

respectively¹⁹). However, the contributions of HDMS and TMDS to the total amount of NDMA precursors in the Yodo River basin were low,¹⁹ and therefore, there is need to identify the primary NDMA precursor(s) in the basin. In addition, since the main source of NDMA precursors appears to be a single STP (designated STP-A), and the precursors were contained in the influent of this STP, it is interesting to clarify the origin of the discharged NDMA precursors.

In this study, the origin of NDMA precursors was investigated by collecting sewage from pipes flowing to STP-A, and then identifying the NDMA precursors in the sewage via ultrahigh performance liquid chromatography–tandem mass spectrometry (UHPLC–MS/MS) and UHPLC–time-of-flight mass spectrometry (TOF/MS). Finally, the contributions of individual NDMA precursors to the total amount of NDMA precursors (i.e., the amount of NDMA formed from the target NDMA precursor to the total amount of NDMA formed during ozonation) in the Yodo River basin were evaluated.

MATERIALS AND METHODS

Reagents and Solutions. Standard solutions of NDMA, *N*-nitrosomorpholine (NMOR), and *N*-nitrosopyrrolidine (NPYR) were purchased from Supelco (Bellefonte, PA, U.S.A.) or Wako Pure Chemical Industries Ltd. (Osaka, Japan). NDMA-*d*₆ was purchased from C/D/N Isotopes (Pointe-Claire, Canada) or Kanto Chemical (Tokyo, Japan). HDMS (>98.0%) and TMDS (>95.0%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). 1,1,5,5-Tetramethylcarbohydrazide (TMCH, >99.5%) is not commercially available and was synthesized on commission by Tokyo Chemical Industry. Other reagents used were of analytical grade and obtained from commercial suppliers. Solutions were prepared from ultrapure water obtained using a Milli-Q Gradient A10 water purification system (Millipore, Bedford, MA, U.S.A.) or a Milli-Q Integral 5 water purification system (Millipore).

Sampling. Sewage in the individual sewer pipes (SW-1 through SW-12) connected to STP-A as well as final STP-A influent was collected in November 2011. In addition, sewage in sewer pipe SW-6, and pipes SW-6–1 to SW-6–4 were collected in February 2012 (SW-6–1 to SW-6–4 are “feeder” pipes and/or sampling locations located upstream of SW-6). The sewer pipes are all connected to STP-A, some in parallel and some in series, but the sum of the flow rates of the individual sewer pipes equals that of the STP-A combined influent. STP-A utilizes a biological treatment system involving a two-stage nitrification–denitrification. Filtration was performed using hydrophilic polytetrafluoroethylene (PTFE) membranes (10 μm, Millipore). The primary, secondary, and final effluents from STP-A were collected in January and February 2014. Chlorine was dosed after the secondary treatment at 2.1–2.2 mg Cl₂/L on the sampling days in January 2014, and at 2.3 mg Cl₂/L on the sampling days in February 2014. The primary effluents were filtered with hydrophilic PTFE membranes, and the filtrates were used for experiment. Various water sample properties [sampling date, pH, total organic carbon (TOC), and ultraviolet absorbance at 260 nm] are given in Supporting Information (SI) Table S1. The water from two WPPs (WPP-L and WPP-M), which use ozone/biological activated carbon (BAC) treatment downstream on the Yodo River from STP-A, was collected from October 2008 to March 2014, and from April 2011 to March 2014, respectively. The sample types collected were raw water,

water after ozonation and BAC treatments, and finished water. In this study, all of the samples were grab samples, except for those from STP-A in January and February 2014. These samples were composites, taken at 24 h intervals. This is because the components of the water from sewage treatment processes fluctuate with time, and composite samples are known to be better for evaluating the fates of the target compounds.

Sewage Concentration and Fractionation. The sewage samples were concentrated and fractionated for NDMA precursor identification. The procedures employed are the same as those previously reported,¹⁹ however, in this study, samples were concentrated via evaporation at 50 °C (R-215; Shibata, Tokyo, Japan) rather than by solid-phase extraction. This is because in the previous study, the primary NDMA precursors were found to be hydrophilic compounds, which were not trapped by the styrene-divinylbenzene copolymer solid-phase extraction cartridges.¹⁹ The concentrated samples were fractionated using HPLC (HP1100; Agilent Technology, Palo Alto, CA, U.S.A.). In addition, standard solutions of NDMA, NMOR, and NPYR were also fractionated via HPLC, and the peak areas of the fractions were analyzed for comparison with the retention times of the NDMA precursors in the sewage samples. Detailed experimental conditions are provided in the SI.

Identification of NDMA Precursors. The precursors which form NDMA in sewage during ozonation were identified using UHPLC–MS/MS (Acquity UPLC system, Acquity TQD tandem mass spectrometer; Waters, Milford, MA, U.S.A.) and UHPLC–TOF/MS (Acquity UPLC H-Class system, Xevo G2-XS mass spectrometer; Waters),²² and the chemical structures were investigated using nuclear magnetic resonance (NMR) spectroscopy (JEOL JNM-ECA600 NMR spectrometer; JEOL, Tokyo, Japan). ¹H NMR, ¹³C NMR, and ¹H–¹³C heteronuclear single-quantum correlation (HSQC) spectra were obtained. Deuteriochloroform (CDCl₃, Sigma-Aldrich, St Louis, MO, U.S.A.) was used as the solvent. Details of the UHPLC–MS/MS, UHPLC–TOF/MS and NMR spectroscopy conditions are given in the SI.

Ozonation. Ozonation experiments were conducted in 1 L glass bottles using a semibatch system with an ozone generator (POX-20; Fuji Electric, Tokyo, Japan), except for the evaluation of the NDMA molar formation yields of the NDMA precursors described below. Ozone was prepared from pure oxygen gas. Ozonation conditions were as follows: sample volume, 600 or 800 mL; ozone concentration in gas phase, 5 or 20 mg/L; ozone gas flow rate, 1 L/min; reaction time, 5–20 min; and temperature, 20 °C. The pH was adjusted to 7 (5 mM phosphate buffer) for fractions of concentrated sewage. Detailed conditions differed depending on the sample type (sewage from pipes and STP-A influents, fractions of concentrated sewage, primary effluent, etc.), and are described in the SI.

Ozonation experiments to evaluate the NDMA molar formation yields of the NDMA precursors (i.e., molar formation of NDMA per molar decomposition of the NDMA precursor) were conducted using a batch system. An ozone solution was prepared by bubbling ozone gas into ultrapure water in an ice bath. The ozonation experiments were initiated by addition of the ozone solution to an aqueous solution of the NDMA precursor. The NDMA precursors in samples from STPs and WPPs coexist with other compounds and are affected by these compounds during ozonation. Thus, the NDMA

molar formation yields were evaluated in a water matrix as in previous studies.^{15,19,21} The raw water from WPP-N [dissolved organic carbon (DOC), 1.3 mg C/L; pH 7.5], dechlorinated tap water (TOC, 0.5 mg C/L; pH 7.3), water from WPP-O after coagulation–sedimentation (DOC, 1.2 mg C/L; pH 7.6), and the secondary effluent from STP-B (DOC, 2.9 mg C/L; pH 6.8) were used as water matrices. The raw water, water after coagulation–sedimentation, and the secondary effluent were used after filtration (Whatman GF/F, GE Healthcare Bio-Sciences, Pittsburgh, PA, U.S.A.). In some cases, the ozonation experiments were conducted in the presence of *tertiary*-butyl alcohol (TBA), a known hydroxyl radical scavenger.²³ Details of these ozonation conditions are also given in the SI.

Measurement of NDMA, TMCH, HDMS, and TMDS. NDMA concentration was determined using UHPLC–MS/MS or gas chromatography (GC)–MS in chemical ionization mode (GCMS-QP2010; Shimadzu, Kyoto, Japan). Solid-phase extraction was conducted, and NDMA-*d*₆ was used as a surrogate. Sample concentration depended on sample volume. The limit of quantification (LOQ) was 5.0–25 ng/L for UHPLC–MS/MS, and 1.0 ng/L for GC–MS. TMCH, HDMS, and TMDS concentrations were determined using UHPLC–MS/MS, without sample concentration. The LOQ of TMCH was 20 ng/L, except for that of the primary effluent (50 ng/L). The LOQs of HDMS and TMDS were 10 ng/L. Detailed information on the analytical methods used to find [NDMA], [TMCH], [HDMS] and [TMDS] can be found in the SI. Other analytical methods employed to analyze the water samples are also described in the SI.

RESULTS AND DISCUSSION

Discharge of NDMA Precursors into Sewage. Table 1 shows the NDMA concentration before and after ozonation of the sewage in sewer pipes SW-1 to SW-12 and the STP-A influents collected in November 2011. NDMA precursors were present, particularly in SW-1, SW-6, and SW-12, as indicated by the sharp increase in NDMA concentration upon ozonation. Taking flow rate into account, the primary source of NDMA

Table 1. NDMA Concentration before and after Ozonation of Sewage in Sewer Pipes and Influent, at STP-A in November 2011

| sample | NDMA concentration (ng/L) | | flow rate (m ³ /h) |
|----------------|---------------------------|-----------------|-------------------------------|
| | before ozonation | after ozonation | |
| STP-A influent | 17 | 4100 (±420) | 7108 |
| SW-1 | 9.5 | 630 | 3337 |
| SW-2 | 11 | 28 | 445 |
| SW-3 | 55 | 47 | 323 |
| SW-4 | <5.0 | 90 (±7.1) | 672 |
| SW-5 | <5.0 | 43 | 344 |
| SW-6 | 18 | 75 000 (±5000) | 347 |
| SW-7 | 5.1 | 48 | 79 |
| SW-8 | <5.0 | 26 | 345 |
| SW-9 | 6.9 (±0.8) | 48 | 727 |
| SW-10 | 120 (±22) | 110 | 344 |
| SW-11 | 13 | 88 | 21 |
| SW-12 | 12 | 3400 (±480) | 66 |

^aOzone concentration in the gas phase, 20 mg/L; ozone gas flow rate, 1 L/min; reaction time, 20 min; temperature, 20 °C. ^bFlow rates are those on sampling days. ^cValue in parentheses is the standard deviation.

precursors is SW-6, so this pipe was investigated further. In February 2012, samples of sewage in sewer pipe SW-6 and those located upstream of SW-6 (SW-6–1 to SW-6–4) were collected, and the NDMA concentration before and after ozonation was investigated (Figure 1). Differences in the

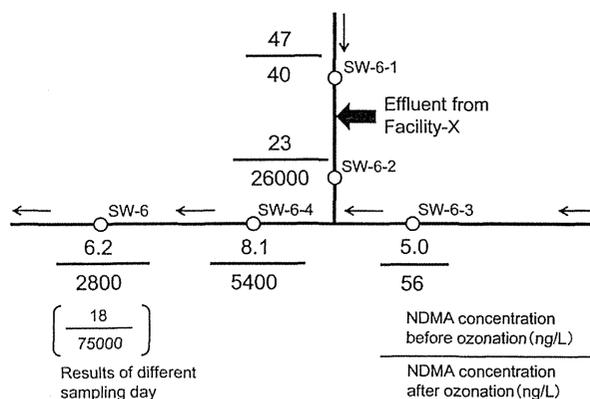


Figure 1. NDMA concentration before and after ozonation in sewage from sewer pipes (ozone concentration in gas phase, 20 mg/L; ozone gas flow rate, 1 L/min; reaction time, 20 min; temperature, 20 °C).

NDMA concentrations after ozonation at SW-6 in November 2011 and February 2012 showed wide fluctuations in the discharge of NDMA precursors. The NDMA concentration after ozonation increased significantly for samples from SW-6–1 to SW-6–2 (40 and 26,000 ng/L, respectively). Between the SW-6–1 and SW-6–2 sampling points, there is a major discharge of effluent from a chemical facility (Facility-X) into the sewage pipe. The effluent from this facility is therefore identified as the possible primary source of the precursor forming NDMA during ozonation at STP-A. Facility-X mainly produces paper (e.g., photographic paper for inkjet printers) and printmaking materials.

