

Distribution of Methyl Mercury in Sediments from Kyeonggi Bay, Namyang Bay, Chinhae Bay, and Lake Shihwa, Korea

KYU-TAE LEE, KURUNTHACHALAM KANNAN,¹ WON-JOON SHIM² AND CHUL-HWAN KOH*

Department of Oceanography, Seoul National University, Seoul 151-742, Korea

¹213 Food Safety and Toxicity Building, Michigan State University, East Lansing, MI 48824, USA

²Chemical Oceanography Division, Korean Ocean Research and Development Institute, Ansan P.O. Box 29, Seoul 425-600, Korea

To elucidate contamination levels and distribution of methyl mercury (Me-Hg) in Korean coastal areas, 126 sediment samples were collected from Kyeonggi Bay, Namyang Bay, Chinhae Bay, and Lake Shihwa during 1995–1996, and the Me-Hg concentrations were determined by cold vapor atomic fluorescence spectrometry (CVAFS). Contamination levels of Me-Hg in sediments from Kyeonggi Bay, Namyang Bay, Chinhae Bay, and Lake Shihwa were 274 ± 990 , 108 ± 24 , 294 ± 342 , and 1080 ± 760 pg/g, respectively. Concentrations of Me-Hg in sediments were significantly correlated with total organic carbon and sulfur contents, but were independent of mud contents and mean grain size. The highest concentration of Me-Hg (7100 pg/g) was observed at Incheon North Harbor (Site K19) in Kyeonggi Bay. This Me-Hg concentration was one or two orders of magnitude higher than those in other Kyeonggi Bay sediments were. The average concentration of Me-Hg in sediments from Lake Shihwa was higher than in those from other study areas. The three peaks of Me-Hg concentrations were observed on three sites (S5, S6, and S10) in Lake Shihwa and gradually decreased in distance-dependent manner around these sites. High concentrations of Me-Hg at surface and 10-cm sediment depth in Chinhae Bay may be due to higher rates of methylation process by active sulfate-reducing bacteria or higher concentrations of total mercury available to sulfate-reducing bacteria.

INTRODUCTION

Environmental methylation of inorganic mercury is a general process to produce methyl mercury (Me-Hg) in the water column and sediment (Berdicevsky *et al.*, 1979; Gilmour *et al.*, 1992). A large assortment of microorganisms is capable of converting inorganic mercury to Me-Hg. The methylation process is stimulated by microbial growth rate, the amount of available inorganic mercury, organic carbon content, sulfide content and others (Craig and Moreton, 1983; Choi and Bartha, 1994). Occurrence of toxic Me-Hg in sediment is of an environmental concern because Me-Hg compounds are uptaken by benthic organisms and accumulated in their tissues (Palmer and Presley, 1993). Therefore, it is important to monitor Me-Hg concentration for the hazard assessment of benthic environment since Me-Hg accumulation may result in adverse biological effects through tropic transfer, even though Me-Hg contamination level is low. Due to the analytical limitation, detection of Me-Hg as low

as sub-nano level in sediment has been hampered; however, cold vapor atomic fluorescence spectrometry (CVAFS) enabled us to elucidate the distribution of Me-Hg in sub-nano level. The present work describes the distribution of Me-Hg in sediments from the Korean coastal areas and evaluates the degree of Me-Hg contamination. This study is the first report on the occurrence of Me-Hg in sediments from the Korean coastal zones.

MATERIALS AND METHODS

Survey areas

The sediment samples were collected from Kyeonggi Bay, Namyang Bay, Chinhae Bay, and Lake Shihwa, west and south coasts of Korea (Fig. 1). Kyeonggi Bay receives large amounts of municipal sewage and waste from Seoul and nearby areas through the Han River, one of the largest river systems in Korea. Seoul is the capital city of which the inhabitants amount to over 10 million. Many

