

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

K. Kosaka (corresponding author)
M. Asami
Department of Environmental Health,
National Institute of Public Health,
2-3-6 Minami, Wako, Saitama 351-0197,
Japan
E-mail: kosaka@niph.go.jp

N. Kobashigawa
Okinawa Prefectural Enterprise Bureau,
1-2-2 Izumizaki, Naha, Okinawa 900-8570,
Japan

R. Nakamura
Yokohama Waterworks Bureau,
1-1 Minatomachi, Naka-ku, Yokohama 231-0017,
Japan

S. Echigo
Graduate School of Engineering,
Kyoto University,
C1 Katsura, Nishikyo-ku, Kyoto 615-8540,
Japan

M. Akiba
National Institute of Public Health,
2-3-6 Minami, Wako, Saitama 351-0197,
Japan

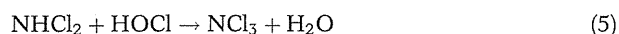
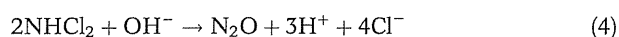
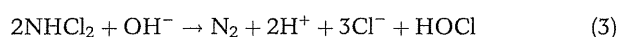
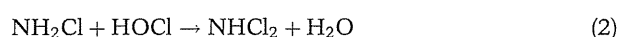
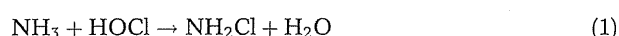
INTRODUCTION

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 $\mu\text{g Cl}_2$ /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 Cl₂/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 Cl₂/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 NCl₃-FP was the difference in NCl₃ concentration between sample and blank solutions. In figures on the results of NCl₃-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 NCl₃ analysis alone. However, in some cases, the standard deviations contained the repetitions of the tests of NCl₃-FPs.

Profiles of NCl₃-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 NCl₃ 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 NH₃ (≥0.1 mg N/L). Unlike the experiments on NCl₃-FP after two-step chlorination, the samples were not filtered to evaluate the change of NCl₃-FP

during the process. The procedures for testing of NCl₃-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 Cl₂/L. Phosphate buffers (pH 7) used for the samples of WPP-9 and WPP-10 were 6 and 1 mM, respectively.

Analysis

NCl₃ 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 × 15 m, 0.25 μm; Agilent Technologies). TCA-d₃ was used as an internal standard. The values of m/z for quantification were 51 for NCl₃ and 100 for TCA-d₃. The limit of quantification of NCl₃ was 15 μg Cl₂/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 NCl₃-FPs in model solutions

Figure 1 shows the NCl₃-FPs of NH₃ solutions (0.05 and 0.1 mg N/L) and glycine solution (0.1 mg N/L) from

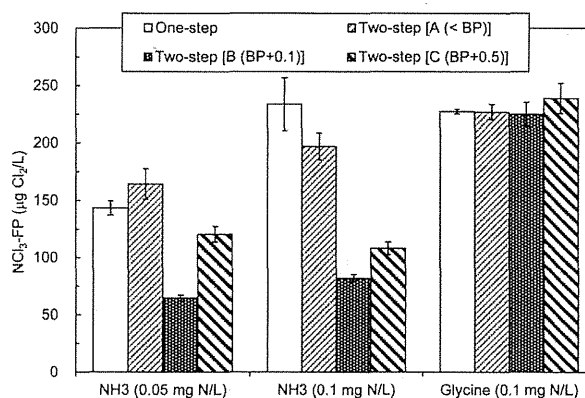


Figure 1 | Effects of two-step chlorination on NCl₃-FPs in NH₃ solutions (0.05 and 0.1 mg N/L) and glycine solution (0.1 mg N/L).

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 $\mu\text{g Cl}_2/\text{L}$ in September and October 2011 and 7–120 $\mu\text{g Cl}_2/\text{L}$ 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,

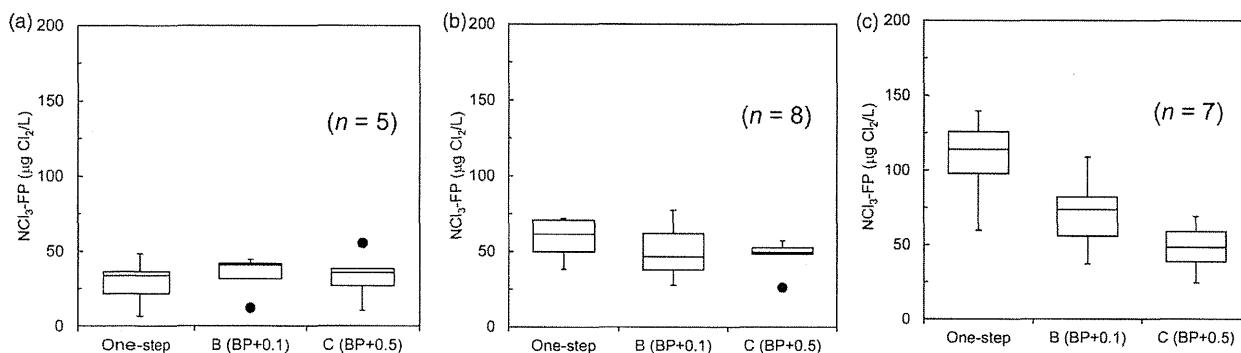


Figure 2 | Effects of two-step chlorination on NCl_3 -FPs in raw waters with NH_3 levels of (a) <0.02, (b) 0.02–0.05 and (c) ≥ 0.1 mg N/L at WPP-1 to WPP-8 [closed circle, value of < 25 percentile – 1.5 × interquartile range) or > (75 percentile + 1.5 × interquartile range)].

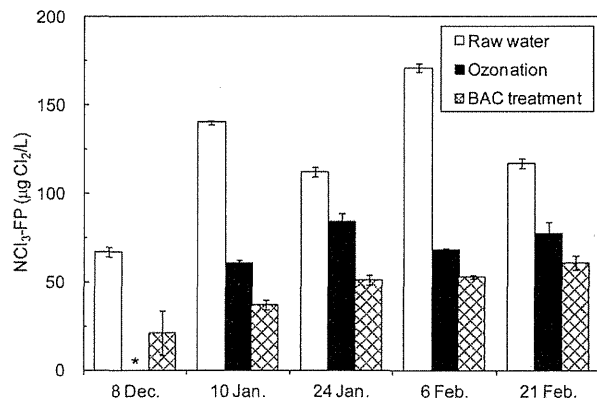


Figure 3 | Profiles of NCl₃-FPs and NH₃ at WPP-10 (*: no data).

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.

ACKNOWLEDGEMENTS

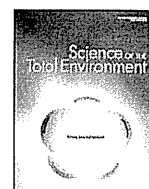
The authors thank Mr H. Egima (Saga City Waterworks and Sewerage Bureau) and Mr Y. Tanaka (Hanshin Water Supply Authority) for help in the experiments. The authors also thank the officials of water utilities for sample collection. The present study was financially supported by Health and Labour Sciences Research Grant (H22-Kenki-Ippan-007, H25-Kenki-Ippan-007) from the Ministry of Health, Labour and Welfare, Japan.