Identification of NDMA Precursors. The SW-6–2 sewage sample was concentrated and fractionated, and the fractions were ozonated. Figure 2(a) shows the NDMA concentration after ozonation of 4 min fractions collected from 0.5 to 40.5 min. The presence of NDMA in the figure means the presence of the NDMA precursors in the fractions because the NDMA concentration before ozonation of the fractions was <5.0 ng/L. The NDMA precursor was present in three fractions (0.5–4.5, 4.5–8.5, and 8.5–12.5 min), but particularly in the 4.5–8.5 min fraction. To increase precision, Figure 2(b) shows the NDMA concentration after ozonation of 1 min fractions collected from 0.5 to 12.5 min. The NDMA precursor was present mainly in the 5.5–6.5 min fraction. The fraction was designated as Fraction-I. It was reported that HDMS and TMDS were present in the fractions at 13.5–14.5 and 14.5–15.5 min, respectively, under the same HPLC conditions.¹⁹ Thus, the possible primary NDMA precursor(s) in SW-6–2 are different, more hydrophilic compounds. In an attempt to classify the NDMA precursor(s), solutions of NDMA, NMOR, and NPYR were fractionated using HPLC with the same conditions, and their retention times were compared. These three compounds were found in the fractions at 2.5–4.5, 3.5–6.5, and 4.5–6.5 min, respectively (details provided in SI Figure S1). The retention times of the unknown NDMA precursors in Fraction-I are significantly longer than those of NDMA and NMOR, and slightly longer than that of NPYR.

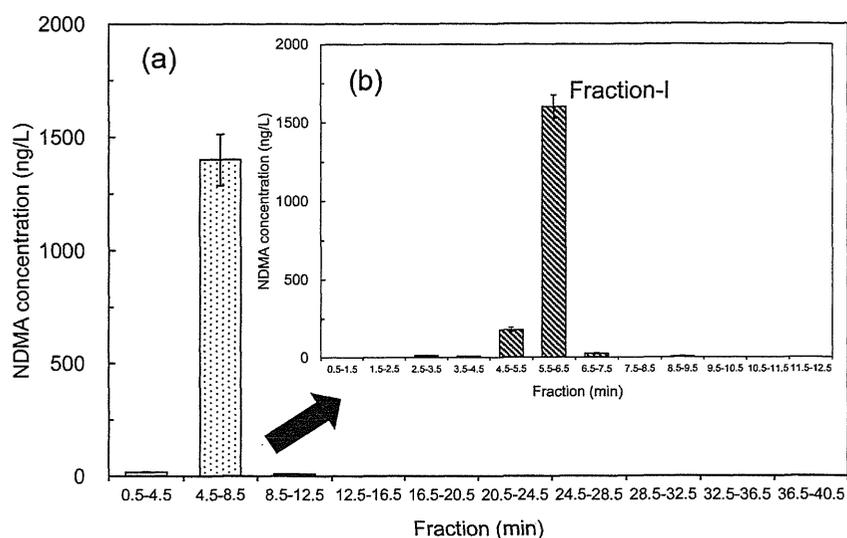


Figure 2. NDMA concentration after ozonation of (a) 4 min fractions from 0.5–40.5 min and (b) 1 min fractions from 0.5–12.5 min [ozone concentration in gas phase, 20 mg/L; ozone gas flow rate, 1 L/min; reaction time, 10 min; pH 7 (5 mM phosphate buffer); temperature, 20 °C].

The retention time of NPYR in UHPLC–MS/MS, using the same mobile phase as for HPLC (ultrapure water and methanol), was around 4.8 min (details concerning gradient conditions (1) can be found in SI Table S3). Although the HPLC and UHPLC columns were different brands (SI Tables S2 and S3, respectively), both had an alkyl reversed-phase. It was presumed that the retention time of the NDMA precursors in Fraction-I in UHPLC–MS/MS was slightly longer than 4.8 min. Fraction-I was purified by further fractionation using UHPLC. The 30-s fractions from 4.0–6.5 min were collected, and each fraction was ozonated (SI Figure S2). NDMA precursors were present in the 5.0–5.5, 5.5–6.0, and 6.0–6.5 min fractions obtained using UHPLC. Analysis of the three fractions shows that the retention times of the NDMA precursors are near the boundary of the 5.0–5.5 and 5.5–6.0 min fractions.

In the total ion chromatogram of Fraction-I obtained via UHPLC–MS, there was a peak at ~5.6 min, with $m/z = 147$ and 239, in the spectrum (data not shown). When the same fraction was analyzed using UHPLC–TOF/MS under the same UHPLC conditions (gradient conditions (1) in SI Table S4), the signals at $m/z 147$ and 239 were found to originate from different compounds.²² The molecular formula predicted by the UHPLC–TOF/MS and chemical database for the compound with $m/z 147$ was TMCH (molecular weight: 146.19).²² TMCH has two *N,N*-dimethylhydrazino functional groups; one of the functional groups transformed into NDMA in high yield upon ozonation.^{15,19,21} The retention time of the $m/z 147$ peak of Fraction-I (7.5 min) obtained using UHPLC–MS/MS agreed with that of an authentic sample of TMCH (Figures 3(a) and (b)). The product ion spectra of $m/z 147$ were also the same (Figures 3(c) and (d)). It is worth noting that the chromatographic conditions employed in generating Figure 3(a),(b) were different from those used for SI Figure S2, and for Figure 3(a),(b), the $m/z 147$ and 239 peaks are separated (conditions were refined and optimized once TMCH was identified and an authentic sample obtained). Additionally, the precise mass of the $m/z 147$ peak in Fraction-I, determined using UHPLC–TOF/MS under gradient conditions (2) (SI Table S4) agreed with that of an authentic sample of TMCH

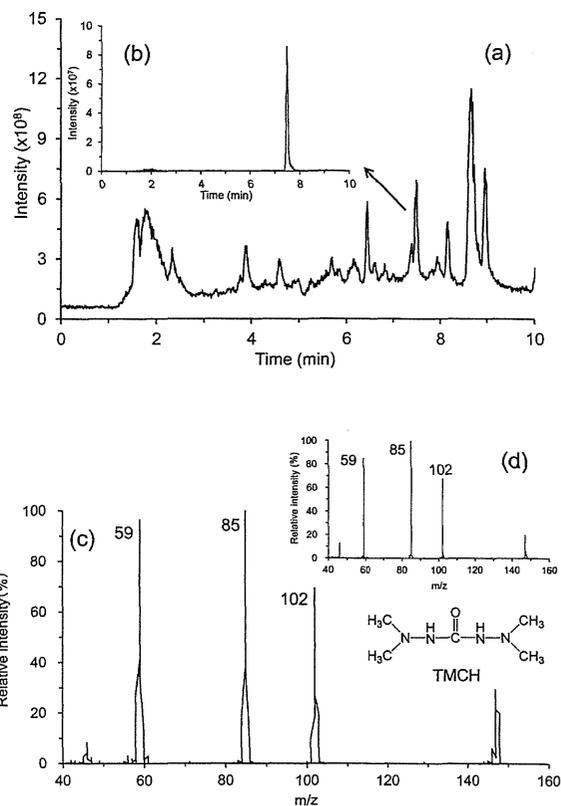


Figure 3. Total ion chromatogram of Fraction-I using (a) UHPLC–MS (scan mode, m/z range 100–300) and (b) UHPLC–MS/MS (product ion scan mode of $m/z 147$, m/z range 40–150). (c) Product ion spectrum of $m/z 147$ peak and (d) authentic sample of TMCH (product ion scan mode of $m/z 147$, m/z range 40–150).

($m/z 147.1246$ and 147.1243 , respectively).²² The presence of TMCH in Fraction-I was also investigated using NMR. The characteristic methyl signal for the *N,N*-dimethylamino functional group of TMCH was assigned using the one-dimensional

(1D) ^1H and ^{13}C NMR spectra of an authentic TMCH sample (Table 2, SI Figure S3). In the ^1H NMR spectrum of Fraction-I,

Table 2. ^1H NMR and ^{13}C NMR Spectroscopic Data for Authentic Sample of TMCH and Fraction-I in CDCl_3 ^a

| No. | Authentic | Fraction-I | Authentic | Fraction-I |
|-----|-----------------|-------------------|--------------|----------------|
| | ^{13}C | $^{13}\text{C}^b$ | ^1H | $^1\text{H}^c$ |
| 1 | 48.24 | 48.2 | 2.54 | 2.54 |
| 2 | 156.45 | - | - | - |

^aSolvent signals at 7.26 and 77.0 ppm were used as internal standards for ^1H and ^{13}C chemical shifts, respectively. ^bIn the NMR spectra, several other signals were observed as impurities. ^c ^{13}C NMR spectroscopic data for Fraction-I were obtained by ^1H - ^{13}C HSQC.

a broad singlet was observed at the same chemical shift of the methyl signal of TMCH, although there were several other signals derived from other compounds (SI Figure S4(a)). However, the ^{13}C NMR spectrum of TMCH in Fraction-I could not be measured due to a small amount of sample. To confirm the presence of TMCH, a 2D HSQC experiment was performed. In the HSQC spectrum of Fraction-I, TMCH was identified by both ^1H NMR and ^{13}C NMR chemical shift values (Table 2, SI Figure S4). The results obtained using UHPLC-MS/MS, UHPLC-TOF/MS,²² and NMR showed that the m/z 147 peaks in Figure 3(a),(c) were due to the presence of TMCH. The UHPLC-MS/MS results showed that TMCH was also present in the 4.5–5.5 min HPLC fraction obtained from SW-6–2 (Figure 2(b)).

NDMA Molar Formation Yield of TMCH during Ozonation. The effect of ozone dose on the NDMA molar formation yield of TMCH in absence and presence of TBA in raw water at WPP-N was then investigated (SI Figure S5). When the raw water in the absence and presence of TBA was ozonated without TMCH addition as a blank, the NDMA concentration was <25 ng/L both before and after ozonation at 1 mg/L of ozone. When TMCH was added to the raw water (45–48 $\mu\text{g/L}$), the TMCH concentrations in the samples in the absence and presence of TBA were 13 and 14 $\mu\text{g/L}$, respectively, after ozonation at 0.25 mg/L of ozone. However, the TMCH concentration in the samples in the absence and presence of TBA was <20 ng/L after ozonation at 0.5–1.5 mg/L of ozone. In case of the absence of TBA, the NDMA molar formation yield was 101% at 0.25 mg/L of ozone dose. The NDMA molar formation yield increased at 0.5 mg/L of ozone (145%) and did not significantly change at 1–1.5 mg/L of ozone. The NDMA molar formation yield of TMCH can exceed 100% due to the presence of two *N,N*-dimethylhydrazino functional groups. Thus, the NDMA molar formation yield became a maximum when TMCH was sufficiently decomposed. In case of the presence of TBA, the NDMA molar formation yields of TMCH at 0.25 and 0.5 mg/L of ozone were similar to those in the absence of TBA (SI Figure S5). However, the NDMA molar formation yields at 1 and 1.5 mg/L of ozone in the presence of TBA (169–173%) were

higher than those in the absence of TBA (136–140%). Since TBA is a known hydroxyl radical scavenger,²³ this indicated that NDMA was formed from the reaction of TMCH with ozone molecule and the NDMA formation was partially inhibited by hydroxyl radical.

The NDMA molar formation yield of TMCH upon ozonation in different water matrices was also investigated (SI Figure S6). When TMCH was not added to the water matrices, the NDMA concentration in the matrices was <25 ng/L both before and after ozonation, except for the secondary effluent. The NDMA concentrations in the secondary effluent were 29 ng/L before ozonation and 49 ng/L at 1.5 mg/L of ozone. When the TMCH was added to the water matrices (44–50 $\mu\text{g/L}$), the TMCH concentration in the samples was <20 ng/L after ozonation, except for the secondary effluent sample (34 ng/L) at 1 mg/L of ozone. As is presented in SI Figure S5, the NDMA molar formation yield in raw water at WPP-N (142%) is the mean of the molar formation yields at 0.5 to 1.5 mg/L of ozone. Similarly, the NDMA formation yield of TMCH in secondary effluents (136%) was the mean of the molar formation yields at 1 and 1.5 mg/L of ozone. The NDMA molar formation yield in dechlorinated tap water and water after coagulation–sedimentation at WPP-O was 144% and 147%, respectively. Thus, the NDMA molar formation yields for the four water samples were similar, and the mean value was rounded to 140%. TMCH is an NDMA precursor, and the NDMA molar formation yield is much higher than that of HDMS (10%) or TMDS (27%), both of which have been found previously in the Yodo River basin.¹⁹ The NDMA molar formation yield is also higher than that of other compounds, such as 1,1-dimethylhydrazine (80%).¹⁵ TMCH is used as an agent to prevent the deterioration of paper (e.g., gas resistance and light resistance),²⁴ and thus, it is not at all surprising that Facility-X would emit this compound.