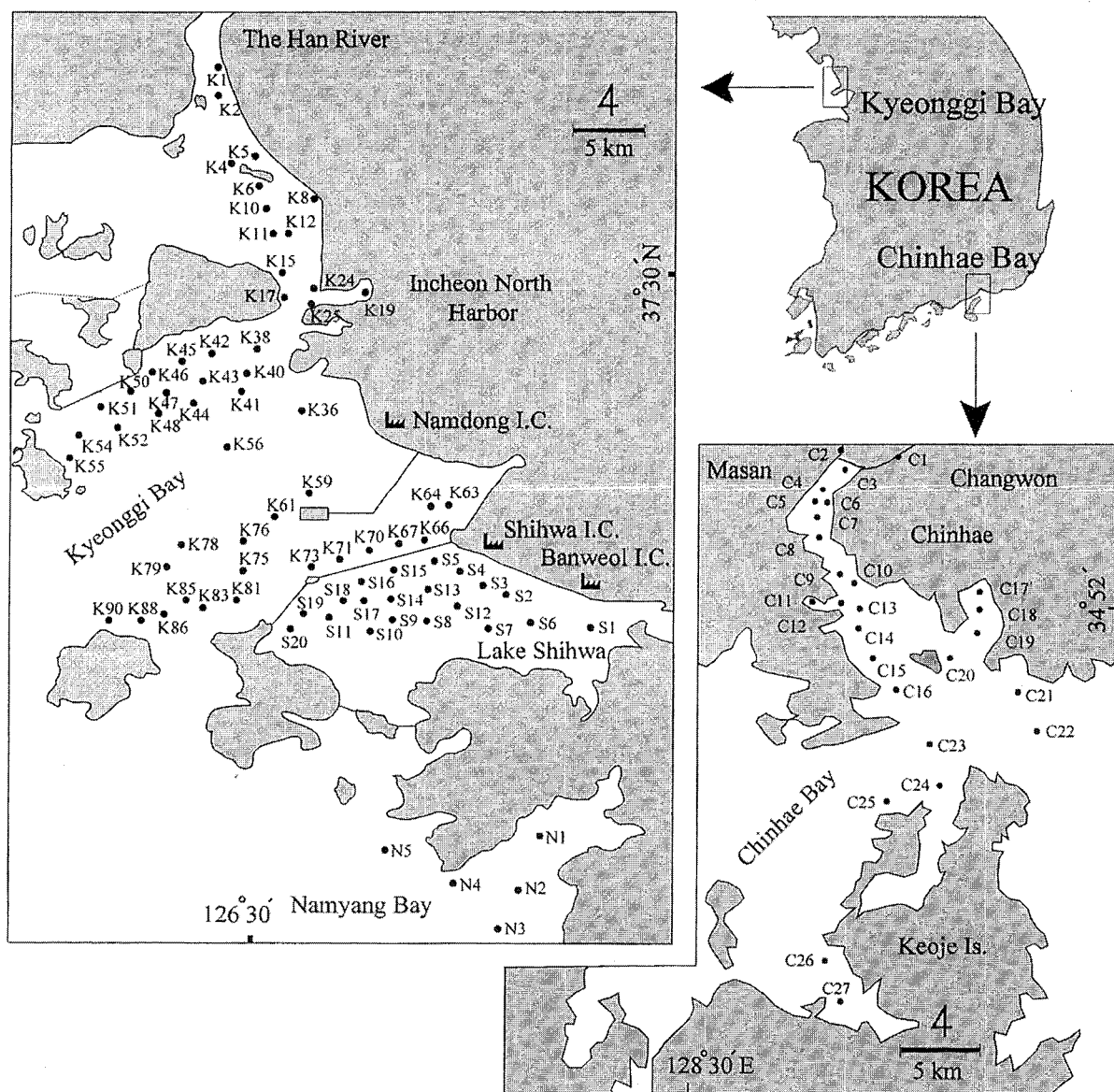


Fig. 1. Map of sampling locations. I.C.=industrial complex.

factories in the vicinity of Incheon North Harbor have distributed pollutants into Kyeonggi Bay since the early period of industrialization in Korea. Intense shipping activities are also common in this region. Additionally, Kyeonggi Bay receives anthropogenic contaminants from Shihwa and Banweol industrial complexes. Chinhae Bay, south coast of Korea, is surrounded by many industrial complexes that discharge a lot of contaminants. Lake Shihwa, which was produced by the 12-km long dike construction in 1994, receives industrial wastes and municipal sewage from neighboring industrial complexes. On the other hand, Namyang Bay remains natural and relatively free of industry.