REFERENCES

- American Water Works Association 2000 *The Drinking Water Dictionary*. American Water Works Association, Denver, CO, USA.
- Bureau of Waterworks, Tokyo Metropolitan Government 2012 Tokyo High Quality Management Program (the Tokyo version of the Water Safety Plan) (in Japanese).
- Chiba Prefectural Waterworks Bureau 2007 Program of Producing Good-tasting Drinking Water (in Japanese).
- Hosoda, N., Yamazaki, M., Noma, T., Matsumoto, K. & Ikushima, K. 2009 Trichloramine reduction control at Asaka water purification plant. In: *Proceedings of 60th Annual Conference*, Japan Water Works Association, pp. 162–163 (in Japanese).
- Jafvert, C. T. & Valentine, R. L. 1992 Reaction scheme for the chlorination of ammoniacal water. *Environ. Sci. Technol.* **26**, 577–586.
- Japan Water Works Association 2011 *Standard Methods for the Examination of Water*. Japan Water Works Association, Tokyo, Japan (in Japanese).
- Kosaka, K., Seki, K., Kimura, N., Kobayashi, Y. & Asami, M. 2010 Determination of trichloramine in drinking water using headspace gas chromatography/mass spectrometry. *Water Sci. Technol.: Water Supply* **10**, 23–29.

- Na, C. Z. & Olson, T. M. 2006 Mechanism and kinetics of cyanogen chloride formation from the chlorination of glycine. *Environ. Sci. Technol.* **40**, 1469–1477.
- Shang, C. & Blatchley III, E. R. 1999 Differentiation and quantification of free chlorine and inorganic chloramines in aqueous solution by MIMS. *Environ. Sci. Technol.* **33**, 2218–2223.
- Shigeeda, T., Hashimoto, H., Yamakoshi, S. & Haigima, T. 2011 Control of trichloramine advanced water treatment process at Asaka water purification plant of Tokyo Metropolitan Government in winter FY 2009. In: *Proceedings of 62nd Annual Conference*, Japan Water Works Association, pp. 616–617 (in Japanese).
- Standard Methods for the Examination of Water and Wastewater* 2005 21st edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.
- Tanaka, T., Mashiko, A., Ozaki, M. & Sato, C. 2010 New findings for chloramines formation and application of their reduction in water purification process. *J. Japan Water Works Assoc.*, **909**, pp. 2–12 (in Japanese).
- White, G. C. 1999 *Handbook of Chlorination and Alternative Disinfectants* 4th edn. Wiley-Interscience, Hoboken, NJ, USA.
- World Health Organization 2011 *Guidelines for Drinking-water Quality* 4th edn. World Health Organization, Geneva, Switzerland.

First received 16 July 2013; accepted in revised form 24 February 2014. Available online 11 March 2014



Formaldehyde formation from tertiary amine derivatives during chlorination



Koji Kosaka ^{a,*}, Mari Asami ^a, Takahiko Nakai ^a, Keiko Ohkubo ^a, Shinya Echigo ^b, Michihiro Akiba ^c

^a Department of Environmental Health, National Institute of Public Health, 2-3-6 Minami, Wako, Saitama 351-0197, Japan

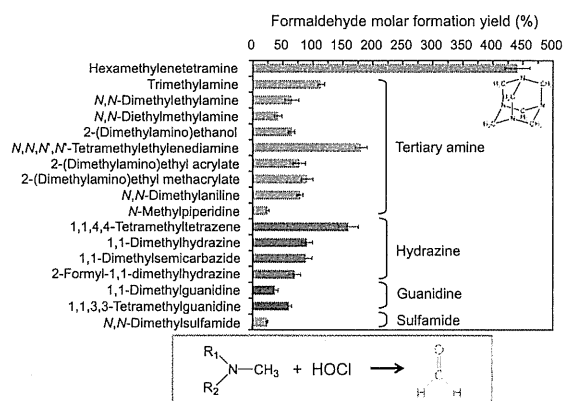
^b Graduate School of Engineering, Kyoto University, C1 Katsura, Nishikyo-ku, Kyoto 615-8540, Japan

^c National Institute of Public Health, 2-3-6 Minami, Wako, Saitama 351-0197, Japan

HIGHLIGHTS

- Formaldehyde precursor contamination caused a large water quality accident.
- Formaldehyde formation yields upon chlorination were evaluated.
- Some tertiary amine derivatives were strong formaldehyde precursors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 January 2014

Received in revised form 24 April 2014

Accepted 24 April 2014

Available online xxx

Editor: Adrian Covaci

Keywords:

Water pollution

Hexamethylenetetramine

Formaldehyde

Tertiary amine derivative

Chlorination

ABSTRACT

In May 2012, formaldehyde (FA) precursor contamination in the Tone River Basin led to the suspension of water supply to approximately 360,000 homes, which affected approximately 870,000 people in the Tokyo Metropolitan Area. The discharge of industrial effluents containing hexamethylenetetramine (HMT), a tertiary amine and FA precursor, without proper treatment resulted in the formation of FA during chlorination at water purification plants. Tertiary amines are known to be the precursors of aldehydes upon chlorination. In this study, FA formation from 29 separate amine derivatives during chlorination was investigated to determine any other potential causes of this water quality accident. The FA formation yield also included FA formation by the autolysis of the target compounds as well as the chlorination of the autolysis products. The FA molar formation yield of HMT was the highest after 24 h of chlorination (440%). Among the various tertiary amine derivatives containing N-methyl groups, tertiary amines and hydrazines were found to be strong FA precursors because the FA molar formation yields per N-methyl group ranged from 25% to 45% (with a mean of 38%) and from 35% to 45% (with a mean of 41%), respectively. Guanidines and sulfamides containing N-methyl groups were also FA precursors but they exhibited lower FA molar formation yields per N-methyl group. The FA molar formation yields of the remaining compounds were <4%. The FA formation yield of HMT was extremely high even on a per weight basis (95 wt.%). The FA weight formation yields of some tertiary amines and hydrazines were greater than 20 wt.%.

© 2014 Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +81 458 6306; fax: +81 458 6305.
E-mail address: kosaka@niph.go.jp (K. Kosaka).

1. Introduction

In Japan, formaldehyde (FA) in drinking water is regulated to not exceed concentrations of 80 µg/L (Water Supply Division (WSD), Health Service Bureau (HSB), Ministry of Health Labour and Welfare (MHLW), 2003). Aldehydes, including FA, are among the various by-products of chlorination and ozonation in particular (Shah and Mitch, 2012).

In May 2012, FA was detected at high concentrations in the drinking water at the water purification plants (WPPs) of several water utilities that obtain raw water from the Tone River or its branches (Figs. S1 and S2) (WSD, HSB, MHLW, 2013). Owing to this water quality accident, water intake and transmission (distribution) were affected at eight large WPPs in the Tokyo Metropolitan Area (Fig. S1). This stoppage of water transmission resulted in the suspension of water supply to approximately 360,000 homes affecting approximately 870,000 people in five cities within the Chiba Prefecture (Table S1).

Hexamethylenetetramine (HMT) was identified as the compound responsible for the water quality accident (Kobayashi et al., 2013). HMT is a tertiary alkylamine that possesses a caged structure in which each of the four nitrogen atoms is connected to three -CH₂- substituents. HMT was present in the raw water and then transformed into FA upon chlorination at the WPPs. On-site inspections by local government agencies indicated that the origin of the HMT was industrial effluents from a chemical facility that produces displays and other electronic products (WSD, HSB, MHLW, 2013).

It was reported that tertiary amines were the precursors of aldehydes upon chlorination and FA was formed from tertiary amines with *N*-methyl functional groups (Figs. 1 and 2) (Ellis and Soper, 1954; Mitch and Schreiber, 2008). Mitch and Schreiber (2008) reported that from the results of three tertiary alkylamines during chlorination, there was no significant regioselectivity among *N*-alkyl functional group and other substituents (R₁ and R₂) for the formation of aldehydes (Fig. 1). Additionally, there have been reports on the formation of aldehydes from primary amines and amino acids during chlorination (Froese et al., 1999; Deborde and von Gunten, 2008; Na and Olson, 2006; Joo and Mitch, 2007). For these compounds, there are several reaction pathways during chlorination and the amounts of the formation of aldehydes were dependent on the compounds and chlorination conditions. The information of the previous studies is useful for understanding importance of amines and their derivatives as the precursors of aldehydes upon chlorination. However, there are wide varieties of amines and their derivatives. Therefore, investigations including a wider range of compounds were needed to predict the consequence of contamination by amine derivatives, particularly tertiary amine derivatives, on drinking water production in the future. Among such investigations, that of FA formation has a priority to prevent water quality accidents similar to that occurred in the Tone River Basin.

