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Concentrations and Distribution of Mercury and Other Heavy Metals in Surface Sediments of the Yatsushiro Sea including Minamata Bay, Japan

Haruhiko Nakata · Hideaki Shimada · Maki Yoshimoto · Rika Narumi · Kazumi Akimoto · Takayuki Yamashita · Tomoya Matsunaga · Keisuke Nishimura · Masakazu Tanaka · Kenju Hiraki · Hideyuki Shimasaki · Kiyoshi Takikawa

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Abstract The concentrations and distribution of heavy metals, such as mercury, zinc, copper, lead, and iron in surface sediments from 234 stations of the Yatsushiro Sea including Minamata bay were investigated. High concentrations of mercury were found in sediments from Minamata bay and its vicinity, but the levels decreased gradually with distance from the bay. The concentrations of mercury in sediments decreased gradually from south to north of the Yatsushiro Sea. These imply the lack of movement of mercury from Minamata bay to the northern Yatsushiro Sea. The geographical profiles of zinc and copper were contrary to that found for mercury, indicating the presence of natural and anthropogenic sources of copper and zinc in the northern Yatsushiro Sea.

Keywords Heavy metals · Mercury · Sediment · Minamata Bay and Yatsushiro Sea

H. Nakata (✉) · K. Nishimura · M. Tanaka · K. Hiraki
Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan
e-mail: nakata@sci.kumamoto-u.ac.jp

H. Shimada · M. Yoshimoto · R. Narumi
Faculty of Education, Kumamoto University, Kurokami 2-40-1, Kumamoto 860-8555, Japan

K. Akimoto · H. Shimasaki · K. Takikawa
Center for Marine Environmental Studies, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

T. Yamashita · T. Matsunaga
Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

It is well-known that Minamata bay located in the southeastern coast of the Yatsushiro Sea, western Japan, had been seriously contaminated by mercury discharged from the Chisso Corporation-Minamata factory for several decades. Inhabitants of Minamata city and its surrounding areas have suffered from exposure to mercury by consuming contaminated seafood from the Minamata bay; 2,265 residents were certified as Minamata disease patients by 2003 (http://www7.ocn.ne.jp/~mimuseum/). A great number of pathological, clinical and epidemiological studies have been conducted so far to understand the etiology and the extent of damage (Harada 1995; Ninomiya et al. 1995). In the late of 1950s, elevated concentrations of mercury were reported in fish, crustaceans, and shellfish from Minamata bay region (Kitamura et al. 1960).

It has also reported that mercury was highly accumulated in sediments of Minamata bay. The residue levels in Minamata bay sediments were in the range of several ten to several hundred μg/g (Irukayama et al. 1964). The highest mercury concentration was 2,010 μg/g (wet wt) in sediment collected from the outflow of the chemical plant (Kitamura et al. 1960). These results strongly suggested that a great amount of mercury had been discharged into Minamata bay, although the total outflow of mercury from this bay to the adjacent areas has not been known (Kudo et al. 2000). In 1977, mercury decontamination project was initiated in Minamata bay, and dredging of sediment was continued until 1990. As a result, mercury concentrations in sediments have dramatically decreased in Minamata bay, but there were suggestions that great amount of mercury have been dispersed from the bay into the Yatsushiro Sea over the past several decades.

