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After Minamata disease occurred in Kumamoto Prefecture, the Minamata Bay Pollution Prevention Project on Minamata Bay area was started to deal with mercury pollution. Beneficial from the project, the mercury content in the bay area has been significantly reduced. However, many studies have shown that the residual trace mercury content around the bay is still high. Furthermore, mercury has migrated from Minamata Bay to the Yatsushiro Sea. Therefore, continuous research on the distribution and content of mercury in this region is required.

In this study, using sediment classification, the relationship between sediment particle size, particle specific surface area, and T-Hg (total mercury) concentration was investigated. Based on the numerical simulation, the particle size effect on the migration of mercury-containing sediments and the T-Hg distribution in the Yatsushiro Sea were studied. The result showed that the larger the particle size, the lower the T-Hg concentration in the sediment. Meanwhile, the larger the particle specific surface area, the higher the T-Hg concentration. Moreover, the smaller the particle size of the mercury-containing sediment, the higher the migration speed as well as the more comprehensive migration range. From the numerical simulation results, it was found that mercury was mainly distributed in the southwest and northeast directions from Minamata Bay. Finally, the simulated mercury distribution, which considers the relationship between particle size and mercury concentration, shows a high agreement with the past measurements of mercury, suggesting the importance of particle size effect in mercury migration.

Key Words: *mercury, particle size, particle specific surface area, migration, the Yatsushiro Sea*

1. BACKGROUND

Mercury has a long and interesting history, stemming from its significant use in medicine and industry, and the resulting toxicity[1)]. Once mercury enters the food chain, it can accumulate in organisms and cause adverse effects, especially seriously affecting human health[2)]. In the 1960s, residents of Minamata City suffered severe neurosis due to eating seafood contaminated with methylmercury (MeHg), which is known as Minamata disease. By 1989, the amount of the cases had been officially confirmed to reach 2217[3)]. To solve this problem, Kumamoto Prefecture started the Minamata Bay Pollution Prevention Project in 1977. The survey conducted after the completion of the project showed that the average T-Hg value at 84 sites in the bay had dropped to 4.7 (0.06-12) μg/g[Note 1)]. However, as reported by Nishimura and Okamoto[Note 2)], large amounts of methylmercury still exist in Minamata Bay. Moreover, the average level of mercury in fish remains still slightly higher than in other regions[4)]. Furthermore, some studies have reported the migration of mercury from Minamata Bay to the Yatsushiro Sea along with sediments[5,6)]. Therefore, it is necessary to study continuously the content and distribution of residual trace mercury in the Yatsushiro Sea including the bay.

Tomiyasu *et al.*[7)] measured the concentrations of

T-Hg and methylmercury (MeHg) in the bottom water, suspended solids, and surface sediments of Minamata Bay. The results showed that sediments were the important source of mercury in the water of the bay. In addition, MeHg concentration in the bottom water was also much higher in the upper and middle layers of the water column, suggesting that methylmercury may be the dominant form of mercury released from sediments into water. Therefore, it is most important to grasp the content and distribution of mercury in the sediment. In many previous studies, the distribution of mercury in the sediments of the sea around the bay was investigated. Sediments are composed of various particles with various particle sizes. However, there are few studies on whether particle size of sediments affects the content of mercury in sediments.

In this study, dependent on sedimentation classification, the relationships between the T-Hg concentration and sediment particle size as well as particle specific surface area were investigated. Also, the numerical simulations of sediment migration with different particle sizes were established to study the effect of particle size on the migration of mercury-containing sediments. Furthermore, based on the simulation results, combined with the relationship between total mercury and particle size, the distribution of T-Hg in the Yatsushiro Sea was determined.

