Initial Environmental Risk Assessment of Japanese PRTR Substances in Treated Wastewater

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ABSTRACT
This study aimed to collect fundamental information on environmental risks posed by Class 1 chemicals under the Japanese Pollutant Release and Transfer Register (PRTR) system. The concentration of the substances in treated wastewater was estimated using the publicly available information in the PRTR system. Initial ecological and human health risk assessments were performed by comparing the estimated concentration and existing toxicity indexes on the basis of a hazard quotient (HQ). The results showed that linear alkylbenzene sulfonate (LAS) and its salts had the highest concentrations (166 μg/L). Thirty-six (e.g., hydrazine) and 11 chemicals (e.g., glutaraldehyde) had high HQ values (≥ 0.1) in initial ecological and human health risk assessments, respectively. Using comparisons between a previous study and this study, an interannual variability of high HQ value chemicals revealed that the composition of chemicals for ecological risk was similar for the different periods; however, it was different for human health risk. Further monitoring and development of countermeasures against the chemicals are required to avoid ecological and health risks.

Keywords: ecological risk, health risk, PRTR system, reclaimed water, treated wastewater

INTRODUCTION
The shortage of water accompanied by global warming, population increase, and other related issues are now of worldwide concern. In recent years, the reuse of treated wastewater as reclaimed water has been investigated to address this problem. Reclaimed water is generally utilized for irrigation and purposes other than human consumption in foreign countries (Asano, 2008; Yamagata, 2008). In Japan, it has also been used for agriculture (Tanaka and Asano, 2006; Tasaka, 2007). Reclaimed water may play an important role in water use, food production and the development of sustainable societies as an alternative water resource.

However, there are concerns that treated wastewater may contain many kinds of chemicals. The uptake of these chemicals may be harmful to human health, and the chemicals that are discharged into aquatic environments may cause adverse effects on aquatic life. Although there are surveys on the concentration of heavy metals (Isozaki et al., 2006), nonylphenols and linear alkylbenzene sulfonate (LAS, Fauser et al., 2003) in treated wastewater, and risk assessments of surfactants in a river derived from treated wastewater and other sources (Miura et al., 2005) in previous studies, no report other than the previous research by Mano et al. (2013) is found on the risk assessment of a variety of chemicals in treated wastewater. Thus, the risks posed by chemicals in treated wastewater are unclear and an assessment of these risks is required.

Treated wastewater contains many kinds of chemicals, and it is impossible to carry out a risk assessment for all chemicals that may be harmful. Therefore, an initial environmental risk assessment was conducted (Ministry of the Environment, 2012a). In...
the assessment, the health and ecological risks are gauged through the estimation of exposure to chemicals. These assessments are made by the comparison with hazard indexes and estimated concentration of the registered chemicals. Then, the results of the comparison are used to clarify which potential hazardous chemicals in treated wastewater should be monitored. An initial environmental risk assessment of the chemicals found in treated wastewater in Japan, under the Japanese Pollutant Release and Transfer Register (PRTR) system was carried out by our previous research; chemicals such as hydrazine that may cause environmental risks were reported by Mano et al. (2013). However, the research did not address 52 wastewater chemicals that had been newly registered to the PRTR system since April 2010; at this time no information is available on the risk assessment of the newly registered chemicals in treated wastewater. In addition, there is no information on the interannual variability of potentially hazardous chemicals in treated wastewater in Japan. These evaluations are needed to obtain the latest information on the risk of potentially hazardous chemicals and to clarify the chemicals that need to be monitored.

The purpose of this study was to suggest a list of chemicals present in treated wastewater that require a detailed risk assessment. An initial health and ecological assessment of chemicals was also conducted using PRTR data. Chemicals to be monitored were suggested based on the results of the assessments and an interannual variability of potentially hazardous chemicals.