Studies on the migration and distribution of mercury in Minamata bay as well as in the Yatsushiro Sea have been reported previously. Kudo et al. (1980) estimated that the amount of mercury moved from Minamata bay into the Yatsushiro Sea was 9 tonnes during 1960 and 1975 (0.6 tonnes/year), and 17 tonnes during 1975 and 1978 (5.7 tonnes/year). The dispersion rate of mercury from Minamata bay into the Yatsushiro Sea was very slow, only 110 m per year, and it was controlled by a sequence of re-suspension, horizontal diffusion, and re-deposition of sediment particle sorption of mercury (Kudo et al. 2000). Tomiyasu et al. (2000) examined mercury concentrations in sediment cores collected from 62 stations in the middle and southern Yatsushiro Sea. They suggested that the mercury-enriched sediment near Minamata bay is still being redistributed, which has caused the increase in the surface mercury concentration at a remote site from the bay. Rifardi et al. (1998) investigated the distribution pattern of mercury content in some layers of sediment cores from the South Yatsushiro Sea, and suggested that the sediment polluted with mercury was transported both northeastward and southward from the Minamata bay in the southern Yatsushiro Sea. Further, the pollutant-transport models, analyzing the mass-balance of mercury in Minamata bay and Yatsushiro Sea, estimated that the total outflow of mercury into the Yatsushiro Sea would be approximately 150 kg Hg per year (Rajar et al. 2004). However, most of these studies had examined either Minamata bay region or the southern part of the Yatsushiro Sea, and little information is available on mercury concentrations and distribution in throughout the sea including northern locations. In addition, previous investigations have focused only on mercury, and a few studies have been concerned with other heavy metals, such as zinc, copper and lead in the Yatsushiro Sea. It has been reported that high concentrations of Zn, Cu, Pb, Cr, and Mn were found in Minamata bay sediments (Suzuki and Takahashi 1983), implying the presence of significant sources of these metals in this bay.

The aim of this study was to examine the concentrations and geographical distribution of mercury, zinc, copper, lead, iron, and carbon content in sediments from throughout the entire Yatsushiro Sea. To achieve this goal, a comprehensive sampling had been conducted; we collected surface sediments in 234 stations from throughout the Yatsushiro Sea.

Materials and Methods

Two hundred and thirty-four surface sediments (<1.0 cm depth) were collected from the Yatsushiro Sea including Minamata bay during October and November, 2004. The sampling stations were accurately identified by using the GPS equipment, which was gridded at a resolution of 1 × 1 min between 32°8′ N–32°38′ N latitude and 130°11′ E–130°33′ E longitude. Details of the sampling stations are shown in Fig. 1. All sediments were taken by using a Honza-type Ekman-Birge grab sampler on the R/V of Kumamoto University, '*Dolphin II*'. The geological characteristics of the sediment samples analyzed in this study, such as mud contents and particle size, have been reported previously (Akimoto et al. 2005). All samples were sealed in polyethylene bags and then stored at −20°C until analysis.

The heavy metals, such as zinc, copper, lead and iron were analyzed according to the method described previously (Prudente et al. 1994) with some modifications. Briefly, sediment samples were dried in the oven at 35°C for overnight and passed through a 0.5 mm sieve in order to eliminate pebbles. Approximately, one gram of dried sediment was digested with a mixture of HNO_3 and $HClO_4$ in a 50-mL thick-walled glass flask. Concentrations of Cu, Zn, Pb and Fe were determined by flame atomic absorption spectrophotometry (AA-6400F, Shimadzu Co. Kyoto, Japan). Total mercury concentrations were determined by the oxygen-combustion-gold amalgamation method (Ohkawa et al. 1977) using an atomic absorption-mercury detector. The total organic carbon (TOC) in sediments was measured by an elemental analyzer (Yanaco, MT-3, Japan).

Quality assurance and quality control (QA/QC) of measures include analysis of standard reference material NIES No. 12 (marine sediment) from the National Institute for Environmental Studies, Japan. The average recoveries of Cu, Zn, Pb, Fe and Hg in triplicate analysis were 97 ± 1.6%, 102 ± 3.8%, 89 ± 8.8%, 101 ± 1.0%, and 91 ± 0.5%, respectively. The detection limits of heavy metals were in the range of several to several ten ng/g (dry wt). In this study, the Speaman's rank test and Wilcoxon *U*-test were used to examine the correlation and significant difference between two groups, respectively. The software of Excel Statistics Ver. 6.0 (Esumi, Tokyo, Japan) was used in this study.

Results and Discussion

Concentrations of heavy metals and organic carbon content in surface sediments from the Yatsushiro Sea as well as in Minamata bay are shown in Table 1. Iron was the most abundant metal analyzed in all samples, ranging from 1.7% to 13% (mean: 4.6%). Zinc, copper, lead and mercury were detected in sediments, with mean concentrations of 69, 13, 14, and 0.28 μg/g dry wt, respectively.