We investigated FA formation from a variety of tertiary amines and their derivatives during chlorination to understand their structural characteristics as FA precursors. FA formation from other amines and their derivatives during chlorination was also examined. HMT is a Class I Designated Chemical Substance which is subject to the Japanese Pollutant Release and Transfer Register (PRTR) system established in 1999 (MOE and Ministry of Economy, Trade and Industry (METI), 1999). Additionally, the origin of the industrial effluents containing HMT was a chemical facility covered in the PRTR system. The Japanese PRTR system was designed to promote the voluntary improvement of the management of chemical substances by business operators as well as to prevent impediments to the preservation

of the environment by taking measures to confirm the amounts of such substances when they are released (MOE and METI, 1999). Therefore, the target compounds were primarily selected to evaluate Class I Designated Chemical Substances and their related compounds.

2. Materials and methods

2.1. Water quality accident in the Tone River Basin

On May 16 2012, during a routine water examination of the Saitama Prefecture Bureau of Public Enterprise, FA was detected at a higher concentration than usual in the finished drinking water supplies at the Showa WPP, which obtains raw water from the Tone River (WSD, HSB, MHLW, 2013). Since the FA concentration was 45 µg/L, more than 50% of the suggested concentration threshold, continuous examination of FA concentration was initiated at several WPPs. The addition of a hypochlorite solution to the raw waters at the WPPs suggested that the high FA concentration in the sample was due to contamination with FA precursors (Fig. S2). The FA concentration in the finished drinking water at the Gyoda WPP exceeded the suggested concentration threshold on May 18, 2012 and the water intake and transmission (distribution) were subsequently halted at this WPP (Figs. S1 and S2). Water intake and transmission were affected at eight large WPPs in five prefectures (Saitama, Chiba, Ibaraki, and Gunma Prefectures as well as the Tokyo Metropolitan Government) located in the Tokyo Metropolitan Area from May 18 to 20 (and until May 23 in some areas) (Figs. S1 and S2). Water transmission was suspended for up to 19 h and residents had to wait in long lines to receive emergency water supplies (Table S1).

Based on the FA concentrations after chlorination and the HMT concentrations in ten storage samples, HMT was identified as the compound responsible for the water quality accident (Kobayashi et al., 2013). HMT is used as a hardening accelerator for thermosetting resins, a stabilizer in pesticide formulation, and a reaction accelerator in the manufacturing of rubber products (MOE, 2012). The production and distribution of HMT in Japan in 2010 was 6,000 tons (MOE, 2012).

The origin of the HMT was industrial effluents from a chemical facility and the amount of industrial effluent was approximately 66 tons including approximately 10.8 tons of HMT. From May 10 to 18, the effluent was intermittently discharged into drainage systems connected to the Karasu River, a tributary of the upper Tone River, without proper treatment from a contracted industrial wastewater treatment facility because the material was sent to the industrial wastewater treatment facility without sufficient prior notice of the contents (WSD, HSB, MHLW, 2013; Asami et al., 2013). The causative chemical and its origin were identified within a relatively short time after the water quality incident because a similar accident associated with HMT contamination occurred in the Tone River Basin in 2003. HMT was not regulated prior to the water quality accident in 2012. However, owing to the large impact of this accident, the MOE immediately added HMT to the list of designated environmental contaminants under the Water Pollution Prevention Act (Environment Management Bureau, MOE, 2012).

In Japan, free chlorine is used as a final disinfectant at most WPPs and the residual free chlorine in tap water is typically maintained at ≥0.1 mg Cl₂/L. Therefore, HMT is unlikely to be detected in tap water. However, when a target value of HMT in drinking water is estimated using 0.15 mg/kg/day of the acceptable daily intake (ADI) (MOE, 2012), 50 kg of body weight, 2 L of daily water intake and 0.1 of allocation of ADI to drinking water, it becomes 375 µg/L. This value is about five times larger than the standard value of FA in Japan.

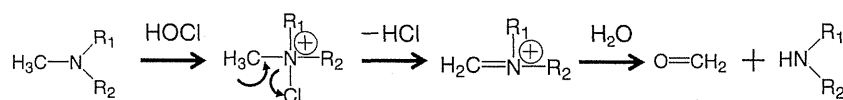


Fig. 1. Reaction scheme of FA formation from tertiary amines during the chlorination process (Ellis and Soper, 1954; Mitch and Schreiber, 2008).