MATERIALS AND METHODS

Target chemicals
Under the Japanese PRTR system, the release and transfer of 30 chemicals such as zinc are legally notifiable by sewerage works. In addition, between April 2011 and March 2012, the discharge amount of 179 chemicals in Japan is estimated as the “Estimated Releases Outside Notification” by sewerage works (Ministry of the Environment, 2014). In this study, the 209 Class 1 chemicals reported in the PRTR document were examined for initial health and ecological risk assessments.

Estimation of concentration of substances under the Japanese PRTR system in treated wastewater
The amounts of chemicals in treated wastewater discharged into receiving water were referred to the data of reported release and transfer, and the “Estimated Releases Outside Notification” in the documents (Ministry of the Environment, 2014). Since the above discharge amounts were determined from the data collected between April 2011 and March 2012, the treatment volume of wastewater in wastewater treatment plants in Japan during the same period (= 1.48 × 10^{10} m^{3}/year, Japan Sewage Works Association, 2013) was used. The estimated concentration of each chemical was obtained from the division of the discharge amount of chemicals by the treatment volume of wastewater. The estimated concentrations were regarded as annual average concentrations in treated wastewater, and were used in the initial health and ecological risk assessments below.

Hazard index
Hazard indexes of the target chemicals were obtained from various documents (Central Advisory Panel, 2003; Ministry of Health, Labour and Welfare, 2003; Ministry of the
Environment, 2015a; Food Safety Commission, 2015a, 2015b; Ministry of the Environment, 2015b; National Institute of Technology and Evaluation, 2015). For an initial health risk assessment, NOAEL (No Observed Adverse Effect Level) or ADI (Acceptable Daily Intake) were obtained from Ministry of Health, Labour and Welfare (2003), Food Safety Commission, Ministry of the Environment, Environmental Health Department, and National Institute of Technology and Evaluation. For an initial ecological risk assessment, NOEC (No Observed Effect Concentration) and PNEC (Predicted No Effect Concentration) were obtained from Central Advisory Panel (2003), Ministry of the Environment (2015a, 2015b), and National Institute of Technology and Evaluation (2015). When Uf (Uncertainty factor) for the NOAEL or NOEC of a target chemical was not specified, Uf for human health and aquatic life was determined based on the calculation method reported by National Institute of Technology and Evaluation (2015) and Ministry of the Environment (2012a), respectively. Then ADI or PNEC were calculated using the Uf based on equation (1) or (2).

$$\text{ADI} = \frac{\text{NOAEL}}{\text{Uf}} \quad (1)$$

$$\text{PNEC} = \frac{\text{NOEC}}{\text{Uf}} \quad (2)$$

When several ADI or PNEC values were found for a chemical, the smallest value was used for the risk assessments.

**Initial health risk assessment**

In this study, a hazard quotient (HQ) was applied to find potential hazardous chemicals in treated wastewater. An HQ value specifies whether a chemical is potentially hazardous or not. The classification of evaluation by HQ values is summarized in Table 1 (Finger et al., 2007).

For safety assessment, the risk of direct drinking of treated wastewater on the assumption of a high risk scenario was examined as an initial health risk assessment. According to the document of Ministry of Health, Labour and Welfare (2009), the assumed conditions were: a person whose body weight is 50 kg drinks 2 L of treated wastewater daily and the contribution rate of drinking for the exposure to a chemical is 10%. A health hazard quotient (HQ$_H$) was calculated by the division of the assumed exposure amount of a chemical by ADI based on equation (3).

$$\text{HQ}_H = \frac{(\text{Estimated exposure amount of a chemical by drinking} [\mu g/\text{kg/day}])}{(\text{ADI} [\mu g/\text{kg/day}] \times 0.1)} = \frac{(\text{Estimated concentration of a chemical in treated wastewater} [\mu g/L])}{2 \times 2 \times (\text{ADI} [\mu g/\text{kg}]/50 \times 0.1) / \text{ADI} \quad (3)}$$
Table 1 - Classification of evaluation of chemicals by HQ.