The highest concentration of mercury was found in a sample collected at St. 205 in Fukuro bay (3.37 μg/g dry wt) near Minamata bay (Fig. 2). Elevated concentrations of mercury were also found in sediments at Sts. 193 (1.73 μg/g), 195 (1.64 μg/g), and 206 (1.70 μg/g) around Minamata

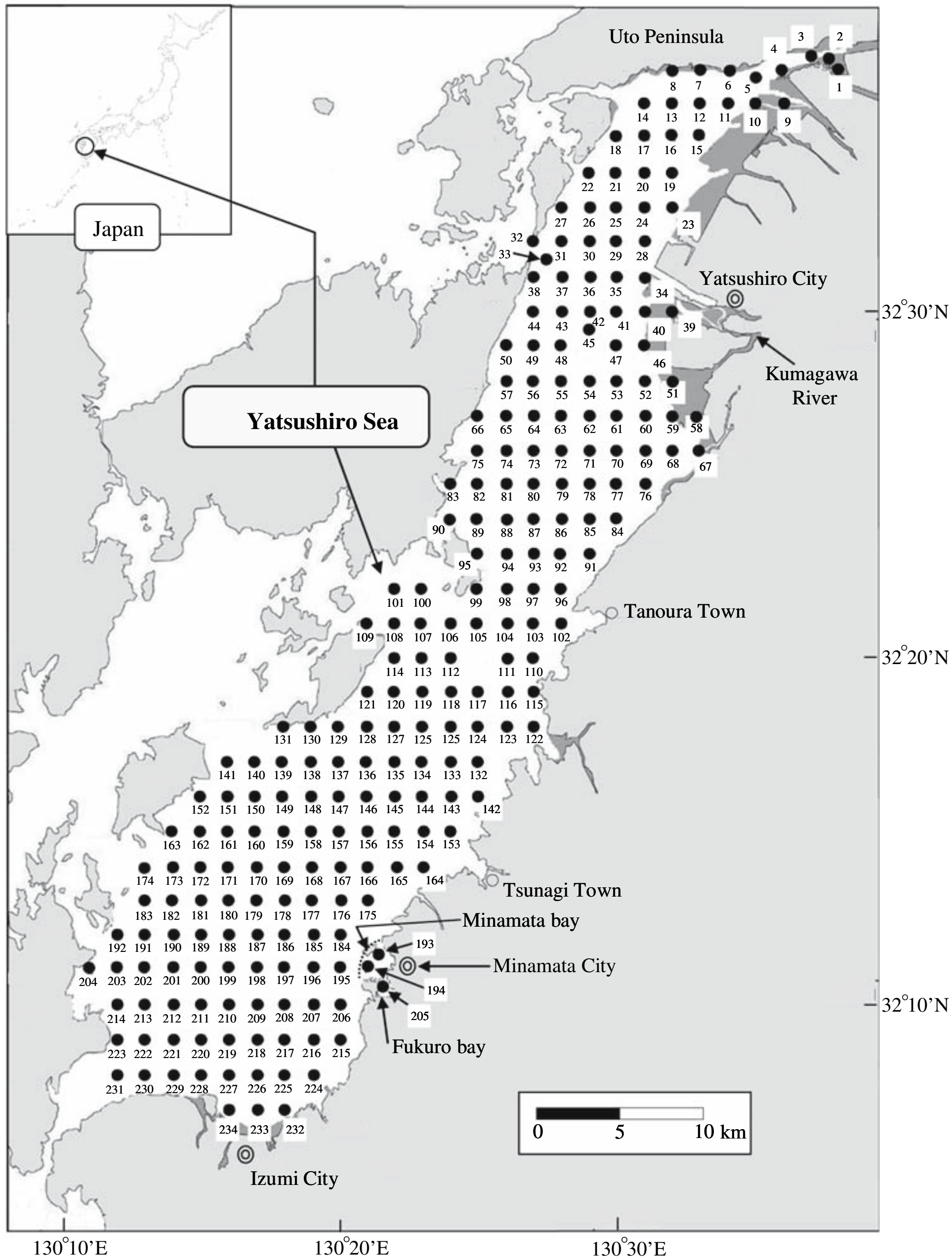


Fig. 1 Map showing the sampling stations of surface sediments in the Yatsushiro Sea, Japan