2. METHODOLOGY

(1) Location of investigation and collection of samples

The area investigated in this study is located in the Yatsushiro Sea. As a closed water system, the Yatsushiro Sea is surrounded by the prefectures of Kagoshima and Kumamoto, and its area is 1,200 km^2 and 22.2 m deep on average[Note 3)]. In the earlier study, Matsunoshita *et al.*[8)] measured the plane distribution of surface sediments in the Yatsushiro Sea. The result indicated that mercury was mainly concentrated in the northeast and southwest regions of the Yatsushiro Sea near Minamata Bay. Therefore, sediment sampling was carried out in the northeast and southwest regions of the Yatsushiro Sea in this study. **Fig. 1** depicts the location of the sampling points. A core sampler (Rigo Co. Ltd., Saitama, Japan) was used to collect the sediment samples. The diameter of the core sample collected at each sampling point is 5 cm, and its maximum thickness is 22 cm.

(2) Classification process of samples

Generally, particle size distribution of marine sediments is not the same. In order to classify sediment samples dependent on particle size, sedimentation classification was conducted as described below. The

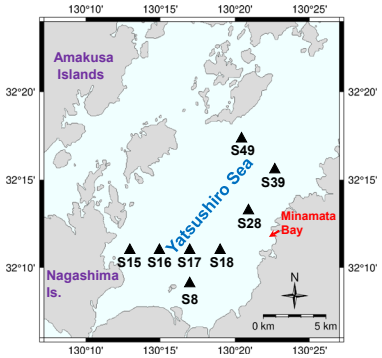

Fig. 1 The location of the sampling points

sediment core samples were cut into 1 cm slices from top to bottom and stored in an ultra-low temperature freezer (< -80 °C). In order to obtain a suitable sample volume, each adjacent two 1 cm sediment slices were mixed together. The pre-prepared sediment sample was put into a 14 mm heat-shrinkable tube that had been plugged at one end with a rubber stopper. After adding the dispersion solvent (glycerol/ethanol, 1:2 v/v) to the tube, the top of the tube was plugged with another rubber stopper. The sample and dispersion solvent in the tube were thoroughly mixed by hand shaking for 1 minute, and then stored in a refrigerator. After two weeks, samples were frozen in liquid nitrogen and cut into 5 mm sections. This process is the same as the one used in the previous research[9)].

(3) Measurement of particle size distribution and calculation of particle specific surface area

Frozen sediment samples were thawed at room temperature and placed in a circulating dryer for drying to remove the water. Thereafter, the sediment samples were thoroughly mixed while impurities in the sediment were manually removed. A laser diffraction particle size analyzer (SALD-3100, Shimadzu Corporation, Kyoto, Japan) was used to analyze the particle size distribution of the samples. The particle specific surface area of each sample can be calculated as follows:

$$m = \sum (G_s \times V \times k) \tag{1}$$

$$V = \frac{4}{3}\pi \left(\frac{D}{2}\right)^3 \tag{2}$$

$$S = \sum (S_n \times k) \tag{3}$$

$$S_n = 4\pi \left(\frac{D}{2}\right)^2 \tag{4}$$

$$S_m = \frac{S}{m} \tag{5}$$

where m is quality; Gs respects particle density[10)] equal to 2.65×10^{-12} g/μm^3; V respects volume; k is the proportion of frequency distribution of each particle size; D is particle size; S respects surface area;

S_n is surface area of each particle, and S_m is particle specific surface area of the sediment sample.

(4) Determination of mercury concentration

T-Hg concentrations in sediments were measured using the method proposed by Akagi and Nishimura[11] and modified by Akagi *et al.*[12]. The accuracy and precision of the method have been calibrated in laboratories[13]. It has been repeatedly validated in the analysis of the IAEA-158 reference standard as well[Note 4]. Using $SnCl_2$ as a reducing agent, the samples were analyzed by a cold vapor atomic absorption spectrometry (Hg-201, Sanso Seisakusho Co., Tokyo, Japan). The water content of the sediment is calculated from the difference in the mass of the sediment before and after drying.

