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Case Study for the Predictive Environmental Risk Assessment of Hexamethylenetetramine Release to the Yodo River during a Massive Tsunami Attack

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Abstract: Untreated hexamethylenetetramine (HMT) was discharged into the Tone River in the central area of Japan, and the risk management plan in the watershed area has been strengthened because HMT is the precursor of formaldehyde (FA) regulated by Japanese water supply law. The release of HMT could occur not only in steady but also in unsteady environmental conditions. In this context, no quantitative environmental risk assessments have dealt with the combined events of FA precursor outflow and natural disasters, such as a massive tsunami attack. In this study, we estimated the time course changes of HMT concentrations at the near water treatment plant (WTP) intakes due to tsunami run-up in the river after HMT discharge from facilities along the river during a massive tsunami attack, then potential ecological and health impacts were estimated. This method has a strong analytical ability to reveal the relationship between wave source and inland water run-up in consideration of 3D density flow. For ecological risk, the half maximal effective concentration (EC$_{50}$) was employed. We found that HMT concentration would not reach a level of concern even after the accident. For potential health risk in terms of the possible maximum inlet concentration of HMT at the WTP, the FA formation amount was $5.3 \times 10^{-2} \text{ mg/L}$, which was below the water quality standard.

Keywords: Natech (Natural hazard-triggered technological accidents); tsunami; water treatment systems; disinfection by-product; risk assessment

1. Introduction

On 11 March 2011, the Great East Japan Earthquake generated massive tsunami waves, then the tsunami propagation caused extreme multiple damages to inland industrial activities. Such a massive tsunami hazard has caused a secondary impact on industrial facilities, such as manufacturing factories that utilize chemicals and metals. Due to the damage caused by the Great East Japan Earthquake, comprehensive measures against natural disasters should be further strengthened due to concerns about the occurrence of large-scale earthquakes, such as the Nankai Trough earthquake. The Ministry of Education, Culture, Sports, Science, and Technology’s Headquarters for Earthquake Research Promotion (2013) estimated that the probability of a Nankai Trough earthquake occurring within 30 years is 70–80%; thus, local governments in areas where damage is expected should take immediate measures against earthquakes [1].

In consideration of the propagation of the impact of natural hazards to industrial facilities, recent research has investigated natural hazard-triggered technological accidents (Natech) that occur frequently worldwide, but such phenomena are not well evaluated and addressed. Moreover, Natech risk evaluation and management methods are still under development. Kishimoto (2014) discussed a broader aspect of these issues, including the
viewpoint of mixed land use, such as industrialization and urbanization, and the diffusion of new technologies [2]. In accordance with the Natech literature survey by Camila et al. (2019), the number of cases of tsunami Natech risk assessment and management is limited compared with that for other natural disasters [3]. Tanaka et al. [4] scrutinized a tsunami hazard in inland areas in terms of intrusion distance and flow discharge in rivers during the 2011 Tohoku Tsunami. This type of analysis is the basis for further risk analysis. Nagashima and Yoneyama (2017) indicated that one of the effects of a tsunami on an inland area is the water intake problem caused by the mixing of salt water at the intake of a water treatment plant (WTP) in a river channel [5]. They quantitatively evaluated the spatial distribution and temporal changes of salt water and the effect of salt water on water intake [5]. In Japan, many industrial activities handle chemical substances. If chemical substances flow into a river from facilities due to an earthquake, chemical substances that are toxic to humans may affect the water intake. The motivation of our research starts here.

In 2012, untreated hexamethylenetetramine (HMT) was discharged into the Tone River, and high levels of formaldehyde (FA) exceeding the water quality standard were detected at a WTP. HMT is classified as a Class I Designated Chemical Substance under Japan’s Pollutant Release and Transfer Register (PRTR) system. Thus, it is harmful to humans and ecosystems. The Tone River distributes water to the Tokyo metropolitan area, and some WTPs without advanced water purification systems, such as ozone water treatment, might be affected by the suspension of water intake [6]. FA can be produced by the reaction between chlorine and HMT injected during the water purification process [6]. Tsuruta et al. (2015) evaluated the effectiveness of ozone treatment and found that an advanced water purification flow in Osaka City could remove about 2 µM of HMT (a concentration near the maximum detectable concentration of HMT at the time of the accident in the Tone River system) [7]. However, only 5.9% of WTPs in Japan use advanced water purification treatment systems [8]. In addition, even if WTPs have ozone treatment equipment, the FA generated may not be fully treated and exceed the standard value because the ozone treatment function may be affected during an earthquake. Therefore, in areas where a large number of chemical facilities are located along the river, risk assessments should be conducted assuming that high concentrations of HMT will be discharged into the rivers due to earthquakes in order to prepare for water quality accidents during emergencies.

For HMT emissions [9], the Ministry of the Environment (2020) estimated that the ratio of non-notified facilities (i.e., facilities with less than 20 employees and handling less than 1 t of chemical substances) to notified facilities is 99:1 [10]. In terms of storage amount, the total number of non-notified facilities is considered to be larger than that of notified facilities. Therefore, a large number of outflows from non-notified facilities may occur during an earthquake. However, risk assessments of spills from non-notified facilities have not been conducted due to the lack of emission data.

