VERTICAL DISTRIBUTION OF MERCURY IN BOTTOM SEDIMENTS AND PARTICLE SIZE EFFECT ON MIGRATION OF MERCURY-CONTAINING SEDIMENTS IN THE YATSUSHIRO SEA

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出版情報：Journal of JSCE. 11 (2), 2023-11-01. 土木学会
バージョン：

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In 1977, the Minamata Bay Pollution Prevention Project was initiated to dispose of sedimentary sludge containing over 25 ppm of total mercury (T-Hg) after the outbreak of Minamata Disease. The sediments containing the high concentration Hg were dredged, but nevertheless, the residual Hg in Minamata Bay has attracted much attention. Moreover, some studies have even indicated that the Hg remaining in the sediments near the bay has migrated to the Yatsushiro Sea.

In this study, the vertical distribution of mercury concentration across sediment layers at different sites was investigated. Developed numerical modeling was used to evaluate the impact of sediment particle size on the migration of Hg-containing sediments from Minamata Bay to the Yatsushiro Sea as well. According to the results, mercury migrated from Minamata Bay to the Yatsushiro Sea, where the mercury migrating to the southwest of the Yatsushiro Sea is more concentrated. Additionally, there were significant differences in mercury concentrations at various depths and locations. The total mercury content varied with the particle size. The migration of mercury-containing sediments with larger particle size was slower and the migration range was limited.

Key Words: *mercury, vertical distribution, sediment particle size, migration, the Yatsushiro Sea*

1. INTRODUCTION

An acetaldehyde-producing factory released mercury-contaminated sewage into Minamata Bay from 1932 and continued for more than 30 years until 1968[1)]. The mercury accumulated in the sediment, bioaccumulated in fish and shellfish, and led to the Minamata Disease[2,3)]. To get rid of sedimentary sludge with over 25 ppm of mercury, the Minamata Bay Pollution Prevention Project was started on October 1st, 1977[4)]. After the remediation project, the mercury concentration was significantly decreased. However, the residual mercury concentrations remained 10 times higher than the background level of the natural environment[5)]. The total mercury content in the sediments of the Minamata Bay area was measured from 2002 to 2010[6)]. It was found that the amount of discharged mercury remaining in the contaminated layer was estimated to be 750 ± 290 kg. In 2012, a detailed survey of mercury concentrations in sediments at the bottom of Minamata Bay was conducted[7)]. The total quantity of mercury was calculated to be 3.4 tons and 2.3 mg/kg dry weight basis in the bottom sediments of Minamata Bay, respectively. Moreover, it was suggested that the mercury that remained in Minamata Bay migrated from Minamata Bay to the Yatsushiro Sea[8)]. Therefore, the vertical distribution of T-Hg in the Yatsushiro Sea is considered extremely important. In addition, mercury is mainly concentrated

in sediments and migrates along with the sediments. The sediment acts as a record of deposition, and its geographic distribution of mercury could indicate the temporal behavior of discharged mercury[9]. Therefore, the prediction of mercury migration based on sediments was regarded as an effective way.

In our previous study, a numerical model, regardless of particle size effect, was established to simulate the transport of bottom sediments from Minamata Bay to the Yatsushiro Sea[10]. However, the different particle sizes of sediments may influence gravity-induced sedimentation and cause various specific surface areas that result in different amounts of absorbed mercury. Hence, in the present study, we investigate the vertical distribution of mercury by measuring its concentration across sediment layers at various sites. In addition, the effect of sediment particle size on the migration of Hg-containing sediment from Minamata Bay to the Yatsushiro Sea is also analyzed by numerical simulation.

2. METHODOLOGY

(1) Sample Collection and Processing

In this study, the sediment samples were collected from the Yatsushiro Sea using a gravity core sampler in August 2017. The sediment sampling points are shown in **Fig.1**. Each core sediment sample was divided into sections with 1cm thickness (**Fig.2**) and then kept in an ultra-low freezer (< -80°C) for storage. Two continuous 1cm sediment sections were mixed to provide an appropriate sample volume. Heat-shrink tubing (50 cm) was progressively rolled to create a tube with a diameter of 14 mm on a hot plate at 110°C. After one end of the tubes had been sealed off with a rubber stopper, the pre-prepared sediment samples were put into the tubes. Thereafter, the dispersion solvent (glycerin/ethanol, 1:2 v/v) was poured into the tubes as well. Then, the tubes should be covered with another rubber stoppers. After that, the samples were shaken by hand for 1 min and then allowed to rest in a refrigerator (4°C). After two-week resting, the samples were solidified by liquid nitrogen and then cut into 5 mm sections (**Fig.2**). The process is the same as the previous paper[11].

