Occurrence and fate of N-nitrosamines and their formation potential in three wastewater treatment plants in Japan
Suchul Yoon, Norihide Nakada and Hiroaki Tanaka

ABSTRACT
N-nitrosamines are well known as carcinogens present in the environment. However, studies of the occurrence and fate of N-nitrosamines and their formation potential (FP) in wastewater treatment plants (WWTPs) are lacking. Therefore, the objectives of this study were to determine the occurrence of N-nitrosamines in WWTPs, the FP of N-nitrosamines on chloramination during wastewater treatment, and the efficiency of FPNH2Cl reduction by biological treatment. Also, the residual FPNH2Cl in the final discharge was investigated. The efficiencies of removal of N-nitrosamines ranged from 35 to 94% (WWTP O; residential area), from 58 to 98% (WWTP E; industrial area), and from 58% to >99% (WWTP N; industrial area). In WWTP O, the rates of production of N-nitrosodimethylamine (NDMA) (42%) and NDBA (58%) were the highest. In WWTP E, only NDBA (34%) was produced. In WWTP N, NPYR and NPIP (both >99%) were produced. NDMA FPNH2Cl values were very high in influent in all WWTPs. The efficiencies of removal of N-nitrosamine FPNH2Cl during biological treatment ranged from 20% to >99%, but there is no obvious explanation for this variability. Residual N-nitrosamine FPNH2Cl ranged from 2 to 22 ng L−1. Thus, N-nitrosamines could be produced in water purification or reclamation plants using discharge from WWTPs.

Key words | N-nitrosamines, formation potential, wastewater treatment plants

INTRODUCTION
N-nitrosamines are well known as carcinogens present in the environment (Hartmetz & Slemrova 1980; Charrois et al. 2004; Cheng et al. 2004; Zhao et al. 2006; Suez Environment Report 2007). They can cause cancer or tumors in laboratory animals, even in trace amounts (Hecht 1999).
N-nitrosamines are formed by chlorination (Valentine et al. 1986; Choi & Valentine 2002; Mitch & Sedlak 2002a, b; WateReuse Foundation 2005; Krasner et al. 2006). The concentration of N-nitrosodimethylamine (NDMA) formed as a byproduct of chlorination appears to depend on the chloramine dose. In a 2001 study (Najm & Trussell 2001), it was found that increasing the chloramine dose from 1 to 5 mg L−1 more than doubled the resultant NDMA concentration.
The formation of other aliphatic, alicyclic, and aromatic nitrosamines such as N-nitrosopyrrolidine (NPYR), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-nitrosodiethyamine (NDEA), N-nitrosodibutylamine (NDBA), and N-nitrosodiphenylamine (NDPhA) via the chlorination or chloramination of water has also been reported (Zhao et al. 2008). The use of other disinfectants such as ozone may also result in the formation of NDMA, albeit at lower concentrations (Zhao et al. 2008; Asami et al. 2009), particularly if specific precursors are present (Schmidt et al. 2008). N-nitrosamines (NDMA, NDEA, NMOR, NDPhA, NPYR, NPIP, and NDBA) have been detected in wastewater (Cheng et al. 2004; Suez Environment Report 2007), NDMA and NMOR in surface water (Hartmetz & Slemrova 1980; Suez Environment Report 2007), and NDMA, NDEA, NMOR, NPYR, NPIP, and NDPhA in drinking water (Charrois et al. 2004; Zhao et al. 2006). However, studies of the occurrence and fate of N-nitrosamines in wastewater treatment plants (WWTPs) are lacking. Furthermore, the formation potential (FP) of N-nitrosamines in WWTPs has not been studied until now. Therefore, the objectives of this study were to...
determine the occurrence of N-nitrosamines in WWTPs, the FP of N-nitrosamines on chloramination during wastewater treatment, and the efficiency of FPNH\textsubscript{2}Cl reduction by biological treatment. Also, the residual FPNH\textsubscript{2}Cl in the final discharge was investigated in this study.

