ARTICLE IN PRESS

Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

# Chemical characteristics of dissolved mercury in the pore water of Minamata Bay sediments

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## ARTICLE INFO

*Keywords:*
Minamata Bay
Methyl-Hg
Total-Hg
Pore water
Partition coefficient Log Kd

## ABSTRACT

Methylmercury concentrations in fish from the historically polluted Minamata Bay remain higher than in fish from other coastal seas around Japan. To obtain a better understanding of this phenomenon, the chemical characteristics of pore water from Minamata Bay sediments were investigated. Samples were taken from two stations over a 1-year period. Total average values in the pore water at the two stations for dissolved total mercury and methylmercury concentrations were 6.64 ± 4.93 and 2.69 ± 2.07 ng/l, respectively. The pore water was centrifuged at 1000 rpm to 3000 rpm. The highest ratio of dissolved methylmercury to dissolved total mercury exceeded 60% for pore water centrifuged at 3000 rpm. Furthermore, because total average values of Log Kd of total mercury and methylmercury in sediment (St1 and St2) were 5.42 and 2.32 (L $kg^{-1}$), methylmercury in Minamata Bay sediment is more eluted than other mercury species.

## 1. Introduction

Minamata disease was discovered at Minamata Bay, Kumamoto Prefecture, in 1956. At that time, Minamata Bay had been polluted by mercury, which had caused severe mercury poisoning. The neurological issues associated with severe mercury poisoning were first identified at Minamata Bay and were subsequently referred to as Minamata disease. Humans and other mammals were poisoned by eating fish and shellfish containing mercury. The source of the mercury was industrial wastewater discharged from Chisso Corporation's chemical factory (Environmental Health Department, Ministry of the Environment, 1999). To remediate the mercury pollution in Minamata Bay, a large dredging project was performed between 1976 and 1990 (Environmental Health Department, Environmental Agency of Japan, 1999). Twenty-six years have elapsed since the completion of the dredging project. However, it has been observed that the edible muscle of fish from Minamata Bay contains total mercury (total-Hg) concentrations exceeding 1 ppm (Kindaichi and Matsuyama, 2005). In Japan, the regulatory limits for mercury for fish and shellfish are 0.4 ppm total-Hg and 0.3 ppm methylmercury (methyl-Hg). To be classified as a mercury-polluted fish or shellfish, both regulatory limits must be exceeded. Based on the results of a 2004 survey of Minamata Bay fish and shellfish, Kumamoto Prefecture (2005) reported an average measurement in excess of the regulatory limits for total-Hg concentrations in edible fish muscle. Matsuyama et al. (2013) reported that average values of total-Hg concentrations in the edible muscle of fish caught in Minamata Bay were several times higher than concentrations in the same fish species caught elsewhere, despite not exceeding the regulatory limits for fish and shellfish in Japan. Matsuyama et al. (2011) studied the seasonal variations of dissolved mercury (diss-Hg) concentrations in vertical layers (0 m, 6 m, 10 m, 15 m, and 20 m) in three monitoring stations in Minamata Bay. Their results revealed that the average annual values of dissolved total-Hg (diss-total-Hg) and dissolved methyl-Hg (diss-methyl-Hg) concentrations were 0.43 ± 0.14 ng/l, 0.10 ± 0.06 ng/l, respectively. To elucidate the above results in terms of Hg found in seawater and Hg migration characteristics in fish, Matsuyama et al. (2013) carried out fish cage experiments using young red sea bream over a two-year period at two locations where there are clear dissolved mercury concentration differences (Minamata Bay in Kumamoto Prefecture, and Nagashima in

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http://dx.doi.org/10.1016/j.marpolbul.2017.10.021
Received 3 May 2017; Received in revised form 6 October 2017; Accepted 7 October 2017

Please cite this article as: Matsuyama, A., Marine Pollution Bulletin (2017), http://dx.doi.org/10.1016/j.marpolbul.2017.10.021

Kagoshima Prefecture as a control). Total-Hg and methyl-Hg concentrations were 0.0008 and 0.0006 mg/kg dry weight, respectively, in the synthesized diet that was prepared for the fish cage experiment. All fish were fed the synthesized diet containing little mercury at a rate of 2% body weight/day. From the fish cage experiment, the initial and final means ($N = 10$) total-Hg content of Minamata Bay was 5.2 ± 0.8 and 5.5 ± 0.3 μg/fish in 2009 and 8.1 ± 0.5 and 6.7 ± 1.0 μg/fish in 2010, respectively. In contrast, in the Nagashima area the corresponding values were 5.2 ± 0.8 and 5.5 ± 0.3 in 2009 and 8.1 ± 0.5 and 8.3 ± 1.0 μg/fish in 2010, respectively. These results suggest that the current levels of Hg concentration in Minamata Bay will not affect the fish living in Minamata Bay (Matsuyama et al., 2013); the current average values of total-Hg concentration in Minamata Bay surface sediment is 2.5 mg/kg dry weight and the methyl-Hg concentration is 1.74 μg/kg dry weight (Matsuyama et al., 2014; Matsuyama et al., 2016). The regulatory limit for Hg concentration in sediment in Japan is based only on total-Hg concentration, and is 25 mg/kg dry weight (Tomiyasu et al., 2008). Therefore, the regulatory standards for Hg pollution of sediment in Japan are met. However, the average total-Hg concentration for Minamata Bay sediment was approximately 47 times that of sediment collected at Isahaya Bay in the northern part of Kyushu (Matsuyama et al., 2016). In addition, methyl-Hg from Minamata Bay was found to be almost 16 times higher than Isahaya Bay (methyl-Hg 0.11 μg/kg dry weight). In general, it has been observed that the chemical species of Hg in edible fish muscle comprises $>$ 90% methyl-Hg (Hight and Cheng, 2006). In addition, it is known that inorganic Hg absorbed by the fish is not converted to methyl-Hg in the fish body (Kikuchi et al., 1976; Nagashima et al., 1984). Therefore, the source of the high total-Hg concentration in fish caught in Minamata Bay is not diss-MeHg from Minamata Bay seawater. It is postulated that the source of methyl-Hg in fish living in Minamata Bay is biological accumulation through the food web in Minamata Bay (U.S. EPA, 2007; Toxicity and Exposure Assessment for Children's Health; Nishimura and Kumagai, 1983). Tomiyasu et al. (2008) reported that the maximum ratio of diss-methyl-Hg concentration to diss-total-Hg concentration in seawater at the bottom of Minamata Bay exceeded 60%. They suggested that the Minamata Bay ecosystem could have been affected by diss-methyl-Hg eluted from Minamata Bay sediment. A better understanding of the effects of methyl-Hg derived from the Minamata Bay sediment is therefore needed. This study addresses this knowledge gap by investigating the distribution of diss-Hg in pore water in Minamata Bay sediment by using a special centrifuge that was developed for this study, and by investigating the characteristics of Hg elution from the sediment.