(2) Sample analysis

Each sediment section was divided into two parts: One was used for the total mercury analysis, while the other was for particle size distribution analysis.

For the total mercury analysis, a technique developed by Akagi and Nishimura[12] and improved by Akagi *et al.*[13] was used to measure the T-Hg concentration in the sediments, where the cold vapor atomic absorption spectrometry (Hg-201, Sanso Seisakusho

Fig.1 The location of sediment sampling points.

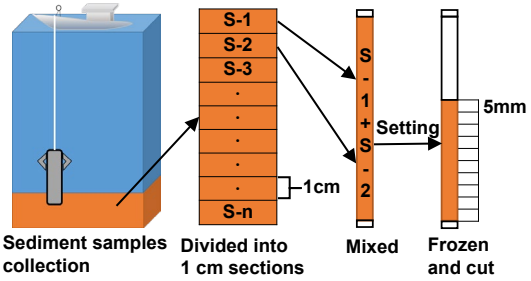

Fig.2 The processing of sediment samples.

Co., Japan) using $SnCl_2$ as a reducing agent. Before sample analysis, the impurities (*e.g.*, stones and small pebbles) in the sample were firstly removed by manual and sieving method, and the samples were thoroughly mixed. Besides, the analysis of the T-Hg concentration of the sample requires the determination of the water content of the sediment. In this experiment, the measurement of the sample's water content was as follows: drying it at 105°C for 24 hours in a convection oven, then determining the difference in sediment mass between the two measurements.

For particle size distribution analysis, the samples were put in plastic bags and kept in an extremely cold freezer (<-80°C). Water in the sediment samples needed to be eliminated prior to particle size analysis. The sediments were dried overnight in a circulating dryer at 105°C. After drying, the impurities (*e.g.*, small pebbles and stones) of the sample were removed by hand, and the samples were thoroughly mixed. Finally, a laser diffraction particle size analyzer (SALD-3100, Shimadzu Corporation, Japan) was used to measure the particle size of sediment samples.

(3) Numerical model

Our numerical model was established based on Delft3D (hydrodynamic model of a coastal region). The calculation domain in the model was defined to contain both the Yatsushiro Sea and the Ariake Sea (**Fig.3**). In the horizontal direction, the variable grid established by Fathya *et al.*[14] was utilized, where the

grid accuracy of Minamata Bay, and its surrounding regions is up to 62.5 m, whereas the grid accuracy of places further from Minamata Bay is 125 m and 250 m, respectively. The vertical grid adopts the σ coordinate system and is composed of five layers, each having 20% of the total depth. Only the 4 main tidal components (M2, S2, K1, and O1) are modified for amplitude and phase in the open boundary condition (Kabashima Suido-Akune). The results of the tide measurement by Yano *et al.*[15] were used to calibrate the harmonic constants. Freshwater inflows come from 8 Class A rivers, 9 Class B rivers, and the north-south discharge gates of the Isahaya Sea Dyke. Class A river flows are derived from hourly flows measured at monitoring stations. The discharge of each Class B river is estimated based on the ratio of the catchment area to the adjacent Class A river. The initial bottom sediment thickness was set to 1 m only in Minamata Bay (the area shown in the red box in **Fig. 4**), and the initial bottom sediment thickness was set to 0 m elsewhere.