<table>
<thead>
<tr>
<th>Classification of evaluation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HQ &lt; 0.1</td>
<td>No adverse effect is expected.</td>
</tr>
<tr>
<td>0.1 ≤ HQ &lt; 1</td>
<td>The hazard is low, but potential for adverse effects should be considered.</td>
</tr>
<tr>
<td>1 ≤ HQ &lt; 10</td>
<td>Some adverse effects or moderate hazard is probable.</td>
</tr>
<tr>
<td>10 ≤ HQ</td>
<td>High hazard is anticipated.</td>
</tr>
</tbody>
</table>

This table referred to Finger et al. (2007).

**Initial ecological risk assessment**

For safety assessment, a risk of direct exposure of aquatic life to treated wastewater, on the assumption of a high risk scenario, was investigated as an initial ecological risk assessment. The risk was evaluated based on an HQ as well as the initial health risk assessment. The ecological hazard quotient HQ$_E$ was calculated by dividing the estimated concentration of a chemical in treated wastewater by PNEC based on equation (4).

$$
HQ_E = \frac{\text{Estimated concentration of a chemical} [\mu g/L]}{\text{PNEC} [\mu g/L]} \tag{4}
$$

**Interannual variability of potential hazardous chemicals**

The health hazard quotient (HQ$_H$) and HQ$_E$ of chemicals in treated wastewater using the PRTR data obtained between April 2008 and March 2009 was evaluated by Mano et al. (2013). Chemicals with an HQ$_H$ and HQ$_E$ ≥ 1 in this study and the previous research were compared to investigate the interannual variability of potential hazardous chemicals.

**RESULTS**

**Estimation of concentration of substances under the Japanese PRTR system in treated wastewater**

Of the 209 chemicals under the Japanese PRTR system, there were no discharge data for 3 chemicals, and therefore the estimated concentrations of 206 chemicals were obtained. The estimated concentrations of the highest 30 chemicals are shown in Fig. 1. The concentration of LAS and its salts was the highest (166 μg/L). Eight chemicals including 2-aminoethanol were ≥ 10 μg/L, 19 chemicals were ≥ 1 μg/L, and 31 chemicals were 0.1 μg/L, respectively. Among the newly registered chemicals, AES (sodium polyoxyethylene dodecyl ether sulfonate), SDS (sodium dodecyl sulfate) and other 6 chemicals showed high concentrations.

**Initial health and ecological risk assessment**

Of the 209 chemicals under the Japanese PRTR system, 122 chemicals were found considering the estimated concentrations and ADI. Figure 2 summarizes the HQ$_H$ of chemicals whose value was ≥ 0.1. Glutaraldehyde had the largest HQ$_H$ value (7.2), followed by molybdenum and its compounds (2.3). The HQ$_H$ values of 9 chemicals such as cobalt and its compounds were between 0.1 and 1.
Fig. 1 - Estimated concentration of chemicals under the Japanese PRTR system in treated wastewater. (Linear alkylbenzene sulfonate (LAS); Polyoxyethylene alkyl ether (AE); Sodium polyoxyethylene dodecyl ether sulfonate (AES); Sodium dodecyl sulfate (SDS); 2,2-Dibromo-2-cyanoacetamide (DBNPA); N,N-Dimethylacetamide (DMAC); Ethylenediamine tetraacetic acid (EDTA); Hexadecyltrimethylammonium chloride (HTAC). The symbol (*) indicates a newly registered chemical to the Japanese PRTR system since April 2010.)
Fig. 2 - Health hazard quotient (HQH) of chemicals on the assumption of direct drinking of treated wastewater. (The symbol (*) indicates a newly registered chemical to the Japanese Pollutant Release and Transfer Register (PRTR) system since April 2010.)