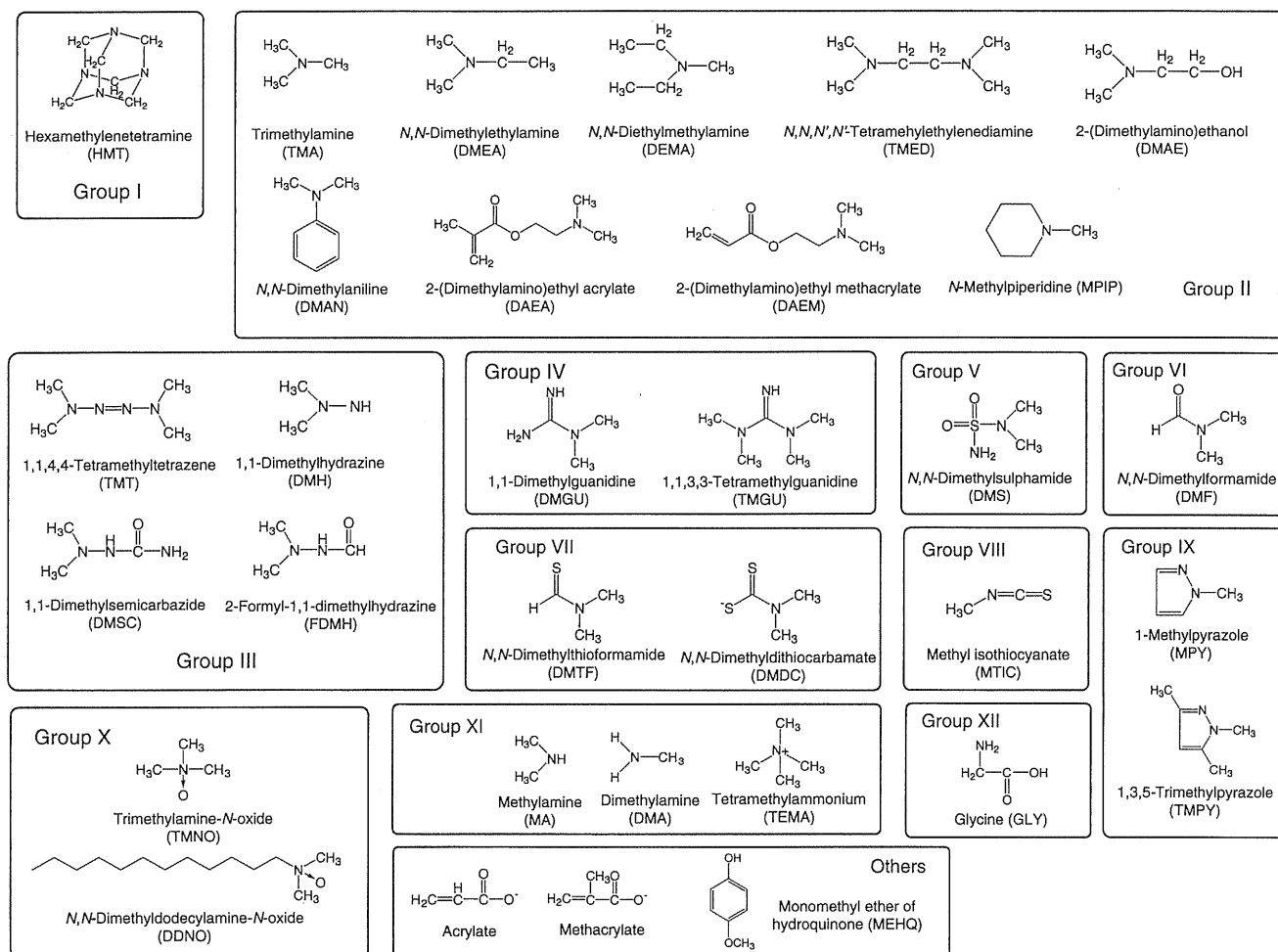


Fig. 2. Chemical structures of the target compounds.

2.2. Reagents and solutions

Ultrapure water used in this investigation was prepared through the purification of tap water using a Gradient A10 ultrapure water system (Millipore, Bedford, MA). Commercially available natural water (Volvic; Danone, Saint-Ouen, France) was used to prepare the FA standard solutions used for calibration. Standard solutions of FA (1 g/L in methanol) and 1-chlorodecane (1 g/L in *n*-hexane) were purchased from Kanto Chemical (Tokyo, Japan) and Wako Pure Chemical (Osaka, Japan), respectively. Sodium hypochlorite (Tsurukuron TW) was obtained from Tsurumi Soda (Yokohama, Japan). Suppliers of the target compounds are listed in the Supplementary Materials. All other reagents used in this study were analytical grade.

2.3. Classification of target compounds

Fig. 2 displays the target compounds in this study. Their usages and origins are listed in Table S2. Based on the reaction scheme of FA formation from tertiary amines during chlorination (Fig. 1) (Ellis and Soper, 1954; Mitch and Schreiber, 2008), amines and derivatives containing *N*-methyl groups were selected for this study, with the exception of HMT and glycine (GLY). GLY has been previously reported to be a possible FA precursor upon chlorination under certain conditions (Na and Olson, 2006). A total of 29 amines and derivatives were classified into Groups I through XII based on their chemical structures, where Groups I and II consisted of tertiary amines (HMT and tertiary amines

containing *N*-methyl groups, respectively), Groups III through X consisted of tertiary amine derivatives, Group XI consisted of primary and secondary amines and quaternary ammonium, and Group XII consisted of amino acids. Groups III through X were classified based on their substituents (Fig. 2). Group III consisted of hydrazines, Group IV consisted of guanidines, Group V consisted of sulfamides, Group VI consisted of amides, Group VII consisted of thioamides, Group VIII consisted of thioisocyanates, Group IX consisted of methylpyrazoles, and Group X consisted of alkylamine oxides. The target compounds were primarily selected to evaluate Class I Designated Chemical Substances and their related compounds as FA precursors during chlorination. Currently, there are 462 Class I Designated Chemical Substances, among which 45 compounds are either HMT or amines and their derivatives containing *N*-methyl groups belonging to Groups I, II, III, VI, VII, VIII, IV, X, and XI. As shown in Table S2, 11 of the 29 amines and their derivatives are Class I Designated Chemical Substances. For Group II, a variety of tertiary amines were selected because tertiary alkylamines were reported to be FA precursors (Mitch and Schreiber, 2008). Groups IV, V, and XII were selected as other examples of amine derivatives.

HMT is highly hydrophilic [$\log K_{ow}$: -4.15 (predicted value)] (Royal Society of Chemistry) (Table S2) and was not removed by the powdered activated carbon added as a control measure in water purification processes during the water quality accident in May 2012. Therefore, it is possible that hydrophilic compounds were responsible for water quality accidents and were subsequently selected as target compounds, except for *N,N*-dimethylaniline (DMAN) ($\log K_{ow}$: 2.31) (Royal Society of Chemistry) and the surfactant *N,N*-dimethyldodecylamine-*N*-oxide

(DDNO) (Chemicals Evaluation and Research Institute (CERI), 2006b). Some of the Class I Designated Chemical Substances possess complex structures and are hydrophobic. Therefore, only simple compounds were used as target compounds in this study [e.g.; 1-methylpyrazole (MPY) and 1,3,5-trimethylpyrazole (TMPY) from Group VI]. Furthermore, three compounds [the monomethyl ether of hydroquinone (MEHQ), acrylate, and methacrylate] were included because 2-(dimethylamino)ethyl acrylate (DAEA) and 2-(dimethylamino)ethyl methacrylate (DAEM) contain MEHQ as an inhibitor, and DAEA and DAEM can be hydrolyzed to (dimethylamino)methanol (DMAE) (CERI, 2006a) and acrylate and to DMAE and methacrylate (CERI, 2007), respectively.

2.4. Formaldehyde formation potential

The formation of FA was evaluated by testing the FA formation potential. The experiments were conducted in glass vials covered with aluminum foil. In some cases, the experiments were conducted using perfluoroalkoxy (PFA) vials covered with aluminum foil. The sample volume was 20 mL and the headspace was approximately 2 mL. However, the results of the FA molar formation yields were similar to those reported in previous studies conducted under headspace-free conditions (Mitch and Schreiber, 2008) (see Results and discussion). In the water quality accident in the Tone River Basin, HMT was detected at levels of several hundred micrograms per liter (several μM) in the raw river water (Kobayashi et al., 2013). Therefore, the concentrations of the target compounds were set to 2 μM in this study. In Japan, the chlorination by-product formation potential is generally tested according to the procedures described by the Standard Methods for the Examination of Water by Japan Water Works Association (JWWA) (2011). The experimental conditions (i.e.; reaction time: 24 h, chlorine concentration at 24 h: 1.0–2.0 mg Cl_2/L , pH 7, temperature: 20 °C) were set to evaluate the amount of chlorination by-products formed under typical conditions. In this study, the experimental conditions specified by JWWA (2011) were used as a reference. The experimental conditions were as follows: chlorine dose: 2.0 ± 0.1 mg Cl_2/L , reaction time: 24 h, pH 7 (2 mM phosphate buffer), temperature: 20 °C. The reaction was initiated by adding small amounts of the hypochlorite solution to the samples with mixing, which was continued for about 20 s and the samples were then stored in the dark at 20 °C. After 24 h of chlorination, the residual chlorine in the sample was quenched by adding 100 μL of a 200 mM sodium thiosulfate solution (Wako Pure Chemical). The experiments were conducted in parallel to determine the amount of residual chlorine in the samples after 24 h of chlorination. Phosphate buffer (2 mM, pH 7) was also prepared in the glass (or PFA) vial and the same amounts of chlorine as those of target compounds were added. The chlorine concentration in the phosphate buffer was used as the chlorine dose for testing the FA formation potential. Additionally, to evaluate the effects of the reaction time, three target compounds [HMT, trimethylamine (TMA), and 1,1-dimethylhydrazine (DMH)] were chlorinated for 1 h. All experiments were conducted at least in duplicate.