Contribution of TMCH to Total NDMA Precursors in Sewage. The TMCH concentration of the primary, secondary, and final effluents from STP-A in January 2014 was nearly constant (73, 77, and 70 ng/L, respectively). Similarly, the values in February 2014 were 95, 90, and 86 ng/L, respectively. Removal of TMCH by biological treatment processes was therefore low. In addition, removal of TMCH with chlorine was low when the chlorine dose for the secondary effluent was set at 2.1–2.3 mg Cl_2/L . During chlorination, removal of HDMS and TMDS was also low (Figure 4 and SI Figure S7). Previously, it was reported that HDMS and TMDS are rapidly decomposed by chlorine.¹⁹ Their residual ratios at 15 min of reaction were 0.1 and 0.2, respectively, under the following chlorination conditions: chlorine dose, 1.2 mg Cl_2/L ; pH 7; temperature, 20 $^\circ\text{C}$.¹⁹ The residual ratios were estimated from the figure in the previous study.¹⁹ From those results, the apparent reaction rate constants of HDMS and TMDS with chlorine at pH 7 were estimated to be about 150 and 100 $\text{M}^{-1} \text{s}^{-1}$, respectively. Again, like HDMS and TMDS, TMCH is a tertiary amine derivative with two *N,N*-dimethylhydrazino functional groups that are reactive with chlorine.^{19,25} Thus, it was viewed as reasonable that removal of TMCH during the chlorination would be low if the apparent reaction rate constant of TMCH with chlorine was similar to those of HDMS and TMCH, and the chlorine dosed was consumed by water matrices in the secondary effluent. Therefore, removal of TMCH should likely not be expected during sewage treatment processes, and other control strategies are desired and necessary (e.g., reduction of TMCH discharge in industrial effluents).

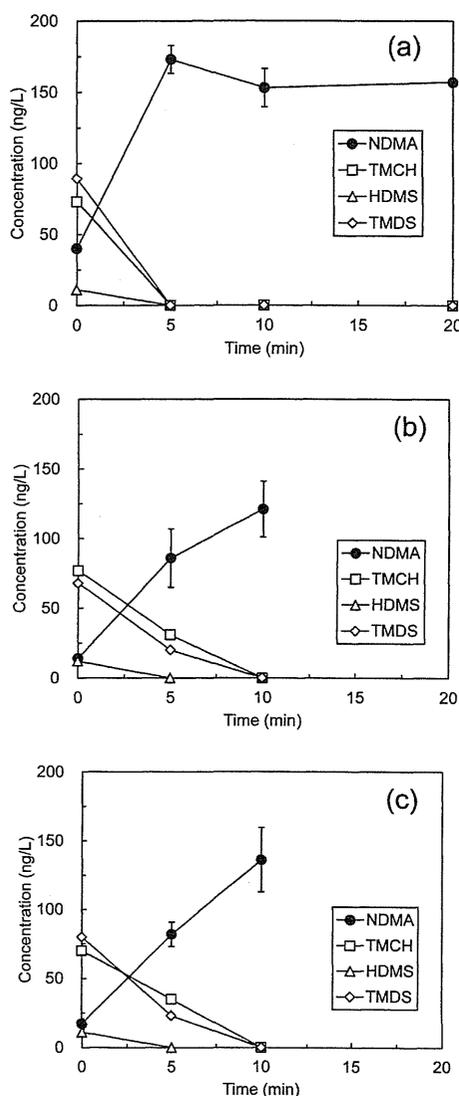


Figure 4. Profiles of concentrations of NDMA, TMCH, HDMS, and TMDS during ozonation of (a) primary, (b) secondary, and (c) final effluent from STP-A in January 2014 (ozone concentration in gas phase, 20 mg/L for primary effluents and 5.0 mg/L for secondary and final effluents; ozone gas flow rate, 1 L/min; temperature, 20 °C).

Figure 4 shows concentration profiles for NDMA, TMCH, HDMS, and TMDS during ozonation of the primary (4a), secondary (4b), and final (4c) effluents from STP-A in January 2014. For example, the initial concentrations of NDMA, TMCH, HDMS, and TMDS in the primary effluent were 40, 73, 11, and 89 ng/L, respectively. The concentration of TMCH, HDMS, and TMDS decreased upon ozonation, and that of NDMA increased. A similar trend was observed in February 2014 (SI Figure S7). In this study, the ozone exhaust concentration was not monitored. However, it was monitored during ozonation of the primary and secondary effluents of STP-B under the same ozonation conditions as those of the primary and secondary effluents of STP-A (details are in the SI). The exhausted ozone concentration increased rapidly during ozonation and became stable in 5 min. The absorption rate of ozone after reaching a steady state during ozonation of

the primary and secondary effluents of STP-B was 4–4.5% and 6%, respectively.

Notably, the NDMA concentration in the effluents of STP-A after ozonation in January and February 2014 (around 100–150 ng/L, Figure 4 and SI Figure S7) was lower than that of the STP-A influents in November 2011 (4100 ng/L, Table 1), as well as that found in previous studies (5300 ng/L in secondary effluent in December 2008¹⁹ and around 3700–4500 ng/L in final effluent in December 2010²⁰). Figure 5 shows the temporal variation in NDMA concentration over time through the water purification steps at WPP-L. The source water for the WPP is the Yodo River, and the intake points are downstream of STP-A. The NDMA concentration in the raw water samples ranged from <1.0 to 8.7 ng/L. The NDMA concentration increases after ozonation, with periodic if not seasonal fluctuations, with an overall decrease in NDMA concentration over the study period. That is, the peak NDMA concentration in the water samples after ozonation until spring 2011 varies between 80 and 140 ng/L, but those thereafter only go up to 25 ng/L. A similar trend was observed at WPP-M (SI Figure S8): the NDMA concentration after ozonation in April 2011 was 110 ng/L, but, after that it was in the range from <1.0 to 26 ng/L. From these data, it is clear that overall, the amount of NDMA precursors discharged from Facility-X decreases over time, for unknown reasons. Seasonal fluctuations in the amount of NDMA precursors discharged from STP-A were not investigated. One explanation for the fluctuations is that the flow rate of the Yodo River decreases in the winter and spring, and thus, the percentage of the final effluent of STP-A in the Yodo River water increases.

The NDMA molar formation yield of TMCH and the concentration of NDMA and TMCH before ozonation and after ozonation were used to estimate the contribution of TMCH to the total NDMA formed during ozonation. This analysis is based on the assumption that the NDMA molar formation yield of TMCH is the same, regardless of source/coexisting compounds/etc. As shown in SI Figure S6, the NDMA molar formation yield of 140% was used because the values were the same for the four water matrices. As discussed above, the NDMA molar formation yield of TMCH was low when TMCH decomposition was insufficient (SI Figure S5). The contributions of TMCH to the total NDMA precursors were only calculated when the TMCH concentration after ozonation was less than its LOQ. In such cases, the TMCH concentration was regarded as zero. The mean TMCH contribution values for all ozonation durations of the primary, secondary, and final effluents in January 2014 were 43% (39–46%), 51%, and 42%, respectively. Those in February 2014 were 72% (63–78%), 72% (64–80%), and 60% (57–62%), respectively. The values in parentheses are the ranges of the contributions of TMCH to the total NDMA precursors. Thus, TMCH was the primary NDMA precursor at STP-A, although the contribution of TMCH to the total NDMA formed during ozonation fluctuated. The mean values for HDMS in the primary, secondary, and final effluents at STP-A were 0.2%, 0.4%, and 0.3%, respectively, in January 2014, and 0.4%, 0.6%, and 0.5%, respectively, in February 2014. The values for TMDS in the primary, secondary, and final effluents at STP-A were 4.0%, 3.5%, and 4.1%, respectively, in January 2014, and 6.0%, 6.9%, and 4.6%, respectively, in February 2014. In these HDMS and TMDS contribution calculations, the NDMA molar formation yields used were 10% and 27%, respectively.¹⁹ It has been reported that the primary origin of contaminants

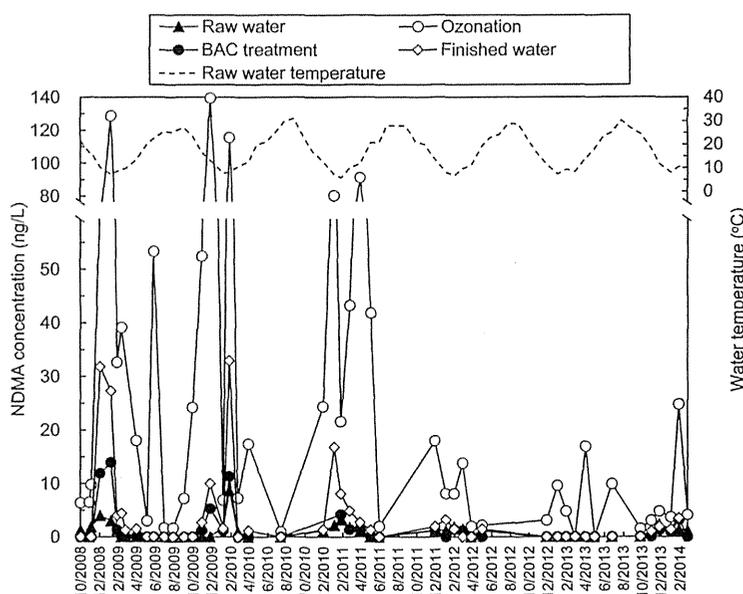


Figure 5. Temporal variation of NDMA concentration in water purification process and raw water temperature at WPP-L from October 2008 to March 2014.

yielding NDMA upon water purification via ozonation in the Yodo River basin is effluent from STP-A.^{17,19} On the basis of the results of the present study, it is concluded that TMCH is the primary NDMA precursor present in the Yodo River basin. Thus, far, aquatic TMCH has received very little attention. However, this study suggests that this chemical unintentionally becomes the primary causative reactant resulting in a toxic compound (NDMA) as a product of the water purification process. Information sharing among the staff of the company discharging this industrial effluent, sewage systems, and water suppliers is important for the protection of safe drinking water.

■ ASSOCIATED CONTENT

Supporting Information

Properties of water samples (Table S1); fractionation of sewage and identification of NDMA precursors (Tables S2–S4); ozonation conditions and analytical methods (Tables S5–S8); distribution of percentages of NDMA, NMOR, and NPYR in fractions obtained by HPLC (Figure S1); NDMA concentrations after ozonation of fractions of Fraction-I (Figure S2); NMR spectra of authentic sample of TMCH and Fraction-I (Figures S3 and S4); NDMA molar formation yield of TMCH upon ozonation (Figures S5 and S6); concentration profiles of NDMA, TMCH, HDMS, and TMDS during ozonation of primary, secondary, and final effluent from STP-A in February 2014 (Figure S7); and temporal variation in NDMA concentration at WPP-M (Figure S8). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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塩水電解による塩素酸及び過塩素酸の生成特性と電極材質に関する検討

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Generation Characteristics of Chlorate and Perchlorate in Electrolysis of Salt Water Using Six Anodes of Different Materials

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Abstract

Chlorate and perchlorate are oxidized substances of chloride, and they exist in the form of anions in water and toxic contaminants that should be controlled, especially in drinking water. To control and minimize the formation of perchlorate in the water purification process, the formation of chlorate and perchlorate in chlorine generation process was studied in electrolysis of salt water. Six electrodes with different properties (main components: A: RuO₂-TiO₂; B: RuO₂-IrO₂-TiO₂; C: IrO₂-SnO₂; D: IrO₂-Pt; E: Pt; and F: PbO₂) were tested. Electric voltage differed among electrodes and the generation of chlorate and perchlorate depended on their electric voltage. When electric current is constant, those electrodes of higher terminal voltage generally showed lower production of chlorine and higher generation of chlorate and perchlorate. It is noted the electrodes, E: Pt and F: PbO₂ are prominent in the generation of chlorate and perchlorate. Therefore, the generation of chlorate and perchlorate should be controlled with the consideration of electrode material, the especially in on-site generation of hypochlorite, industrial electrolysis, water purification devices, and hypochlorite generation devices that involve electrolysis.