Of the 209 chemicals under the Japanese PRTR system, 144 chemicals were found considering the estimated concentrations and PNEC. The chemicals whose HQE values were ≥ 0.1 are shown in Fig. 3. The largest HQE value was 1,920 for hydrazine, then 296 for hydroquinone. The HQE values of 6 chemicals including polyoxyethylene alkyl ether (AE) were between 10 and 100. The HQE values of 10 chemicals including cobalt and its compounds were between 1 and 10. The ecological hazard quotient (HQE) values of 18 chemicals such as arsenic and its inorganic compounds were between 0.1 and 1.

The number of chemicals whose HQE value was ≥ 0.1 was much larger than that of chemicals whose HQH value was ≥ 0.1. For both assessments, the only chemical with both HQH and HQE values ≥ 1 was glutaraldehyde. Similarly, the chemicals with both HQH and HQE values ≥ 0.1 were glutaraldehyde, cobalt and its compounds, pyridine, formaldehyde, bromodichloromethane, chloroform, dinitrotoluene, hydroquinone and vanadium compounds.

**Interannual variability of potentially hazardous chemicals**

Our previous research (Mano et al., 2013) revealed that the chemicals with an HQH value ≥ 1 were hydrazine (39.2) and 1,3-dichloro-2-propanol (3.0, classified into Class 2 since April 2010). A comparison of that report and the results given here in Fig. 2 suggest that the health risk from potentially hazardous chemicals has significant temporal variation.
Fig. 3 - Ecological hazard quotient (HQ$_E$) of chemicals on the assumption of direct exposure of aquatic living things to treated wastewater. (Polyoxyethylene alkyl ether (AE); Polyoxyethylene nonylphenyl ether (NPE); Linear alkylbenzene sulfonate (LAS); N,N-dimethyldodecylamine N-oxide (DDNO); Hexadecyltrimethylammonium chloride (HTAC); Polyoxyethylene octylphenylether (OPE); Bis (2-ethylhexyl) phthalate (DEHP). The symbol (*) indicates a newly registered chemical to the Japanese Pollutant Release and Transfer Register (PRTR) system since April 2010.)
Table 2 summarizes the HQ\textsubscript{E} values during different data periods. The values of hydroquinone and DDNO (N,N-dimethyldodecylamine N-oxide) in this study were larger and smaller than those in the previous report (Mano \textit{et al}., 2013), respectively. The values of other chemicals were similar between this study and the previous research.

**Table 2 - Interannual variability of HQ\textsubscript{E} of chemicals. Abbreviations are shown in Fig. 3.**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>HQ\textsubscript{E} Apr 2011 – Mar 2012</th>
<th>HQ\textsubscript{E} Apr 2008 – Mar 2009$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrazine</td>
<td>1,920.6</td>
<td>1,569</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>296.3</td>
<td>36.7</td>
</tr>
<tr>
<td>AE (C = 12 – 15)</td>
<td>59.9</td>
<td>54.0</td>
</tr>
<tr>
<td>NPE</td>
<td>58.6</td>
<td>73.8</td>
</tr>
<tr>
<td>Zinc compounds (water-soluble)</td>
<td>58.0</td>
<td>58.9</td>
</tr>
<tr>
<td>LAS and its salts (C = 10 – 14)</td>
<td>44.9</td>
<td>55.3</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>25.1</td>
<td>11.6</td>
</tr>
<tr>
<td>DDNO</td>
<td>16.5</td>
<td>1,722</td>
</tr>
<tr>
<td>2-aminoethanol</td>
<td>3.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Fenitrothion</td>
<td>0.97</td>
<td>1.65</td>
</tr>
</tbody>
</table>

$^*$ Data from Mano \textit{et al} (2013)
DISCUSSION

The estimated concentrations of LAS and its salts, and AE, in treated wastewater were found to be high (Fig. 1) and their HQ_E values were ≥ 10 (Fig. 3). Linear alkylbenzene sulfonate (LAS) and its salts have been added to the environmental standard for the preservation of aquatic living things (Ministry of the Environment, 2013), and AE is regulated by Water Supply Act in Japan. Although there is no standard for 2-aminoethanol, it should be noted that its estimated concentration is the second highest (Fig. 1) and its HQ_E value was ≥ 1 (Fig. 3). Detailed monitoring and investigation of the environmental fate of these chemicals are required.