Sample collection

By using van Veen grab sampler of 0.1 m², a total of 107 surface sediment samples were collected from Chinhae Bay (n=27) in January 1995, Kyeonggi Bay (n=50) in December 1995, Namyang Bay (n=5) in February 1996, and Lake Shihwa (n=25) in February 1996. The top 1–3 cm of surface sediments was taken with metal spoon. Additionally, sediment core samples were retrieved at Sites C6 and C13 in Chinhae Bay. The cores were sliced from top to 20-cm at 2-cm interval. Sediment samples were frozen below –20°C for the Me-Hg analysis. Separate samples were also taken for

determining grain size distribution and total organic carbon and sulfur contents.

Chemical analysis

Sediments from Kyeonggi Bay, Namyang Bay, and Chinhae Bay were air-dried prior to chemical analysis whereas those from Lake Shihwa were analyzed in wet phase. Grain size distribution was determined by dry- and wet-sieving method (Galehouse, 1971; Ingram, 1971). Total organic carbon and total sulfur contents were measured by using CHNS analyzer (CHNS-962, LECO). All concentrations were calculated on pg/g dry wt. basis.

All the processes for low-level Me-Hg determination were performed under extremely clean conditions. PTFE vials were heated in concentrated HNO₃ and thoroughly rinsed with tap water prior to use. The contamination by mercury in tap water was negligible. The residues of Me-Hg in sediments were determined following the method described by Liang *et al.* (1994). An aliquot (2 g wet wt. or 1 g dry wt.) of homogenized sediment was weighed into a 30-ml PTFE vial, followed by the addition of 5-ml tap water, 0.2 ml of 20% KCl, and 0.5 ml of 8M H₂SO₄. The mixture was diluted to 10 ml and distilled at a rate of 7 ml/hr under an argon flow of 60 ml/min rate and heating block temperature of 145°C. The distillate was collected in a 30-ml PTFE vial that was kept in an ice-cooled water bath. Prior to distillation, 5 ml of tap water was placed in the collection vial.

An aliquot of the distillate was added to tap water of 100 ml in a 250-ml reaction (ethylation) flask. The sample was buffered to pH 4.9 with 2M acetic acid-sodium acetate solution, and then 50 µl of 1% aqueous sodium tetraethylborate solution was added. The flask was immediately closed and connected to collection trap (Tenax) on one end and argon on the other. The mixture was allowed to react for 15 min without bubbling. The ethylation reaction resulted in the formation of ethylmethyl mercury from reactive Me-Hg. After the reaction, the solution was purged for 12 min at a flow-rate of 250 ml/min with Hg-free, high-purity argon. The outflowing gas stream was passed through a 100-mg Tenax trap (20/35 mesh; Alltech Associates Inc., IL, USA), which adsorbed the organomercury species. After the sample was purged, dry argon was flushed through the Tenax trap for 5 min for the removal of traces of condensed water vapor, which cause a strong inter-

Table 1. Interlaboratory comparison of results of Me-Hg determination for certified reference material

Reference material	Me-Hg conc. (ng/g)			⁵ Total Hg conc. (µg/g)
	² Lab. 1	³ Lab. 2	⁴ Lab. 3	
¹ PACS-1	8.47±0.63 n=8	7.99±0.42 n=3	8.00±0.66 n=6	4.57±0.16

¹Certified reference material (harbor marine sediment) from National Research Council Canada.

²Brooks Rand, Seattle, WA, USA; distillation, followed by aqueous phase ethylation, GC separation, and CVAF detection method. From Horvat *et al.* (1993).

³Academy of Natural Sciences, Benedict, MD, USA; alkaline digestion, followed by aqueous phase ethylation, GC separation, and CVAF detection method. From Horvat *et al.* (1993).

⁴Skidaway Institute of Oceanography, Savannah, GA, USA (present study); distillation, followed by aqueous phase ethylation, GC separation, and CVAF detection method.

⁵Certified value ±95% confidence limit.

ference during chromatographic elution and atomic fluorescence detection.

The mercury species on the Tenax trap was released by thermal desorption into an isothermal gas chromatography column that is a 60-cm-long, U-shaped, salinized glass column filled with 15% OV-3 Chromosorb W, acid washed and dimethyldichlorosaline treated at 100°C. Under a flow of argon, the eluted mercury species was converted at 900°C into elemental Hg by thermal decomposition and then detected by CVAFS (Model 2500, Tekran Inc., Ontario, Canada). The output from the detector was quantified using an integrator (Model HP3394A, PA, USA). Me-Hg concentration was quantified by comparing peak areas of standards with those of samples.