Keywords: Electrolysis; Hypochlorite; Perchlorate; Chlorate; Terminal voltage

1. はじめに

水道では、遊離塩素または結合塩素の残留が義務付けられていることから、最終消毒剤として塩素剤が用いられている。水道統計¹⁾によると、水道事業者が使用している塩素剤のうち、92.6%が購入した次亜塩素酸ナトリウム溶液（以下、次亜塩素酸または次亜）で、このとき、次亜は塩水の電気分解（電解）によって製造されている。また、国内の浄水場では最終消毒剤として用いる次亜を電解によって塩水から現場生成する場合があります。5.4%は主に現場で隔膜式電気分解法を用いて生成される次亜である。加えて、配水網や貯水槽^{2,3)}において、水道水中の塩化物を電解により酸化して、残留塩素を増加させることも実用化されている。

電解による消毒・殺菌は身近なところでも活用されている。水中の塩化物等を酸化し、殺菌作用を利用する電解処理では、陽極水、陰極水、両極水（陽極と陰極で電気分解された水を合わせたもの）など、多くの種類の電解水が利用されている⁴⁾。そのうち強電解水とは、軟水

器等を通水した水に、電解補助剤として塩化ナトリウムを少量含む水を電解し、陽極側から得られる水である。生成された水は強酸性で、塩素を高濃度（例えば20～60 mg・L⁻¹）に含む強酸性水であり、手指洗浄用殺菌水、食品添加物殺菌料、農業用特定防除資材等として利用されている⁴⁻⁷⁾。一方、微酸性～弱酸性電解水は少量の塩化ナトリウムまたは塩化カリウムと少量の塩酸を含む水溶液を、無隔膜電解槽等を用いて電解した水である。生成された水は、弱酸性（pH 4～6）を示し、塩素も水道水中と同程度の濃度で含まれる。このpH範囲は、次亜塩素酸（HOCl）を最も有効に利用できる範囲であり、塩素による強力な殺菌効果が期待できる⁸⁾。また、食塩水を電解液とし無隔膜電解により微アルカリ性次亜塩素酸水溶液を生成し、生成液に適量の炭酸水を加えることにより、微酸性次亜塩素酸水溶液を生成する場合もある。

このように、塩化物を含む水を電解すると消毒剤・殺菌剤である次亜塩素酸が生成するが、一部はさらに酸化され、二酸化塩素、亜塩素酸（ClO₂⁻）、塩素酸（ClO₃⁻）、過塩素酸（ClO₄⁻）へと変換する（Table 1）。特に、電解

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Table 1 Reaction of electrolysis of chloride.

| | | | |
|----------------------|---------------------------------------|--|----------|
| Oxidation at anode | 2Cl^- | $\rightarrow \text{Cl}_2 + 2\text{e}^-$ | …Ref(8) |
| | $\text{Cl}_2 + \text{H}_2\text{O}$ | $\rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^-$ | …Ref(8) |
| Dismutation reaction | $6\text{OCl}^- + 3\text{H}_2\text{O}$ | $\rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 6\text{H}^+ + 3/2\text{O}_2 + 6\text{e}^-$ | …Ref(27) |
| Chemical reaction | $2\text{HOCl} + \text{OCl}^-$ | $\rightarrow \text{ClO}_3^- + 2\text{Cl}^- + 2\text{H}^+$ | …Ref(27) |
| | $\text{HOCl} + \text{ClO}_3^-$ | $\rightarrow \text{ClO}_4^- + \text{Cl}^- + \text{H}^+$ | …Ref(27) |
| | $\text{ClO}_3^- + \cdot\text{OH}$ | $\rightarrow \text{ClO}_4^- + \text{H}^+ + \text{e}^-$ | …Ref(34) |
| | $\text{ClO}_3^- + \text{H}_2\text{O}$ | $\rightarrow \text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^-$ | …Ref(34) |

プロセスでの安定性から塩素酸、過塩素酸の蓄積が報告され、これらの化合物自体も、それぞれ塩水、塩素酸溶液の電解によって工業生産が行われている⁹⁾。なお、これらの亜塩素酸、塩素酸、過塩素酸は、水中ではイオンで存在するが、水道水質基準等の表記と合わせ、本稿では亜塩素酸、塩素酸、過塩素酸と記述する。

塩素酸化合物は、塩素酸ナトリウム、塩素酸カリウム等の形態で農薬類や火薬等に用いられている¹⁰⁾。水道水中の塩素酸の主な起源は、次亜中の不純物であることが知られ、その影響により浄水、給水栓水における検出事例が多いことが報告されている^{9, 11~13)}。次亜が高温で長期間保存された場合は、高い濃度で検出されることがあり、注意喚起が出されている^{14~16)}。塩素酸は甲状腺濾胞中のコロイドを枯渇させ甲状腺機能を低下させる毒性が指摘され、世界保健機関 (WHO) 飲料水水質ガイドラインでは、その暫定ガイドライン値として $700 \mu\text{g}\cdot\text{L}^{-1}$ を定めている¹⁷⁾。米国環境保護庁 (USEPA) では最大許容濃度 (MCL) は定めていないが、カリフォルニア州環境健康影響評価局 (OEHHA) は、同様の毒性の観点から $200 \mu\text{g}\cdot\text{L}^{-1}$ の目標値を推奨する意見も提出されている¹⁸⁾。国内では、内閣府食品安全委員会による毒性評価結果¹⁹⁾を受けて、2007年度の水質基準の改正で、水道水質基準項目に指定されている (水道水質基準値: $600 \mu\text{g}\cdot\text{L}^{-1}$)¹⁴⁾。

過塩素酸化合物は、過塩素酸アンモニウム、過塩素酸ナトリウム等の形態で、ロケットやミサイルの推進剤の他、エアバッグ、火薬、花火、マッチ等に用いられている¹¹⁾。水道水中の過塩素酸の存在は国内外で報告されている²⁰⁾が、国内の場合、上流域の発生源の影響で、利根川流域の広い範囲で存在していることが報告されている^{9, 11)}。過塩素酸は、甲状腺におけるよう素の取り込みを抑制することから、2005年2月、米国科学アカデミー (NAS) は、過塩素酸の参照用量 (RfD) として、 $0.7 \mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ を勧告した²¹⁾。塩素酸同様に第3次規制物質候補リスト (CCL3) に指定され、2008年12月、USEPAは暫定健康勧告濃度として $15 \mu\text{g}\cdot\text{L}^{-1}$ を公表し²²⁾、その後も規制方法について検討を続けている。過塩素酸の飲料水中の州のMCLとして、カリフォルニア州では $6 \mu\text{g}\cdot\text{L}^{-1}$ ²³⁾を、マサチューセッツ州では $2 \mu\text{g}\cdot\text{L}^{-1}$ ²⁴⁾を定めており、幾つかの州では、 $1\sim 18 \mu\text{g}\cdot\text{L}^{-1}$ の範囲で、過塩素酸の勧告レベルを設定している。国内では、2009年度より水道水質基準関連の要検討項目に指定され、2011年度には目標値 $25 \mu\text{g}\cdot\text{L}^{-1}$ が設定された²⁵⁾。国際連合食糧農業機関 (FAO) と WHO の FAO/WHO 合同食品添加物専門家会議においても、暫定最大耐容一日摂取量を基に、目標値として $25 \mu\text{g}\cdot\text{L}^{-1}$ を定めている²⁶⁾。

これまで、電解における次亜の生成特性に対し、電解条件、電解装置、電極種等の様々な観点から検討が行われ、同様に、塩素酸や過塩素酸の生成特性についても検討されてきた。Jungら²⁷⁾は、無隔膜式でプレート型の白金/チタン (Pt/Ti) 電極を用いて、異なる pH 条件 (pH 3.6~9.0) 下で、塩化物を含む水の電解中の塩素酸および過塩素酸の生成特性を検討した。その結果、塩化物濃度に比例して、塩素酸、過塩素酸が生成したこと、一般的な pH 状態 (pH 7.2~9.0) では、過塩素酸濃度と塩素酸濃度の比率は低かったこと、pH はこの比率に影響を及ぼさなかったことを報告した。Neodoら²⁸⁾は、塩水の電解において、塩素、塩素酸、過塩素酸いずれも水温が低い場合の方が生成したことを示した。このとき、二酸化ルテニウム・二酸化スズ ($\text{RuO}_2\cdot 2\text{SnO}_2/\text{Ti}$) 電極と Pt/Ti 電極の比較では、塩素濃度は $\text{RuO}_2\cdot 2\text{SnO}_2/\text{Ti}$ 電極の方が高かったが、塩素酸及び過塩素酸濃度は Pt/Ti 電極の方が高かったことも示した。「/Ti」は、チタン金属を基板としていることを示す。さらに、Tockら²⁹⁾や Bergmannら³⁰⁾は、ポロンドープダイヤモンド (BDD) 電極や Ti 電極を用いた場合、特に BDD で比較的高い過塩素酸が生成されたことを報告している。神崎³¹⁾は、中性付近でパラジウム (Pd) を用いて陽分極すると塩素が効率よく生成し、塩素酸も電解で合成され、強酸性での塩素ガスの発生を除けば、熱力学的には塩素の原子価が最も高い過塩素酸が優先的に生成する可能性を指摘した。これらのことは、電解条件によって塩素、塩素酸、過塩素酸の生成は影響を受けること、電極の種類は重要な因子の一つであることを示している。しかし、これまで次亜製造用として一般的に用いられる電極についての検討は限定的であり、特に、次亜製造時の不純物として生成する塩素酸、過塩素酸の生成に関する知見は少ない。

本研究では、塩水の電解による次亜生成過程における副生成物としての塩素酸及び過塩素酸の生成特性について、電極種の視点から検討を行った。すなわち、現在、塩素発生、次亜製造や電解工程に用いられる主な電極6種 [ルテニウム (Ru)、チタン (Ti)、イリジウム (Ir)、錫 (Sn)、白金 (Pt)、鉛 (Pb) あるいはその化合物のそれぞれ単独及び混合電極] について比較した。

2. 実験方法

2.1 試薬及び溶液

本研究で用いた精製水は、超純水製造装置 (Gradient A10 water purification system; Millipore 製) で製造したものをを用いた。塩化ナトリウムは和光純薬製を、塩素酸、過塩素酸の標準液はそれぞれ関東化学製、GFS Chemicals 製を用いた。 $^{18}\text{O}_4^-$ 過塩素酸ナトリウムは、Cambridge Isotope Laboratories 製を用いた。その他、本

研究で用いた試薬は特級以上であった。

2.2 電極

陽極は、現在、塩素発生、次亜製造や主な電解工程に関連する6種の電極を用いた。実際の塩素発生電極を供給しているベルメック電極株式会社に特性の異なる電極の製作を依頼した。各電極の材質は、A:二酸化ルテニウム-二酸化チタン ($\text{RuO}_2\text{-TiO}_2/\text{Ti}$)、B:二酸化ルテニウム-二酸化イリジウム-二酸化チタン ($\text{RuO}_2\text{-IrO}_2\text{-TiO}_2/\text{Ti}$)、C:二酸化イリジウム-二酸化スズ ($\text{IrO}_2\text{-SnO}_2/\text{Ti}$)、D:二酸化イリジウム-白金 ($\text{IrO}_2\text{-Pt}/\text{Ti}$)、E:白金 (Pt/Ti)、F:二酸化鉛 (PbO_2/Ti)であった。これらは材質から想定される酸素過電圧が異なり、その値の小さい方から電極A~Fとする。電極の予測酸素過電圧の順としたのは、塩素酸、過塩素酸の生成と関連している可能性を考えたためである。陰極はTiを用い、精製水で洗浄して繰り返し使用した。電極は、幅1cmの金属基板の柄に、縦4cm、横5cmの平板部分をコーティングしたもので、平板部分が十分浸漬するよう設置し、浸漬面積は約20 cm^2 であった。