The FA formation yield was estimated from the potentials of the FA formation from the target compounds added to water under typical chlorination conditions. The FA molar formation yield (%) was defined as the difference between the FA concentration per concentration of target compound in the samples before chlorination and after 24 h of chlorination. In this study, concentrations of target compounds before and after chlorination were not measured. Therefore, the FA formation yield includes FA formation derived from the autolysis of the target compounds as well as the chlorination of the autolysis products. Additionally, the FA formation yield of a target compound with a low reactivity towards chlorine becomes lower than that of the decomposed target compound. The FA concentrations in the 2 mM phosphate buffer at pH 7 were below the limit of quantification (LOQ), <2.0 $\mu\text{g}/\text{L}$, both before and after 24 h of chlorination. Therefore, the effects of FA contamination from ambient air during the calculation of the FA formation

yield were considered to be negligible. If the FA concentration was <2.0 $\mu\text{g}/\text{L}$, it was regarded as 0 when calculating FA formation yield. When the FA concentrations before and after chlorination were <2.0 and 2.0 $\mu\text{g}/\text{L}$, respectively, the FA molar formation yield was calculated to be 4%. Thus, when the FA concentrations both before and after chlorination were <2.0 $\mu\text{g}/\text{L}$, the FA molar formation yield was described as $<4\%$.

Additionally, the FA formation yield was expressed by weight because the concentrations of the chemicals in raw and drinking waters are typically expressed by weight per liter. Therefore, chemicals with higher FA weight formation yields are more significant as potential causative chemicals of water quality accidents even if their FA molar formation yields were the same.

2.5. Analytical methods

The FA concentrations in the samples were determined by gas chromatography with mass spectrometry (GC – MS) after derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) (Wako Pure Chemical) (JWWA, 2011). Before derivatization, the pH of the sample was adjusted to approximately 4–5 using 1 N HCl. 1-Chlorodecane was used as an internal standard. An Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) connected to an Agilent 5973 mass spectrometer (Agilent Technologies) was used in selective ion monitoring (SIM) mode with an HP-5MS capillary column (0.25 mm \times 30 m, 0.25 μm , Agilent Technologies). The LOQ of FA was set at 2.0 $\mu\text{g}/\text{L}$ because the relative standard deviation of 2.0 $\mu\text{g}/\text{L}$ for FA in natural water ($n = 5$) was less than 10%. HMT is known to be hydrolyzed under acidic conditions and transformed into FA (Painter and King, 1986). The FA concentrations of the HMT sample before chlorination were 30–50 $\mu\text{g}/\text{L}$ because acid was added to the samples during the pretreatment portion of the FA analysis. That is, HCl was added to the sample before derivatization to adjust the pH of the sample to 4–5. Also, H_2SO_4 was added to the sample after derivatization to decompose residual PFBOA in the sample. However, the peak areas of FA by GC – MS were not significantly different regardless of acid additions (i.e., additions of HCl and H_2SO_4 , addition of only H_2SO_4 , and no acid addition) when 20 $\mu\text{g}/\text{L}$ of FA was added to 2 mM phosphate buffer (pH 7). Therefore, it was considered that the effects of acid addition on derivatization rate of FA were small under the analytical conditions of this study and no acid was added to the HMT sample during the pretreatment stage. Additionally, the FA concentrations of the sample were determined using the absolute calibration curve method because the peak areas of the internal standard occasionally increase. Alternatively, FA concentrations in samples of HMT after 1 h of chlorination were not significantly different by the addition of acid, and the FA concentrations were determined using the same procedure as the other target compounds. FA concentration in sample of HMT after chlorination was determined after 10-fold dilution because of its high concentration. FA concentration in sample was also decreased by chlorination. Therefore, from these reasons, it was considered that the effects of acid addition on FA analysis in sample of HMT after chlorination were small. Free chlorine concentration was determined by titration using *N,N*-diethyl-*p*-phenylene diamine (Wako Pure Chemical) and ferrous ammonium sulfate (Wako Pure Chemical) (American Public Health Association (APHA) et al., 2005).

3. Results and discussion

3.1. FA formation yields from target compounds during chlorination

Table 1 lists the FA molar formation yields of the target compounds after 24 h of chlorination. The FA molar formation yields for the 29 amines and their derivatives ranged from $<4\%$ to 440%. The residual chlorines at 24 h were ≥ 0.6 mg Cl_2/L and those of most compounds were ≥ 1.0 mg Cl_2/L . Chlorine consumptions per target compound ranged from 0.1 to 8.7 mol/mol when considering the chlorine

Table 1
FA molar formation yields of target compounds.

Target compounds	FA molar formation yield (SD) (%)
Group I	
Hexamethylenetetramine (HMT)	440 (21)
Group II	
Trimethylamine (TMA)	110 (5.8)
<i>N,N</i> -Dimethylethylamine (DMEA)	65 (11)
<i>N,N</i> -Diethylmethylamine (DEMA)	43 (6.5)
<i>N,N,N',N'</i> -Tetramethylethylenediamine (TMED)	180 (10)
2-(Dimethylamino)ethanol (DMAE)	65 (5.4)
<i>N,N</i> -Dimethylaniline (DMAN)	79 (5.1)
2-(Dimethylamino)ethyl acrylate (DAEA)	78 (10)
2-(Dimethylamino)ethyl methacrylate (DAEM)	91 (9.8)
<i>N</i> -Methylpiperidine (MPIP)	25 (2.9)
Group III	
1,1,4,4-Tetramethyltetrazene (TMT)	160 (17)
1,1-Dimethylhydrazine (DMH)	90 (8.3)
1,1-Dimethylsemicarbazide (DMSC)	89 (11)
2-Formyl-1,1-dimethylhydrazine (FDMH)	70 (9.8)
Group IV	
1,1-Dimethylguanidine (DMGU)	38 (7.1)
1,1,3,3-Tetramethylguanidine (TMGU)	61 (4.7)
Group V	
<i>N,N</i> -Dimethylsulfamide (DMS)	24 (1.4)
Group VI	
<i>N,N</i> -Dimethylformamide (DMF)	<4
Group VII	
<i>N,N</i> -Dimethylthioformamide (DMTF)	<4
<i>N,N</i> -Dimethyldithiocarbamate (DMDC)	<4
Group VIII	
Methyl isothiocyanate (MITC)	<4
Group IX	
1-Methylpyrazole (MPY)	<4
1,3,5-Trimethylpyrazole (TMPY)	<4
Group X	
Trimethylamine- <i>N</i> -oxide (TMNO)	<4
<i>N,N</i> -Dimethyldodecylamine- <i>N</i> -oxide (DDNO)	<4
Group XI	
Methylamine (MA)	<4
Dimethylamine (DMA)	<4
Tetramethylammonium (TEMA)	<4
Group XII	
Glycine (GLY)	<4
Other	
Acrylate	<4
Methacrylate	<4
Monomethyl ether of hydroquinone (MEHQ)	<4

1) Experimental conditions: target compound, 2 μ M; chlorine dose, 2.0 ± 0.1 mg Cl_2/L ; reaction time, 24 h; pH, 7; temperature, 20 $^\circ\text{C}$.

2) SD: standard deviation.

consumption in the phosphate buffer after 24 h of chlorination (0.16 mg Cl_2/L). The FA molar formation yields varied among the different types of amines and their derivatives and between groups. The results of each group are discussed below.

3.1.1. Group I

The FA molar formation yield of HMT was 440%, which was the highest among all the target compounds tested in this study. Chlorine consumption per HMT concentration was 6.6 mol/mol. Before chlorination, the FA concentration of the sample was 4.9 $\mu\text{g}/\text{L}$. HMT possesses four tertiary amines, each of which is connected to three $-\text{CH}_2-$ substituents. The FA molar formation yield of HMT per nitrogen atom was 110%. Considering FA formation mechanism from tertiary amines during chlorination (Fig. 1), it was presumed that nitrogen atom of HMT was initially attached by chlorine and FA was formed from the $-\text{CH}_2-$ substituents. It was also implied that one mole of FA was formed from the $-\text{CH}_2-$ substituents per nitrogen atom.