**MATERIALS AND METHODS**

**Chemicals**

N-Nitrosodimethylamine (NDMA), N-nitroso-n-methylhexylamine (NMEA), N-nitrosodimethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA), N-nitrosopyrrolidine (NPYR), N-nitrosopipерidine (NPIP), N-nitrosomorpholine (NMOR), and N-nitrosodi-n-butylamine (NDBA) were purchased from Supelco (Bellefonte, PA, USA). Deuterated NDMA (NDMA-d\textsubscript{6}), NDPA (NDPA-d\textsubscript{14}), and NPYR (NPYR-d\textsubscript{8}) were used as internal standards, and toluene-d\textsubscript{8} was used as an injection internal standard; these chemicals were purchased from CDN Isotopes (Pointe-Claire, PQ, Canada). As isotope-labeled analogs were not available for some of the compounds, we used NDPA-d\textsubscript{14} for quantification of NDBA, and NPYR-d\textsubscript{8} for NMEA, NDEA, NPIP, and NMOR. Individual stock solutions of the standards were prepared at 1 mg L\textsuperscript{-1} in dichloromethane (DCM) and stored at −20°C. Working standard mixtures (10 to 250 μg L\textsuperscript{-1}) of the compounds were prepared daily and used in standard curve preparation. Gas chromatography–mass spectrometry (GC-MS)-grade DCM was obtained from Wako Pure Chemical Industries (Tokyo, Japan). Ultra pure water (Milli-Q) was obtained from Milli-Q-Plus (Millipore, Billerica, MA, USA). The detailed information of characteristics of target N-nitrosamines, and optimized analytical parameters are shown in Table 1.

**Wastewater treatment plants**

In our previous study, the occurrence and removal of NDMA and its FPNH\textsubscript{2}Cl in 12 WWTPs were investigated (Yoon et al. 2013). Two WWTPs (E and N) located in industrial areas and one WWTP in a residential area (O), which all had a very high NDMA FPNH\textsubscript{2}Cl in influent were selected.
in our previous study (Yoon et al. 2011). The three WWTPs represent a variety of treatment methods (Table 2) and influent properties (Table 3). Influent, secondary effluent, and final discharge were sampled automatically using 24-h-flow proportional composite collection techniques, every 1 h for 24 h. Sodium thiosulfate (Na$_2$S$_2$O$_3$ at 10 mg per 1,000 mL) was added into the final discharge samples to eliminate residual chlorine and ozone. All the samples were collected in 1-L amber glass bottles, kept in the dark at 4°C, and analyzed within 10 h.

**Pretreatment procedure**

First, 200 mL of each sample was filtered through a glass fiber filter (GF/B, pore size: 1.0 μm, Whatman, Osaka, Japan) (Figure 1). Then NDMA-$d_6$, NDPA-$d_{14}$, and NPYR-$d_8$ were added to all filtrate samples as internal standards, and the N-nitrosamines in the filtrate were concentrated in a Sep-Pak NH$_2$ cartridge (for sample cleanup) and then an AC-2 cartridge at 10 mL min$^{-1}$. The NH$_2$ cartridge (silica-based polar-bonded phase with basic character) substantially reduces the amount of co-extracted acidic interference. The cartridges were conditioned in advance with 5 mL each of DCM, methanol, and Milli-Q water. After concentration, the AC-2 cartridge was deactivated by pneumatic pump (DA-6-S; Ulvac, Osaka, Japan) for 2 h. N-nitrosamines were eluted from the dehydrated cartridge with 2 mL of DCM. The eluate was further concentrated under a gentle stream of N$_2$ gas at 35°C to just before dryness. The residue was reconstituted in 200 μL of DCM and assayed for N-nitrosamine by GC-tandem mass spectrometry (GC-MS/MS). To correct for fluctuations in the GC-MS/MS apparatus, we added toluene-$d_8$ as an injection internal standard just before injection of the samples into the system (Yoon et al. 2012).

**Measurement of N-nitrosamines by GC-MS/MS**

The eight N-nitrosamines, the three internal standards, and the injection internal standard were analyzed on a Varian 300 triple-quadrupole mass spectrometer (Varian, Tokyo, Japan) coupled to a Varian 450 gas chromatograph (full details in Table 4).

**N-nitrosamines FP test during chloramination**

The FP of N-nitrosamines by chloramination (FP$_{NH_2Cl}$) was defined as the increase in N-nitrosamine concentration during 10 days’ chloramination. The test for N-nitrosamine FP$_{NH_2Cl}$ followed Mitch & Sedlak (2002a), Mitch et al. (2003) with a minor modification (Yoon et al. 2011).