それぞれの電極の用途や特徴³²⁾を示す。電極A(主たる成分: $\text{RuO}_2\text{-TiO}_2$)は、最も一般的な塩素発生反応の陽極であり、全てのソーダ電解プロセス、塩化物浴電解並びに塩素電解等広範囲に使用されている。電極B(同: $\text{RuO}_2\text{-IrO}_2\text{-TiO}_2$)はイオン交換膜法ソーダ電解用として開発された、塩素ガス中の酸素含有量が低く且つ長寿命の陽極とされている。その他の塩素発生電解プロセスにも使用される。電極C(同: $\text{IrO}_2\text{-SnO}_2$)は、無隔膜法で、希薄塩水及び海水を電解して次亜を生成する場合に使用され、低温でも高い電流効率を維持し、長寿命の陽極とされている。電極D(同: $\text{IrO}_2\text{-Pt}$)は、主として酸性電解浴中で、陽極で酸素発生または酸化反応を必要とする場合に使用する陽極で、陽極電位が高い。これら電極A~Dは、寸法安定性陽極(DSA[®];ベルメック電極株の登録商標)と呼ばれ、通常格子状のチタン金属基板上に導電性で耐食性の金属酸化物を薄くコーティングして用いられる。電極E(同: Pt)は、電極D(同: $\text{IrO}_2\text{-Pt}$)と同様に陽極電位が高い電極とされている。電極F(同: PbO_2)は、安価であるため、高酸化型で有機物分解やオゾン発生に用いられ、工業用に亜鉛の精錬等に用いられている¹¹⁾。電極E、Fもチタンを金属基板としている。なおここまでの電極の材質は文献¹¹⁾等に表示された表記を用いており、同社製品コードではAはJP-130、BはJP-202、CはJP-330、DはJL-403、EはJL-510、FはJL-701に相当する電極をそれぞれ基本とした³²⁾。以下、電極材質の酸化物が明確に表記されている文献を引用する場合を除き、実験に用いた電極については、A~Fで表記する。

2.3 塩水电解実験の操作手順

塩水电解実験における実験条件は、Jungら²⁷⁾の文献を元に、比較的安定的に次亜が生成される塩化物濃度、試料水量、電流値等の実験値を設定した。実際の次亜製造においては多くは隔膜法が用いられ、電極のコーティングの特性によっても電流効率が変化するため、単純比較は困難であるが、2A(電極20 cm^2 に対し0.1 $\text{A}\cdot\text{cm}^{-2}$)の通電電流量で電流効率60~70%として、30 $\text{g}\cdot\text{L}^{-1}$ 以上の希塩水の電解を行った場合、2時間程度で有効塩素

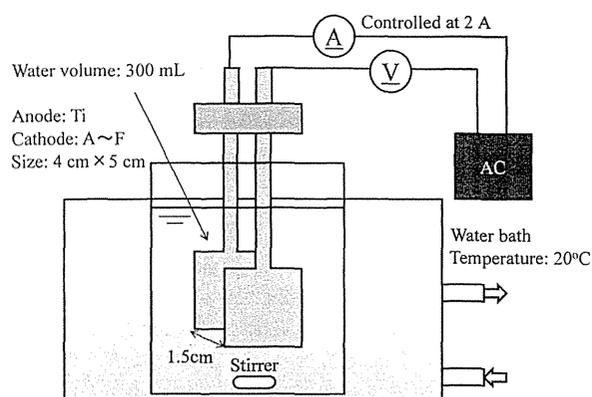


Fig. 1 Experimental apparatus.

濃度として10,000 $\text{mg}\cdot\text{L}^{-1}$ を見込むことができる条件とした。試料水量は異なるが、荻原ら³³⁾の塩水の電解実験においても、塩化ナトリウム濃度3%、電流値2Aの条件が用いられている。本実験では、精製水に塩化ナトリウムを30 $\text{g}\cdot\text{L}^{-1}$ (塩化物濃度:18 $\text{g}\cdot\text{L}^{-1}$)に調製したものを対象水とし、電解実験に用いた。実験装置の概要をFig. 1に示す。実験は、対象水量が300 mL、水温が20°C、電極間が1.5 cmの条件で行った。電流値は2Aに設定し、実験中、対象水は攪拌子で攪拌し続けた。試料水は、実験開始から5、15、30、60、90、120分後に採取し測定した。試料水は採取後、速やかに精製水で希釈し、塩素濃度を測定するとともに、その一部は塩化物及び塩素酸、過塩素酸の測定用に、それぞれフェノール及びアスコルビン酸ナトリウム(いずれも和光純薬製)を添加して脱塩素した。塩化物イオン測定用試料の脱塩素剤にフェノールを用いた理由は、塩素との反応が塩素付加反応であり、脱塩素時に塩化物濃度を増加させないためである。実験開始前と終了時に試料水のpHを測定した。実験は、2回以上繰り返し行った。

2.4 測定方法

塩素濃度は、DPD/FAS滴定法で測定した³³⁾。塩化物濃度は、イオンクロマトグラフ(IC)法(DX-500;Dionex製)で測定した。塩素酸、過塩素酸濃度は、IC-タンデム質量分析(MS/MS)法(IC:ICS-2000;Dionex製、MS/MS:API 3200 QTrap;Applied Biosystems製)で測定した¹²⁾。過塩素酸濃度の測定では、 $^{18}\text{O}_4\text{-}$ 過塩素酸ナトリウムを内部標準物質として用いた。MRM(Multiple Reaction Monitoring(多重反応モニタリング))モードにおけるモニタリング質量数は、塩素酸が m/z 83 \rightarrow 67、過塩素酸が m/z 99 \rightarrow 83、 $^{18}\text{O}_4\text{-}$ 過塩素酸は m/z 107 \rightarrow 89であった。このとき、試料水中の塩化物によるイオン化阻害を防ぐため、前処理として、試料水はOnGuard IIカートリッジAg/H(Dionex製)に通水して塩化物を除去するか、試料水の希釈を行った。

3. 結果及び考察

3.1 塩水电解における次亜の生成

塩水电解における塩素濃度の経時変化をFig. 2に示す。いずれの電極においても、20分間程度で塩素濃度は約3 $\text{g}\cdot\text{L}^{-1}$ 生成し、その後も上昇を続けた。5~15分間では、電極間に大きな濃度差は認められなかった。しかし、30分を過ぎた頃から、電極E、Fの塩素の生成は

他の電極に比べて低下し、120分後では約 $2\text{ g}\cdot\text{L}^{-1}$ 低かった。これは、DSA[®]電極である($\text{RuO}_2\cdot 2\text{SnO}_2/\text{Ti}$)電極とPt/Ti電極との比較結果²⁷⁾と類似の傾向であったが、本実験では、この報告ほど塩素濃度に違いは認められなかった。pHは、実験開始時は5.4～5.8の範囲であったが、120分後は8.9～9.3の範囲にあった。このことから、塩素は、次亜塩素酸イオンの形態で存在していると言える。また、塩化物濃度(初期濃度: $18\text{ g}\cdot\text{L}^{-1}$)は時間と共に低下したが、120分後でも $15\sim 16\text{ g}\cdot\text{L}^{-1}$ の範囲にあり、大きくは変わらなかったため、揮発による影響等は小さいと考えられた。

全ての電極において電流値はほぼ一定で設定値に近い値であったが、電圧は電極によって異なった。すなわち、実験開始時について見ると、電圧値は5.2～6.8Vの範囲にあり、120分後は、いずれの電極でも0.3～0.4V上昇していた。

本実験のように $30\text{ g}\cdot\text{L}^{-1}$ の希薄塩水の場合、陽極では酸素の生成が主な反応であると考えられるが、電極では、同時に塩素の生成も起こっている。したがって、今回計測された電圧値はいわゆる「混成電位」に位置付けられる。このため、この値は酸素過電圧が高い電極において高い傾向にあったが、必ずしもその順番(A～Fの順番)とは一致しない場合も認められたと推測された。なお、純粋に塩素発生電位あるいは酸素発生電位を比較測定するには、前者であれば塩酸中もしくは酸性の高濃度食塩中で、後者であれば希硫酸中で測定することとなり、実際の電解溶液での値とはかけ離れた値になってしまう恐れがある。このため、本研究では、実験開始時と120分後における実測値の平均値を「端子間電圧 (terminal voltage)」とし、解析に用いることとした (Table 2)。Fig. 3に、端子間電圧と60及び120分後の塩素濃度との関係を示す。電極Dは電極Aと端子間電圧値が近く、

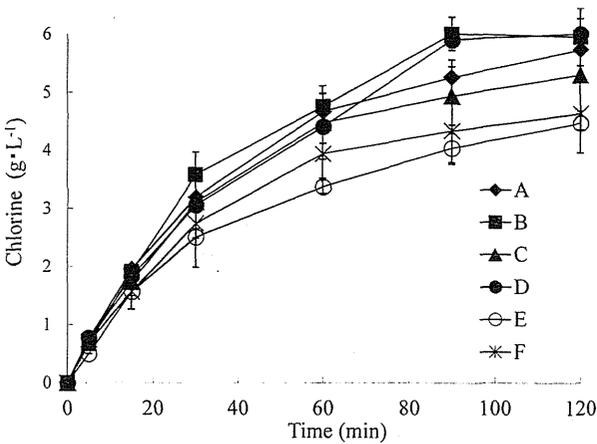


Fig. 2 Generation of chlorine during electrolysis of salt solution using different anodes.

Table 2 Terminal voltages at 2A.

| Voltage (V) | A | B | C | D | E | F |
|-------------|-----|-----|-----|-----|-----|-----|
| Initial | 5.4 | 5.2 | 5.8 | 5.5 | 6.8 | 6.3 |
| Final | 5.7 | 5.6 | 6.1 | 5.8 | 7.1 | 6.7 |
| Mean | 5.6 | 5.4 | 6.0 | 5.7 | 7.0 | 6.5 |

塩素生成濃度も近いいため僅かに逆転したがその場合を除き、60分及び120分後において、塩素生成濃度は、B, (A, D), C, F, Eの順に低かった。すなわち、端子間電圧の順に塩素濃度が低くなる傾向にあった。端子間電圧が最も低い電極Bと最も高い電極Eの端子間電圧の差は約1.5Vであるが、生成した塩素濃度は2.5割から3割低かった。

3.2 塩水電解における塩素酸及び過塩素酸の生成

塩水電解における塩素酸及び過塩素酸濃度の経時変化をそれぞれFigs. 4及び5に示す。実験開始時の濃度は、いずれも定量下限値以下であったが、時間の経過と共にほぼ単調に増加した。120分後の塩素酸及び過塩素酸濃度は、それぞれ $140,000\sim 800,000$ 及び $70\sim 45,000\text{ }\mu\text{g}\cdot\text{L}^{-1}$ の範囲であった。したがって、塩素、塩素酸、過塩素酸のいずれも電極によってその生成が異なり、その違いは過塩素酸、塩素酸、塩素の順に大きく、特に過塩素酸は電極種の影響が非常に大きいことが示された。

Figs. 6及び7に、それぞれ端子間電圧と60及び120分後の塩素当たり塩素酸及び過塩素酸生成率との関係を示す。塩素酸の場合、電極Cを除き、端子間電圧が高い場合に塩素当たり塩素酸生成率が高いことが示された。これは、Fig. 3と逆の傾向であったが、端子間電圧が高いとより酸化が進み、次亜塩素酸イオンが塩素酸へと変換されたことを示していると考えられた。一方、過

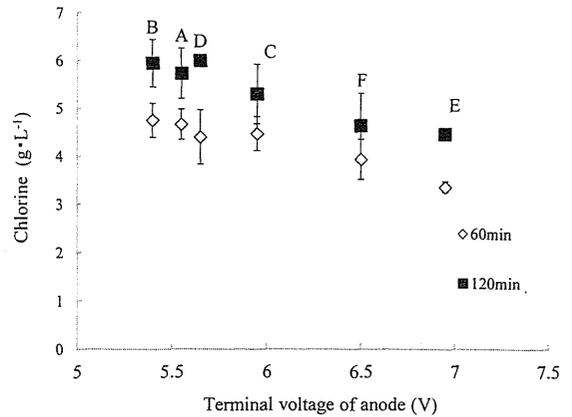


Fig. 3 Relationship between terminal voltages and chlorine concentration at 60 and 120 min of reaction.

