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Distribution and characteristics of methylmercury in surface sediment in Minamata Bay

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ABSTRACT

This study was carried out to evaluate the present-day chemical properties of methylmercury in surface sediment in Minamata Bay where a dredging project was completed 28 years ago. Present-day sediment from Minamata Bay consists of sandy silt, and the average loss-on-ignition in surface sediment was 7.0 ± 2.3%. The average methylmercury concentrations in the upper sediment layers were significantly higher than those in the lower sediment layers. Currently, the concentrations in sediments in Minamata Bay do not exceed the Japanese regulatory standard value for mercury. The average concentration of methylmercury in Minamata Bay surface sediment was 1.74 ± 1.0 ng/g on a dry weight basis ($n = 107$). The methylmercury concentration in Minamata Bay surface sediment was almost 16 times higher than that in surface sediment from Isahaya Bay surface sediment, which was 0.11 ± 0.045 ng/g on a dry weight basis ($n = 5$).

1. Introduction

Minamata Bay sediment was heavily contaminated by mercury (Hg) originating from wastewater discharged from the Chisso Corporation's chemical factory in Minamata city. Almost all of the Hg contamination was removed by the large-scale dredging project that was carried out from 1976 to 1990 (Environmental Health Department, Environmental Agency of Japan, 1999). Results of a survey carried out by Kumamoto Prefecture on Minamata Bay surface sediment in 1991 confirmed that the dredging was effective, and the remaining total mercury (total-Hg) concentration in the surface sediment was reported to be 4.1 mg/kg on a dry weight (d.w.) basis (Kumamoto Prefecture, 2010). Later, it was reported that the weighted average value of total-Hg concentration was 2.9 mg/kg d.w., and, when reinvestigated, Matsuyama et al. (2014) reported that the amount of mass-Hg in Minamata Bay was 3.4 t. This reinvestigation also showed that >95% of the total Hg discharged from the factory had been removed by dredging. Nevertheless, the total-Hg concentration of monitored fish in Minamata Bay (*Sebastiscus marmoratus*, Japanese stingfish, and *Pseudolabrus japonicas*, Bambooleaf wrasse) is thought to be higher than the same species caught in Tokyo Bay and other places. That is, the total-Hg concentrations in *S. marmoratus* and in *Pseudolabrus japonicus* in Minamata Bay were almost three and five times higher, respectively, than in other sea areas (Matsuyama et al., 2013). Although we still need to gain a better insight into this phenomenon, results of a fish cage experiment performed in Minamata Bay with high dissolved methylmercury (methyl-Hg) concentrations (Matsuyama et al., 2013) showed that the dissolved methyl-Hg in seawater did not move directly into fish bodies. Other researchers also reported that inorganic Hg taken into the fish body is not converted to methyl-Hg (Kikuchi et al., 1976; Nagashima et al., 1984). Therefore, it is thought that the increase in the total-Hg concentration in fish is not from Hg that is absorbed directly from seawater, but via the food web in the bay. As no rivers flow into Minamata Bay, it is thought that the sediment supplies Hg to the food web. Also, >90% of the mercury in marine fish muscle is methyl-Hg (Hight and Cheng, 2006). To obtain a better understanding of why fish in Minamata Bay have high total-Hg concentrations in comparison with fish in other sea areas, the methyl-Hg concentration in Minamata Bay sediment, as well as the total-Hg concentration, should be thoroughly investigated as sediment may be an important source of methyl-Hg. Therefore, first, to demonstrate the status of methyl-Hg in the Minamata Bay sediments, we have presented the current distribution of methyl-Hg concentrations in Minamata Bay surface sediment graphically in this contribution. We compared the average concentration of methyl-Hg in Minamata Bay surface sediment with the average methyl-Hg concentrations in surface sediments from Isahaya Bay and from

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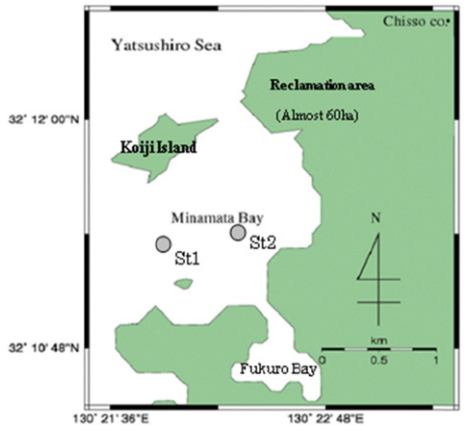

Fig. 1. Surface sediment sampling sites in Minamata Bay (St1, St2).