(5) Establishment of numerical model

The numerical model was established using the Delft3D hydrodynamic model. The calculation domain in the model was defined to contain both the Yatsushiro Sea and the Ariake Sea. The horizontal grid is a variable grid established by Fathya *et al.*[14], and the grid precision is 62.5 m, 125 m, and 250 m, respectively. The vertical grid adopts the σ coordinate system and consists of five layers, each of which is 20% of the total depth. The bathymetric map in the calculation area is shown in **Fig. 2**. In the open boundary condition (located on the line connecting Kabashima Suido and Akune.), the 4 main tidal components (M2, S2, K1, and O1) are modified for amplitude and phase. The results of the tide measurement by Yano *et al.*[15] were used to calibrate the harmonic constants. Freshwater inflow was provided by 8 Class A rivers, 9 Class B rivers, and the north-south discharge gates of the Isahaya Sea Dyke (**Fig. 2**). The data of freshwater, including inflow, salinity, temperature, etc., was obtained from the Hydrology and Water Quality Database of MLIT.

According to the Shields formula and friction velocity formula, the critical shear stress was determined from the following equation:

$$\tau_{*C} = \frac{\frac{\tau_{Cr,e}}{\rho}}{\left(\frac{\sigma}{\rho}-1\right) g d_m} \tag{6}$$

where τ_{*C} denotes dimensionless critical tractive force, which is 0.05; $\tau_{cr,e}$ respects the critical shear stresses for erosion; σ is particle density; ρ denotes water density; g respects gravity acceleration; d_m is the median grain size of sediment samples.

The Rubey's theoretic equation can be used to calculate the sedimentation rate of suspended particles:

$$w_s = \left(\sqrt{\frac{2}{3}+\frac{36\nu^2}{d_*}} - \sqrt{\frac{36}{d_*}}\right)\sqrt{(\sigma_s-1)gD} \tag{7}$$

$$d_* = \frac{(\sigma_s-1)gD^3}{\nu^2} \tag{8}$$

where w_s denotes the sedimentation velocity; ν is the kinematic viscosity coefficient, D respects the median grain size; g is gravity acceleration, and σ_s denotes particle density.

According to the distribution of particle sizes in sediments, several particle sizes are selected for calculation in this simulation. The critical shear stresses $\tau_{cr,e}$ and the sedimentation rate w_s of different particle sizes are shown in **Table 1**.

The erosion rate parameters were used from our previous studies, which were obtained based on *in-situ* measurement[16]. The initial bottom sediment thickness was set to 1 m only in Minamata Bay (The area shown in the red box in **Fig. 2**).

3. RESULTS AND DISCUSSION

(1) Relationship between total mercury concentration and particle size of sediments

The relationship between the T-Hg concentration and the particle size of the sediment is shown in **Fig. 3**. The particle size is mainly distributed from 7 μm to 12 μm. It indicates that the migration depends on the smaller particles. There is a negative correlation between the total mercury concentration and particle size, indicating the significant influence of particle size on the distribution of total mercury in sediments.

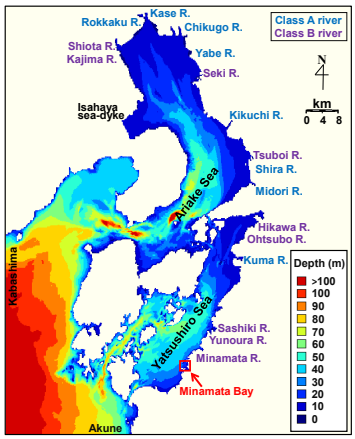

Fig. 2 The bathymetric map in the calculation area

Table 1 The critical shear stresses and the sedimentation rate of different particle sizes

Particle sizes (μm)	The critical shear stresses (Pa)	The sedimentation rate (m/s)
5	3.97×10^{-3}	2.25×10^{-5}
10	7.94×10^{-3}	8.99×10^{-5}
15	1.19×10^{-2}	2.02×10^{-4}
25	1.99×10^{-2}	5.61×10^{-4}
50	3.97×10^{-2}	2.23×10^{-3}
75	5.96×10^{-2}	4.91×10^{-3}
100	7.95×10^{-2}	8.40×10^{-3}
200	1.59×10^{-1}	2.53×10^{-2}

The larger the particle size, the lower the total mercury concentration in the sediment. There may be two main possible reasons for this: 1) The larger the particle size, the smaller the particle specific surface area, and the weaker the ability of the particles to adsorb mercury. 2) The larger the particle size, the lower the migration speed of sediment particles due to the gravity effect, and the weaker the migration ability of T-Hg with sediments.