Quality control

Analytical quality control was performed by routine analysis of certified reference material (CRM), *e.g.* PACS-1, harbor marine sediment which is certified for total Hg. Procedural blanks ran in each set of sample analysis. The instrumental detection limit, three times greater than the instrumental noise, was about 1 pg. Interlaboratory comparison of the recovery results of Me-Hg for the same commercial CRM is summarized in Table 1.

RESULTS AND DISCUSSION

Environmental parameters affecting Me-Hg distribution

In total mercury distribution in watershed/runoff

Table 2. Relationships between Me-Hg concentrations and environmental parameters

	Mud (%)	Mz (ϕ)	TOC (%)	TS (%)
Me-Hg (pg/g)	$r^2=0.04$ $p>0.05$ $n=39$	$r^2=0.04$ $p>0.05$ $n=38$	$r^2=0.43$ $p<0.05$ $n=77$	$r^2=0.19$ $p<0.05$ $n=55$
Mud (%)		$r^2=0.82$ $p<0.05$ $n=38$	$r^2=0.18$ $p<0.05$ $n=24$	$r^2=0.19$ $p<0.05$ $n=24$
Mz (ϕ)			$r^2=0.23$ $p<0.05$ $n=23$	$r^2=0.43$ $p<0.05$ $n=23$
TOC (%)				$r^2=0.49$ $p<0.05$ $n=55$

waters and soils, published data showed that the contents of mercury and organic carbon in soil were closely related (Aastrup *et al.*, 1991; Lee and Iverfeldt, 1991; Hurley *et al.*, 1995). The relationship between methyl mercury and environmental parameters in sediments with sub-nanogram Me-Hg concentrations has been scarcely studied. We investigated the relationship between Me-Hg concentrations and environmental parameters such as total organic carbon content, total sulfur content, mud content, and mean grain size to evaluate the most influencing environmental factors on methyl mercury distribution in marine sediments (Table 2). Concentrations of Me-Hg in sediments were significantly correlated with total organic carbon contents and total sulfur contents but were independent of mud contents and mean grain size. Total organic carbon contents in sediments explained 43% of Me-Hg distribution. Total sulfur contents in sediments showed significant correlation with Me-Hg concentrations but explained only 19% of Me-Hg distribution. It has been reported that distribution of Me-Hg was affected by total mercury concentrations, organic carbon contents, and sulfide concentrations in sediments (Choi and Bartha, 1994). Other major factors influencing Me-Hg distribution such as sulfate concentration and microbial activity *in situ* should be investigated in future study.

Distribution of Me-Hg in sediments

Contamination levels of Me-Hg in sediments from Kyeonggi Bay, Namyang Bay, Chinhae Bay, and Lake Shihwa are summarized in Table 3. The average concentrations in each area were 274, 108,

294, and 1080 pg/g, respectively. The lowest contamination level was observed in the Namyang Bay sediment.

In Kyeonggi Bay, the highest concentration of Me-Hg was measured 7100 pg/g at Site K19, innermost part of Incheon North Harbor. Concentration of Me-Hg was sharply declined to about 300 pg/g in the middle part of the harbor and decreased further below 100 pg/g off the harbor. From the same sediment sample at Site K19, Lee *et al.* (1997a, 1997b) reported large amounts of organic compounds like polychlorinated biphenyls (PCBs; 330 ng/g), dichlorodiphenyltrichloroethanes (DDTs; 32 ng/g), and chlordanes (66 ng/g). Incheon North Harbor was the most contaminated region in Kyeonggi Bay in respect of the contamination levels of Me-Hg and organochlorine compounds. This region was designated as a potential area of adverse biological effect by the study of equilibrium partitioning approach in terms of PCBs contamination (Lee *et al.*, 1997c).