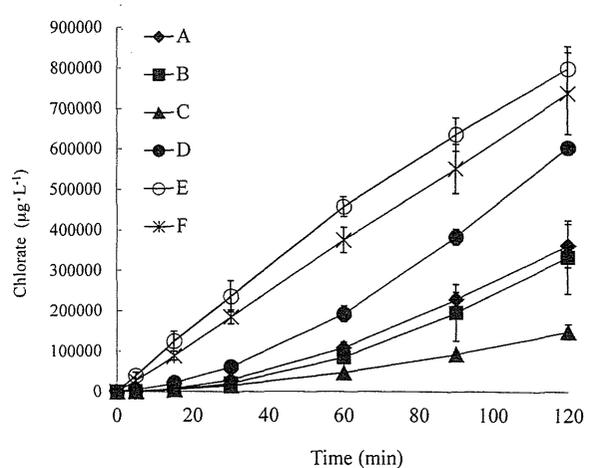


Fig. 4 Generation of chlorate during electrolysis of salt solution.

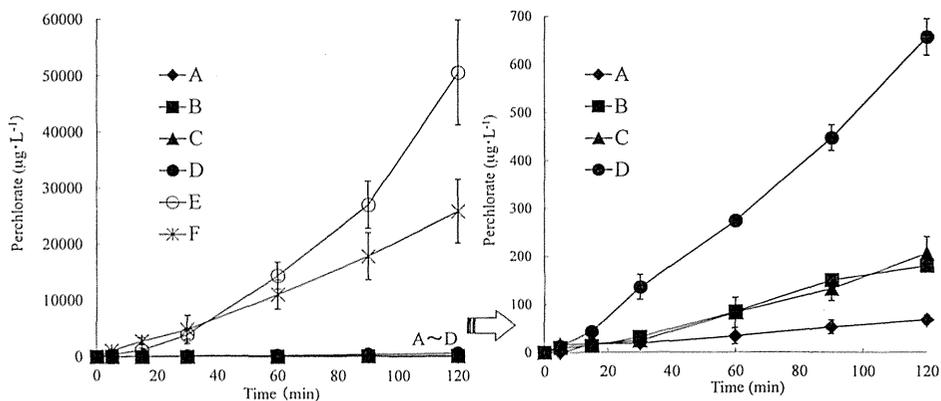


Fig. 5 Generation of perchlorate during electrolysis of salt solution.

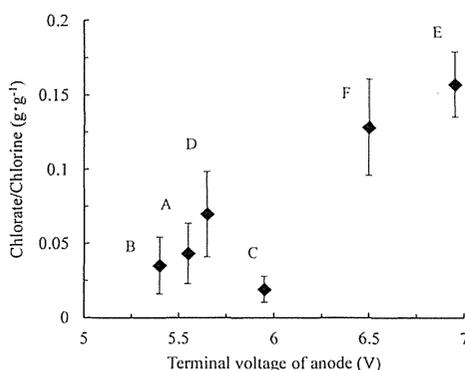


Fig. 6 Relationship between terminal voltages and the ratio of chlorate generation to chlorine generation during 60-120 min of reaction.

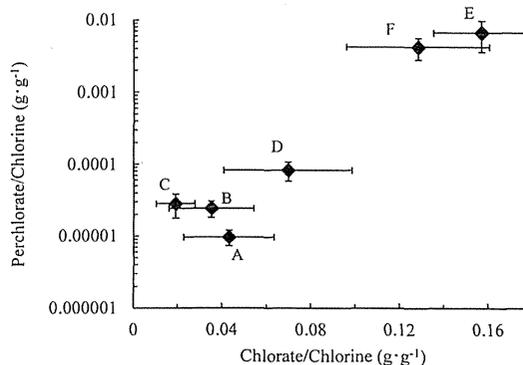


Fig. 8 Relationship between chlorate per chlorine and perchlorate per chlorine.

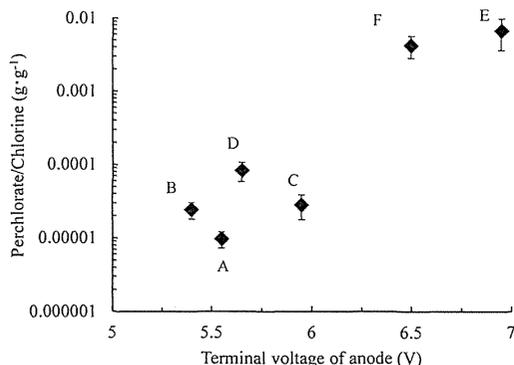


Fig. 7 Relationship between terminal voltages and the ratio of perchlorate generation to chlorine generation during 60-120 min of reaction.

塩素酸の場合、全体的に見ると端子間電圧が高い場合に塩素当たり過塩素酸生成率が高い傾向にあったが、電極 A ~ D の過塩素酸生成率は、電極 E, F に比べるとオーダーで 2 ~ 3 桁低く、電極 A ~ D の間では、電極 A, B, D に比べ、特に電極 C が塩素濃度当たりの過塩素酸生成率が低く、端子間電圧との間に明確な関連性は認められなかったことから、それ以外の要因も関連していると推測された。

電解における塩素酸、過塩素酸の生成には複数の経路があることが報告されている^{28, 34, 35)}。塩素酸の場合、次亜や亜塩素酸等の塩素化オキソ酸が酸化される経路、塩化物が直接塩素酸になる経路、電解によって生成され

た活性酸素種 [オゾンやヒドロキシルラジカル ($\cdot\text{OH}$)] が係わる経路がある³⁵⁾。過塩素酸の場合、塩素酸が $\cdot\text{OH}$ によって酸化される経路が知られている³⁵⁾。このうち、 $\cdot\text{OH}$ の生成に関しては、BDD, Pt, PbO_2 等の電極では生成しやすく、特に BDD 電極では高いこと³⁶⁾、これら電極では過塩素酸の生成率が高かったことが報告されている。一方、具体的な種類については言及されていなかったが、一部の DSA[®] 電極では、過塩素酸の生成率が低かったことが報告されている³⁶⁾。これは、Fig. 7 における電極 A ~ D と E, F の間における塩素当たり過塩素酸生成率の違いと類似しており、 $\cdot\text{OH}$ の生成しやすさによるものと考えられた。このことから、次亜製造に広く用いられている DSA[®] 電極 (電極 A ~ D) は、いずれも過塩素酸までは塩素化オキソ酸の酸化が進みにくいことが示された。

DSA[®] 電極である電極 A ~ D の間でも過塩素酸は生成されたが、端子間電圧と過塩素酸の間に関連性は認められず、過塩素酸濃度のオーダーは 1 桁異なった。塩素当たりの塩素酸と過塩素酸生成率の関係についても、DSA[®] 電極とその他の電極を比較すると、全体的には塩素酸濃度が高い場合に過塩素酸濃度も高い傾向が認められた (Fig. 8)。しかしながら、DSA[®] 電極の中では、その関連性は認められなかった。いずれの濃度も電極 D において最も高かったが、最も濃度が低かったのは、塩素酸では電極 C、過塩素酸では電極 A であった。電極 D は、端子間電圧は最も高くないが、材質の一部に Pt を用いているため、DSA[®] の中では塩素酸、過塩素酸濃度も高かった可能性が考えられた。一方、上述したように塩

素酸、過塩素酸の生成経路は複雑であり、塩素酸は過塩素酸の前駆物質でもあるため、塩素酸と過塩素酸が蓄積しにくい材質の組み合わせは異なると考えられる。

本実験は、次亜製造を目的とした段階（塩素濃度が時間とともに上昇しているあるいは一定となる範囲）を対象とし、塩素濃度は電極により違いはあったものの大きくは異なる範囲での検討であった。実験結果から、その段階でも、副生成物としての塩素酸、過塩素酸の生成に違いが認められ、特に過塩素酸において顕著であり、概して電解における端子間電圧と関連性があることが示された。今回の実験結果は無隔膜式の反応装置で、希塩水電解を行っているため、実際の場合には塩濃度や電位の違いにより生成状況は異なると考えられるが、端子間電圧が高い場合は塩素酸、過塩素酸の濃度が高くなるため、浄水場等の現地で生成する次亜塩素酸や、電解工程を有する工場廃水、電解を用いる浄水器等でもこのような傾向があると考えられた。

3.4 電解における塩素酸・過塩素酸の制御

塩素酸は水質基準項目、過塩素酸は、現在水道水質基準の要検討項目に位置づけられており、目標値も設定されている。Fig. 7の結果から、電極 E, F においては、本条件における塩素当たり過塩素酸生成率が $0.0025 \text{ g} \cdot \text{g}^{-1}$ を超えている。すなわち、次亜の注入率 $10 \text{ mg} \cdot \text{L}^{-1}$ に対し、過塩素酸濃度が $25 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ を超えることに相当する。特に水道における次亜の注入率が $10 \text{ mg} \cdot \text{L}^{-1}$ 程度となる場合もあることを考慮すると、次亜の生成等に Pt 電極や PbO_2 電極を用いた場合の過塩素酸濃度に留意が必要である。

なお、今回の実験は、無隔膜式の電解であるため、実際の次亜製造時とは条件が異なる。また、配水過程等における電解処理により追加塩素添加を行う場合など²⁾は塩化物イオン濃度が低いため、生成特性も異なることが考えられ、実際の適用には更なる検討が必要である。

4. まとめ

1) 6種類の異なる電極を用いて実験を行ったところ、生成装置の電極の種類により反応時の電位が異なり、次亜塩素酸の生成にともなって生成する塩素酸、過塩素酸の生成量が異なることが分かった。

2) 電流値が一定の条件では、白金電極や二酸化鉛電極において、端子間電圧が高く、塩素（次亜塩素酸）の生成量が少なく、塩素酸、過塩素酸の生成量が多くなることが分かった。

3) 電解における電極の違いにより、塩素酸、過塩素酸の濃度が高くなる場合があるため、生成次亜、工場における電解工程等でもこのような傾向があると考えられた。

4) 塩素酸は水道水質基準項目、過塩素酸は、現在水道水質基準の要検討項目に位置づけられており、目標値も設定されている。電極種により、生成する次亜塩素酸濃度に対する塩素酸、過塩素酸濃度が高い場合があるため、特に次亜の生成等に白金電極や二酸化鉛電極を用いた場合の塩素酸、過塩素酸濃度に留意が必要である。

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[論文要旨]

塩水电解における次亜塩素酸の生成における塩素酸, 過塩素酸の特性を把握するための検討を行った。6種類の異なる電極(主たる成分 A:RuO₂-TiO₂, B:RuO₂-IrO₂-TiO₂, C:IrO₂-SnO₂, D:IrO₂-Pt, E:Pt, F:PbO₂)を用いて塩水电解を行ったところ, 生成装置の電極の材質により反応時の電位が異なり, 次亜塩素酸の生成にともなって生成する塩素酸, 過塩素酸の生成量が異なることが分かった。電流値が一定の条件では, 端子間電圧が高い電極で電圧が高く, 塩素(次亜塩素酸)の生成量が少なく, 塩素酸, 過塩素酸の生成量が多くなった。特に, 白金電極(E)や二酸化鉛電極(F)において, 次亜塩素酸あたりの過塩素酸の生成が顕著であった。電解における電位の違いにより, 塩素酸, 過塩素酸の濃度が高くなるため, 次亜塩素酸を生成する工程, 工場における電解等でも注意が必要である。

キーワード: 電解; 次亜塩素酸; 過塩素酸; 塩素酸; 端子間電圧

Control of trichloramine formation by two-step chlorination in water purification processes

K. Kosaka, N. Kobashigawa, R. Nakamura, M. Asami, S. Echigo and M. Akiba

ABSTRACT

Chlorinous odour in drinking water is of great concern in Japan. Some water utilities use trichloramine (NCl_3) as an index of chlorinous odour and are attempting to control its levels in drinking water. In the present study, the effects of two-step chlorination, involving addition of chlorine twice, on NCl_3 control were investigated. The results regarding ammonia (NH_3), glycine solutions and raw waters at water purification plants (WPPs) indicated that NCl_3 -formation potentials (FPs) were reduced by two-step chlorination when NH_3 was a primary NCl_3 precursor and the 1st chlorine addition was set at an excess breakpoint (BP). However, no effect on NCl_3 -FP was observed when the 1st chlorine addition was set below BP. Two-step chlorination was not effective for NCl_3 control regardless of the amounts of the 1st chlorine addition when organic nitrogen compounds were the primary NCl_3 precursors. Moreover, the NCl_3 -FPs in raw water with relatively high NH_3 were reduced at actual WPPs when two-step chlorination was applied.