(2) Relationship between total mercury concentration and particle specific surface area of sediments

To verify the analysis above, the relationship between T-Hg concentration and particle specific surface area of sediments was obtained (**Fig. 4**). It can be seen that the particle specific surface area at various sampling points was proportional to the total mercury concentration in the sediments. In other words, the larger the particle specific surface area, the higher the T-Hg concentration. It is mainly because of the following two reasons: 1) Mercury can be fixed on the particle surface through adsorption in the sediment. Due to the larger particle specific surface area of particles, the ratio of surface area to volume is higher, and there is more surface area available for adsorption. Therefore, the larger the particle specific surface area of particles, the more mercury they can adsorb, leading to a higher total mercury concentration in sediments. 2) The larger the particle specific surface area of particles, the lower their settling rate, and thus the more mercury they can carry, resulting in a higher total mercury concentration in sediments.

In addition, T-Hg concentration dispersion degree corresponding to each specific surface area is low for the sampling points far away from Minamata Bay (*e.g.*, the maximum concentration is 755 ng/g while the minimum is 139 ng/g at S15.), while it's opposite for the sites close to Minamata Bay (*e.g.*, for S28, maximum: 1,621 ng/g; minimum: 157 ng/g). This is mainly because the closer to Minamata Bay, the greater the impact of mercury discharged from Minamata Bay. On the other hand, the dispersion degree difference between the sites in different direction (*e.g.*, S18 and S39) is due to the influence of different currents and topography. Compared to the sites in the southwest direction from Minamata Bay like S18, the sites in the northeast direction (*e.g.*, S39) has high dispersion degree due to baroclinic current, the larger bottom slope (**Fig. 2**) and higher residual current velocity.

(3) Migration of mercury-containing sediments with different particle sizes

The migration of mercury-containing sediments with different particle sizes is shown in **Fig. 5.** The migration areas (deposited thickness $> 3 \times 10^{-5}$ m) for particle size from 5 μm to 200 μm are about 190 km^2, 130 km^2, 30 km^2, 10 km^2, 0.2 km^2, 0.06 km^2, 0.025 km^2, and 0.016 km^2, respectively. The smaller the particle size of the sediments, the more comprehensive the migration range. It is mainly due to the fact that the sediments in small particle sizes have a larger particle specific surface area, which contributes to providing the sediments with more areas to interact with water bodies. It is easier to be transported and diffuse under the action of water flow. Additionally, when the inertial mass of small particles is smaller, the movement resistance becomes smaller, which leads to its faster movement speed as well. After one year of simulation, it can be found that sediments

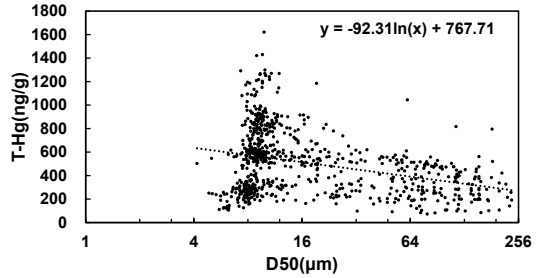

Fig. 3 The relationship between the T-Hg concentration and the particle size in the sediment