Many studies have conducted risk assessment based on the direction of river flow under normal conditions [11]. However, no study has performed risk assessments assuming that chemical substances from downstream industrial facilities reach upstream water intakes due to tsunami run-up.

Thus, it is necessary to use data that reflect the reality as much as possible to analogize the upper limit of damage and evaluate the risk under a complex event for clarifying whether enormous damage is necessary to assume. The purpose of this paper is to reveal the importance of this combined risk estimation for chemical and natural hazards by merging established methodologies for chemical risk assessment and numerical analysis. In this study, we quantitatively evaluated the risk of water supply damage by predicting the time course changes of HMT concentration at a WTP intake and the possible volume of HMT intake due to the tsunami run-up in a river channel under the release of HTM by the Nankai Trough earthquake.
2. Target Area

As described in Figure 1, the target area is the western part of Japan that includes the Yodo River area. The Yodo River has the largest water supply population in Japan, and the Kunijima WTP has a water supply population of 2,725,006 [12], so many households may be affected. The Great Yodo River Weir (Figure 1) is located 9.8 km from the mouth of the Yodo River and consists of four central water control gates (55 m wide) and one flow control gate on each side (40 m wide) [13]. The Great Yodo River Weir prevents salt water from flowing upstream. The initial tide level was set to Tokyo Peil (a commonly used elevation standard in Japan) +0.9 m, which is the high-water level at Osaka Bay [5].

![Figure 1. Aerial view of the Great Yodo River Weir area. (a) The whole picture of the target area, the western Japan. dx shows the areal range of calculation. (b) The area around Osaka City (the target area). (c) The area around the Great Yodo River Weir, which is located at the junction of the Yodo River and its tributary, the Okawa River, and the industrial and domestic water intakes of the Kunijima WTP.](image)

3. Methods

The entire numerical simulation methods employed here were developed by previous papers [5,14,15]. Their feature was to predict the propagation of the wave source to inland areas in a 2D way and in river channels. A 3D analysis was conducted in consideration of density flow. With these models, successful estimation of flow behavior was achieved, and physically meaningful results were justified [5,14]. The detail of the analytical conditions and basic governing equations was explained there. Therefore, parameter calibration and model validation were performed, and the feasibility of these methods was examined. However, parameter calibration and model validation for specific substances have not yet been performed because of the lack of observation results of HMT in an ambient water environment. Considering its physicochemical property, the authors supposed that the behavior of HMT was similar to that of salt, and emphasized the simulation studies. Here, only some of the specific important items are explained.

3.1. Framework of Analysis

Figure 2 shows the framework of the analysis. In the disaster and emission scenario, we assumed that the ground liquefied due to the earthquake and that the chemicals stored in the facilities were discharged into the river. In the emission estimation model, we estimated the handling amount of HMT using emission factors based on the PRTR data. We used the number of employees in all industries as a sorting index to estimate the storage amount of HMT in each mesh, and we selected the meshes that were thought to store the most HMT. We used the sum of the storage amounts of those meshes as the discharge to the river. We applied the discharge into the river to the tsunami model [5] to estimate the time changes of the concentration distribution of HMT. We estimated the amount of HMT that is ultimately taken to the WTP, the amount of FA produced from HMT by chlorination, and the concentration of FA in the feed water. Subsequently, we compared the HMT concentrations with the current Japanese water quality standards. We used these
analytical procedures to assess the potential impact of post-earthquake HMT discharged into rivers on social infrastructure, human health, and aquatic organisms.

Figure 2. Analysis framework. The arrows indicate the flow of risk assessment. The emission estimation model was incorporated into the disaster and emission scenarios and applied to the tsunami model. Each rounded box indicates the calculation process, and each parallelogram indicates the input data.

The liquefaction risk was evaluated using the liquefaction potential factor $P_L$, which is defined as follows (Equations (1)–(4)) [16]:

$$P_L = \int_0^{20} F \times W(Z) dZ$$  \hspace{1cm} (1)

$$F = \begin{cases} 1 - F_L & (F_L < 1.0) \\ 0 & (F_L \geq 1.0) \end{cases}$$  \hspace{1cm} (2)

$$W(Z) = 10 - 0.5Z$$  \hspace{1cm} (3)

$$F_L = \frac{R}{L}$$  \hspace{1cm} (4)

where, $Z$ is the depth in meters, $R$ is the in situ resistance (or undrained cyclic strength) of a soil element to dynamic loads, and $L$ is the dynamic load induced in the soil element by a seismic motion [16].

We integrated the 250 m mesh maps of liquefaction risk for the Nankai Trough earthquake in Osaka Prefecture (2020) into a 1 km mesh [17]. We adopted the average of the
median $P_L$ of the respective 250 m mesh maps (each mesh was classified by $P_L$ in 5) as the $P_L$ for the 1 km mesh; the $P_L$ for meshes with $P_L$ of 25 or more was uniformly set to 27.5.