Key words | ammonia, chlorination, chlorinous odour, drinking water, two-step chlorination, trichloramine

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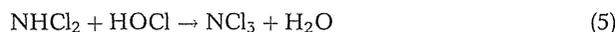
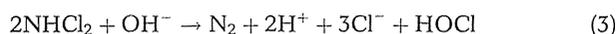
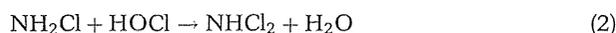
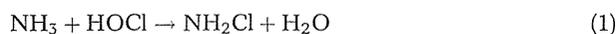
INTRODUCTION

Trichloramine (NCl_3), formed by the chlorination of ammonia (NH_3) and some organic nitrogen compounds (Shang & Blatchley III 1999), is one of the major chlorinous odour compounds in drinking water (Tanaka *et al.* 2010). It was reported that the odour threshold concentration of NCl_3 was 20 $\mu\text{g Cl}_2/\text{L}$ (World Health Organization 2011). Concentrations of free chlorine and chloramines [monochloramine (NH_2Cl), dichloramine (NHCl_2) and NCl_3] are generally expressed by weight of chlorine ($\mu\text{g Cl}_2/\text{L}$) (Standard Methods 2005). In Japan, some water utilities use NCl_3 as an index of chlorinous odour and are attempting to control its levels in drinking water (Chiba Prefectural Waterworks Bureau 2007; Bureau of Waterworks Tokyo Metropolitan Government 2012).

The characteristics of NCl_3 formation in water have been investigated by several groups (Jafvert & Valentine

1992; Tanaka *et al.* 2010). These studies indicated that reduction of residual chlorine and high pH are viable options for NCl_3 control. In addition, two-step chlorination has been applied for NCl_3 control at several water purification plants (WPPs) of the Bureau of Waterworks Tokyo Metropolitan Government (Hosoda *et al.* 2009; Shigeeda *et al.* 2011). During two-step chlorination, chlorine is added twice and free chlorine concentrations after the 1st chlorine addition are set at a slight excess above breakpoint (BP). BP chlorination is a known process to reduce NH_3 in water through the continuous addition of free chlorine (American Water Works Association 2000). Initially, NH_2Cl is formed by the reaction of NH_3 and chlorine, followed by NHCl_2 formation (Equations (1) and (2)) (White 1999). The NHCl_2 formed is decomposed by several pathways including

Equations (3) and (4), and concentrations of the sum of free chlorine and chloramines have a minimum value at BP. After BP, the sum of free chlorine and chloramines increases because free chlorine concentration increases with free chlorine addition. In this region, NCl_3 is also formed by Equation (5). The concept of two-step chlorination is to reduce NCl_3 formation after the 2nd chlorine addition by promoting NHCl_2 decomposition through the reaction of Equations (3) or (4) (Tanaka *et al.* 2010). However, there have been few studies regarding the characteristics of two-step chlorination.



In the present study, NCl_3 -formation potentials (FPs) by one- and two-step chlorination in model solutions containing known NCl_3 precursors and raw waters at WPPs were compared to investigate the effects of two-step chlorination on NCl_3 control. In addition, the effects of the amounts of the 1st chlorine addition of the two-step chlorination were examined. Moreover, profiles of NCl_3 -FPs at actual WPPs both with and without two-step chlorination were compared.

METHODS

Reagents and solutions

Ultrapure water used was prepared with a Gradient A10 ultrapure water system (Millipore, Bedford, MA, USA). 1,1,2-Trichloroethane- d_3 (TCA- d_3) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Sodium hypochlorite (NaOCl ; Tsurukuron TW) was obtained from Tsurumi Soda (Yokohama, Japan). Standard

NCl_3 solution was prepared from NaOCl and ammonium chloride solutions by the procedures described previously (Shang & Blatchley III 1999; Kosaka *et al.* 2010). The NCl_3 concentration in the standard solution was determined by titration using *N,N*-diethyl-*p*-phenylene diamine and ferrous ammonium sulphate (Standard Methods 2005).

Test of NCl_3 -FPs

Raw waters at eight WPPs (WPP-1 to WPP-8) were collected in September and October 2011. The eight raw waters were collected again in January and February in 2012, except for that at WPP-3. Instead, raw water at WPP-3' was collected using the same lake water as the source. The raw water at WPP-4 was also collected in July 2011. All of the raw waters were surface water and were filtered with glass filters (GF/F; Whatman, Springfield Mill, UK) and the filtrates were used for the experiments. The water qualities are listed in Table S1 (available online at <http://www.iwaponline.com/ws/014/017.pdf>).

The scheme of the test of NCl_3 -FPs consisted of one- and two-step chlorination and is shown in Figure S1 (available online at <http://www.iwaponline.com/ws/014/017.pdf>). Model solutions and the raw waters at WPP-1 to WPP-8 were used for this part. In some cases, 0.1 mg N/L of NH_3 was added to the raw waters before the tests. NH_3 solutions (0.05 and 0.1 mg N/L) were used as model solutions because the concept of two-step chlorination is to reduce NCl_3 formation by promoting NHCl_2 decomposition (Tanaka *et al.* 2010). Glycine solution (0.1 mg N/L) was also used as a model solution because glycine is a typical organic nitrogen compound known as an NCl_3 precursor (Shang & Blatchley 1999).

The one-step chlorination test was similar to the procedures for testing FPs of chlorination by-products (Japan Water Works Association 2011). The experimental conditions were as follows: reaction time, 24 h; free chlorine concentration at 24 h, 1.0 ± 0.2 mg Cl_2/L ; pH, 7 (1 mM phosphate buffer); temperature, 20 °C. A blank solution was prepared by addition of chlorine to phosphate buffer under the same conditions as those of the samples. NCl_3 concentration in the blank solution was around 20 $\mu\text{g Cl}_2/\text{L}$.

The two-step chlorination test was also conducted at pH 7 prepared with 1 mM phosphate buffer at 20 °C. Firstly, the 1st chlorine addition was performed for each sample at three different doses based on the residual chlorine

concentration after 30 min. For the slightly greater-than-BP condition and the greater-than-BP condition, free chlorine concentration after 30 min was set at around 0.1 and 0.5 mg Cl_2/L , which were designated as B (BP + 0.1) and C (BP + 0.5), respectively. For the less-than-BP condition, the chlorine dose was half of B (BP + 0.1), which was designated as A (<BP). After 4 h of the 1st chlorine addition, chlorine was added again (2nd chlorine addition) so that the free chlorine concentration after 24 h of the second chlorine addition was 1.0 ± 0.2 mg Cl_2/L . The duration of the 1st chlorination was set to 4 h to simulate the general hydraulic retention time from pre-chlorination to sedimentation/sand filtration at WPPs. The blank solution was prepared by one-step chlorination of 1 mM phosphate buffer as described above.

The NCl_3 -FP was the difference in NCl_3 concentration between sample and blank solutions. In figures on the results of NCl_3 -FPs, their standard deviations are also shown as error bars (see 'Results and discussion'). In many cases, the standard deviations were based on the repetitions of NCl_3 analysis alone. However, in some cases, the standard deviations contained the repetitions of the tests of NCl_3 -FPs.

Profiles of NCl_3 -FPs at water purification plants

Raw and processed waters at WPP-9 and WPP-10 were collected in February 2011 and in December 2011 to February 2012, respectively. These two WPPs employed rapid sand filtration with advanced purification processes (ozone/biological activated carbon (BAC) processes). At WPP-9 chlorine was added only after BAC treatment. Raw water, waters after sedimentation, sand filtration, ozonation, and BAC treatment were collected from the WPP. In contrast, chlorine was added twice in the treatment train at WPP-10: chlorine was added at the settlement reservoir for NCl_3 control at a slight excess above BP, and after BAC treatment to ensure residual chlorine (Shigeeda *et al.* 2011). Raw water before chlorination and the waters after ozonation and BAC treatment were collected from the WPP. The water qualities of the samples are summarized in Table S2 (available online at <http://www.iwaponline.com/ws/014/017.pdf>). Raw waters at WPP-9 and WPP-10 had relatively high levels of NH_3 (≥ 0.1 mg N/L). Unlike the experiments on NCl_3 -FP after two-step chlorination, the samples were not filtered to evaluate the change of NCl_3 -FP

during the process. The procedures for testing of NCl_3 -FPs were the same of those of one-step chlorination described above. Note that residual free chlorine at 24 h in the water after ozonation on 21 February 2012 was 1.3 mg Cl_2/L . Phosphate buffers (pH 7) used for the samples of WPP-9 and WPP-10 were 6 and 1 mM, respectively.

Analysis

NCl_3 concentration was determined by headspace gas chromatography with mass spectrometry (Agilent 6890/5975C; Agilent Technologies, Palo Alto, CA, USA) (Kosaka *et al.* 2010) with an HP-1MS capillary column (0.25 mm \times 15 m, 0.25 μm ; Agilent Technologies). TCA- d_3 was used as an internal standard. The values of m/z for quantification were 51 for NCl_3 and 100 for TCA- d_3 . The limit of quantification of NCl_3 was 15 $\mu\text{g Cl}_2/\text{L}$. Analytical methods of other water quality items are described in Supplementary Material (available online at <http://www.iwaponline.com/ws/014/017.pdf>).

RESULTS AND DISCUSSION

Effects of two-step chlorination on NCl_3 -FPs in model solutions

Figure 1 shows the NCl_3 -FPs of NH_3 solutions (0.05 and 0.1 mg N/L) and glycine solution (0.1 mg N/L) from

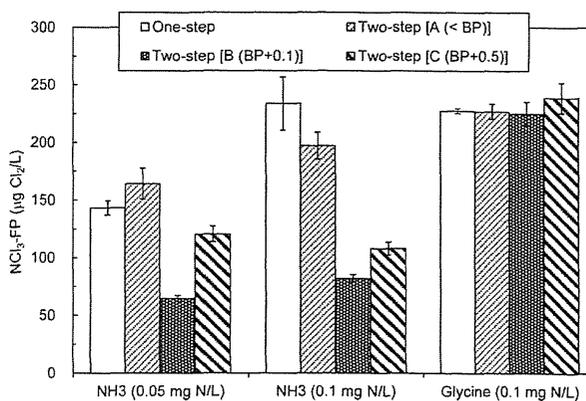


Figure 1 | Effects of two-step chlorination on NCl_3 -FPs in NH_3 solutions (0.05 and 0.1 mg N/L) and glycine solution (0.1 mg N/L).

one- and two-step chlorination. The NCl_3 -FPs in 0.05 and 0.1 mg N/L of NH_3 solutions from one-step chlorination were close to those from two-step chlorination of A (<BP). NH_2Cl and NHCl_2 were present after 4 h of the 1st chlorine addition of A (<BP), but NH_2Cl was dominant. The sums of NH_2Cl and NHCl_2 of 0.05 and 0.1 mg N/L of NH_3 solutions were 0.24 and 0.44 mg Cl_2 /L, respectively. On a nitrogen-weight basis, these values (i.e., 0.047 and 0.086 mg N/L, respectively) were almost identical to the initial NH_3 concentrations. Since NH_3 , NH_2Cl and NHCl_2 are NCl_3 precursors (reaction (1), (2) and (5)), it was considered that in the case of A (<BP), the amounts of the NCl_3 precursors did not change until the 2nd chlorine addition and the NCl_3 -FPs were similar to those from one-step chlorination.