A 20 mmol L$^{-1}$ stock solution of monochloramine (NH$_2$Cl) was prepared for chloramination. Unfiltered wastewater samples (900 mL) with pH adjusted to 6.9 with 10 mmol L$^{-1}$ phosphate buffer were dosed with 100 mL of monochloramine stock solution (final concentration of 2.0 mmol L$^{-1}$, or 142 mg L$^{-1}$ as Cl$_2$), and the samples were stored for 10 days at 20°C. The concentrations of monochloramine were analyzed every day by N,N-diethyl-p-phenylenediamine colorimetry (Eaton et al. 1998).

**Table 2 | Characteristics of the three WWTPs**

<table>
<thead>
<tr>
<th>WWTP</th>
<th>Service area (km$^2$)</th>
<th>Average flow (m$^3$/d)</th>
<th>Service population</th>
<th>SRT$^b$ (days)</th>
<th>Secondary treatment</th>
<th>Disinfection</th>
<th>Sampling date</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>14.71</td>
<td>94,900$^a$</td>
<td>108,600</td>
<td>20</td>
<td>CAS$^c$</td>
<td>NaClO</td>
<td>2011 Jan 11</td>
</tr>
<tr>
<td>E</td>
<td>12.15</td>
<td>326,000$^a$</td>
<td>149,000</td>
<td>6.6</td>
<td>AO$^d$</td>
<td>NaClO</td>
<td>2011 Feb 16</td>
</tr>
<tr>
<td>N</td>
<td>18.69</td>
<td>288,000$^a$</td>
<td>292,500</td>
<td>3.8</td>
<td>CAS</td>
<td>NaClO</td>
<td>2011 Feb 18</td>
</tr>
</tbody>
</table>

$^a$Average dry weather value of the studied period.
$^b$Sludge retention time.
$^c$Conventional activated sludge.
$^d$Anaerobic–aerobic activated sludge.

**Table 3 | Characteristics of the influent properties in three WWTPs**

<table>
<thead>
<tr>
<th>WWTP</th>
<th>pH</th>
<th>BOD (mg L$^{-1}$)</th>
<th>COD$^e$ (mg L$^{-1}$)</th>
<th>SS (mg L$^{-1}$)</th>
<th>T-N (mg L$^{-1}$)</th>
<th>NH$_4$-N (mg L$^{-1}$)</th>
<th>NO$_2$-N (mg L$^{-1}$)</th>
<th>NO$_3$-N (mg L$^{-1}$)</th>
<th>T-P (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>7.3</td>
<td>183</td>
<td>136</td>
<td>202</td>
<td>26.0</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>ND$^b$</td>
<td>3.0</td>
</tr>
<tr>
<td>E</td>
<td>7.3</td>
<td>170</td>
<td>83</td>
<td>120</td>
<td>25.8</td>
<td>16</td>
<td>ND</td>
<td>ND</td>
<td>3.0</td>
</tr>
<tr>
<td>N</td>
<td>7.4</td>
<td>120</td>
<td>75</td>
<td>120</td>
<td>34.8</td>
<td>28</td>
<td>0.01</td>
<td>0.05</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$^e$COD$_{Mn}$.
$^b$Not detected.
matter (OM) in the form of suspended solids (SS) in the wastewater contained substantial concentrations of N-nitrosamine precursors. The water samples were not filtered, so as to retain the OM. The NH₂Cl stock solution was added intermittently to react with any N-nitrosamine precursors present in the OM. The rate of NH₂Cl consumption revealed the concentration of initial N-nitrosamine precursors present in the samples. The N-nitrosamine FP_NH₂Cl concentrations were adjusted for the values of controls (analysis without spiking of any amines). The residual concentration at the end of each test was approximately 0.14 mmol L⁻¹ (10 mg L⁻¹ as Cl₂), implying that the NH₂Cl concentration was sufficient for N-nitrosamines formation throughout the chloramination process. Therefore, the formation of N-nitrosamines under these conditions can be used as a surrogate for N-nitrosamine FP_NH₂Cl.