3.1.2. Group II

FA was formed from all of the nine tertiary amines in Group II after 24 h of chlorination. Tertiary amines containing *N*-methyl groups were the FA precursors upon chlorination despite their substituents (R_1 and R_2 in Fig. 2) being different. The FA molar formation yields ranged from 25% to 180% and the highest value was observed for *N,N,N',N'*-tetramethylethylenediamine (TMED), a compound containing four *N*-methyl groups. The chlorine consumption per target compound ranged from 2.6 to 6.5 mol/mol. The FA molar formation yields of TMA and *N,N*-diethylmethylamine (DEMA) were 110% and 43%, respectively. These two compounds have been previously reported to exhibit FA molar formation yields of 105% and approximately 30%, respectively (Mitch and Schreiber, 2008). The FA molar formation yield of DEMA in the previous study was estimated from the figure in the previous study. The FA molar formation yield of these two compounds in this study were not so markedly different despite the experimental conditions being different (TMA and DEMA: 50 μM , chlorine dose: 200 μM , reaction time: 30 min for TMA and 15 min for DEMA, pH 7 for TMA and pH 9 for DEMA) (Mitch and Schreiber, 2008).

DAEA and DAEM were hydrolyzed to acrylate and DMAE, and to methacrylate and DMAE, respectively (CERI, 2006a, 2007). The half-lives of DAEA and DAEM were reported to be 12.5 h and 4.5 days at pH 7, respectively. DAEA and DAEM also contained MEHQ as an inhibitor. The FA molar formation yields of DAEA, DAEM, and DMAE in this study were 78%, 91%, and 65%, respectively. Those of acrylate, methacrylate, and MEHQ were <4% which implies that the effects of these three compounds as FA precursors were negligible. The FA molar formation yields of DAEA and DAEM were slightly higher than that of the hydrolyzed product, DMAE.

The number of *N*-methyl groups of the tertiary amines in Group II ranged from one to four. Based on the results of TMA, DEMA, DAME, and triethylamine, Mitch and Schreiber (2008) reported that there was no significant regioselectivity among the *N*-alkyl groups, R_1 and R_2 , for aldehyde formation from tertiary alkylamines. In this study, the FA molar formation yields per *N*-methyl group in Group II ranged from 25% to 45% with a mean value of 38% (Fig. 3). Therefore, the FA molar formation yields per *N*-methyl group were largely close to 33%, a stoichiometric value of the FA molar formation yield per *N*-methyl group, although the FA molar formation yields varied among the target compounds. This result implied that the FA formation from *N*-methyl groups was completed under simulated typical chlorination conditions,

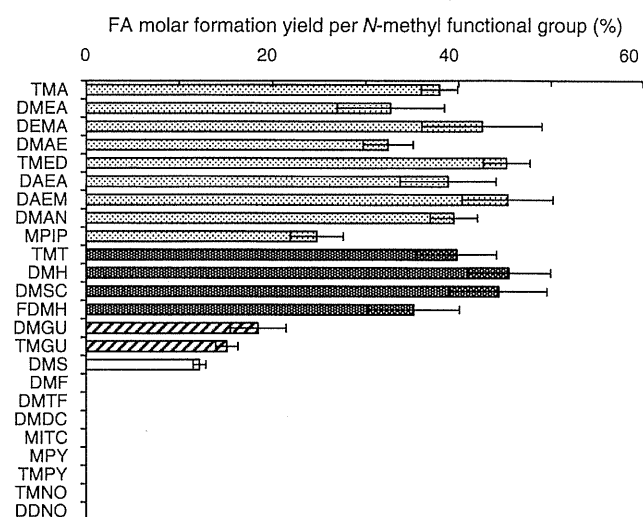


Fig. 3. FA molar formation yields of the tertiary amines and their derivatives per *N*-methyl group (target compound: 2 μM , chlorine dose: 2.0 ± 0.1 mg Cl_2/L , reaction time: 24 h, pH 7, temperature: 20 $^\circ\text{C}$).

and the reaction of the target compounds in Group II did not exhibit any significant regioselectivity (Mitch and Schreiber, 2008).

3.1.3. Groups III through V

Among the various tertiary amine derivatives, the FA molar formation yields in Groups III through V were $\geq 4\%$. For Group III, the FA molar formation yields of the four tertiary amine derivatives ranged from 70% to 160%. The highest FA molar formation yield was produced by 1,1,4,4-tetramethyltetrazene (TMT) which contained four *N*-methyl groups. Prior to chlorination, FA was only detected in TMT at a concentration of 7.0 $\mu\text{g/L}$. The FA molar formation yields of the target compounds per *N*-methyl group in Group III ranged from 35% to 45% with a mean of 41% (Fig. 3). TMT and FDMH were the transformation products of DMH (Carlsen et al., 2008). The FA molar formation yields per *N*-methyl group of these compounds were slightly lower than that of DMH. As shown in Fig. 3, as in the case of the target compounds in Group II, there was no significant regioselectivity among the *N*-methyl groups, R_1 and R_2 .

In Groups IV and V, the FA molar formation yields of 1,1-dimethylguanidine (DMGU), 1,1,3,3-tetramethylguanidine (TMGU), and DMS were 38%, 61%, and 24%, respectively (Table 1). The FA molar formation yields per *N*-methyl group were 19%, 15%, and 12%, respectively (Fig. 3). These values were lower than those of Groups II and III. The reaction sites of DMS with chlorine were believed to be the primary amines of DMS which subsequently formed chlorinated DMS (von Gunten et al., 2010). The nitrogen atoms of the tertiary amine derivatives of DMS were considered to be a minor reaction site. It was also assumed that chlorinated DMS and its chlorination by-products were less reactive in the presence of chlorine. Therefore, the FA molar formation yields of DMS per *N*-methyl group were lower than 33%. Since DMGU and TMGU have primary or secondary amines, tertiary amine derivatives containing *N*-methyl groups are likely to be less reactive towards chlorine.

3.1.4. Groups VI through X

The FA concentrations of all eight tertiary amine derivatives containing *N*-methyl groups in Groups VI through X after 24 h of chlorination were $< 2.0 \mu\text{g/L}$, i.e.; their FA molar formation yields were $< 4\%$. The amides (Group VI) were electron-withdrawing substituents and their reactivity towards chlorine was low (Kamiguchi and Miyata, 2008; Deborde and von Gunten, 2008), which was the primary reason for their low FA molar formation yields ($< 4\%$). Based on the chlorine consumption levels at 24 h (Fig. S3), the reactivities of the methylpyrazoles (Group IX) and the alkylamine oxides (Group X) with chlorine were quite low. Alternatively, chlorine consumption of thioamides (Group VII) and methyl isothiocyanate (MTIC) (Group VIII) were quite high (4.8–8.7 mol/mol). All of these compounds contain sulfur in their structure, and sulfur-containing compounds can be easily oxidized in the presence of chlorine (Deborde and von Gunten, 2008). It was assumed that the reaction sites of the target compounds in Groups VII and VIII during chlorination were primarily the sulfur of thioamide or isothiocyanate groups. Chlorine was not attached to the nitrogen atoms of the *N*-methyl groups or the reaction was a minor pathway and the FA molar formation yields of the target compounds in Groups VII and VIII were subsequently $< 4\%$.

