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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. Ip², Gan Zhang³,

Gui-bin Jiang¹, Xiang-dong Li^{2*}

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

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

*³State 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

23

24

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

35

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

37

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

40

41 **1. Introduction**

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

50 China plays an important role in global anthropogenic Hg emissions. Hg
51 emissions in China were estimated to total approximately 696 tons in 2003, with an
52 average rate of increase of 2.9% per year during the period 1995-2003 (Wu et al.,
53 2006). A large amount of the Hg emissions obviously correlates with the rapid
54 economic development that has taken place in the region during the last three decades.
55 The increase in emissions of Hg has also caused the air, water, and soil in China to
56 become seriously polluted (Feng, 2005; Jiang et al., 2006).

57 The Pearl River Estuary (PRE), located in south China, is created by the inflows
58 of fresh water to the South China Sea. The estuary covers an area of 8000 km², with
59 the distance from north to south averaging about 49 km, and from east to west varying
60 from 4 to 58 km (Zhang et al., 2003; Ip et al., 2004). The PRE has been found to be
61 contaminated by a number of metal and organic pollutants, a result of the rapid
62 urbanization and industrialization that has been occurring in the Pearl River Delta

63 (PRD) region during the last a few decades (Hong et al., 1999; Fu et al., 2003; Ip et al.,
64 2005; Liu et al., 2005; Mai et al., 2005; Chen et al., 2006). The PRD region,
65 consisting of part of Guangdong Province as well as China's two special
66 administrative regions of Hong Kong and Macao, is known as one of the most
67 industrialized and urbanized regions in China. A large number of factories have been
68 set up in the PRD region to produce a wide range of goods, including electronic
69 products, medicines, cars, toys, clothing, and others. In 2002, exports from the PRD
70 accounted for 35% of China's total exports (Streets et al., 2006). Without effective
71 treatment, the pollutants from the PRD would enter the PRE through direct discharge
72 or with the run-off of river water. Several studies have demonstrated that PRE is the
73 main reservoir of persistent organic pollutants, such as OCPs, PAHs, PCBs, and
74 PBDEs (Chen et al., 2006; Guan et al., 2007; Guan et al., 2009). An estimated 23
75 metric tons of PBDEs have been discharged into the PRE in the last 20 years (Guan et
76 al., 2007). Meanwhile, high concentrations of trace metals have also been found in the
77 sediments and aquatic organisms of the PRE (Ip et al., 2005; Ip et al., 2006). However,
78 Hg has largely been ignored in most studies of pollutants in the region, and thus the
79 extent to which the PRE is contaminated with Hg is still unknown. Our previous
80 investigation in Victoria Harbour, a part of the PRE, showed that the total Hg
81 concentrations in surface sediments ranged from 47 to 855 ng/g (dry wt.), indicating
82 the possible contamination of Hg in this area (Shi et al., 2007).

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

85 technique, the historical changes in the concentrations and influxes of Hg in the last
86 100 years were also investigated.

87

88 **2. Materials and methods**

89 2.1 Sample collection

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

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

102

103 2.2 Determination of Hg in sediments

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

107 and shaken frequently. After cooling down, the solutions were diluted to 25 mL with
108 Milli-Q water and then centrifuged at 3000 rpm for 15 min. The Hg concentrations
109 were determined by the Flow Injection Mercury System (FIMS, Perkin Elmer) using
110 SnCl₂ for the reduction step.

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

117 2.3 ²¹⁰Pb dating

118 The ²¹⁰Pb radiometric technique was used to estimate the chronology of the
119 sediment cores. A constant rate of the ²¹⁰Pb supply (CRS) model was applied to date
120 the sediment cores, to obtain sediment influxes over time (McCall et al., 1984). The
121 detailed method and results of ²¹⁰Pb dating have been described elsewhere (Ip et al.,
122 2004).

123

124 2.4 Geochemical mapping

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

129

130 **3. Results and discussion**

131 3.1 Spatial distribution

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

144 Table 1 shows the content of Hg in different marine sediments. Compared with
145 the reported background total Hg levels in marine sediments (50-80 ng/g, (Fuji,
146 1976); 20-100 ng/g, (Lindqvist et al., 1984)), the sediments collected from the PRE
147 were significantly contaminated with Hg. However, the concentrations of Hg in most
148 sediments from the coastal area were still within the background range (<80 ng/g, see
149 Fig. 2). As a whole, the concentrations of Hg in the study area were higher than those
150 in sediments from the Arctic Ocean Basin, South Florida Estuaries (USA), and the