**RESULTS AND DISCUSSION**

**Limits of detection and quantification**

The limit of detection (LOD) and limit of quantification (LOQ) were determined by measuring standard solutions with N-nitrosamine concentrations of 5, 10, 20, 50, and 100 μg L⁻¹ by GC-MS/MS. From five measurements of each solution, the mean standard deviation (SD) and relative SD (RSD) were calculated. Using the SD (σ) of the solution with the lowest concentration and a RSD of <20%. LOD ranged from 0.1 to 1.0 ng L⁻¹, and LOQ of the eight N-nitrosamines ranged from 0.4 to 3.3 ng L⁻¹ (Table 5).

**Method validation and recovery analysis**

To investigate the rates of recovery of the N-nitrosamines and internal standards, we added standard solution with 200 ng L⁻¹ of each of the eight N-nitrosamines and three internal standards into influent, secondary effluent, final discharge, and Milli-Q water (n = 5). Furthermore, the rates of recovery of the N-nitrosamines with and without internal standards were compared. The rates of recovery were calculated as:

\[
\text{Recovery} \% = \left( \frac{C_a - C}{\alpha} \right) \times 100
\]

where \(C_a\) is the concentration of each N-nitrosamine in the sample with standard solution added (ng L⁻¹), \(C\) is...
the concentration in the original sample, and \( \alpha \) is the concentration in the standard solution. In our previous study, the recovery rates of internal standards from WWTPs and Milli-Q water using five different cartridge sequences were studied (Yoon et al. 2014). From our results, we decided that mode 3 (NH\(_2\) cartridge connected with an AC-2 cartridge) was the optimum for SPE. Absolute recoveries of the internal standards in mode 3 ranged from 98 to 152%, with 2 to 10% reproducibility (RSD; \( n = 5 \)), even in wastewater samples; these are higher than the reported values (e.g. 20 to 119% in wastewater and 38 to 118% in drinking water samples) (Krauss & Hollender 2009; Krauss et al. 2009). The recovery rates are shown in Table 6.

### Investigation of \( N \)-nitrosamine fate

\( N \)-nitrosamines were removed by secondary treatment, but concentrations of some increased again from the secondary effluent to the final discharge. NDMA was produced in WWTP O but not in WWTP E or N (Figure 2). This result resembles that of our previous study (Yoon et al. 2014), in which NDMA was not detected or was below the LOQ in WWTPs E and N.

The rate of \( N \)-nitrosamine production during chlorination or ozonation was defined as:

\[
\text{Production rate (\%)} = \left( \frac{C_d}{C_S} - 1 \right) \times 100
\]

where \( C_d \) is the concentration of \( N \)-nitrosamine in the final discharge and \( C_S \) is the concentration in the secondary effluent.

In WWTP O, NDMA, NPYR, NPIP, and NMOR were removed from influent at efficiencies of 35 to 94% (Figure 2(d)). The concentrations of NDMA, NDEA, NPYR, NMOR, and NDBA in the final discharge ranged from 2 to 237 ng L\(^{-1} \) (Figure 2(a)). The rates of production of NDMA, NDEA, NMOR, and NDBA ranged from 19 to 58% (Figure 2(e)). NMEA and NDPA were not detected or were below the LOQ in all samples from all WWTPs.

In WWTP E, NDMA, NPYR, NPIP, and NMOR were removed at efficiencies of 58 to 98% (Figure 2(d)). The concentrations of NDMA, NDEA, NPYR, NMOR, and NDBA in the final discharge ranged from 7 to 53 ng L\(^{-1} \) (Figure 2(b)). The rate of production of NDEA was 34%, but the other \( N \)-nitrosamines were not detected or not produced (Figure 2(e)).

In WWTP N, NDMA, NPYR, NPIP, and NMOR were removed at efficiencies of 58% to \( >99\% \) (Figure 2(d)). The concentrations of NDMA, NDEA, NPYR, NPIP, NMOR, and NDBA in the final discharge ranged from 7 to 53 ng L\(^{-1} \) (Figure 2(c)). The rates of production of NPYR and NPIP were both \( >99\% \) (Figure 2(e)).