We selected four meshes whose liquefaction risk was particularly high and the estimated HMT storage amount was 2 km $\times$ 2 km in size as the outflow areas. We assumed that the HMT discharged from the chemical facility would flow into a virtual channel set up in the mesh and then into the river [18].

3.2. Estimation of HMT Outflow during Disasters and Accidents

We estimated the mesh-specific storage amount of HMT at non-notified facilities based on the methods of Nakakubo [11]; the Ministry of the Environment [10,19]; and the Ministry of Economy, Trade and Industry [20]. The notified releases $E$ (kg/year) and the non-notified releases $E_n$ (kg/year) represent the amount of HMT released to the atmosphere, public water, soil, and landfill from notified and non-notified facilities in Osaka Prefecture, respectively. We estimated the transfers of non-notified facilities in Osaka Prefecture ($Tr_n$ (kg/year)) from $E_n$ (kg/year) [10] using the ratio of $E$ (kg/year) to $Trans$ (kg/year) [21] (Equation (5)). The storage amount of chemical substances depends on the handling amount at the industrial facility, but the releases and transfers do not include the amount of chemical substances shipped as products. Therefore, we calculated the handling amount from the releases and transfers by using the emission factor (Equation (6)). The emission factor $EF$ is the ratio of the total amount of releases and transfers at the notified facilities to the handling amount $HA$ [22] (Equation (6)). We calculated the HMT handling amount $HA_n$ (kg/year) at the non-notified facilities (Equation (7)), assuming that the HMT emission factor of the non-notified facilities is equal to that of the notified facilities [11]. Fuji et al. [23] adopted the median of the data obtained from the interview survey conducted by the Kyoto City Water Supply and Sewerage Bureau on factories as the storage amount conversion factor and set it to two weeks. However, in the actual survey, some facilities stored three years’ worth of handling amount; thus, we adopted one year’s worth of handling amount for a safer estimation (Equation (8)). We used the number of employees in all industries, $W$ [24], as a sorting index and calculated the HMT storage amount $S_m$ (kg/day) by mesh in non-notified facilities from the HMT storage amount $S$ [kg/day] for Osaka Prefecture as a whole (Equation (9)) and input data for each equation are shown in Table 1:

$$Tr_n = E_n \times \frac{Trans}{E} \quad (5)$$

$$EF = \frac{E + Trans}{HA} \quad (6)$$

$$HA_n = \frac{E_n + Tr_n}{EF} \quad (7)$$

$$S = HA_n \quad (8)$$

$$S_m = \frac{W_m}{W} \times S \quad (9)$$

| Variables | Meaning |
|-----------|---------|
| $Tr_n$    | Transfers (non-notified facilities in Osaka Prefecture) (kg/year) |
| $E_n$     | Releases (non-notified facilities in Osaka Prefecture) (kg/year) |
| $Trans$   | Transfers (notified facilities in Osaka Prefecture) (kg/year) |
| $E$       | Releases (notified facilities in Osaka Prefecture) (kg/year) |
| $HA$      | Handling amount (notified facilities in Osaka Prefecture) (kg/year) |
| $EF$      | Emission factor [-] |
| $HA_n$    | Handling amount (non-notified facilities in Osaka Prefecture) (kg/year) |
| $S$       | Storage amount (non-notified facilities in Osaka Prefecture) [kg/day] |
| $S_m$     | Storage amount by mesh (non-notified facilities) [kg/day] |
| $W$       | Number of employees in all industries in Osaka |
| $W_m$     | Number of employees in all industries by mesh |
Table 1. The data used for estimating the HMT storage amount of non-notified facilities.

| Parameter                                                                 | Value          |
|---------------------------------------------------------------------------|----------------|
| Releases (notified facilities in Osaka Prefecture) (kg/year) [21]         | 5              |
| Transfers (notified facilities in Osaka Prefecture) (kg/year) [21]       | $4.8 \times 10^3$ |
| Handling amount (notified facilities in Osaka Prefecture) (kg/year) [21] | $2.3 \times 10^5$ |
| Releases (non-notified facilities in Osaka Prefecture) (kg/year) [10]    | 95             |
| Number of employees in all industries [24]                               | $9.2 \times 10^6$ |

3.3. Leakage from Facilities

A large amount of chemical substances flowing into a river in a short time period will lead to higher concentrations in the environment and more damage than a small amount flowing into a river for a long time period. Therefore, we assumed that the entire storage amount would leak out in a short time period due to a damaged storage tank during the earthquake. Equation (10) represents the outflow rate $q$ (m$^3$/s) of the chemical per unit time at time $t$. We assumed that the total amount of chemical $V_{\text{tot}}$ (m$^3$) will flow out at a constant rate from time 0 (s) to the ending time $T_{\text{release}}$ (s):

$$q = \frac{V_{\text{tot}}}{T_{\text{release}}}$$

However, if $t > T_{\text{release}}$, $q = 0$.