The erosion rate parameters determined by Chi *et al.*[10], which were obtained based on *in-situ* measurement, were used. Regarding the selection of different graded particle sizes, we consider using the particle size corresponding to the maximum mercury concentration at each sampling point and the particle size with the most distribution. There are two considerations for this choice below: (a) The particle size corresponding to the maximum mercury concentration: This particle size is significantly affected by the mercury discharged from Minamata Bay and may migrate faster and more widely. (b) The most widely distributed particle size: This particle size is the primary particle size in the process of mercury discharge from Minamata Bay to the Yatsushiro Sea. The particle sizes corresponding to the maximum mercury concentrations at different sampling points and the average particle sizes with the largest particle size distribution are shown in **Table 1**. Except for the particle size corresponding to the maximum mercury concentration of YS49, the other particle sizes are all distributed from 7 μm to 9 μm, and the numerical values are relatively small (**Table 1**). For better evaluating the effect of particle size on migration, the particle sizes including 7.3 μm, 8.6 μm, 9.8 μm, and 57.9 μm were selected for simulation analysis.

According to the Shields formula,

$$\tau_{*C} = \frac{{U_{*C}}^2}{\left(\frac{\sigma}{\rho} - 1\right) g d_m} \tag{1}$$

and shear velocity formula,

$$U_{*C} = \sqrt{\frac{\tau_{cr,e}}{\rho}} \tag{2}$$

The critical shear stress was calculated according

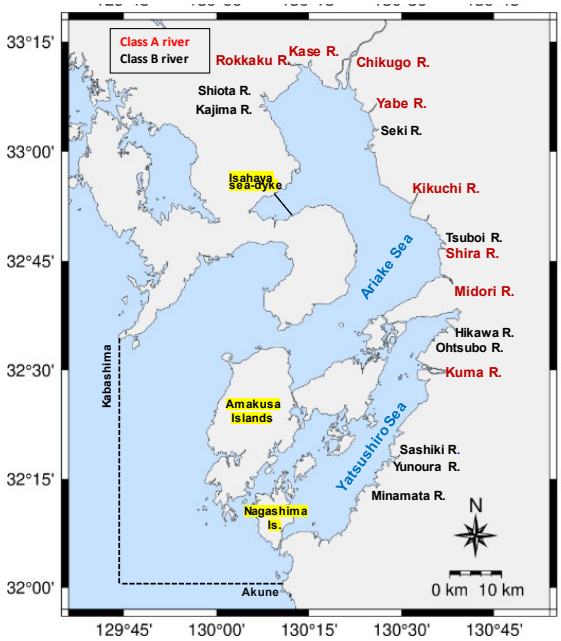

Fig.3 The calculation domain of the model

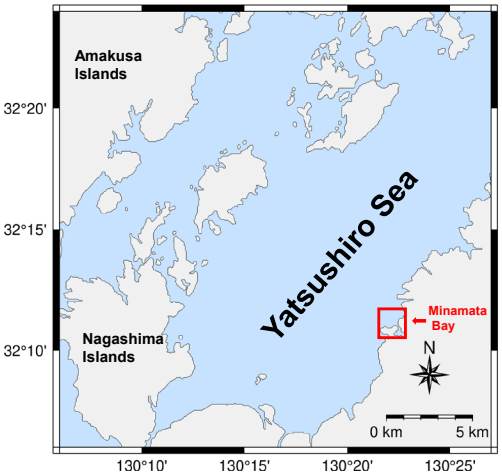

Fig.4 Initial sediment distribution setting

to the formula as follows:

$$\tau_{cr,e} = \left(\frac{\sigma}{\rho} - 1\right) \rho g d_m \tau_{*C} \tag{3}$$

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

The sedimentation rate of suspended particles can be obtained by the following Rubey formula:

$$\frac{w_0}{\sqrt{(\sigma_s - 1) g D}} = \sqrt{\frac{2}{3} + \frac{36}{d_*}} - \sqrt{\frac{36}{d_*}} \tag{4}$$

$$d_* = \frac{(\sigma_s - 1) g D^3}{v^2} \tag{5}$$

where w_0 respects the sedimentation velocity, σ_s is particle density, D is the median grain size, g respects gravity acceleration, and v donates the kinematic viscosity coefficient.

Table 1 The representative particle size of different sampling points

Sampling point	The particle size corresponding to the maximum mercury concentration (μm)	The particle size with the most distribution (μm)
YS8	9.6	8.5
YS15	8.6	8.6
YS16	8.0	9.4
YS17	8.2	8.4
YS18	9.4	9.5
YS28	9.8	9.6
YS39	7.3	7.7
YS49	57.9	7.5

Table 2 The critical shear stresses τ_{cr} and the sedimentation rate of different particle sizes

Particle sizes (μm)	The critical shear stresses (Pa)	The sedimentation rate (m/s)
7.3	5.8×10^{-3}	4.8×10^{-5}
8.6	6.8×10^{-3}	6.6×10^{-5}
9.8	7.8×10^{-3}	8.7×10^{-5}
57.9	4.6×10^{-2}	3.0×10^{-3}

The critical shear stresses τ_{cr} and the sedimentation rate of different particle sizes are shown in **Table 2**.