\( N \)-nitrosamines were formed from the reaction between amine-based materials and monochloramine indicating that it should be considered a potential disinfection by-product. The formation of \( N \)-nitrosamines increased with increased

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**Table 4** | Detailed analytical parameters for GC-MS/MS

<table>
<thead>
<tr>
<th>Gas chromatograph (Varian 450 GC)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary column</td>
<td>FactorFour VF-17 ms, 30 m × 0.25 mm i.d., 0.25 ( \mu )m film thickness</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1 mL min(^{-1} )</td>
</tr>
<tr>
<td>Oven program</td>
<td>40 °C, hold 1 min; to 80 °C at 5 °C min(^{-1} ), to 280 °C at 20 °C min(^{-1} ), hold 3 min</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Interface temperature</td>
<td>280 °C</td>
</tr>
<tr>
<td>Injection mode</td>
<td>Splitless, hold 1 min</td>
</tr>
<tr>
<td>Injection volume</td>
<td>2 ( \mu )L</td>
</tr>
</tbody>
</table>

**Mass spectrometer (Varian 300 MS)**

- Ionization mode: Positive chemical ionization
- Detector range: 600 to 2,000 V
- Ion source temperature: 220 °C
- Transfer line temperature: 250 °C
- Carrier gas: Helium, constant 50 kPa, 1.5 mL min\(^{-1} \)
- Chemical ionization gas: Methane, 1 Pa
- Filament current: 50 \( \mu \)A
- Ionization energy: 70 eV

**Table 5** | Limit of detection (LOD) and limit of quantification (LOQ) for \( N \)-nitrosamines

<table>
<thead>
<tr>
<th></th>
<th>NDMA</th>
<th>NMEA</th>
<th>NDEA</th>
<th>NDPA</th>
<th>NPYR</th>
<th>NPIP</th>
<th>NMOR</th>
<th>NDBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD (ng L(^{-1} ))</td>
<td>0.1</td>
<td>0.4</td>
<td>1.0</td>
<td>0.9</td>
<td>0.4</td>
<td>0.5</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>LOQ (ng L(^{-1} ))</td>
<td>0.4</td>
<td>1.3</td>
<td>3.2</td>
<td>2.9</td>
<td>1.3</td>
<td>1.5</td>
<td>3.3</td>
<td>2.9</td>
</tr>
</tbody>
</table>
monochloramine concentration and showed maximum in yield when amine-based materials were varied at fixed monochloramine concentrations (Choi & Valentine 2002).

Most of the N-nitrosamines were removed from influent to secondary effluent except for NDEA and NDBA. In a study of N-nitrosamines in 21 sewage treatment plants (STPs) in Switzerland (Krauss et al. 2009), the concentrations of NDEA and NDBA were in general <5 ng L⁻¹ in secondary effluent in all STPs but one, where they were produced at 24 and 19 ng L⁻¹, respectively. In the USA, the efficiencies of removal of NDMA ranged from 50 to 75% at some WWTPs but rated little or none at others (Deeb et al. 2006). In Switzerland, all N-nitrosamines studied were removed during activated sludge treatment, but the variation among plants and among sampling dates at the Regensdorf plant was considerable (Krauss et al. 2009). At all 21 STPs, the average removal efficiencies increased in the order of NMOR (43%) < NDMA = NDEA (65%) < NDBA (74%) < NPIP (89%). Among the 20 STPs

| Table 6 | Recovery rates of N-nitrosamines and internal standards in influent, secondary effluent, final discharge, and Milli-Q water

<table>
<thead>
<tr>
<th>N-nitrosamine</th>
<th>Influent</th>
<th>Secondary effluent</th>
<th>Final discharge</th>
<th>Milli-Q water</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDMA</td>
<td>104 ± 4</td>
<td>90 ± 4</td>
<td>95 ± 9</td>
<td>98 ± 5</td>
</tr>
<tr>
<td>NDMA-ｄ6</td>
<td>99 ± 12</td>
<td>112 ± 10</td>
<td>105 ± 10</td>
<td>98 ± 7</td>
</tr>
<tr>
<td>NMEA</td>
<td>107 ± 2</td>
<td>97 ± 9</td>
<td>100 ± 5</td>
<td>100 ± 5</td>
</tr>
<tr>
<td>NDEA</td>
<td>110 ± 1</td>
<td>118 ± 7</td>
<td>122 ± 12</td>
<td>109 ± 7</td>
</tr>
<tr>
<td>NDPA</td>
<td>91 ± 12</td>
<td>97 ± 2</td>
<td>111 ± 4</td>
<td>104 ± 3</td>
</tr>
<tr>
<td>NDPA-ｄ14</td>
<td>123 ± 12</td>
<td>126 ± 10</td>
<td>152 ± 10</td>
<td>112 ± 7</td>
</tr>
<tr>
<td>NPYR</td>
<td>92 ± 6</td>
<td>130 ± 8</td>
<td>95 ± 5</td>
<td>131 ± 8</td>
</tr>
<tr>
<td>NPYR-ｄ6</td>
<td>137 ± 12</td>
<td>118 ± 10</td>
<td>105 ± 10</td>
<td>113 ± 7</td>
</tr>
<tr>
<td>NPIP</td>
<td>102 ± 3</td>
<td>112 ± 6</td>
<td>111 ± 2</td>
<td>105 ± 4</td>
</tr>
<tr>
<td>NMOR</td>
<td>81 ± 14</td>
<td>124 ± 6</td>
<td>106 ± 8</td>
<td>111 ± 3</td>
</tr>
<tr>
<td>NDBA</td>
<td>80 ± 9</td>
<td>95 ± 5</td>
<td>91 ± 12</td>
<td>91 ± 3</td>
</tr>
</tbody>
</table>