Where $q$ (m$^3$/s) is the amount of chemical substance released per unit time at time $t$, $V_{\text{tot}}$ (m$^3$/s) is the storage amount of chemical substance, and $T_{\text{release}}$ (s) is the ending time of the outflow.

Therefore, $dV$ (m$^3$) can be expressed as follows (Equation (11)):

$$dV = q \times \Delta t$$

where $dV$ (m$^3$) is the volume of chemicals leaking from the storage tank at time $\Delta t$, which shows an increment of calculation time.

3.4. Discharge into River

We used the method of Takubo et al. [15] shown below to determine the concentration of HMT in a river (Equations (12)–(14)):

$$\tilde{V}_t = V_t + dV$$

$$\tilde{C}_t = \frac{C_t \times 10^3 V_t + \rho_c dV}{V_t} \times 10^{-3}$$

$$\tilde{\rho}_t = \frac{\rho_0 V_t + \rho_c dV}{V_t}$$

$$= \rho_0 + \tilde{C}_t \left(1 - \frac{\rho_0}{\rho_c}\right) \times 10^3$$

where $V_t$ (m$^3$) is the volume at time $t$ ($\leq T_{\text{release}}$) of the chemical discharge cell, $\tilde{V}_t$ (m$^3$) is the volume at time $t$ ($\leq T_{\text{release}}$) of the chemical discharge cell after release, $C_t$ (mg/L) is the chemical concentration, $\rho_c$ (kg/m$^3$) is the density of the chemical substance, $\tilde{C}_t$ (mg/L) is the concentration of the chemical discharge cell after release, $\tilde{\rho}_t$ (kg/m$^3$) is the density of the chemical discharge cell, $\tilde{\rho}_t$ is the density of the chemical discharge cell, and $\rho_0$ (kg/m$^3$) is the density of water.

In the case of a chemical spill, if $\tilde{V}_t$ exceeds the cell volume of the chemical discharge cell, the excess volume is assumed to be added to the cell one level above in the vertical direction. In that added cell, the chemical concentration and density are also set to $\tilde{C}_t$ and $\tilde{\rho}_t$, respectively [15].
3.5. River Runoff and Tsunami Analysis Models and Settings

Data used for this analysis were geographical, roughness, and embankment data based on plane Cartesian coordinates from reported documents [15].

The model used in this study was a combination of a 3D numerical analysis method and a planar 2D analysis method based on nonlinear long wave theory [5]. Wide-area tsunami propagation, in-channel saline water behavior [5], and in-channel saltwater and substance behavior analyses were conducted on the basis of continuity, motion, turbulence evaluation, and convection diffusion equations as the governing equations in consideration of density flow. In the river channel, 3D analysis can be actualized. Substance behavior was estimated using convection diffusion equations; the application of the combination of these equations has already been carried out, and the feasibility of this method has already been evaluated [15]. In the current study, we replaced salinity with HMT in the analysis. The densities of HMT and seawater are approximately 1331 and 1020–1035 kg/m$^3$, respectively, and are expected to show similar behavior.

The details of the analysis area and boundary conditions have been explained in previous research [5,14]. As to the 2D tsunami propagation analysis, a five-layer nesting analysis was performed, and the grid sizes were 810, 270, 90, 30, and 10 m. The boundary condition was assumed to be fixed end for the north end, and others were assumed to be free end [14]. As to the river channel analysis, 3D analysis with 5 m for horizontal and 1 m for vertical was conducted (Table 2).

| Analysis Area | Computational Grid Size | Coordinate of the South–West End | Range End–West South–North |
|---------------|-------------------------|----------------------------------|----------------------------|
| Horizontal 2D | 810                     | (−716,000, −720,000)            | 1,215,000 801,900           |
|               | 270                     | (−173,300, −298,800)            | 186,300 178,200             |
|               | 90                      | (−108,500, −196,200)            | 81,000 72,900               |
|               | 30                      | (−61,700, −161,100)             | 32,400 34,200               |
|               | 10                      | (−58,100, −150,150)             | 26,300 21,150               |
| 3D            | 10/5                    | (−45,500, −142,180)             | 2950 2100                   |

((unit: m).

3.6. Risk Assessment of HMT to Riverine Aquatic Organisms

We evaluated the ecological risk of exposure of riverine aquatic organisms to HMT for a very short period of time by defining a Risk score as shown in Equation (15) and comparing the cumulative exposure during the peak period from time $t_1$ (s) to $t_2$ (s):

$$
\text{Risk score} = \sum_{t=t_1}^{t_2} \frac{C_{\text{HMT}}^t \Delta t}{C_{\text{acute}} \times T_{\text{acute}}}
$$

where $C_{\text{HMT}}^t$ (mg/L) is the concentration of HMT at time $t$ at the concentration measurement point, $C_{\text{acute}}$ (mg/L) is the acute toxicity values in the HMT toxicity test results, and $T_{\text{acute}}$ (s) is the duration in the toxicity test. We calculated the product of concentration and duration by adding the time width $\Delta t$ from time $t_1$ to $t_2$ when the high concentration was estimated. A risk score greater than or less than 1 indicates an impact or no impact on riverine aquatic organisms, respectively.