3.1.5. Groups XI and XII

The FA molar formation yields of MA (primary amine), DMA (secondary amine), TEMA (quaternary ammonium), and GLY (amino acid) were $< 4\%$. Among them, TEMA was low reactive with chlorine due to the neighboring electron-withdrawing substituents (Mitch and Sedlak, 2004). Cyanogen chloride (CNCl), FA, and trichloronitromethane were identified as chlorination by-products of MA and its degradation pathway has been previously elucidated (Joo and Mitch, 2007). The FA molar formation yield at pH 7 after 7 d was quite low (1.1%) and this value was not significantly different than the value in this study.

However, it has been reported that the propionaldehyde molar formation yields ranged from 9% to 29% after 4 d. Therefore, other aldehydes may be produced from primary amines at higher molar yields when using longer reaction times. The reaction pathway during the chlorination process was also reported for GLY (Na and Olson, 2006). CNCl, *N*-chloromethylimine, and FA were reported to be chlorination by-products. The chlorination by-product formation was dependent on the amount of chlorine and the pH. When an excess of chlorine was present, as it was in this study, then GLY was converted into *N,N*-dichloroglycine which was then converted into CNCl and *N*-chloromethylimine. Therefore, the FA molar formation yield was $< 4\%$ in this study. Alternatively, it has been reported that FA was formed through the hydrolysis of *N*-chloromethylimine (Na and Olson, 2006; Joo and Mitch, 2007). Therefore, the FA molar formation yield may exceed 4% when using longer reaction times. It is important to note that for both MA and GLY, the CNCl decays through the hypochlorite-catalyzed hydrolysis during chlorination (Na and Olson, 2006; Joo and Mitch, 2007).

Next, the FA weight formation yields of the target compounds were calculated from their FA molar formation yields. Additionally, of the 45 Class I Designated Chemical Substances containing *N*-methyl groups, nine compounds belonged to Groups I through III (one in Group I, seven in Group II, and one in Group III). The FA weight formation yields of the four compounds from Group II for which experimental data was not obtained [cartap, thiocyclam, *N,N*-dimethyldodecylamine (DMDA), and dazomet] (Fig. S4) were estimated using the mean FA molar formation yield per *N*-methyl group of Group II. The underlying assumption of this estimation was that the FA molar formation yields per *N*-methyl functional group of the compounds in Group II were not significantly different. One of the two *N*-methyl groups of dazomet was considered to belong to Group II, while the other was considered to belong to Group VII.

The FA weight formation yields ranged from 7.5 wt.% to 95 wt.% (Fig. 4). Even on a per weight basis, the FA formation yield of HMT was extremely high. The FA weight formation yields of TMA, TEMD, DMH, and TMT ranged from 41 wt.% to 58 wt.%, and those of DMEA, DMSC, FDMH, DMAE, and DMAN ranged from 20 wt.% to 27 wt.%. HMT, DMH, and DMAN are classified as Class I Designated Chemical Substances (Chemical Management Policy Division, Manufacturing Industries Bureau, METI). Additionally, TMA, TEMD, DMEA, and DMAE are commonly used in industrial applications (The Chemical Daily, 2013). Therefore, these compounds are possible causative chemicals of

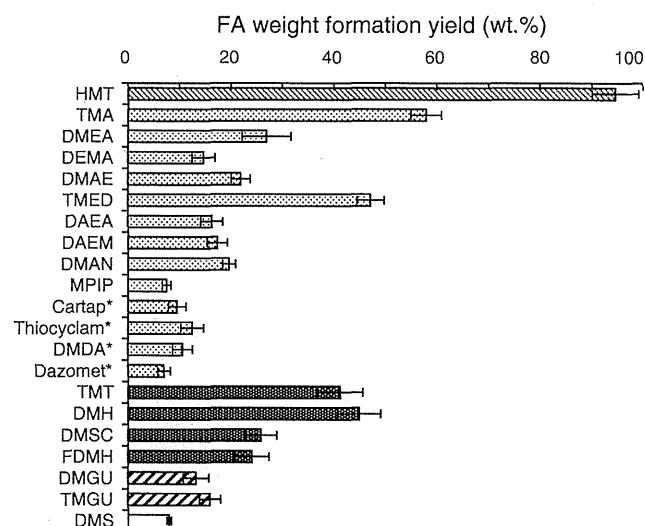


Fig. 4. FA weight formation yields of the tertiary amines and their derivatives (target compound: 2 μM , chlorine dose: $2.0 \pm 0.1 \text{ mg Cl}_2/\text{L}$, reaction time: 24 h, pH 7, temperature: 20 $^\circ\text{C}$, *: estimated value).

water quality accidents involving FA precursors. They are highly hydrophilic ($\log K_{ow}$: up to 0.70) (Royal Society of Chemistry), with the exception of DMAN, and therefore their removal during water purification processes is often quite difficult.

The acetaldehyde (AA) weight formation yields were estimated based on the FA molar formation yields. Twelve Class I Designated Chemical Substances contained *N*-ethyl functional groups. Of these 12 compounds, 2-(diethylamino)ethanol and triethylamine belonged to Group II and were hydrophilic [$\log K_{ow}$: 0.05 (predicted value) and 1.45, respectively] (Royal Society of Chemistry) (Fig. S4). The basic structures of 2-(diethylamino)ethanol and triethylamine were the same as those of DMAE and TMA, respectively, and the difference in the structures corresponded to the different types of *N*-alkyl functional groups. The AA weight formation yields of 2-(diethylamino)ethanol and triethylamine, estimated from the FA molar formation yields of DMAE and TMA, respectively, under the assumption that the molar formation yields of the aldehydes were similar regardless of the *N*-alkyl functional groups, were estimated to be 24 wt.% and 50 wt.%, respectively.

3.2. Effects of the chlorination reaction time on the FA molar formation yield

Fig. S5 displays the FA molar formation yields of HMT, TMA, and DMH at 1 h and 24 h after chlorination. These compounds were selected because of their high FA weight formation yields (Fig. 4). The FA molar formation yields of these three compounds at 1 h were 410%, 8.9%, and 66%, respectively. The FA molar formation yields of HMT at 1 h and 24 h after chlorination were not so different, indicating that the FA formation from HMT was nearly completed within 1 h at pH 7. HMT has four nitrogens of tertiary amine. It was presumed that HMT has several reaction sites with chlorine and its FA formation rate was faster. Chlorine consumption at 1 h was lower than that at 24 h and it has been hypothesized that other by-products were also formed between 1 h and 24 h after chlorination.

For TMA and DMH, the FA molar formation yields at 1 h after chlorination were lower than those after 24 h of chlorination, particularly for TMA. Therefore, the FA molar formation yield of TMA was greater than that of DMH at 24 h, but the order was reversed at 1 h. In a previous study (Mitch and Schreiber, 2008), the FA molar formation yield by chlorination reached approximately 100% within 30 min. The chlorine level in the previous study [200 μM (14 mg Cl_2/L)] was greater than that in this study (2.0 mg Cl_2/L) and therefore the rate of FA formation was faster. The apparent rate constant of TMA and chlorine at pH 7 was previously reported to be $69 \text{ M}^{-1} \text{ s}^{-1}$ (Deborde and von Gunten, 2008). Thus, the half-life of TMA at 2 mg Cl_2/L at pH 7 was calculated to be approximately 6 min, and TMA was almost completely chlorinated within 1 h in this study. Therefore, the dehydrohalogenation and subsequent hydrolysis of a chlorinated TMA intermediate were the rate-limiting steps for FA formation by TMA (Fig. 1) (Ellis and Soper, 1954; Mitch and Schreiber, 2008). For DMH, the chlorine consumption rates at 1 h and 24 h were not significantly different among the three compounds. However, the FA molar formation yield at 1 h was 74% of that at 24 h. As in the case of TMA, the reaction after the formation of a chlorinated DMH intermediate was assumed to be the rate-limiting step. These results indicated that the difference of FA formation rates between TMA and DMH were due to the difference of stability of their chlorinated intermediates. All substitutes of TMA connected to nitrogen are the same (*N*-methyl functional groups), and the distribution of electrons among the substitutes were equal. Therefore, the chlorinated TMA intermediate was more stable than the chlorinated DMH intermediate and the FA formation rate of TMA was lower. The results of this study suggested that the formation rates were different among the various compounds, and in some cases the FA concentration would increase throughout the distribution system. However, it has been suggested that FA formation from the *N*-methyl groups of tertiary amines and their derivatives was completed under typical chlorination conditions when considering the retention within the distribution system (24 h).