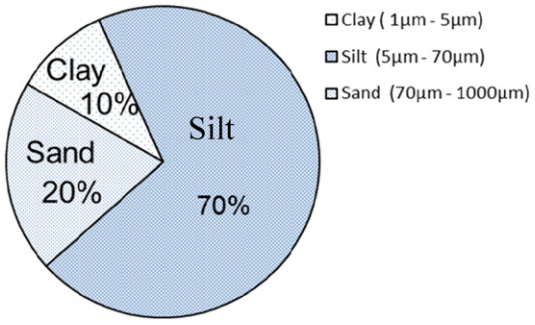

Fig. 3. Grain size distribution pattern in surface sediments of Minamata Bay (0–5 cm).

the Yatsushiro Sea. We also investigated seasonal variations in Hg concentrations in surface sediments from Minamata Bay.

2. Materials and methods

2.1. Survey locations and sediment sampling

To obtain the average methyl-Hg concentration in Minamata Bay surface sediment, we used an approach similar to that described by Matsuyama et al. (2014). Seasonal variations in Hg concentrations in the sediment were examined in samples collected from two locations (Fig. 1). To compare Hg concentrations in Minamata Bay surface sediments, five samples were collected from the bottom of Isahaya Bay (Fig. 2).

2.2. Sediment sample collection

2.2.1. Minamata Bay

We used surface sediment samples collected in Minamata Bay ($n = 107$) in a previous study (Matsuyama et al., 2014) to determine the average methyl-Hg concentration in Minamata Bay surface sediments. We also collected core sediment samples to investigate seasonal variations in methyl-Hg concentrations using the sampling method that was used in our earlier study (Matsuyama et al., 2014). We travelled in a fishing vessel to two sampling points identified by GPS (Fig. 1). We collected samples over a period of 1.5 years, from June 2013 to October 2014. The sediment was extracted every month at maximum ebb tide using a gravity core sampler. After sampling, and to avoid oxidation by atmospheric oxygen, the samples were kept in a vinyl bag that was evacuated with a small hand pump. The evacuated vinyl bags were cooled with ice bricks in a cooling box and transported to the laboratory within 60 min. Samples for analysis were removed from a depth of 15 cm below the surface of the core samples (30 ± 10 cm [$n = 28$] average length). After cutting, these sediment samples were stored in an ultra-freezer (−80 °C).

2.2.2. Isahaya Bay

The method used to collect surface sediments was almost the same as that used in Minamata Bay. However, we only used an Ekman-Birge-grab (Type 5141, Rigosha Co. Ltd., Tokyo, Japan) to collect the samples in Isahaya Bay. We travelled to the sampling sites that were identified by GPS in a fishing vessel (Fig. 2). After sampling, and to avoid oxidation by atmospheric oxygen, the samples were kept in a vinyl bag that was evacuated with a small hand pump. The evacuated vinyl bags were cooled with bricks of ice in a cooling box and transported from Isahaya Bay to our institute. The sediment samples were collected in Isahaya Bay in mid-July 2015.

2.3. Determination of Hg concentration in sediment

2.3.1. Pretreatment of sediment

After defrosting the samples at room temperature, small stones and small broken shellfish were removed by hand. Pretreatment involved mixing the sample using the quarter-mixing-method based on the soil chemistry to obtain a homogeneous sample. Samples were then analyzed for their Hg concentrations and chemical properties without drying.

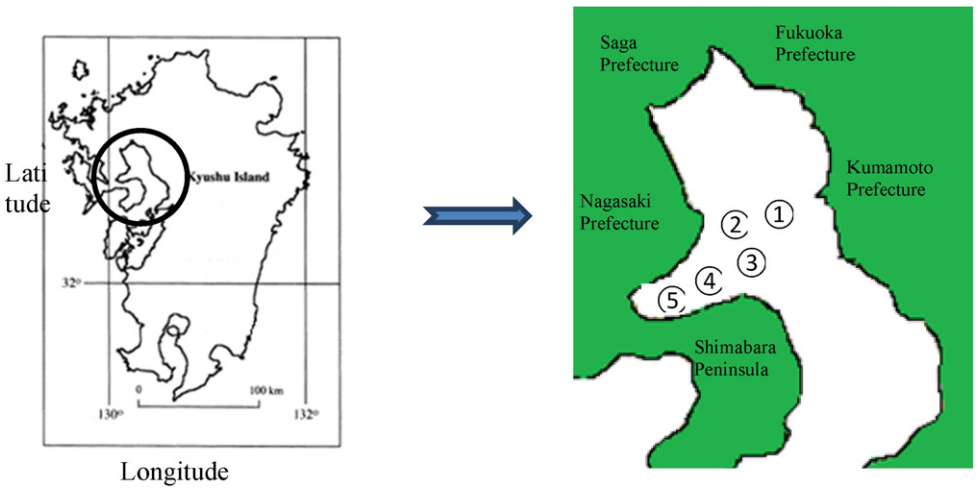

Fig. 2. Surface sediment sampling sites in Isahaya Bay (St1–St5).