The average contamination level of Me-Hg in Lake Shihwa was relatively higher than those in other study areas. The average of Me-Hg concentrations in August 1996 were similar to that in February 1996 though there were 2–3 times differences in Me-Hg concentrations between sites. Distribution of Me-Hg in surface sediments is illustrated with concentration contours in Fig. 2. The three peaks of Me-Hg concentrations were observed on three sites (S5, S6, and S10) in Shihwa Lake and gradually decreased in distance-dependent manner around these sites. Site S5 was near to Shihwa industrial complex, implying that the industrial complex might have affected Me-Hg contamination. Concentration of Me-Hg as much as 2200 pg/g at Site S5 was decreased to 1200 pg/g at Site S13, around 300 pg/g at Sites S4 and S15, and finally to 60 pg/g at Site S16. Another site (S6) with high concentration was located near Banweol industrial complex, indicating that the industrial complex may have affected high Me-Hg residues in the adjacent areas. Concentration of Me-Hg was 1970 pg/g at Site S6, and decreased to 1830 pg/g at Site S7 and 52.9 pg/g at Site S12. The third site (S10) was observed at mid-western part of the lake, where no explicit mercury contamination source was present. Me-Hg concentration was found 2250 pg/g at Site S10, about 1700 pg/g at Sites S17 and S18, 958 pg/g at Site S9, about 500 pg/g at Sites S8 and S14, 173 pg/g at Site S11, and finally 62.7 pg/g at Site S16.

Table 3. Me-Hg concentrations (pg/g dry wt.) in surface sediments from Kyeonggi Bay, Namyang Bay, Chinhae Bay, and Lake Shihwa

Site	Me-Hg conc.	TOC (%)	Sampling date (yr/mon)	Site	Me-Hg conc.	TOC (%)	Sampling date (yr/mon)
<i>Lake Shihwa</i>				K46	35.7	0.143	95/12
S1	1910	0.824	96/08	K47	259	0.199	95/12
S2	1160	1.08	96/08	K48	13.9		95/12
S3	571	0.660	96/08	K50	45.6	0.272	95/12
S4	367	0.420	96/08	K51	63.5	0.419	95/12
S5	2200	1.09	96/08	K52	263		95/12
S6	1970	0.880	96/08	K54	222		95/12
S7	1830	0.782	96/08	K55	81.8		95/12
S8	479	0.379	96/08	K56	59.2	0.436	95/12
S9	958	1.42	96/08	K59	40.0	0.147	95/12
S10	2250	0.629	96/08	K61	41.1	0.196	95/12
S11	173	0.196	96/08	K63	120		95/12
S12	52.9	0.282	96/08	K64	56.1	0.241	95/12
S13	1200	0.708	96/08	K66	88.8		95/12
S14	580	0.696	96/08	K67	90.1		95/12
S15	313	0.286	96/08	K70	224		95/12
S16	62.7	0.215	96/08	K71	167		95/12
S17	1580	1.12	96/08	K73	386		95/12
S18	1900	1.19	96/08	K75	139		95/12
S19	555	0.649	96/08	K76	134	0.44	95/12
S20	1460	0.798	96/08	K78	56.6		95/12
Average	1080		96/08	K79	36.9	0.23	95/12
S2	1570	1.31	96/02	K81	96.5		95/12
S11	300	0.561	96/02	K83	50.9		95/12
S13	1360		96/02	K85	271	0.50	95/12
S15	822		96/02	K86	20.1		95/12
S17	928	1.11	96/02	K88	53.4	0.31	95/12
Average	996			K90	262		95/12
				Average	274		
<i>Namyang Bay</i>				<i>Chinhae Bay</i>			
N1	94.2	0.467	96/02	C1	176		95/01
N2	121	0.428	96/02	C2	1690		95/01
N3	142	0.479	96/02	C3	255		95/01
N4	104		96/02	C4	215		95/01
N5	80.6		96/02	C5	172		95/01
Average	108			C6	1060		95/01
				C7	94.9		95/01
<i>Kyeonggi Bay</i>				C8	131		95/01
K1	386	0.259	95/12	C9	150		95/01
K2	119	0.296	95/12	C10	255		95/01
K4	178	0.494	95/12	C11	183		95/01
K5	202	0.346	95/12	C12	128		95/01
K6	160		95/12	C13	67		95/01
K8	290	0.399	95/12	C14	128		95/01
K10	238		95/12	C15	105		95/01
K11	242	0.421	95/12	C16	265		95/01
K12	133		95/12	C17	369		95/01
K15	204		95/12	C18	198		95/01
K17	115		95/12	C19	292		95/01
K19	7100	1.54	95/12	C20	597		95/01
K24	287	0.487	95/12	C21	164		95/01
K25	339	0.620	95/12	C22	276		95/01
K36	31.4	0.201	95/12	C23	157		95/01
K38	80.5	0.284	95/12	C24	140		95/01
K40	66.5		95/12	C25	393		95/01
K41	20.1	0.654	95/12	C26	122		95/01
K42	47.5	0.252	95/12	C27	144		95/01
K43	52.1		95/12	Average	294		
K44	17.0	0.551	95/12				
K45	37.1	0.317	95/12				

Depth profiles of Me-Hg concentration from two sediment cores in Chinhae Bay are illustrated in Fig.