Table 1 Concentrations of heavy metals (μg/g dry wt) and carbon content (%) in surface sediments from the Yatsushiro Sea and Minamata bay region

	Hg	Zn	Cu	Pb	Fe*	Carbon*
Yatsushiro Sea (Numbers of samples)	232	226	234	200	200	234
Concentration±sd	0.28 ± 0.31***	69 ± 27	13 ± 6.5	14 ± 7.0	4.6 ± 1.6	2.6 ± 1.5
Range (min–max)	0.02–3.4	4.9–155	3.2–64	nd ~ 56	1.7–13	0.09–9.2
Minamata bay region (n = 4)**	4	4	4	4	4	4
Concentration ± sd	1.8 ± 1.2***	51 ± 46	14 ± 9.1	14 ± 4.4	5.1 ± 1.6	2.4 ± 0.43
Range (min–max)	0.49–3.4	4.9–110	3.7 ~ 25	10–19	3.6–7.0	2.0–3.0

*Concentration unit: %

**Samples were collected from Sts. 193, 194, 195, and 205 in Fig. 1

***Significantly different ($p < 0.001$)

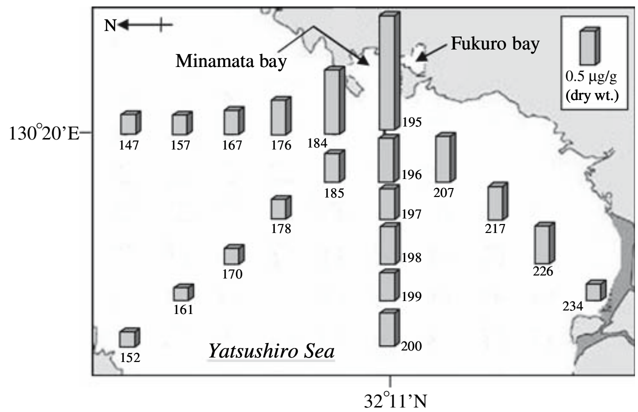


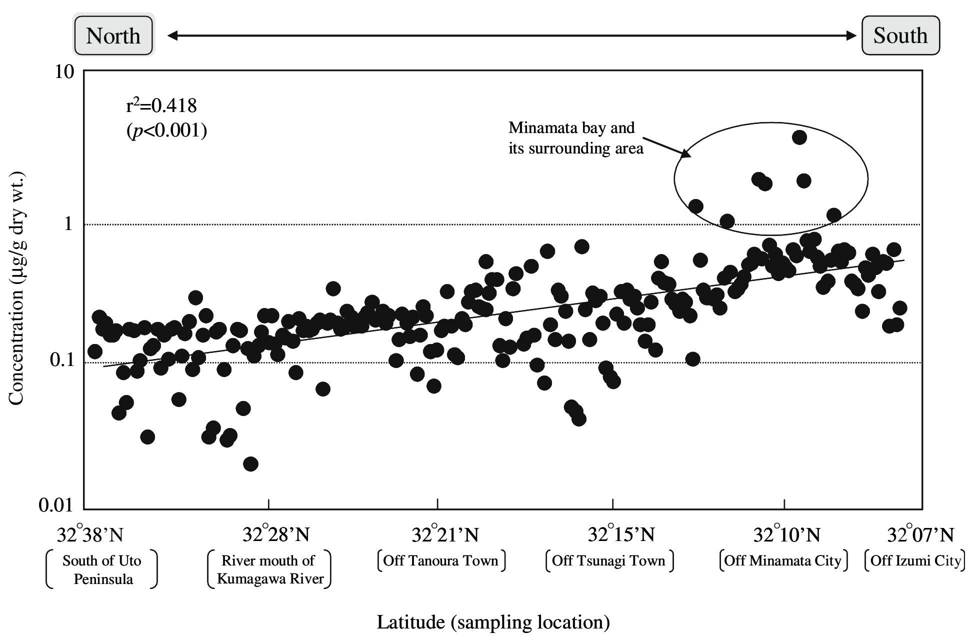
Fig. 2 Concentrations of mercury (μg/g dry wt) in surface sediments in the southern Yatsushiro Sea