Given that the minimum toxicity data available for HMT for aquatic organisms is the 48 h EC$_{50}$ of 104 mg/L, which is an index of swimming inhibition for the crustacean Daphnia magna [25], we set $C_{\text{acute}}$ and $T_{\text{acute}}$ as 104 mg/L and 172,800 s (48 h), respectively.
3.7. Risk Assessment of Potential FA Production at WTP

We assumed that river water containing HMT is taken to a WTP and reacts with chlorine in the chlorination process to produce FA. Moreover, we estimated the FA concentration in the water supply during the peak period from time $t_1$ (s) to $t_2$ (s). To calculate the potential FA production at the WTP, we assumed that the water treatment functions capable of decomposing HMT, such as ozone treatment, were damaged due to the earthquake. At the Kunijima WTP, we focused on the domestic water intake because no chlorination is performed at the industrial water intake. The FA concentration in the water supply, $C_{FA}$ (mg/L), is the estimated concentration under the condition of complete mixing (Equation (16)):

$$C_{FA} = \frac{K_{production} \times \sum_{i=1}^{t_2-t_1} C_{HMT}^{HMT} \Delta t \times Q_{intake}}{Q_{supply} \times (t_2-t_1)}$$

where $K_{production}$ is the mass of the largest FA produced by HMT per unit mass, $Q_{intake}$ (L/s) is the amount of water intake per second, and $Q_{supply}$ (L/s) is the amount of water supply per second. The speed of water intake and water supply was calculated from the respective quantities per day, assuming that their speed per hour is constant.

The mass of FA generated from HMT per unit mass is about 0.6–1.1 g according to studies that evaluated the amount of FA generated by chlorination of HMT [26–29]. We adopted the case with the largest amount of generation to estimate the safe side and set $K_{production}$ to 1.1. According to the Osaka City Waterworks Bureau (2019), the average water intake in January, when the intake volume is the lowest during the low-water-temperature period, is 64,041 m³/day for industrial water [13]. $Q_{intake}$ for industrial water was calculated as $7.4 \times 10^2$ L/s. Meanwhile, domestic water is taken from the Kunijima and Hitotsuya intakes, of which the average amount in January was 581,132 m³/day. The ratio of intake capacity of the pumps at Kunijima and Hitotsuya intakes was 88:12 [12]. Thus, $Q_{intake}$ for domestic water was calculated as $5.9 \times 10^3$ L/s. On the other hand, the average water supply in January was 461,881 m³/day [12]; therefore, $Q_{supply}$ was calculated as $5.3 \times 10^3$ L/s. We also compared the FA concentration in the water supply ($C_{FA}$) with the Japanese water quality standard for FA ($8.0 \times 10^{-2}$ mg/L) [30] to assess the risk. Water quality standards are established based on chronic toxicity indicators [31,32].

3.8. Threshold for Risk Determination

The concentration of HMT in river water under normal conditions is estimated to be $3.0 \times 10^{-3}$ mg/L [33]. We took the significant figures into account and calculated the Risk score for the concentration that changes the first significant figure of the concentration in river water under normal conditions, that is, when the concentration of HMT in river water increases by more than $5.0 \times 10^{-5}$ mg/L due to the outflow. If the increase was smaller than this value, we did not perform a risk assessment because rounding would equal to the normal HMT concentration.

4. Case Study

4.1. Analysis Conditions

In this study, we based our analysis on the method of Nagashima and Yoneyama [5], assuming that the HMT is discharged into the river channel around the Great Yodo River Weir. We assumed the case that would cause the most damage. We used the case with the highest tsunami height reaching near the mouth of the Yodo River in the “Study Group on the Great Earthquake Model of the Nankai Trough” [34] as the tsunami fault model. We assumed a river flow rate of 62 m³/s, which is the minimum amount during a drought when the tsunami is expected to have an impact farther upstream [5]. At this case, the river water flow over the Great Yodo River Weir is 0 m³/s, and the river water flows into its tributary (the Okawa River) [5].

We set the river water as freshwater with 0 mg/L salinity for the upstream and downstream sides of the Great Yodo River Weir. The water temperature was set to 15 °C,
assuming a period of low water temperature when chemical decomposition in water and volatilization from the water surface to the atmosphere are unlikely to occur [15].

We set the molecular diffusivity of HMT to be $2.0 \times 10^{-9} \text{ m}^2/\text{s}$ as in Nagashima and Yoneyama [5]. In this study, we did not consider the decomposition or reaction of HMT in water, its volatilization into the atmosphere, or its adsorption on suspended solids in water. Therefore, the analysis in this study focuses only on the estimation of the maximum concentration that appears in a short time. During calculation, only the increased concentration due to the outflow was added, not the background concentration of HMT ($3.0 \times 10^{-3} \text{ mg/L}$) [33]. However, the total concentration of HMT was taken into account at the stage of risk assessment (see Sections 5.2.2 and 5.3.2).