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

153

154 3.2 Temporal distribution

155 Three sediment cores were collected from the study area and dated using the
156 ^{210}Pb technique. The vertical distributions of Hg in sediment cores and the year in
157 which they are estimated to have become present are shown in Fig. 3. Cores 14 and 25
158 are located around the two zones with high concentrations of Hg. Core 30 is located in
159 the South China Sea outside the PRE and close to Hong Kong. Therefore, the
160 concentrations of Hg in cores 14 and 25 were significantly higher than those in core
161 30. In core 14, the concentrations of Hg were relatively higher in the upper 45 cm,
162 corresponding to the period from 1972 to the present, and then decreased with the
163 depth in the rest of the core. The concentrations of Hg in core 25 decreased slightly
164 with depth in the profile, but were significantly high in the top 10 cm of sediments
165 (after 1980). In these two cores, the concentrations of Hg in the sediments of the PRE
166 increased during the last century, especially in the last 2-3 decades. However, in core
167 30, the change in Hg concentrations with depth was not significant, except that the
168 concentrations of Hg in 5-7 cm (1990-1993) and 27-31 cm (1970-1974) were slightly
169 higher than in other layers.

170

171 3.3 Influx of Hg

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

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

$$175 \quad \text{Influx} = \sum A_i \rho_{it} D_{it} C_{it}, \quad (1)$$

176 where A_i is the area of the sediment core (cm^2), ρ_{it} is the sediment dry density for
177 interval t (e.g., decade) (g/cm^3), D_{it} is the thickness of the sediment for interval t
178 within decade j in core i (cm), and C_{it} is the concentration of Hg for interval t (ng/g).

179 The changes of Hg influxes in sediment cores in the last 100 years are shown in Fig. 4.

180 The influxes of Hg in core 14 increased gradually in the last century, but rapidly after
181 the 1970s, especially in the 1990s. The influx of Hg in the 1990s was approximately 9

182 times that in the 1900s and 3 times that in the 1950s. In core 25, high influxes of Hg

183 were also found after the 1970s, despite a small reduction in the 1980s and 1990s. The

184 increase in influxes of Hg in cores 14 and 25 obviously correlates with the economic

185 development and urbanization of the PRD region, especially in the last three decades.

186 In core 30, which is located outside of the PRE, the influx of Hg increased from the

187 1950s and peaked in the 1960s. The influx of Hg in the 1990s was only 45% of that in

188 the 1960s and even less than that in the 1950s. This showed that the Hg in this core

189 probably came from discharges related to Hong Kong, because the development of

190 Hong Kong's industry started in the 1950s and rapidly increased in the 1960s and

191 1970s. During this period, a large number of factories were established, which

192 produced basic industrial chemicals, paints, electroplating, enamelware, batteries, and

193 so forth. In the early 1980s, many factories were moved to mainland China, and

194 industrial activities in the territory declined significantly in the last few decades.

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

197

198 **4. Conclusions**

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

207

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214

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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