bay. These levels of mercury were approximately 6 to 12-fold greater than the overall mean concentration determined in this study (0.28 μg/g), and also 27 to 57-fold higher than the background level in Yatsushiro Sea sediment (0.059 μg/g dry wt; Tomiyasu et al. 2006). In Minamata bay, mercury-contaminated sediment had been dredged and removed during 1977 and 1990, and mercury concentrations in sediments have dramatically decreased. However, the results suggest that mercury contamination exists until now in Minamata bay and its surrounding area. Recent studies have also reported high concentrations of mercury in surface and core sediments in Minamata bay region, at concentrations of several μg/g dry wt (Tomiyasu et al. 2006).

The concentrations of mercury in sediments decreased with distance from Minamata bay. As described earlier, the mercury concentration in St. 195 was 1.64 μg/g, whereas the levels at Sts. 184, 176, 167, 157, and 147, located north of the bay, decreased gradually to at the levels of 0.91, 0.49, 0.33, 0.28 and 0.28 μg/g, respectively (Fig. 2). The mercury concentrations at Sts. 152 and 234, located toward the northwest and southwest of Minamata bay, also decreased by one-seventh of the level found at St. 195. On the other hand, mercury concentrations in sediment at Sts. 196–200, located west of the bay, decreased, although the concentrations at St. 200 were only one-third of the concentration determined at St. 195 (Fig. 2). In addition, elevated concentrations of mercury (>0.4 μg/g dry wt) were found at Sts. 201–203, 204, 208, 208–211, 215, 216, 218, 219, 224, 227, 229, 230, and 232, located toward the west and south-southwest of Minamata bay. These observations imply that mercury has been mainly transported from Minamata bay to western and southwestern parts of the South Yatsushiro Sea. Rifardi et al. (1998) reported elevated concentrations of mercury in sediments from the southern Yatsushiro Sea, due to migration of mercury by tidal current in the sea. The vertical profile of mercury concentrations in sediment cores suggested that mercury-enriched sediment of Minamata Bay is still being transported to remote areas in the Yatsushiro Sea (Tomiyasu et al. 2000).

In order to understand the concentrations and distribution of mercury throughout the Yatsuhiro Sea, the relationship between the latitude of sampling locations (station numbers in Fig. 1) and mercury concentrations in sediments was investigated (Fig. 3). Interestingly, the correlation was significantly positive ($p < 0.001$), which indicates that the concentrations of mercury in sediments decreased from the

Fig. 3 Geographical distribution of mercury concentrations (μg/g dry wt) in surface sediments from the Yatsushiro Sea



south to north of the Yatsushiro Sea. Elevated mercury concentrations were identified in sediments in the Minamata bay region (Fig. 3), suggesting the presence of mercury source in this bay. On the other hand, the average mercury concentration in northern Yatsushiro Sea sediments (32°27′ N–32°38′ N; station numbers: 1–66; n = 66) was 0.13 ± 0.05 μg/g (dry wt), which value was approximately one order of magnitude lower than that in Minamata bay area. Further, mercury concentrations in sediments of the northern Yatsushiro Sea were apparently lower than those in Osaka bay (0.34 ng/g; Nagaoka et al. 2004), and comparable with those in other Japanese coastal waters, such as Sendai bay (0.12 ng/g; n = 5), Suruga bay (0.12 ng/g; n = 6), Toyama bay (0.11 ng/g; n = 3), Ise bay (0.15 ng/g; n = 5), and Seto-Inland Sea (0.11 ng/g; n = 6) (Japan Coast Guard 2005, http://www1.kaiho.mlit.go.jp/). The low concentrations of mercury in northern Yatsushiro Sea sediments may imply that mercury has not been migrated from Minamata bay to this area.