4.2. Case Setting

We considered the following two cases. Figure 4 shows a 1 km mesh map of the storage amount of HMT at non-notified facilities around the Yodo River in Osaka Prefecture and the outflow area and location of the water intake for each case.

Case 1
We assessed the impact of an HMT discharge on the right bank downstream of the Great Yodo River Weir.

During drought when the weir is completely closed, the flow rate over the weir is zero. Therefore, if HMT is discharged downstream of the weir, it will not be diluted by the flow of the river, and the high concentration of HMT will stay just below the weir until the tsunami arrives.

Case 2
We assessed the impact of an HMT discharge on the water surface with a domestic water intake at the Kunijima WTP.

In both cases, the outflow duration was set to 60 s, and the analysis was conducted until 18,000 s (5 h) after the earthquake.

5. Results and Discussion

5.1. Examination of Water Flow at the Yodo River Weir, HMT Storage Amount, and Outflow Amount

The estimated water flow at the location of the Yodo River weir is shown in Figure 3. In this figure, a plus value means the flow direction, and a minus value means the run-up direction in the river. The figure depicts that the first tsunami attack was approximately 11,000 s.

![Figure 3. Overflow rate at the Yodo River weir.](image)

The non-notified transfers of HMT in Osaka Prefecture were estimated to be $9.2 \times 10^4 \text{ kg}$ from Equation (5), which is about 19 times higher than the notified transfers of HMT in Osaka Prefecture. The emission factor is 0.021 from Equation (6). The handling amount of non-notified facilities in Osaka Prefecture calculated from Equation (7) was $4.3 \times 10^6 \text{ kg}$, which is
also about 19 times larger than that of notified facilities. Table 3 shows the estimation results of the non-notified storage amount in the target mesh area using Equations (8) and (9).

Table 3. Estimation results of the non-notified storage amount of HMT by mesh.

| Mesh Number | Number of Employees [24] | Non-Notified Storage Amount (kg) | $P_L$ |
|-------------|---------------------------|----------------------------------|-------|
| 1           | $3.9 \times 10^4$         | $1.8 \times 10^4$                | 26.9  |
| 2           | $1.2 \times 10^4$         | $5.6 \times 10^3$                | 25.9  |
| 3           | $3.9 \times 10^4$         | $1.8 \times 10^4$                | 25.9  |
| 4           | $1.4 \times 10^4$         | $6.7 \times 10^3$                | 23.3  |

The outflow amount is the sum of the estimated non-notified storage amount of HMT in the four meshes surrounded by the white dotted lines in Figure 4, which is $4.9 \times 10^4$ kg. The $P_L$ was larger than 15, indicating a large liquefaction potential for all meshes (Table 2).

Figure 4. Locations of discharge facilities, river discharge points, and estimated storage amount. Mesh shading indicates non-notified storage of HMT, with darker red meshes indicating higher estimated storage.

Figure 4 shows the mesh map of the non-notified storage amount, and Table 4 shows the discharge points for case settings 1 and 2 determined from the storage amount per mesh (Figure 4).

Table 4. Case setting.

| Case | Outflow | Discharge Point * | Distance from Discharge Point to Water Intakes [m] |
|------|---------|-------------------|-----------------------------------------------|
| 1    | The total storage amount of a 2 km × 2 km mesh with both high storage amount and liquefaction risk along the Yodo River | Right bank downstream of the Great Yodo River Weir | 300 (industrial) |
| 2    |         | Water surface just above the domestic water intake | 1000 (domestic) |

* The details of the points are shown in Figure 4.
The storage amount was especially large in the area southwest of the Great Yodo River Weir, with an estimated storage amount of over 30 t per mesh. These areas had large storage amount due to their large population and large number of employees (Figure 4). Given that the Kunijima WTP intakes are all located on the right bank of the Yodo River, a large amount of HMT is expected to flow into the right bank intake when discharged from the right bank mesh into the Yodo River. Therefore, as a scenario, we assumed that all the HMT stored in the outflow area on the right bank (as shown in Figure 4) would be discharged into the right bank of the Yodo River in 60 s due to an earthquake.

In Case 1, we assumed that the HMT is discharged from the right bank downstream of the Great Yodo River Weir. Given that no water flows over the weir during drought, if the HMT flows out at this point, it will not be diluted, and high concentrations of HMT will remain until the tsunami arrives. In Case 2, we set the outflow point assuming that the outflow would be in the vicinity of the domestic water intake.

5.2. Case 1
5.2.1. Behavior and Concentration Distribution of HMT

Figure 5a–d show the concentration distribution of HMT in the Yodo River channel. Comparing Figure 5a–d, we can see that the highest HMT concentration is located around the outflow point immediately after the outflow. Figure 5b shows the diagram just before the arrival of the tsunami, which is diffused about 350 m downstream by the undertow of the tsunami. Figure 5c shows the diagram when HMT is pushed upstream the most by the tsunami, and the concentration is about 2.0 × 10⁻⁴ mg/L from the Great Yodo River Weir to about 400 m upstream. In Figure 5d, the HMT concentration is less than 1.0 × 10⁻⁴ mg/L up to 1 km upstream from the Great Yodo River Weir. Therefore, the HMT concentrations during the tsunami will be diluted by the tsunami flow, and the concentrations will be smaller than those in the case of normal river flow.