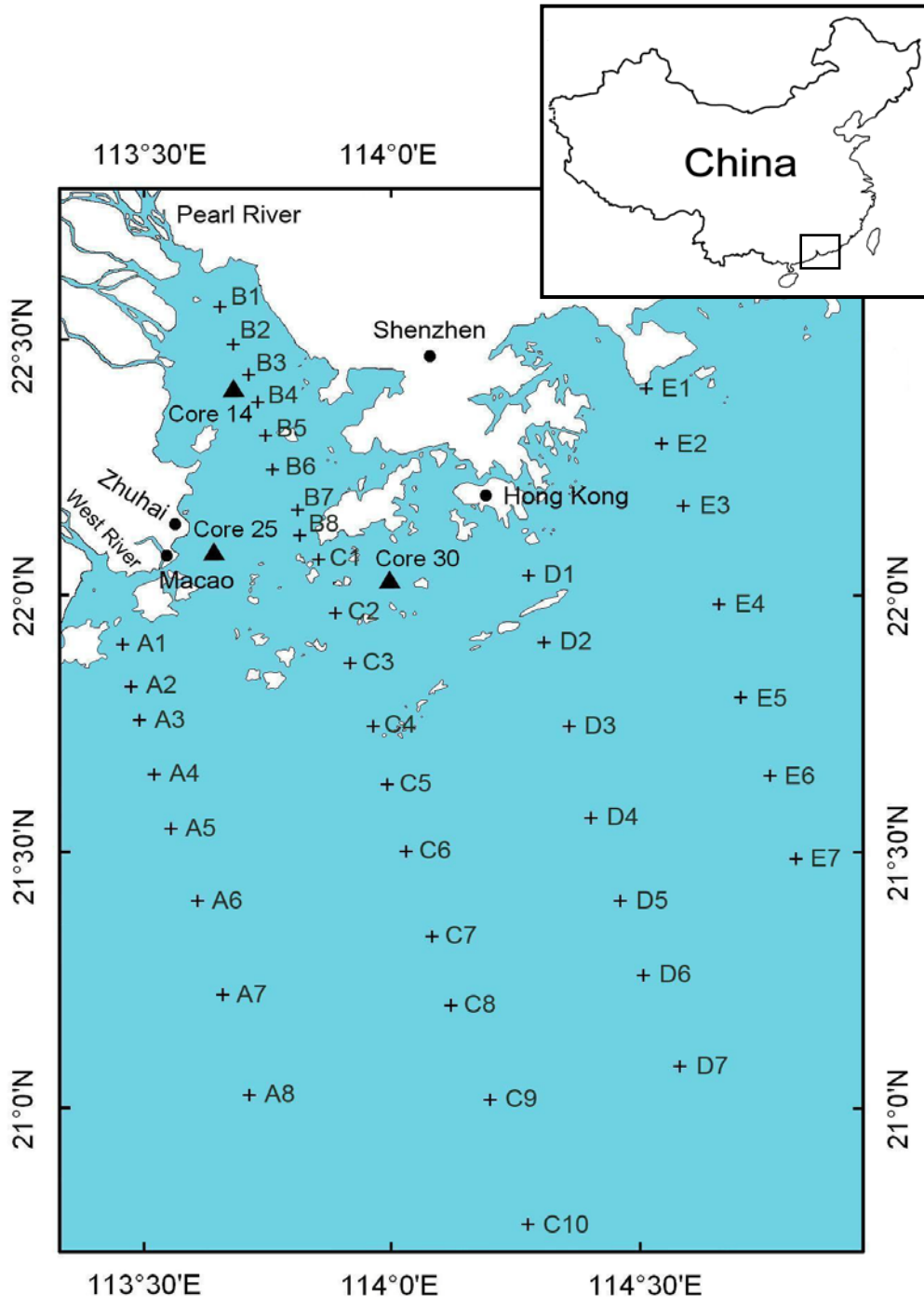


Fig. 1

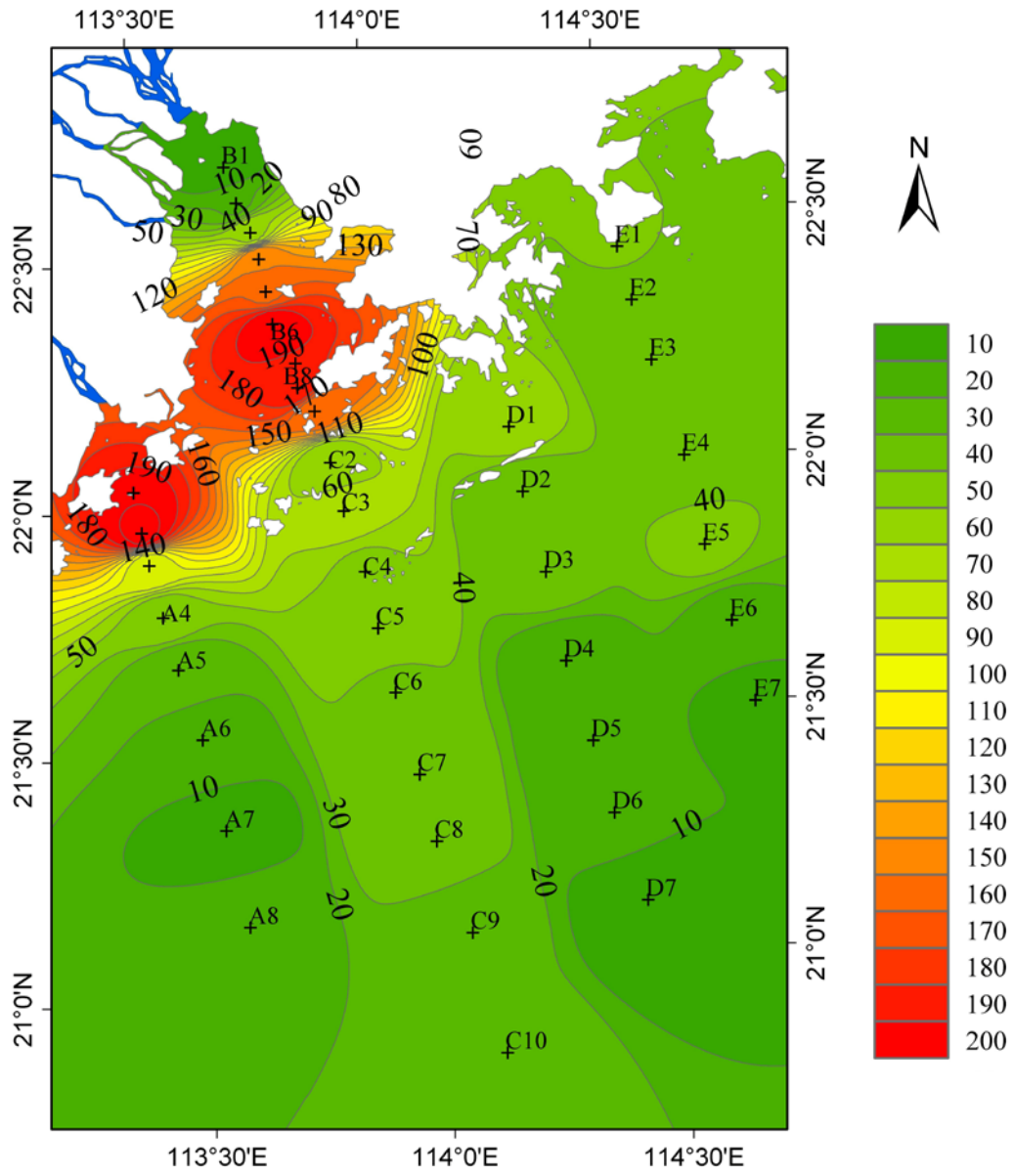


Fig. 2