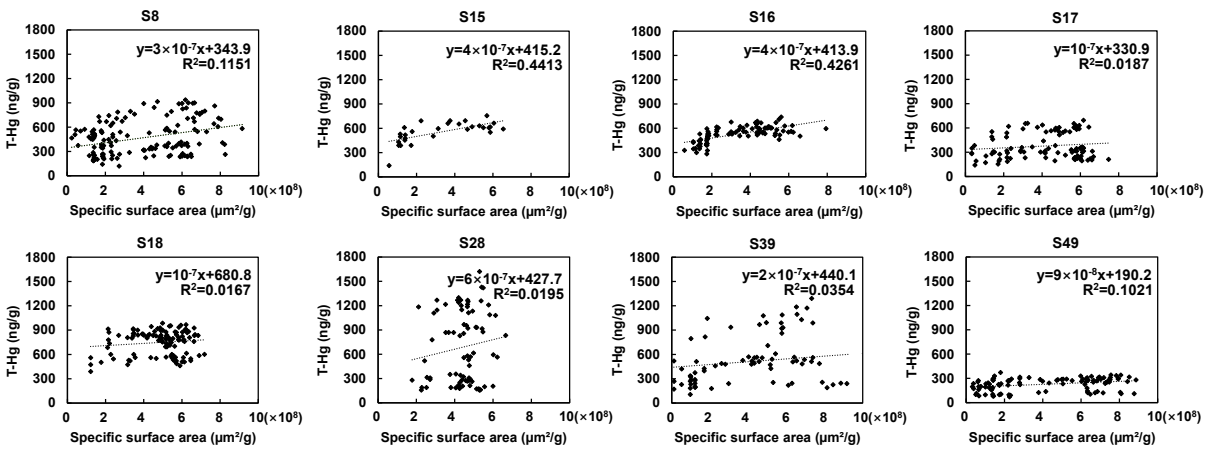

Fig. 4 The relationship between T-Hg concentration and particle specific surface area

with a particle size greater than 50 μm migrated almost exclusively around Minamata Bay, illustrating that once the particle size is bigger than 50 μm, much longer time is needed for the sediments to transport to the Yatsushiro Sea while their migration range is also tiny. Furthermore, it confirms again that the sediments with smaller particle sizes are the main force for migration.

(4) Mercury concentration distribution in the Yatsushiro Sea

Based on the migration simulations in Section 3 (3), combined with the relationship between particle size and mercury concentration, the mercury concentration distribution in the Yatsushiro Sea was obtained, where the distribution rules of different particle sizes and the weighted settlement were used (**Fig. 6**). It is important to note that each average size was selected including 5 μm, 10 μm, 15 μm, 25 μm, 50 μm, 75 μm, 100 μm, and 200 μm. Based on the selected average sizes, their corresponding ranges of particle size were determined. The percentage for each particle size range was calculated based on each particle size range amount and the total amount, where the amount of 5-mm segment *Bi* (*i*=1, 2, …) for each particle size range was obtained from the previous research[9]. It can be seen that mercury is mainly distributed in the southwest and northeast directions from Minamata Bay. Meanwhile, mercury exceeding 0.5 ppm is distributed within about 100 km^2 southwest direction from Minamata Bay, while it is only distributed within about 55 km^2 northeast direction from Minamata Bay. Southwest direction from Minamata Bay is considered to be mainly affected by barotropic current, while northeast direction by baroclinic current[17]. Meanwhile, the bottom slope in the southwest direction from Minamata Bay is generally smaller than that in the northeast direction (**Fig. 2**). Therefore, the mercury distribution in the two regions is significantly different. In addition, due to the complex topography and vegetation in the shore area, the water flow is relatively slow, which makes mercury more likely to distribute in the shore area. On the other hand, the more sediments and suspended matter in the coastal area, which are more likely to absorb mercury, may be another reason for the accumulation of mercury in the coastal area. In the earlier study, Matsuyama *et al*. measured the plane distribution of sediment with a T-Hg concentration range of 0.5-2.0 mg/kg dry weight in the Yatsushiro Sea[6]. Compared