Figure 5. Concentration distribution of HMT (Case 1). The color bars in the right part of the figures indicate the concentration of HMT. T (s) in the figures indicates the elapsed time after the earthquake, (a) immediately after the outflow (300 s), (b) before the arrival of the tsunami (8700 s), (c) after being diffused by the tsunami (11,100 s), and (d) after returning to normal flow (18,000 s).
Figure 6 shows the changes in HMT concentrations at the industrial and domestic intakes of Kunijima WTP in Case 1. In Case 1, the tsunami reached the Great Yodo River Weir about 2 h and 30 min after the earthquake, causing a temporary increase in HMT concentration at the intake of the industrial water of Kunijima WTP. The maximum HMT concentration at the industrial intake was $1.3 \times 10^{-4}$ mg/L. After the HMT concentration at the industrial intake started to increase, it remained above $1.0 \times 10^{-5}$ mg/L for $2.2 \times 10^3$ s. The concentration at the domestic intake was lower than the estimated concentration in river water under normal conditions ($3.0 \times 10^{-3}$ mg/L) [33].

![Time change of HMT concentration near the intakes of Kunijima WTP (Case 1). The blue and orange lines indicate the time change of concentration at the industrial and domestic water intakes from the time of the earthquake to 18,000 s later, respectively. The asterisk (*) indicates the time when the overflow of the Great Yodo River Weir by the tsunami was first estimated.](image)

### 5.2.2. Risk Assessment of HMT to Riverine Aquatic Organisms and Humans

The risk score for aquatic organisms around the industrial water intake was calculated as the duration of the concentration of one-tenth of the maximum HMT concentration ($1.3 \times 10^{-5}$ mg/L). The duration of the concentration was 1889 s, from 9986 s to 11,874 s. The risk score was calculated by adding the estimated background HMT concentration under normal conditions ($3.0 \times 10^{-3}$ mg/L), which was $3.2 \times 10^{-7}$, indicating that the risk to aquatic organisms was not a concern even near the industrial water intake where the highest concentration was estimated.

Osaka City (2020) does not provide a specific concentration of HMT or FA for the water quality standard of industrial water supply [35], and the toxicity of dermal HMT administration has not been evaluated in animals. However, the results of patch tests on workers exposed to HMT have shown positive reactions [36]. In addition, allergic contact dermatitis, such as erythema, papules, pruritus, urticaria, and edema, as well as asthma, allergic rhinitis, and allergic conjunctivitis, have been reported, suggesting that HMT is a sensitizing substance to humans [36]. According to the results of this study, the maximum HMT concentration in river water at the industrial water intake is smaller than the estimated concentration in river water under normal conditions ($3.0 \times 10^{-3}$ mg/L) [33]. Thus, the risk of handling industrial water was not considered to be a concern.

Given that the HMT concentration at the domestic water intake was less than $5.0 \times 10^{-5}$ mg/L, we did not assess the risk of FA produced.
5.3. Case 2

5.3.1. Behavior and Concentration Distribution of HMT

Figure 7a–d show the concentration distribution of HMT in the Yodo River channel. Comparing Figure 7a–d, the HMT concentration around the outflow point immediately after the outflow was the highest, with a maximum concentration of $2.5 \times 10^{-1}$ mg/L. In addition, Figure 7b shows the figure just before the arrival of the tsunami, where about $3.0 \times 10^{-4}$ mg/L of HMT flowed 400 m in the downstream direction. Figure 7c shows the figure when the HMT is pushed upstream the most by the tsunami, and the concentration is about $2.0 \times 10^{-4}$ mg/L from the outflow point to 100 m upstream. In Figure 7d, the water is flowing down the river again, and the HMT concentration is less than $2.0 \times 10^{-4}$ mg/L. When the tsunami ran up the river, the HMT concentration was about 1/1000 of that immediately after the spill.

![Figure 7a](image1)

![Figure 7b](image2)

![Figure 7c](image3)

![Figure 7d](image4)

**Figure 7.** Concentration distribution of HMT (Case 2). The color bars in the right part of the figures indicate the concentration of HMT, which ranges from 0 mg/L to $1.0 \times 10^{-3}$ mg/L. T (s) in the figures indicates the elapsed time after the earthquake, (a) immediately after the outflow (300 s), (b) before the arrival of the tsunami (8700 s), (c) after being diffused by the tsunami (11,100 s), and (d) after returning to normal flow (18,000 s).