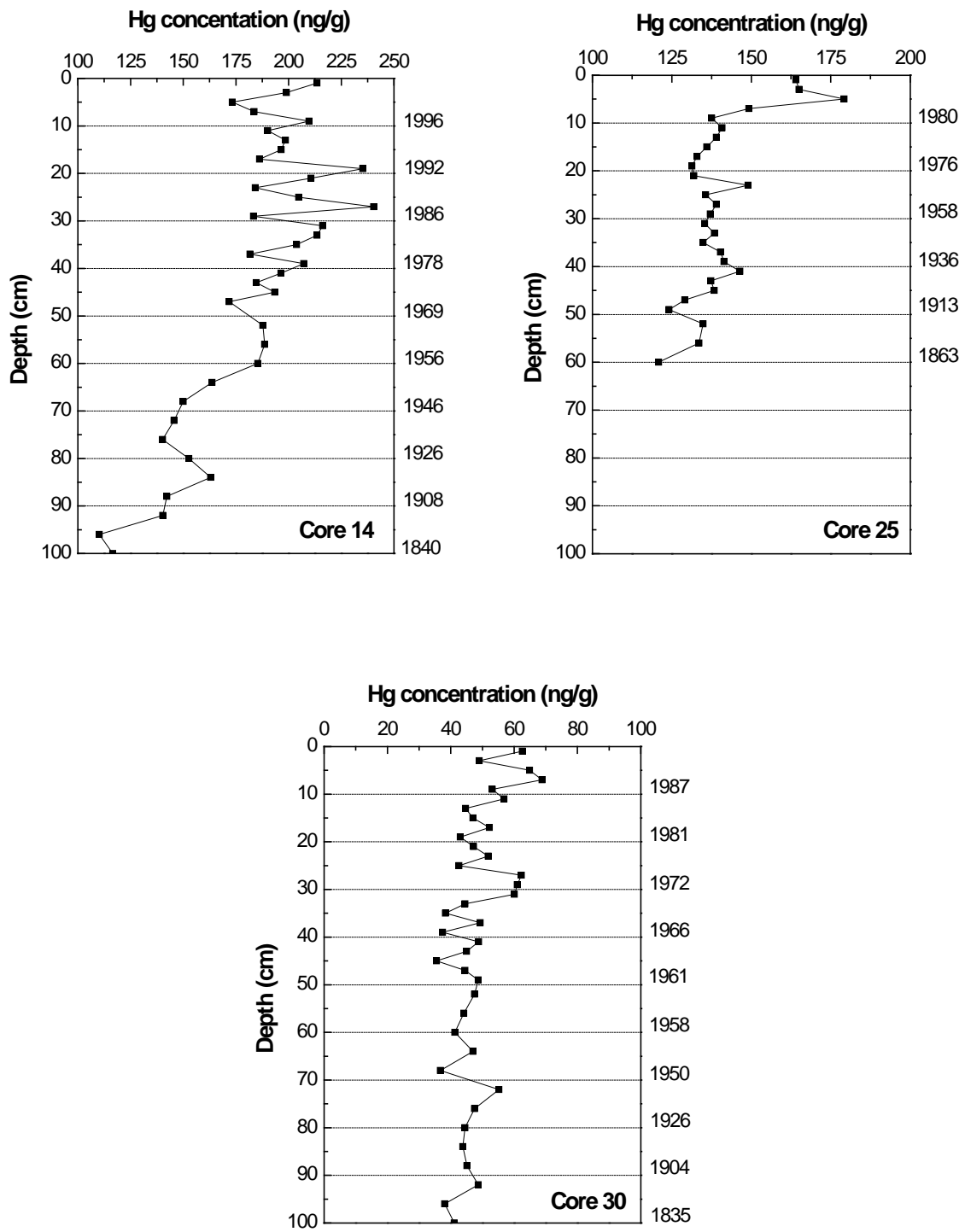


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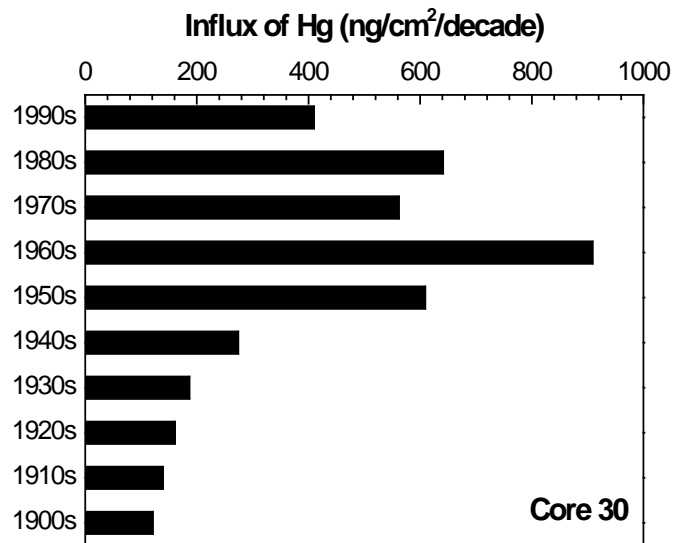