Figure 2 | Concentrations of N-nitrosamines in three WWTPs: (a) WWTP O, (b) WWTP E, (c) WWTP N. (d) Removal efficiency. (e) Production rate. (The full colour version of this figure is available in the online version of this paper, at http://www.iwaponline.com/wst/toc.htm.)
except Regensdorf, the average removal efficiencies ranged widely, for example from <5% to 95% for NDMA and from <5% to 83% for NMOR. The variation among sampling dates at Regensdorf showed similar ranges, for example from 18 to 96% for NDMA and from 11 to 77% for NMOR (Krauss et al. 2009). Clearly, the capability to degrade N-nitrosamines varies not only among different plants, but also within the same plant. This observation is in line with findings by Deeb et al. (2006), who reported 0 to 75% removal of NDMA in the same STP on different days, and 34 to 95% in other plants.

*N-nitrosamine FP_{NH2Cl} fate*

During the 10-day batch-test (pH 7.0 ± 0.2, temperature 24 ± 1°C), the FP_{NH2Cl} values of NDMA in influent in WWTPs E (1,388 ng L\(^{-1}\)) and N (1,209 ng L\(^{-1}\)) were much lower than those in our previous study (8,230 and 7,020 ng L\(^{-1}\); Yoon et al. 2011). We attribute the difference to the time of year: our previous study was carried out in August, whereas this work was carried out in February. More study of the FP_{NH2Cl} of N-nitrosamines at different times of year is needed.

The NDMA FP_{NH2Cl} in influent ranged from 1,209 ng L\(^{-1}\) in WWTP N to 1,935 ng L\(^{-1}\) in WWTP O (Figure 3). In WWTP O, NDEA FP_{NH2Cl} (518 ng L\(^{-1}\)) and NPYR FP_{NH2Cl} (615 ng L\(^{-1}\)) were high, but the values of the other N-nitrosamines ranged between not detected and 70 ng L\(^{-1}\) (Figure 3(a)). In WWTP E, NPYR FP_{NH2Cl} (258 ng L\(^{-1}\)) and NMOR FP_{NH2Cl} (212 ng L\(^{-1}\)) were high, but the other values were either not detected or below the LOQ (Figure 3(b)). In WWTP N, NPYR FP_{NH2Cl} (78 ng L\(^{-1}\)), NPIP FP_{NH2Cl} (24 ng L\(^{-1}\)), and NMOR FP_{NH2Cl} (98 ng L\(^{-1}\)) were moderate, but the other values were not detected (Figure 3(c)). N-nitrosamines are formed unintentionally in a range of industrial processes in which amines come into contact with nitrogen oxides, nitrous acid, or nitrite. Their formation during rubber manufacturing and processing, leather tanning, metal casting, metalworking using semisynthetic cutting fluids, and food processing has been recognized (Ducos et al. 1988; WHO 2002). Hence, we expected the FP_{NH2Cl} values to be much higher in WWTPs E and N, which are located in industrial areas, than in WWTP O, in a residential area. However, the values of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and SS, which are associated with secondary amines, ammonium, and nitrite, were higher in WWTP O than in WWTP N (Table 3; data for E not available). We consider this the reason for the high NDMA FP_{NH2Cl} found in WWTP O.

