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Determination of dissolved gaseous mercury in seawater of Minamata Bay and estimation for mercury exchange across air–sea interface

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ABSTRACT

Dissolved gaseous Hg (DGM) in seawater and atmospheric gaseous Hg were measured at six sites in Minamata Bay to investigate mercury (Hg) evasion flux from the sea surface. Minamata Bay was severely polluted with mono-methyl Hg (MMHg). Total Hg and MMHg, seawater characteristics such as water temperature and salinity, and meteorological parameters were also observed to estimate the air–sea exchange of Hg. The mean concentration of DGM was 116 ± 76 pg L^{-1} (N = 75), ranging from 19 to 442 pg L^{-1}, and the concentrations were higher in summer than in other seasons. DGM concentration showed a significantly positive correlation with solar radiation, and air and water temperatures. Inversely, DGM showed a significantly negative correlation with salinity and redox potential (ORP). Hg evasion fluxes from the sea surface of the bay were calculated using a two-layer gas exchange model and ranged between 0.11 and 33 ng m^{-2} h^{-1} (mean, 5.4 ± 6.3 ng m^{-2} h^{-1}). The estimated flux was slightly higher in the spring and fall when wind speed increased because the gas exchange coefficient used for estimating Hg evasion flux strongly depends on wind speed. The annual evasion flux of Hg from the sea surface of Minamata Bay was estimated to be 47 ± 56 μg m^{-2}, which was on the same order of magnitude as the direct atmospheric deposition flux of Hg (24 μg m^{-2}) during the observation period. Therefore, Hg evasion from the sea surface likely plays an important role in the Hg cycle of Minamata Bay.

1. Introduction

In recent years, there has been growing interest in the emission sources, distribution and long-range transport of atmospheric mercury (Hg). Active discussions on the reduction of Hg emission from human activities have been undertaken by UNEP (United Nations for Environmental Programs) and the Minamata Convention most recently held in October, 2013 (UNEP, 2013). To assess the risks of long-term exposure to human health, much more knowledge of emission sources, transport and deposition of atmospheric Hg is necessary. Although atmospheric Hg is emitted as a result of human activities such as the combustion of fossil fuels, waste incineration and gold mining, Hg is also emitted from natural sources such as volcanic activity and soil weathering (Nriagu, 1989). In addition, re-emission of Hg (both natural and anthropogenic) that had been previously deposited into soil and the oceans also plays an important factor in the global Hg cycle (Amos et al., 2013; UNEP, 2013). Amos et al. (2013) suggested that re-emission of legacy anthropogenic Hg from surface reservoirs accounts for 60% of present-day atmospheric deposition, compared to 27% from current human activities, which has been estimated at about 2000 ton $year^{-1}$ (Pacyna et al., 2006; Streets et al, 2011). In order to determine the cost-effectiveness of measures to reduce the environmental risk of Hg emissions due to human activities, it is important that Hg amounts released by legacy impacts and natural sources should be estimated as precisely as possible.

In Japan, the annual Hg emission attributable to human activities such as coal-fired power plants and waste incinerators was estimated at 19 to 35 ton based on Hg emission data from each source (Kida and Sakai, 2005), but only limited data is available on Hg emissions from natural sources and the re-emission of deposited Hg (Nakagawa, 1999; Marumoto and Sakata, 2005; Narukawa et al., 2006).

Minamata Bay is located in the southwestern part of the Kyushu Islands and was the site of a significant discharge of mono-methyl Hg (MMHg) in contaminated wastewater from the Chisso Corporation's Minamata factory into the bay from 1932 to 1965 (Kumamoto Prefecture, 1998). People living in the coastal areas around the bay and Yatsushiro Sea ate contaminated seafood harvested in these areas and suffered nervous disorders caused by MMHg poisoning. From 1977 to 1990, environmental pollution controls, including a reclamation project in which sediment containing more than 25 ppm (μg g^{-1}) of total Hg was dredged from the bay and deposited along the coastline (Kumamoto Prefecture, 1998). However, the average concentration of total Hg in the surface sediment of the bay in 2010 remained high at 3.1 μg g^{-1} (Tomiyasu et al., 2014). This value is higher than the average concentration in the surface sediment in Tokyo Bay (0.43 ± 0.09 μg g^{-1}), which receives inflow from the largest metropolitan area (Sakata et al., 2006). In addition, Kindaichi and Matsuyama (2005)

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reported that the Hg concentration in some fish harvested from Minamata Bay exceeded 1 ppm, which is more than two times higher than the 0.4 ppm set by Japanese provisional regulation for total Hg in fish muscle (Ministry of Health and Welfare, Japan, 1973). The main source of MMHg in seawater remains unclear and comprehensive research including estimation of the input and output of Hg in the bay is needed to understand the sources and chemical reactions of Hg species.

To investigate Hg evasion from the sea surface of Minamata Bay, which one of the removal processes of Hg from the bay, we measured volatile dissolved gaseous Hg (DGM) in surface seawater twelve times over a period of 1 year. In addition, total Hg and MMHg in the surface seawater were also measured. Moreover, atmospheric Hg concentration at the sea surface, meteorological parameters and water conditions were also monitored and used to calculate the Hg evasion flux using a gas exchange model across the air–sea interface (Liss and Slater, 1974).