Glutaraldehyde is used for as tanning agent and fixing reagent for papers and plastics etc. (Ministry of the Environment, 2012b), and its HQ_H and HQ_E values were ≥ 1. Hydrazine and hydroquinone also had high HQ_E values; hydrazine is used for as rocket fuel (Ministry of the Environment, 2012b) and as an initiating agent for air bags (National Institute of Technology and Evaluation, 2015). Hydroquinone is used in the development of photos, as an antioxidant of rubber, and so on in some other applications (Ministry of the Environment, 2012b). These chemicals are used industrially and their use and careful discharge could lead to a decrease in their HQ values. It is assumed that hydrazine becomes hydrazine monohydrate in receiving water areas (Environmental Risk Assessment Office, 2002). The chemical is used as a raw material of a blowing agent for synthetic resins (Ministry of the Environment, 2012b).

Although hydrazine monohydrate should also be assessed, the PNEC of the chemical was not reported and therefore the ecological risk could not be studied. The toxicity evaluation and risk assessment of hydrazine monohydrate would be of importance for the preservation of aquatic life.

Comparison between previous research (Mano et al., 2013) and this study (Fig. 1) revealed some differences, for example, the concentration of DDNO was the second highest (66 μg/L) in the previous report, while low (0.66 μg/L) in this study. However, the comparison also suggests that the composition of high-concentration chemicals was similar between this study and the previous research. The concentrations of LAS and its salts, 2-aminoethanol, AE and some other chemicals were high in both studies. In addition, most of the chemicals with a high HQ_E value were almost the same and the HQ_E values were similar in both studies (Table 2). The results indicate that there has been no improvement in the risk and discharge of the chemicals, and therefore further monitoring and countermeasures against the discharge of the chemicals are required. On the other hand, the results of the high HQ_H chemicals were totally different between the previous research and this study. Furthermore, some newly registered chemicals were found in the results in Figs. 1, 2 and 3. These points suggest that the risk assessments should be continued into the future to clarify and address these potentially hazardous chemicals.

In this study, it was supposed that the contribution rate of drinking for the exposure to a chemical is constant (= 10%) for all chemicals based on the document of Ministry of Health, Labour and Welfare (2009). However, it should be noted that the rate might be different from chemicals, and that HQ_H value shown in this study may be changed due to the uncertainty.
An initial environmental risk assessment is regarded as a screening evaluation to find the chemicals that a further detailed risk evaluation is required (Hirai et al., 2006). The risk assessment does not reproduce an actual discharge amount or concentration of chemicals in aquatic environments because higher or lower HQ would be shown in some regions. The discharge amount of chemicals was calculated based on the “Estimated Releases Outside Notification” and the degradation or adsorption of chemicals in aquatic environments was neglected in the HQ calculation. Therefore, for those chemicals whose estimated concentration and/or HQ value was larger than 1, detailed surveys on discharge through actual recordings of the chemicals in treated wastewater and countermeasures to decrease the discharge are required in further studies to conduct more comprehensive health and ecological risks.

CONCLUSIONS
Initial health and ecological assessments based on the estimated concentrations of chemicals in treated wastewater under the Japanese PRTR system were conducted. The results showed that 11 and 36 chemicals had high HQ values (≥ 0.1) for health and ecological risks, respectively. An interannual variability of potential hazardous chemicals suggests that the composition of potentially hazardous chemicals for aquatic life was almost the same, whereas they were totally different for human health risk. Further monitoring and evaluation are required to avoid environmental risks by potentially hazardous chemicals.

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