**Efficiency of FP_{NH2Cl} reduction by each process**

The efficiency of reduction of N-nitrosamine FP_{NH2Cl} values were calculated during biological treatment from the values

![Figure 3](https://iwaponline.com/wst/article-pdf/68/10/2118/471553/2118.pdf)
of FPNH2Cl in the influent and secondary effluent (Figure 4). The efficiencies of NDMA FPNH2Cl removal were 82% in WWTP O and 99% in E and N. That of NDEA FPNH2Cl removal was 20% in WWTP O. Those of NPYR FPNH2Cl were 93 to 96% in all three WWTPs. Those of NPIP FPNH2Cl removal were 61% in WWTP O and 81% in WWTP N. Those of NMOR FPNH2Cl removal were 66% in WWTP O, 100% in E, and 89% in N. That of NDBA FPNH2Cl removal was 85% in WWTP O. NMEA FPNH2Cl was below the LOD in all samples in all WWTPs. NDBA FPNH2Cl was detected in the influent of WWTPs O and N. We did not detect NDPA FPNH2Cl in any sample in any WWTP, NDEA FPNH2Cl in WWTP E or N, NPIP FPNH2Cl in WWTP E, or NDBA FPNH2Cl in WWTP N. These results confirm that N-nitrosamine FPNH2Cl was not removed completely by biological treatment. Furthermore, regardless of treatment process, the efficiencies of NDMA FPNH2Cl removal were 82 to 99%, those of NPIP FPNH2Cl were 61 to 81%, and those of NMOR FPNH2Cl were 66 to 89% in WWTPs O and N (Figure 4). Hence, the type of biological treatment process did not notably affect the efficiency of N-nitrosamine FPNH2Cl removal, as our previous study found (Yoon et al. 2011).

Residual N-nitrosamines FPNH2Cl in the final discharge

The residual FPNH2Cl defined in this study indicates that N-nitrosamines FPNH2Cl remains in the final discharge. If N-nitrosamine FPNH2Cl remains in the final discharge, N-nitrosamines could be produced subsequently in water purification or reclamation plants. Although most N-nitrosamine FPNH2Cl values were removed completely, NPYR FPNH2Cl (5 ng L\(^{-1}\)) and NPIP FPNH2Cl (2 ng L\(^{-1}\)) were discharged from WWTP O; NDMA FPNH2Cl (14 ng L\(^{-1}\)), NPYR FPNH2Cl (16 ng L\(^{-1}\)), and NPIP FPNH2Cl (2 ng L\(^{-1}\)) from WWTP E; and NDMA FPNH2Cl (22 ng L\(^{-1}\)) and NMOR FPNH2Cl (7 ng L\(^{-1}\)) from WWTP N. Thus, N-nitrosamines could be produced in water purification or reclamation plants.

CONCLUSIONS

1. In WWTP O (residential area), the efficiencies of removal of NDMA, NPYR, NPIP, and NMOR ranged from 35 to 94%. The concentration of NDEA (237 ng L\(^{-1}\)) in the final discharge was the highest after chlorination. In WWTP E (industrial area), the efficiencies of removal of the same N-nitrosamines were 58 to 98%. In WWTP N (industrial area), the efficiencies of removal were 58 to >99%.
2. In WWTP O, the rates of production of NDMA (42%) and NDBA (58%) were the highest. In WWTP E, only NDBA (34%) was produced. In WWTP N, NPYR and NPIP (both >99%) were produced.
3. The concentrations of NDMA FPNH2Cl in the influent in WWTPs E and N were much smaller than in our previous study (Yoon et al. 2011). We attribute the difference to time of year.
4. NDMA FPNH2Cl values were very high in influent in all WWTPs. NDEA FPNH2Cl and NPIP FPNH2Cl were high in WWTP O. NPYR FPNH2Cl and NMOR FPNH2Cl were high in WWTP E. NPYR FPNH2Cl, NPIP FPNH2Cl, and NMOR FPNH2Cl were moderate in WWTP N.
5. The efficiencies of removal of N-nitrosamine FPNH2Cl during biological treatment ranged from 20% to >99%, but there is no obvious explanation for this variability.
6. Residual N-nitrosamine FPNH2Cl ranged from 2 to 22 ng L\(^{-1}\). Thus, N-nitrosamines could be produced in water purification or reclamation plants using discharge from WWTPs.

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