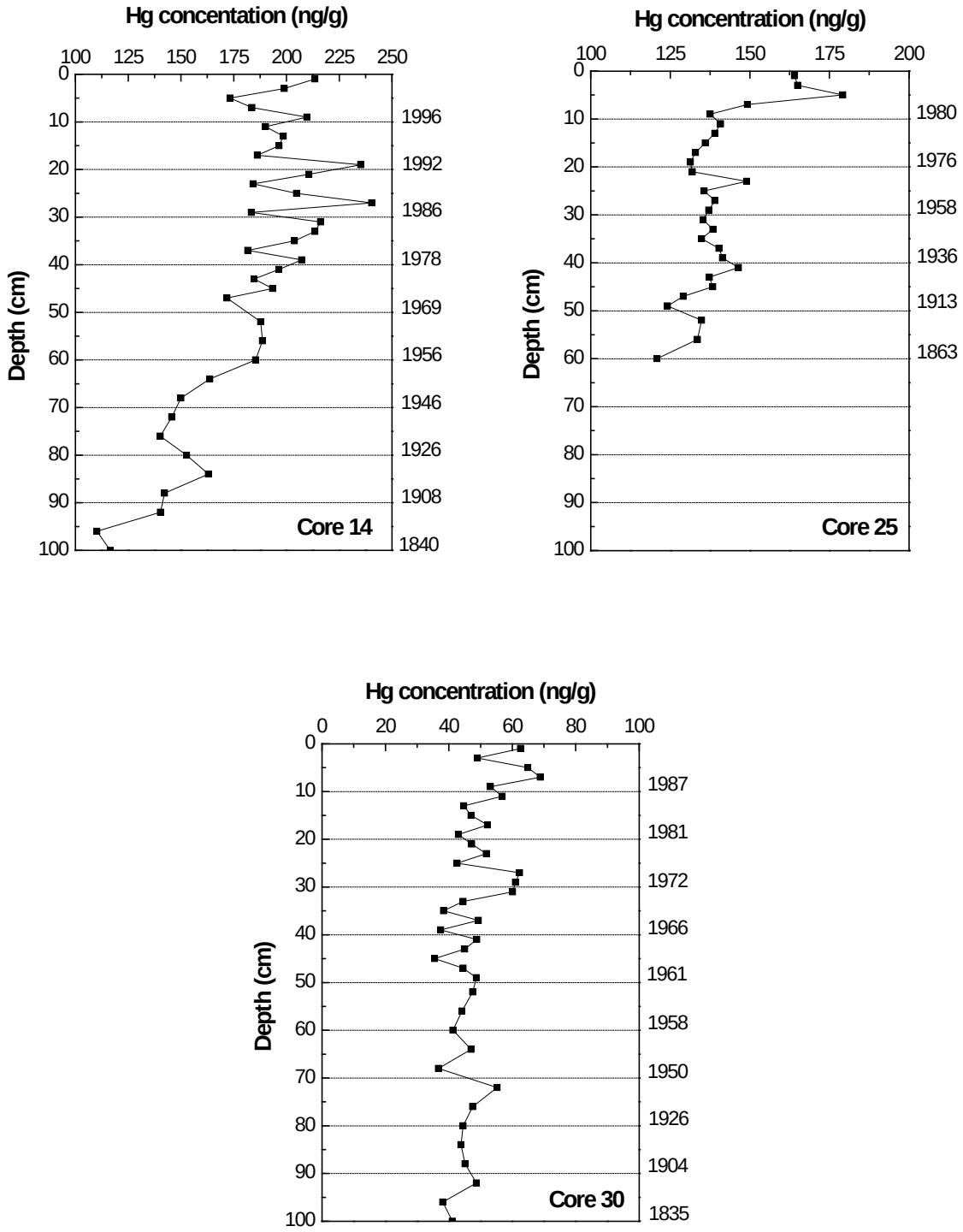
Hg concentation (ng/g)
100 125 150 175 200 225 250
0 10 20 30 40 50 60 70 80 90 100
Depth (cm)
1996 1992 1986 1978 1969 1956 1946 1926 1908 1840
Core 14
Hg concentration (ng/g)
100 125 150 175 200
0 10 20 30 40 50 60 70 80 90 100
Depth (cm)
1980 1976 1958 1936 1913 1863
Core 25
Hg concentration (ng/g)
0 20 40 60 80 100
0 10 20 30 40 50 60 70 80 90 100
Depth (cm)
1987 1981 1972 1966 1961 1958 1950 1926 1904 1835
Core 30