## 2. Materials and methods

### 2.1. Survey locations and sediment sampling

Seasonal Hg variations were measured for pore water of sediments collected from two locations in Minamata Bay (Fig. 1).

### 2.2. Sediment sample collection in Minamata Bay

Core sediment samples were collected to investigate seasonal Hg variations. We travelled in a fishing vessel to the two sampling points identified using GPS (Fig. 1). Sediment samples were collected from June 2013 to July 2014. Monthly sediment samples were obtained during the maximum of an ebb tide using a gravity core sampler. As a result, 22 seasonal samples (St1 = 11, St2 = 11) were taken. To satisfy the requirements for sediment volume for mercury analysis, more than two core samples were taken at each sampling point. The average total core length was 29.2 ± 5.1 cm ($n = 51$). To avoid oxidation after sampling, the inner tube of the gravity core sampler was kept in a vinyl bag that had been evacuated using 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. To avoid the destruction of the sediment structure by freezing, all the sediment samples were stored in a refrigerator at 2 °C. Before analyzing, sediment core samples were brought to room temperature, and were then cut into two samples; the upper layer is 0 (surface) to −15 cm from the surface and the lower layer is −15 to approximately −30 cm from the surface.

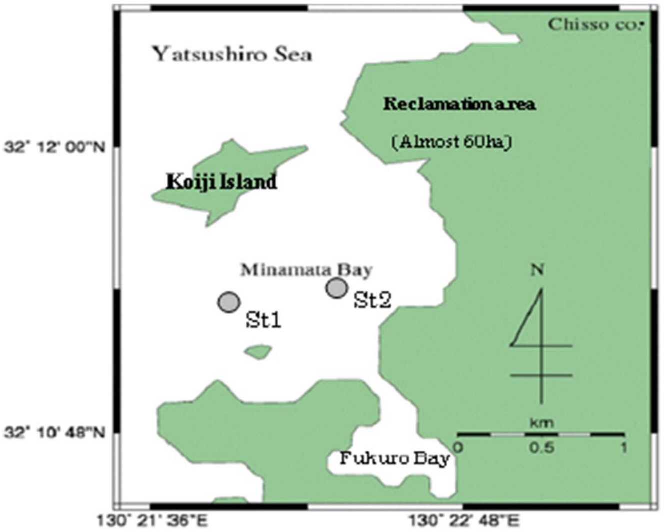

**Fig. 1.** Surface sediment sampling sites (St1, St2) in Minamata Bay.

### 2.3. Determination of dissolved Hg concentration in pore water of sediment

### 2.3.1. Pore water separation method

Pore water was separated from the sediment using a centrifuge prepared specifically for this study. A filtration device was developed for collecting pore water from sediment. To avoid compaction of the sediment by the rotation of the centrifuge, the centrifuge was set to gradually increase in speed until the pre-set speeds were achieved. The centrifuge was set to run at the pre-set speed for 1 h before gradually increasing to the next pre-set speed. To separate pore water from the sediment, three centrifuge rotations steps were used: the first rotation was at 1000 rpm, the next rotation was at 2000, and the final rotation at 3000 rpm. Prior to centrifuging, a 0.45 μm membrane filter was put on the bottom of a perforated stainless steel container to ensure that the

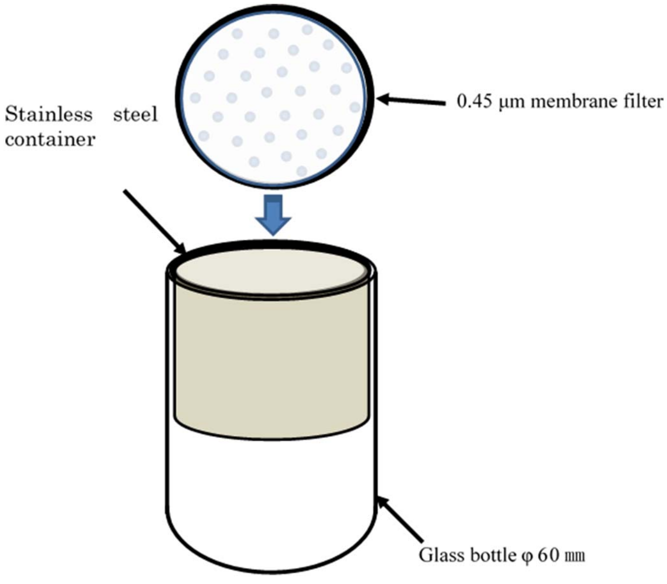

**Fig. 2.** Filtration device for separating pore water.