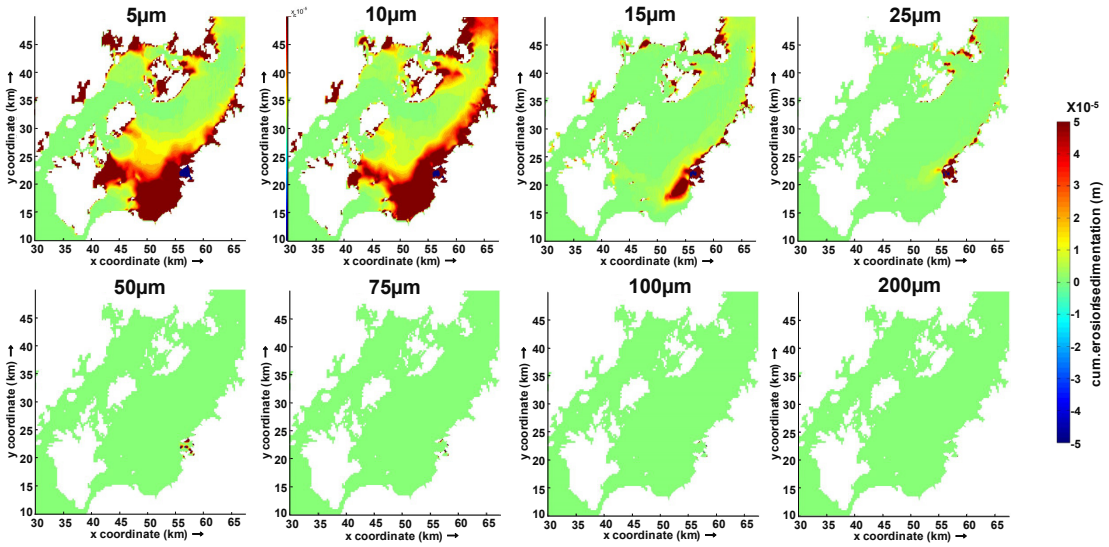

Fig. 5 The migration of sediments with different particle sizes

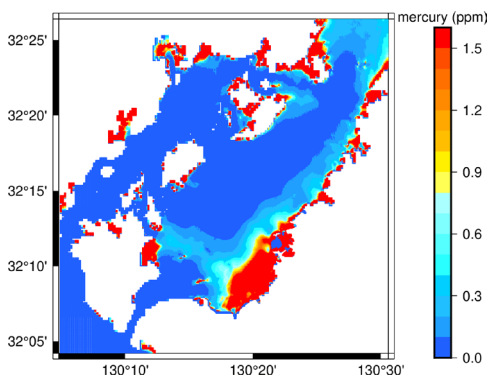

Fig. 6 The mercury concentration distribution in the Yatsushiro Sea

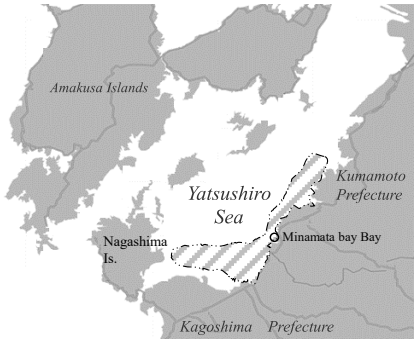

Fig. 7 The plane distribution of sediment with T-Hg concentration range of 0.5–2.0 mg/kg dry weight (area filled with gray lines) (from Matsuyama *et al*. [6])

with their experimental result of T-Hg distribution (**Fig. 7**), it concludes that the simulated distribution (**Fig. 6**) agreed reasonably well with the measured one.

4. CONCLUSIONS

In this study, the relationships between T-Hg concentration and particle size as well as particle specific surface area were investigated. The result showed that the large particle size and the smaller particle specific surface area could lower the T-Hg concentration in the sediment. In addition, numerical simulations were performed on the migration of mercury-containing sediments with different particle sizes in the Yatsushiro Sea, indicating that the smaller the particle size of the sediments, the more comprehensive the migration range. Furthermore, based on the numerical simulation of the migration, considering the relationship between particle size and mercury concentration, the concentration distribution of mercury in the Yatsushiro Sea was calculated, and it was found that mercury is mainly distributed in the southwest and northeast directions from Minamata Bay. Meanwhile, the simulated distribution shows high agreement with the experimental measurements.

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NOTES

Note 1) Minamata City: Minamata Disease -Its History and Lessons- 2022, 66p., 2022.

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