Fig. 3

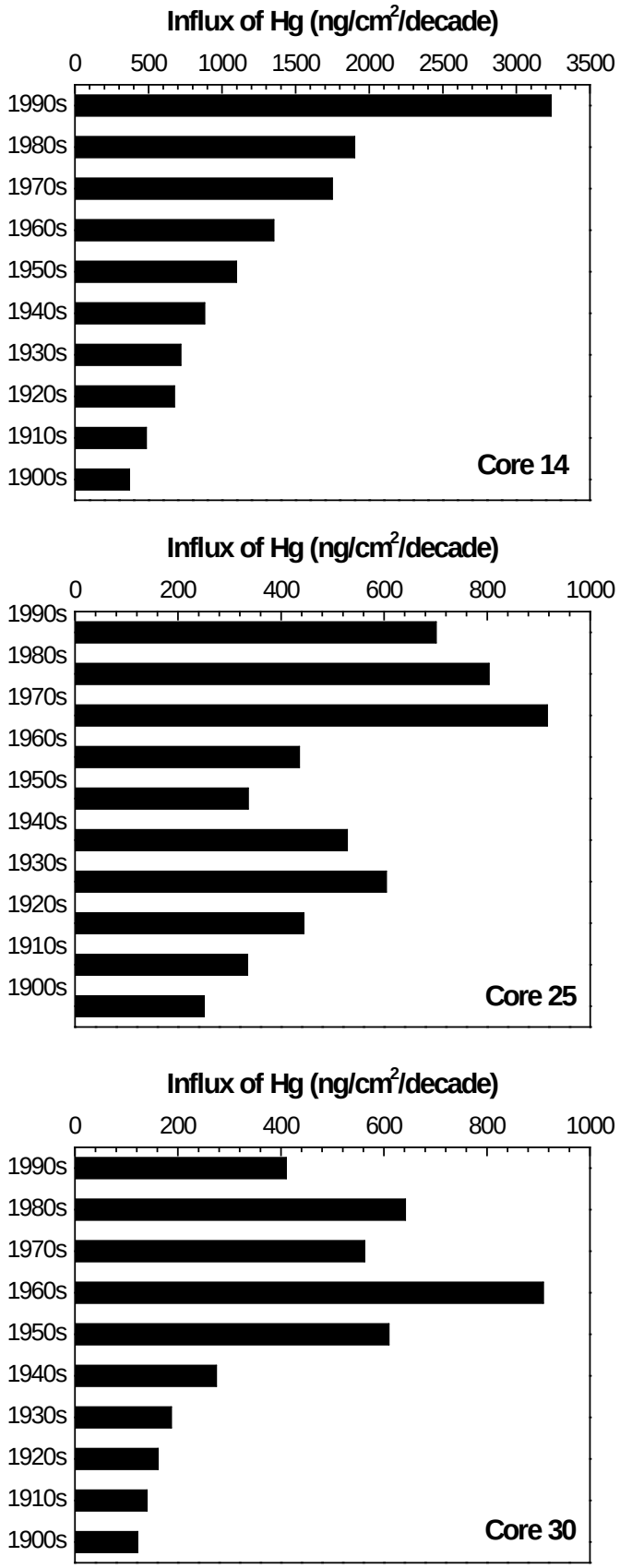
Influx of Hg (ng/cm2/decade)
0
500
1000
1500
2000
2500
3000
3500
1990s
1980s
1970s
1960s
1950s
1940s
1930s
1920s
1910s
1900s
Core 14
Influx of Hg (ng/cm2/decade)
0
200
400
600
800
1000
1990s
1980s
1970s
1960s
1950s
1940s
1930s
1920s
1910s
1900s
Core 25
Influx of Hg (ng/cm2/decade)
0
200
400
600
800
1000
1990s
1980s
1970s
1960s
1950s
1940s
1930s
1920s
1910s
1900s
Core 30

Fig. 4