The NCl_3 -FPs of NH_3 solutions from two-step chlorination of B (BP + 0.1) and C (BP + 0.5) were lower than those from one-step chlorination. After 4 h of the 1st chlorine addition of B (BP + 0.1) and C (BP + 0.5), levels of the sums of NH_2Cl and NHCl_2 were much lower than initial NH_3 concentrations. These results indicated that the amounts of the NCl_3 precursors decreased prior to the 2nd chlorine addition (e.g., reaction (3) or (4)) to lead to lower NCl_3 -FPs. As for the difference between NCl_3 -FPs of B (BP + 0.1) and C (BP + 0.5), those of C (BP + 0.5) in both 0.05 and 0.1 mg N/L of NH_3 solutions appeared to be slightly greater than those of B (BP + 0.1). The residual free chlorine level of C (BP + 0.5) of 0.05 mg N/L of NH_3 solution after 4 h of the 1st chlorine addition was higher than that of B (BP + 0.5) (i.e., 0.03 and 0.58 mg Cl_2 /L, respectively). It is implied that the reactions (3) to (5) are competitive, and NHCl_2 is likely to be transformed into NCl_3 at higher free chlorine concentration. That is, the 1st chlorine additions of C (BP + 0.5) in NH_3 solutions were probably in excess, and, as a result, the NCl_3 -FPs of C (BP + 0.5) were greater than those of B (BP + 0.1).

On the other hand, for the glycine solution, NCl_3 -FPs from one-step chlorination, A (<BP), B (BP + 0.1) and C (BP + 0.5) were similar. Na & Olson (2006) reported that when free chlorine was present in excess, glycine was transformed into *N*-chloroglycine and *N*-chloroglycine was further transformed into *N,N*-dichloroglycine. From the *N,N*-dichloroamino functional group of *N,N*-dichloroglycine, NH_2Cl was formed as one of the transformation products after several reaction steps, followed by NHCl_2 and NCl_3 formations through reactions (2) and (5).

For A (<BP), the glycine concentration was greater than the chlorine dose and was partially transformed into *N*-chloroglycine. *N*-chloroglycine was relatively stable in the absence of free chlorine (Na & Olson 2006). Thus, the amounts of NCl_3 precursors did not change until the 2nd chlorine addition, and the NCl_3 -FP did not decrease. Under the conditions B (BP + 0.1) and C (BP + 0.5), the chlorine dose was higher than the initial glycine concentration. Considering the results of NH_3 solutions, it is reasonable to expect lower NCl_3 -FPs if there was sufficient time for the formation and decomposition of NHCl_2 prior to the 2nd chlorine addition. In other words, 4 h of the 1st chlorination was not enough for these reactions, and the NCl_3 -FPs did not decrease by two-step chlorination.

Effects of two-step chlorination on NCl_3 -FPs in raw waters at WPPs

In this section, the effects of two-step chlorination on NCl_3 -FPs in raw waters at WPP-1 to WPP-8 were evaluated. Considering the results shown in Figure 1, two-step chlorination of A (<BP) was not conducted. The NCl_3 -FPs by one-step chlorination were 22–87 $\mu\text{g Cl}_2$ /L in September and October 2011 and 7–120 $\mu\text{g Cl}_2$ /L in January and February 2012 (Figure S2, available online at <http://www.iwaponline.com/ws/014/017.pdf>). The Wilcoxon signed-rank test, a nonparametric test, suggested seasonal variations of NCl_3 -FPs: NCl_3 -FPs in January and February 2012 were significantly larger than those in September and October 2011 (probability (P) < 0.05). The NCl_3 -FPs of WPP-3 and WPP-3' were excluded from the Wilcoxon signed-rank test because the points of their water intakes were different. NH_3 levels in raw waters in January and February 2012 were higher than those in September and October 2011. Thus, the larger NCl_3 -FPs in January and February 2012 could be due to the higher levels of NCl_3 precursors in the water.

Two-step chlorination under the conditions B (BP + 0.1) and C (BP + 0.5) were effective for some raw waters on NCl_3 control. The general tendency was that the effects of two-step chlorination were observed in the raw waters with relatively high levels of NH_3 . To further confirm the difference of the NCl_3 -FPs among the three groups (i.e., one-step chlorination and two-step chlorination of B (BP + 0.1) and C (BP + 0.5)), the Friedman test, a nonparametric analysis of variance,

was performed. The data set for this analysis included NCl_3 -FPs in raw waters after the addition of 0.1 mg N/L of NH_3 at WPP-4 in July 2011 and WPP-1, WPP-4 and WPP-5 in September and October 2011 (Figures S3 and S4, available online at <http://www.iwaponline.com/ws/014/017.pdf>) (note that for the raw water at WPP-4 in July 2011, the NCl_3 -FP from two-step chlorination of A (<BP) was also included as the NCl_3 -FP of A (<BP) was similar to that of one-step chlorination like the case of NH_3 solution (Figure 1)).

The number of samples of raw waters was 20 and the samples were categorized into three cases based on their NH_3 levels: NH_3 level <0.02, 0.02–0.05 and ≥ 0.1 mg N/L (there were no raw waters with NH_3 level of 0.05–0.1 mg N/L). The numbers of the raw water samples with NH_3 levels of <0.02, 0.02–0.05 and ≥ 0.1 mg N/L were 5, 8 and 7, respectively. In the cases of <0.02 and 0.02–0.05 mg N/L of NH_3 , the NCl_3 -FPs from one- and two-step chlorination were not significantly different (Figure 2). For these cases, other compounds (i.e., organic nitrogen compounds) seemed to be the primary NCl_3 precursors. For the NCl_3 -FPs reduction, sufficient time would be required for the formation and the following decomposition of NHCl_2 prior to the 2nd chlorine addition as was discussed in the reaction with glycine (Figure 1).

On the other hand, in the case of ≥ 0.1 mg N/L of NH_3 , the NCl_3 -FPs among the groups (one-step chlorination and two-step chlorination of B (BP + 0.1) and C (BP + 0.5)) were significantly different ($P < 0.01$). The Bonferroni test was subsequently performed as a post-hoc test to investigate which pairs of the three groups were different. The NCl_3 -FPs from one-step chlorination were significantly different to those

from two-step chlorination of B (BP + 0.1) and C (BP + 0.5) ($P < 0.01$), indicating that NH_3 was a main NCl_3 precursor of this case (≥ 0.1 mg N/L of NH_3). Thus, it was found that two-step chlorination was effective for NCl_3 control when NH_3 is the primary NCl_3 precursor in raw water.

No significant difference was observed between the NCl_3 -FPs of B (BP + 0.1) and C (BP + 0.5) by the Bonferroni test. This tendency was different from those of NH_3 solutions (Figure 1) although the results of the NH_3 solutions were not statistically evaluated. One possible reason for these results were other constituents in the raw waters. As described in the previous subsection, reactions (3) to (5) are competitive, and NCl_3 formation proceeds at higher free chlorine levels. Raw waters generally contain other constituents reactive to chlorine than NH_3 , and the chlorine levels in raw waters after 4 h of the first chlorine addition tend to be lower than those in NH_3 solutions. Thus, free chlorine of C (BP + 0.5) in raw waters was not preferentially used for NCl_3 formation through reaction (5) after 4 h of 1st chlorine additions.

Profiles of NCl_3 -FPs in water purification processes

To confirm the effects of two-step chlorination on NCl_3 -FPs in actual water purification processes, profiles of NCl_3 -FPs in raw waters with relatively high NH_3 were investigated at WPP-9 and WPP-10. Chlorination processes applied at WPP-9 and WPP-10 were one- and two-step chlorination, respectively (see 'Methods').

The NH_3 level and NCl_3 -FP in raw water at WPP-9 were 0.14 mg N/L and 140 $\mu\text{g Cl}_2/\text{L}$, respectively (Figure S5,

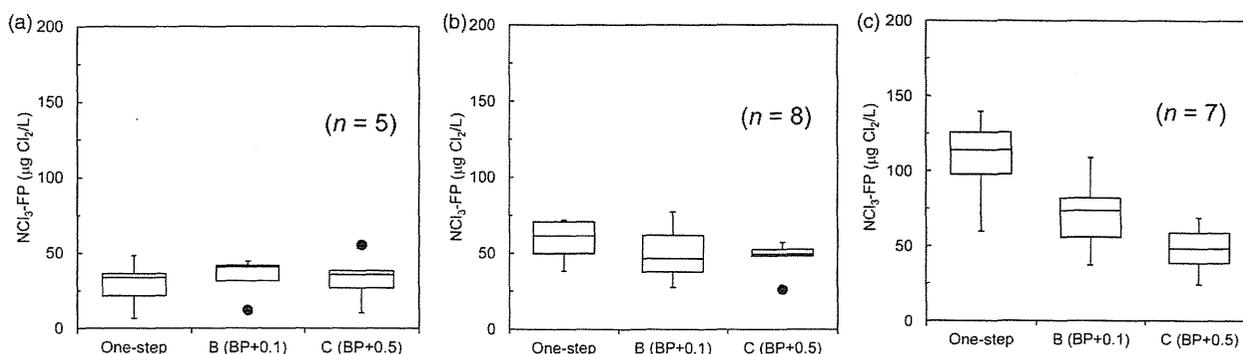


Figure 2 | Effects of two-step chlorination on NCl_3 -FPs in raw waters with NH_3 levels of (a) <0.02, (b) 0.02–0.05 and (c) ≥ 0.1 mg N/L at WPP-1 to WPP-8 [closed circle, value of < 25 percentile – 1.5 × interquartile range) or > (75 percentile + 1.5 × interquartile range)].

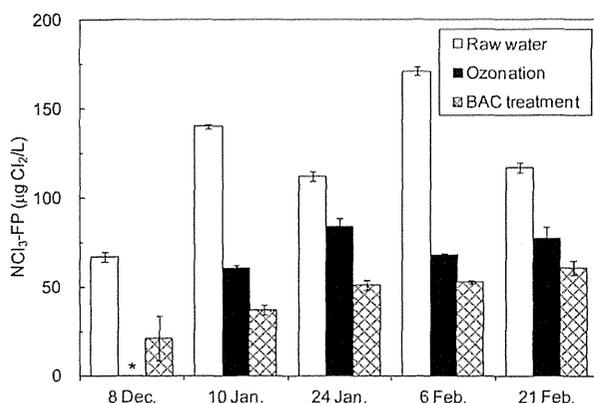


Figure 3 | Profiles of NCl₃-FPs and NH₃ at WPP-10 (*: no data).

available online at <http://www.iwaponline.com/ws/014/017.pdf>). NH₃ decreased gradually during the water purification process, but the level in water after BAC treatment was still 0.08 mg N/L. Because of the low removal of the NCl₃ precursors, the NCl₃-FP did not change during the water purification process (e.g., NCl₃-FP in water after BAC treatment, 130 µg Cl₂/L) (Figure S5).

Figure 3 shows the profiles of NCl₃-FPs at WPP-10. NH₃ levels and the NCl₃-FPs in raw waters were 0.16–0.47 mg N/L (Figure S6 and Table S2, available online at <http://www.iwaponline.com/ws/014/017.pdf>) and 67–170 µg Cl₂/L, respectively. In many cases, the NCl₃-FPs in raw waters effectively decreased in waters after ozonation. NH₃ levels in waters after ozonation at WPP-10 were mostly <0.02 mg N/L (Figure S6 and Table S2), and were much lower than that at WPP-9 (Figure S5). Thus, it was assumed that the reduction of NCl₃-FPs was due to chlorination at the settlement reservoir. It was confirmed that the two-step chlorination was effective for NCl₃-FPs reduction at the actual WPP when the NH₃ level in raw water was relatively high.

CONCLUSIONS

- (1) NCl₃ precursors were ubiquitous in raw water. NCl₃-FPs in raw waters with higher NH₃ were generally higher.
- (2) The results of the NCl₃-FPs in NH₃ solutions and raw waters at WPPs indicated that two-step chlorination of which the 1st chlorine addition was above BP was effective for NCl₃ reduction when NH₃ was the primary NCl₃ precursor. On the other hand, two-step chlorination was not

effective for NCl₃ reduction when organic nitrogen compounds (e.g., glycine) were the primary NCl₃ precursors.

- (3) When chlorine was only added at the final stage of treatment, the NCl₃-FPs in the raw water with relatively high NH₃ did not change markedly during water purification processes. When chlorine was added at a slight excess above BP at the initial stage of the treatment, the NCl₃-FPs markedly decreased during water purification processes.

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