3. RESULTS AND DISCUSSION

(1) Vertical distribution of mercury in bottom sediments

Fig.5 describes the vertical distribution of mercury in sediments at different sampling points in the Yatsushiro Sea. Comparing the results at various points, in the horizontal direction, the T-Hg concentration gradually decreased from Minamata Bay to the northeast and southwest of the Yatsushiro Sea, indicating that mercury migrated from Minamata Bay to the Yatsushiro Sea, consistent with the previous numerical simulation results[10]. At sampling point YS28 which is closest to Minamata Bay, the mercury concentration increased rapidly from the surface layer to the depth of 9 cm, and then decreased rapidly. Its dramatic change reflects the human intervention on mercury-containing sewage discharge and control. In other words, the T-Hg of sediments far away from the surface layer (depth >20 cm) is considered close to the background value due to no disposal of mercury-containing sewage. With continuous mercury pollution, the mercury concentration in the vertical direction increased distinctly (9 cm<depth<12 cm) whereas, and sharply reduced when stopping the swage discharge and carrying out the mercury-containing sediment dredging (depth<9 cm). At points YS39 and YS18, where there is a certain distance from Minamata Bay, the high mercury concentration at a certain depth indicated that the mercury discharged into Minamata Bay had migrated to the northeast and southwest of the Yatsushiro Sea as well. It should be noted that the different changes between those two sampling points were considered due to the change of sewage outlet in 1958. At YS8 and YS17, similar T-Hg concentration changes in the vertical direction were obtained, that is, the mercury concentration remained stable from the surface layer to 8 cm deep and decreased rapidly after the depth exceeded 8 cm. However, although the point YS8 is farther away from Minamata Bay, its higher T-Hg at the same depth compared to YS17 may cause by the geomorphic effect. At points YS16, YS15, and YS49, the mercury concentration was relatively stable as well as low. As the distance from Minamata Bay increases, the amount of migrated mercury becomes smaller. Moreover, the mercury concentration at

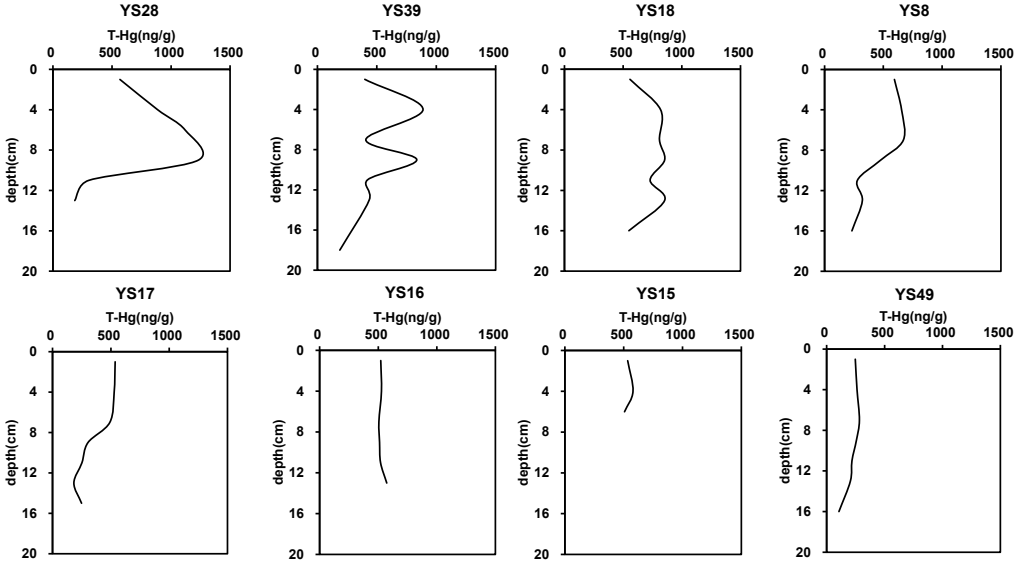

Fig.5 The vertical distribution of mercury in bottom sediments

YS16 and YS15 is significantly higher than that at YS49, indicating that the mercury migrated to the southwest of the Yatsushiro Sea and is more concentrated. This was mainly because the mercury in the southwest of the Yatsushiro Sea could not migrate to a wider area due to the impact of the closure of the islands, while the northeast of the Yatsushiro Sea had a wider range of migration, and the mercury was more dispersed with lower concentration.