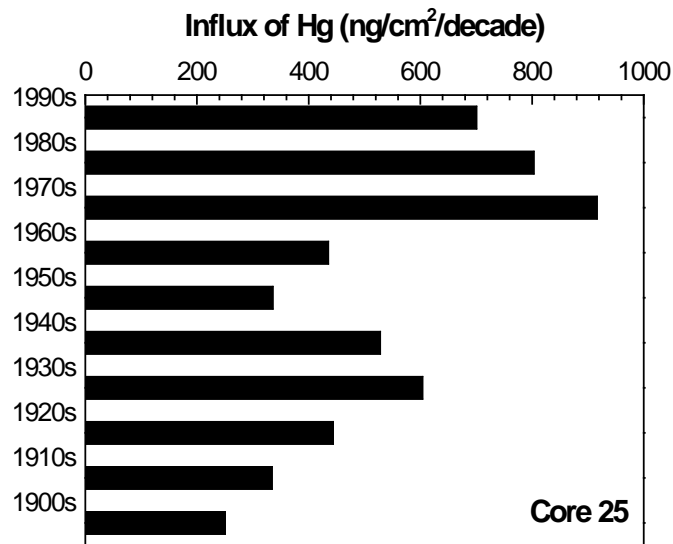
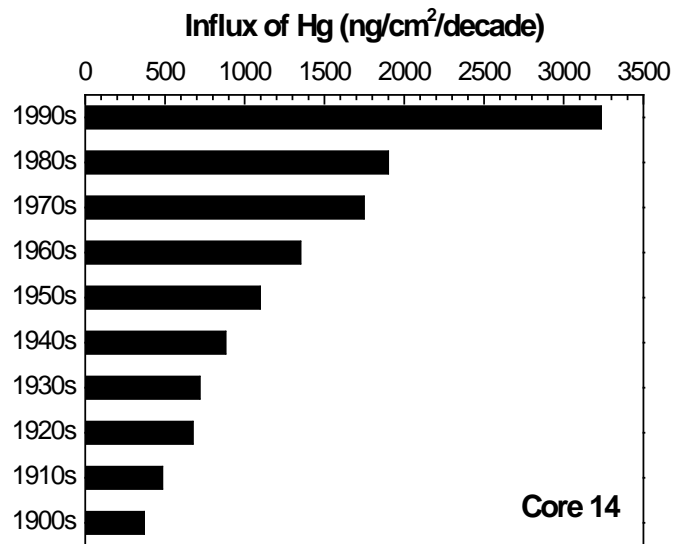


Fig. 4