3. Me-Hg concentration at Site C6 was one order of magnitude higher than that at Site C13, indicating

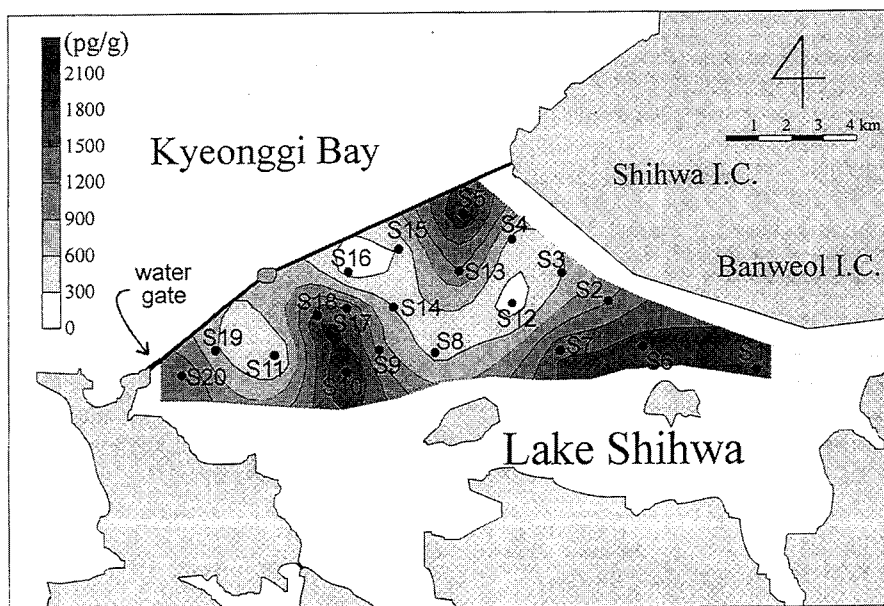


Fig. 2. Contour map of Me-Hg concentrations in sediments from Lake Shihwa. I.C.=industrial complex.

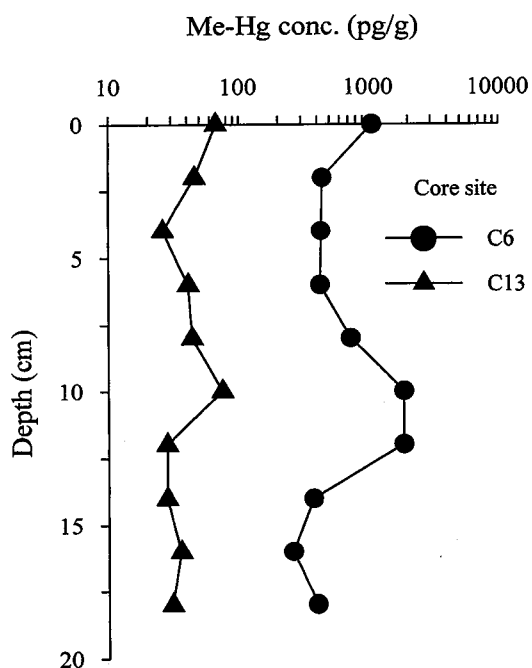


Fig. 3. Depth profiles of Me-Hg concentrations from Chinhae Bay sediments.

more serious Me-Hg contamination. Variation patterns of Me-Hg concentration profiles of the two cores were alike, indicating similar mercury exposure events or methylation processes at similar depths. Relatively high concentrations were measured at the surfaces and 10-cm depths. Compared to those of other sediment layers, Me-Hg concentrations around 10-cm depth were about 3–6 fold higher, while the concentrations at the top sediment layers

were 2–3 times higher. High concentrations of Me-Hg at surface and 10-cm depths may be due to higher rates of methylation process by active sulfate-reducing bacteria or higher concentrations of total mercury available to sulfate-reducing bacteria.

ACKNOWLEDGEMENTS

This work was supported by grants from the project "Methodologies for the quality assessment of benthic environment of Korean coastal waters; Code No. 96-941-2".

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Manuscript received June 13, 1998

Revision accepted August 18, 1998