(2) Relationship between particle size and total mercury concentration

The relationship between particle size and total mercury concentration is shown in **Fig. 6**. At point YS28, the particle size is in a minor range from 6 μm to 25 μm, suggesting there is no significant change in particle size, subsequently resulting in an inconspicuous relationship between T-Hg concentration and particle size. Except for point YS28, the total mercury concentration at various sampling points was inversely proportional to the particle size of the sediments. Overall, with the increase of particle size, the T-Hg decreased gradually. It completely demonstrates that particle size has a great influence on the distribution of T-Hg. The smaller the particle size of sediments, the larger the specific surface area, which provides more effective sites for mercury absorption. On the other hand, the migration speed of sediments with smaller particle sizes is considered higher because of the gravity effect, leading to a higher amount of Hg accumulation. Therefore, sediments with small particle sizes have a high T-Hg concentration.

(3) Migration simulation of different particle sizes

Fig. 7 depicts the effect of particle size on the sediment migration simulation, where the particle sizes

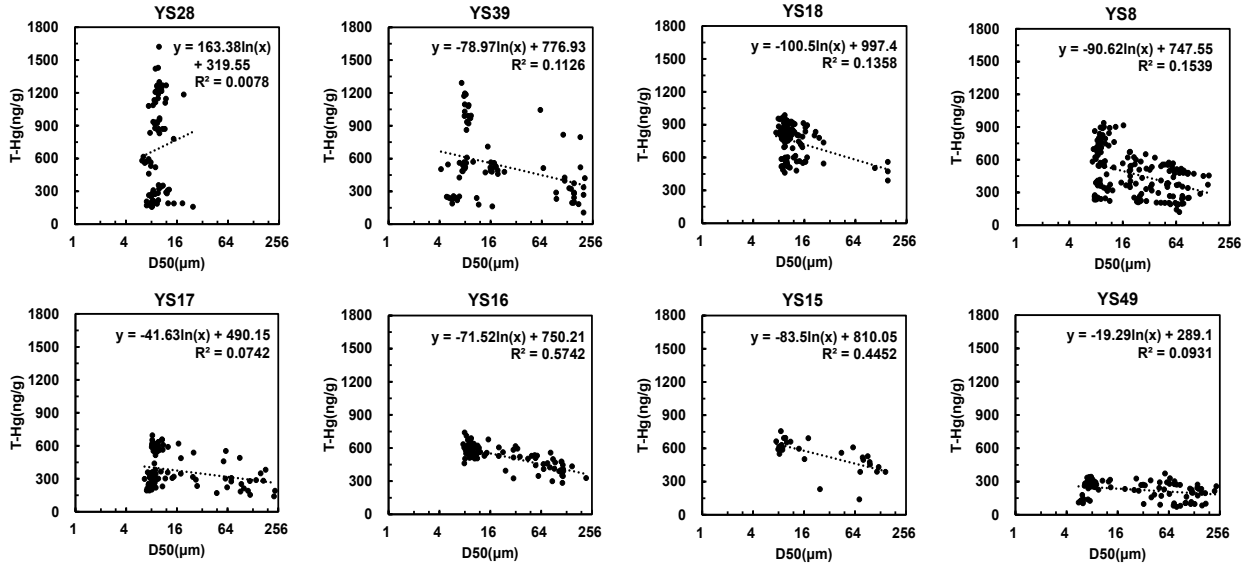

Fig.6 Relationship between particle size and T-Hg concentration

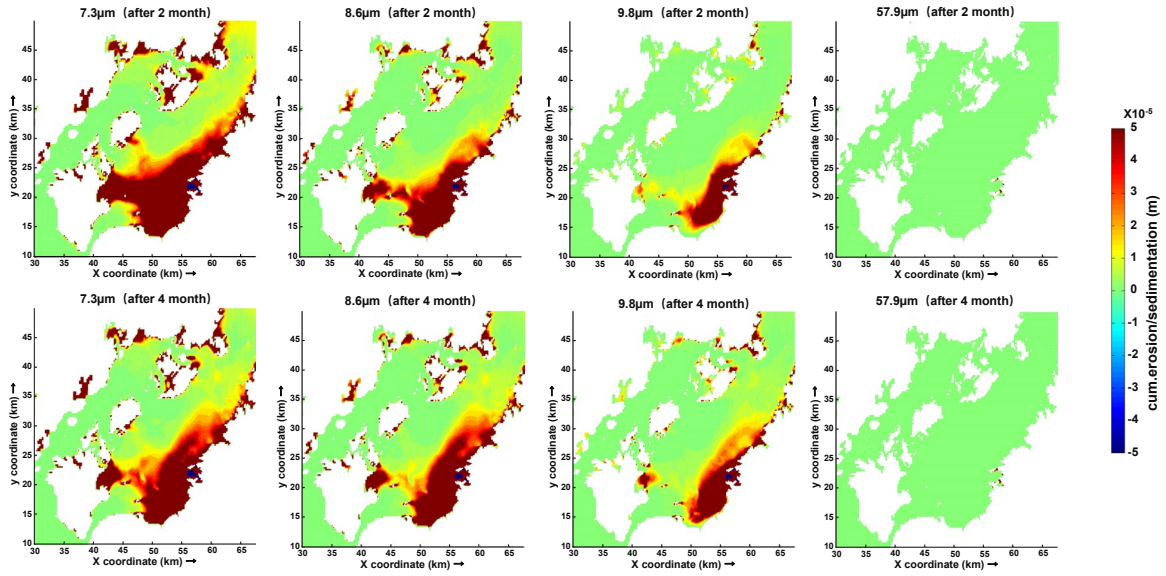

Fig.7 Numerical simulation of the migration of mercury-containing sediment

of sediments were 7.3 μm, 8.6 μm, 9.8 μm, and 57.9 μm, respectively. When the particle size is smaller than 10 μm, the Hg-containing sediments first spread to the area around Minamata Bay, and then gradually transported to the northeast and southwest of the Yatsushiro Sea. Compared to the small particle size, the migration speed and scale of Hg-adsorbed sediments with big particle sizes were smaller. For particle sizes of 57.9 μm, the Hg-containing sediments, a certain amount of