Figure 8a,b shows time change of HMT concentration near the intakes of Kunijima WTP in Case 2. In Case 2, high concentrations of HMT flowed downstream immediately after the outflow, and we can see high concentrations at the domestic water intake. The maximum HMT concentration at the domestic water intake was $8.5 \times 10^{-2}$ mg/L. The reason for the multiple peaks immediately after the outflow is that the outflow of HMT continued for 60 s and had the same speed; thus, minor fluctuations were observed in the values until steady state was reached. However, the concentration temporarily increased again when the tsunami arrived. The maximum HMT concentration observed in the tsunami run-up was about $2.4 \times 10^{-4}$ mg/L, which was less than one hundredth of the concentration immediately after the outflow. At the industrial water intake, the concentration was less than $5.0 \times 10^{-3}$ mg/L.
5.3.2. Risk Assessment of HMT to Riverine Aquatic Organisms and Humans

From the time of the earthquake until 18,000 s after the earthquake, the HMT concentration at the industrial water intake of the Kunijima WTP was less than $5.0 \times 10^{-5}$ mg/L. Therefore, we concluded that the handling risk of industrial water intake was not a concern. We calculated the risk score for aquatic organisms in the vicinity of the domestic water intake based on the duration of the peak concentration. The peak was 78 s, from 12 s to 90 s, when the concentration was greater than $8.5 \times 10^{-3}$ mg/L, which is one tenth of the maximum HMT concentration. Even if the risk score is calculated by adding the estimated HMT concentration under normal conditions ($3.0 \times 10^{-3}$ mg/L), it is still $2.3 \times 10^{-2}$. Thus, the risk to aquatic organisms is not at a level of concern.

The amount of HMT taken up at the domestic water intake during the period of the same peak as the risk score was $2.6 \times 10^4$ mg, including the background HMT. On this basis, the $C_{FA}$ was estimated to be $5.3 \times 10^{-2}$ mg/L. This concentration is on the same order of magnitude as the water quality standard value for FA of $8.0 \times 10^{-2}$ mg/L [30]. However, the water quality standard value is based on the chronic toxicity value for rats [32], whereas the FA concentration in this study was of the same order as the standard value for 78 s. Thus, the risk is not considered to be of concern. In the case of Osaka Prefecture (where the liquefaction risk is high, facilities are located near the water intake, and the storage amount is relatively large), the entire amount of HMT is discharged into the water surface directly above the domestic water intake during an earthquake. This case is based on the assumption that the maximum HMT concentration is taken at the intake. However, there is room for further consideration in the evaluation method because the initial concentration right after the outflow depends on the amount of diluted water at the input. In this case, the risk of FAs being produced exceeding the water quality standards was not at a level of concern.

6. Conclusions

In this study, tsunami attack model and chemical risk assessment method were combined, and we estimated HMT released from the facilities in the Yodo River caused by a tremor of the Nankai Trough earthquake. We estimated the risk of acute toxicity for human and aquatic organisms, which would be caused by HMT outflow under the maximum...
risk in the input condition, that is, the outflow of the entire amount of HMT stored in a 2 km × 2 km area would occur during a drought.

We compared cases where the discharge was downstream of the intake (Case 1) and near the intake and reached the intake before the tsunami run-up (Case 2).

In Case 1, where the highest HMT concentration was estimated, the risk score was $3.2 \times 10^{-7}$ during the peak period, which is considered to be of low concern for aquatic organisms. At the domestic water intake, the increased HMT concentration due to the discharge was lower than $5.0 \times 10^{-5}$ mg/L. Thus, the concern for aquatic organisms was similarly low, and we did not assess the risk of FA that was taken up.

In Case 2, at the industrial water intake, the HMT concentration increased by the discharge was lower than $5.0 \times 10^{-5}$ mg/L. Thus, there was no risk from the intake. The Risk score for the duration of the peak at the domestic water intake was $2.3 \times 10^{-7}$, suggesting no risk to aquatic organisms even in the vicinity of the outflow point, where the highest HMT concentration is expected. Furthermore, the concentration of FA that can be produced by chlorination at the WTP after domestic water intake is $5.3 \times 10^{-2}$ mg/L, which does not exceed the water quality standard value ($8.0 \times 10^{-2}$ mg/L). In the calculation process of the concentrations, the difference between the volume of HMT for the input and that of the water mass of the river would result in underestimation, which requires further study.

The risk assessment model developed in this study can be applied to other chemical outflow scenarios in Nankai Trough earthquake by changing the parameters related to physical properties, outflow volume, and location and can quantitatively assess the risk arising from each event.

Author Contributions: Conceptualization, S.H., L.I., N.Y. and A.T.; Data curation, S.H.; Formal analysis, S.H.; Methodology, S.H., L.I., N.Y. and A.T.; Software, N.Y.; Supervision, A.T.; Validation, L.I., N.Y. and A.T.; Visualization, S.H.; Writing—original draft, S.H.; Writing—review & editing, L.I., N.Y. and A.T. All authors have read and agreed to the published version of the manuscript.

Funding: The Environment Research and Technology Development Fund of the Environmental Restoration and Conservation Agency of Japan, grant number JPMEERF18S11702.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: This research was supported by the Environment Research and Technology Development Fund of the Environmental Restoration and Conservation Agency of Japan.

Conflicts of Interest: The authors declare no conflict of interest.

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