2. Methods

2.1. Sampling

The sampling sites in Minamata Bay are shown in Fig. 1. Seawater sampling for the measurement of DGM and other parameters was carried out three times in each season from July 2012 to May 2013: summer (June–August), fall (September–November), winter (December–February) and spring (March–May). Observations on 18 October 2012 were conducted only at the coastal sites from St. 4 to St. 6 due to an approaching typhoon. Seawater was collected in a sampler that prevents volatilization loss of DGM from the sample (Marumoto et al, 2012). A schematic of the DGM sampler is presented in Fig. 2. Briefly, the DGM sampler has a Teflon ball in the bottom that is pushed up when the sampler takes in water and falls down, closing the opening, when the sampler is pulled from water. The sampler can be used to collect surface seawater without disturbing the water column and any decanting processes. The mean volatilization loss of DGM due to decanting processes is $-15 \pm 10\%$ (Marumoto et al, 2012). Separate from DGM sampling, 500 ml of surface seawater was collected in a Teflon bottle for analysis of total Hg and MMHg.

Solar radiation above and in the sea was recorded using a pyrheliometer (Prede Co., Ltd.; PCM-01W) and water temperature, water density, salinity, conductivity, pH and oxidation–reduction potential (ORP) in the surface seawater were observed using a multi-parameter water quality measurement system with six sensors (Horiba, Co., Ltd.; U-22XD). Wind speed was recorded continuously using an ultrasonic anemometer and a vane-type anemometer at the rooftop of the Minamata Disease Archives (at a height of 23 m above sea level),

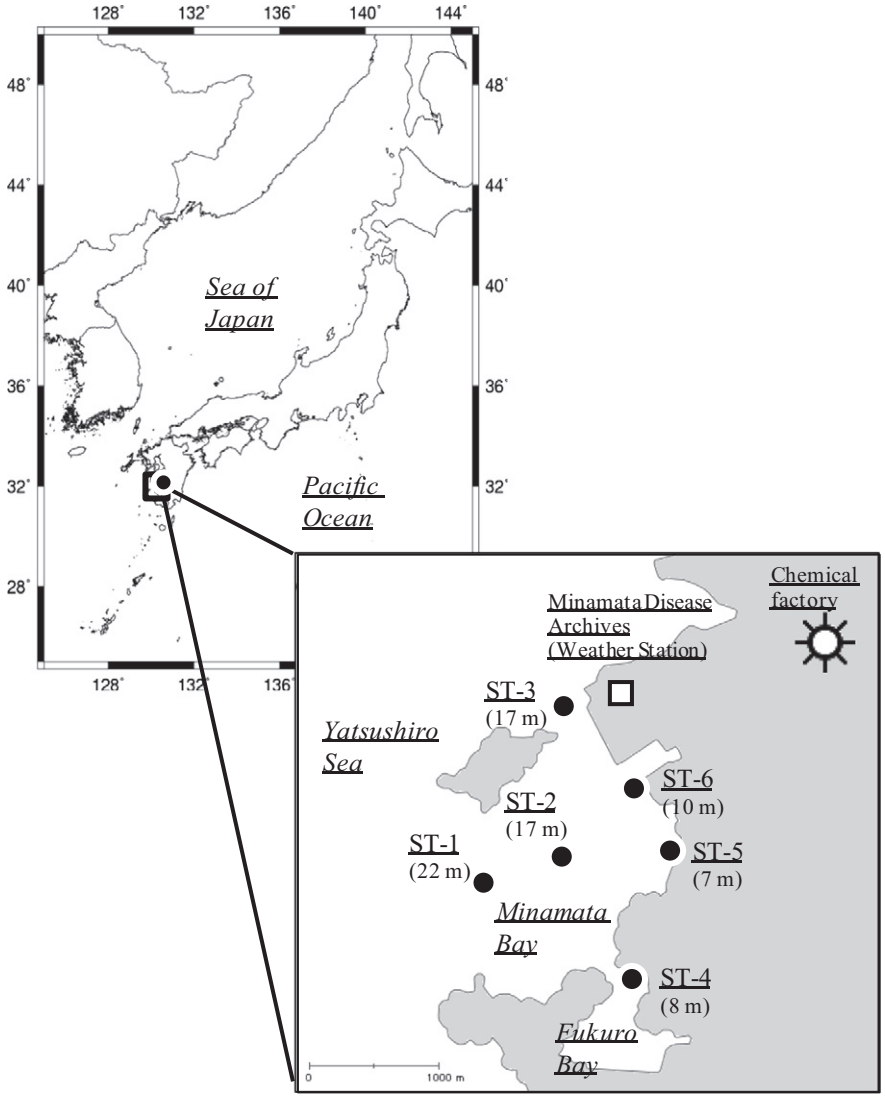

Fig. 1. Location of Minamata Bay and sampling sites in the bay. The water depths at each sampling site at high tide are indicated in parentheses. The tidal range of the bay is about 2 m. Meteorological parameters were continuously measured on the roof top of the Minamata Disease Archives.