erosion and accumulation of sediments occurred only in Minamata Bay. It should be noted that sediments with larger particle size are considered to migrate over a long distance with relatively long time. In other words, for such larger particle size sediments (57.9 μm), it may take many years to migrate to the Yatsushiro Sea, which is also consistent with the fact that the larger particle size sediments in the Yatsushiro Sea are less abundant. Overall, the smaller the particle size of the sediment, the faster the migration speed and the wider the migration range. Once the particle size exceeds a certain value, the migration of the sediments becomes extremely difficult. The gravity-induced high weight caused by particle size hinders sediment transport.

6. CONCLUSIONS

This study investigated the vertical distribution of mercury by measuring its concentration across sediment layers at different sites. Based on the T-Hg concentration changes, the transport of mercury from Minamata Bay to the Yatsushiro Sea was confirmed, and the mercury migrated to the southwest of the Yatsushiro Sea is more concentrated mainly due to the geomorphic effect. Moreover, there were significant variations in mercury levels at various depths and locations.

On the other hand, the total mercury concentration decreased gradually with the increase of particle size. Considering the effect of particle size, our previous numerical model was developed for predicting the mercury migration from Minamata Bay to the Yatsushiro Sea with time. The smaller the particle size of the sediments, the faster the migration speed and the wider the migration range, while the migration of the sediment exceeding a certain particle size becomes quite difficult.

ACKNOWLEDGMENTS: This work was supported by JST SPRING, Grant Number JPMJSP2136 and JSPS KAKENHI, Grant Number JP21K05162, JP21H05178 and JP22K18832.

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(Received March 16, 2023)
(Accepted July 20, 2023)