The temporal trend of mercury concentrations in surface sediments of the Yatsushiro Sea was examined by comparing the concentrations determined in this study with those reported previously (Kudo and Miyahara 1986; Kudo et al. 1998; Fig. 4). As described earlier, mercury residues in southern Yatsushiro Sea sediments were greater than those in middle and northern Yatsushiro Sea samples collected in 2004. However, the mercury concentrations in southern sediments, St. H, and I have decreased since the

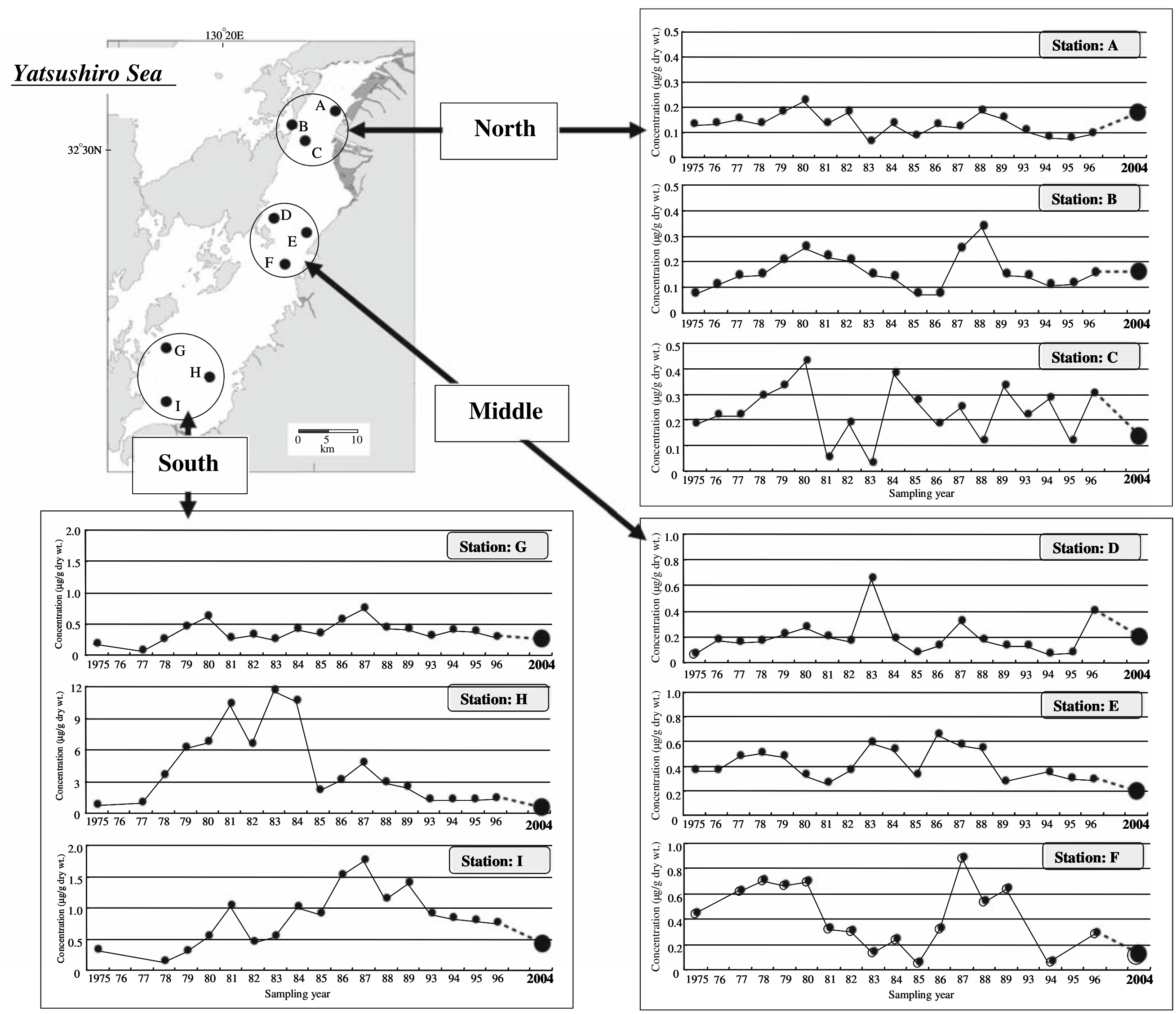


Fig. 4 Geographical and temporal variations of mercury concentrations (μg/g dry wt) in surface sediments from the northern, middle and southern Yatsushiro Sea. Information on Hg concentrations in sediment collected during 1977 and 1996 were cited from Kudo et al. (1998) and Kudo and Miyahara (1986)

late 1980s and the early 1990s. These results suggest that the migration of mercury from Minamata bay has declined after the dredging project was completed in 1990. It was shown that Minamata bay represents an insignificant source of mercury to the Yatsushiro Sea in recent years (Rajar et al. 2004). In the middle Yatsushiro Sea, mercury residues have also decreased in sediments at Sts. E and F during the past 20 years, but little variation in the concentrations was found at St. D. The mercury levels in northern Yatsushiro Sea sediments, Sts. A, B, and C, were generally low, ranging from 0.13 to 0.18 μg/g dry wt in 2004 (Fig. 4). Further, the mercury concentration in St. A has been consistent since the 1970s. Considering that the lower concentrations and less temporal variation of mercury concentrations in sediments from the northern Yatsushiro Sea, it could be concluded that mercury has not migrated from Minamata bay into the northern area of the sea.

It has been reported that the concentrations of heavy metals, in addition mercury, in Minamata bay sediments were extremely high before the dredging operation. The mean concentrations of zinc, copper, and lead in sediments from the northern part of Minamata bay in 1980 ($n = 7$) were 450 μg/g dry wt (range: 133–1,330 μg/g), 145 μg/g (43–382 μg/g), and 208 μg/g (40–459 μg/g), respectively (Suzuki and Takahashi 1983). This strongly suggests that Minamata bay was seriously contaminated by not only mercury but also zinc, copper, and lead in the past. In addition, elevated concentrations of Cd, Cr, and Mn were detected in sediments from Minamata bay in 1980, suggesting the occurrence of significant sources of these metals in this area (Suzuki and Takahashi 1983). In this study, the concentrations of zinc, copper, and lead in station 193 (Minamata bay) was 26.7 μg/g, 10.7 μg/g, and 10.6 μg/g, respectively, which is approximately one order of magnitude lower than the residue levels reported in 1980. This reduction may be due to the dredging of sediment in Minamata bay during the 1970s–1990. In contrast, the average concentrations of iron in sediments of Minamata bay in 1980 (3.5%; Suzuki and Takahashi 1983) were comparable with that obtained in this study (4.0%).

The spatial distribution of zinc, copper, lead, iron, and organic carbon in sediments was examined throughout the Yatsushiro Sea. Interestingly, the relationship between the latitude of sampling stations and Cu or Zn concentrations were negatively correlated. This indicates that the levels of zinc and copper in sediments increased gradually from southern to northern parts of the Yatsushiro Sea. This spatial pattern of copper and zinc was contrary to that of mercury, although these metals originated from a major source in Minamata bay. The differences in the distribution of these metals may be caused by the large amounts of natural and anthropogenic outflows of copper and zinc into the northern Yatsushiro Sea in recent years. The concentrations of copper and zinc found in sediments from southern part of Uto peninsula (Stations 1–7; Cu: 22 ± 3.0 μg/g, Zn: 109 ± 15 μg/g) were higher than the average values found in the Yatsushiro Sea (Table 1). On the contrary, the mean concentrations of zinc, copper, and lead in sediments in this study were lower than those reported for Tokyo Bay (Zn: 153 μg/g, Cu: 47 μg/g, Pb: 29 μg/g dry wt) and Osaka Bay (Zn: 222 μg/g, Cu: 51 μg/g, Pb: 43 μg/g dry wt; Japan Coast Guard 2005, http://www1.kaiho.mlit.go.jp/). These results suggest less significant contamination of these heavy metals in the Yatsushiro Sea, although their recent inputs may be presented in the northern part of the sea.

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