4. Conclusions

In this study, the FA formation yields of amine derivatives during chlorination were investigated. The FA formations by the autolysis of the target compounds as well as the chlorination of the autolysis products were included in the FA formation yield.

- (1) The FA molar formation yield and the FA weight formation yield of HMT after 24 h of chlorination were 440% and 95 wt.%, respectively. Both values were the highest value among the 29 amine derivatives examined.
- (2) The tertiary amine derivatives containing *N*-methyl groups in Groups II and III were strong FA precursors. Some of the FA weight formation yields were more than 20 wt.%. The FA molar formation yields per *N*-methyl group for Groups II and III ranged from 25% to 45% (mean: 38%) and from 35% to 45% (mean: 41%), respectively. It can be concluded that the reaction after the addition of chlorine to the nitrogen atoms of tertiary amine derivatives exhibited no significant regioselectivity.
- (3) FA molar formation yields per *N*-methyl group for Groups IV and V were up to 19%. The FA molar formation yields of the remaining tertiary amine derivatives (Groups VI through X), primary and secondary amines, quaternary ammonium, and amino acids were <4%.
- (4) FA formation rates upon chlorination varied among the target compounds. The FA formation of HMT was nearly completed within 1 h of chlorination. Alternatively, the FA formation of TMA and DMH after 1 h of chlorination was lower than those at 24 h, particularly for TMA. It can be concluded that the FA formation from the *N*-methyl groups of tertiary amine derivatives was completed under typical chlorination conditions when considering the retention in the distribution system.

Acknowledgments

The authors thank Mr. Kazuyuki Ishiwatari (Chiba Prefectural Waterworks Bureau) and Mr. Yoshihiro Iwami (Kanagawa Water Supply Authority) for help with the experiments. This study was financially supported by the Health and Labour Sciences Research Grant (H25-Kenki-Ippan-007) from MHLW.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.04.105>.

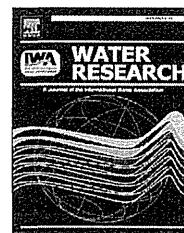
References

- APHA, American Water Works Association, Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. 21st ed. Washington DC: APHA; 2005.
- Asami M, Kosaka K, Ohno K. Risk management framework related to the accidental formaldehyde contamination in water supplies along the Tone River Basin. *Jpn J Risk Analysis* 2013;23:71–6. [in Japanese].
- Carlsen L, Kenessov BN, Batyrbekova SY. A QSAR/QSTR study on the environmental health impact by the rocket fuel 1,1-dimethyl hydrazine and its transformation products. *Environ Health Insights* 2008;1:11–20.
- CERICER Assessment Report 2-(Dimethylamino)ethyl acrylate; 2006a. [in Japanese].
- CERICER Assessment Report N, N-dimethyldodecylamine-N-oxide; 2006b. [in Japanese].
- CERICER Assessment Report 2-(Dimethylamino)ethyl methacrylate; 2007. [in Japanese].
- Chemical Management Policy Division, Manufacturing Industries Bureau, METI. List of Class 1 Designated Chemical Substances. Accessed on May 8, 2014 http://www.meti.go.jp/policy/chemical_management/law/prtr/pdf/engsindai1.pdf.
- Deborde M, von Gunten U. Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review. *Water Res* 2008; 42:13–51.
- Ellis AJ, Soper FG. Studies of *N*-halogeno-compounds. Part VI. The kinetics of chlorination of tertiary amines. *J Chem Soc.* 1954:1750–5.
- Environment Management Bureau, MOE. Enforcement of cabinet order for partial revision of enforcement regulations of the Water Pollution Prevention Act (Kansuiaisui 121001300). <https://www.env.go.jp/hourei/add/e031.pdf>, 2012. [(in Japanese). Accessed on May 8, 2014].

- Froese KL, Wolanski A, Hrudey SE. Factors governing odorous aldehyde formation as disinfection by-products in drinking water. *Water Res* 1999;33:1355–64.
- Joo SH, Mitch WA. Nitrile, aldehyde, and halonitroalkane formation during chlorination/chloramination of primary amines. *Environ Sci Technol* 2007;41:1288–96.
- JWWA. Standard Methods for the Examination of Water. Tokyo, Japan: JWWA; 2011 [in Japanese].
- Kamiguchi H, Miyata M. Occurrence of dimethylformamide in the Yodo River Basin and its treatability during water purification processes. Proc 52th Res Conf Kansai Regional Group at JWWA 2008; 2008. p. 94–7. [in Japanese].
- Kobayashi N, Sugimoto N, Kubota R, Nomoto M, Ikarashi Y. Identification of the cause of formaldehyde water pollution and the future issues on the management of unregulated chemicals in drinking water. *Jpn J Risk Analysis* 2013;23:65–70. [in Japanese].
- Mitch WA, Schreiber IM. Degradation of tertiary alkylamines during chlorination/chloramination: Implications for formation of aldehydes, nitriles. *Environ Sci Technol* 2008;42:4811–7.
- Mitch WA, Sedlak DL. Characterization and fate of *N*-nitrosodimethylamine precursors in municipal wastewater treatment plants. *Environ Sci Technol* 2004;38:1445–54.
- MOE Interim Report for Meeting on Future Measures against Interruption of Water Intake in Tone River Basin; 2012. [in Japanese].
- MOE, METI. Act on Confirmation, etc. of Release Amounts of Specific Chemical Substances in the Environment and Promotion of Improvements to the Management Thereof; 1999 [in Japanese].
- Na C, Olson TM. Mechanism and kinetics of cyanogen chloride formation from the chlorination of glycine. *Environ Sci Technol* 2006;40:1469–77.
- Painter HA, King EF. The need for applying stability tests in biodegradability assessments. *Chemosphere* 1986;15:471–8.
- Royal Society of Chemistry. ChemSpider - Search and share chemistry, <http://www.chemspider.com/>, [Accessed on May 8, 2014]
- Shah AD, Mitch WA. Halonitroalkanes, halonitriles, haloamides, and *N*-nitrosamines: A critical review of nitrogenous disinfection byproduct formation pathways. *Environ Sci Technol* 2012;46:119–31.
- The Chemical Daily. 16313 Chemicals. Tokyo: The Chemical Daily Co, Ltd; 2013 [in Japanese].
- von Gunten U, Salhi E, Schmidt SK, Arnold WA. Kinetics and mechanisms of *N*-nitrosodimethylamine formation upon ozonation of *N*, *N*-dimethylsulfamide-containing waters: bromide catalysis. *Environ Sci Technol* 2010;44:5762–8.
- WSD, HSB, MHLW. Standard items and their standard values (50 items). <http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/kijun/kijunchi.html#01>, 2003. [in Japanese]. Accessed on May 8, 2014].
- WSD, HSB, MHLW. Final Report of Control Measures for Contamination by Precursors of Disinfection By-products in Water Source; 2013. [in Japanese].

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Mechanisms of trichloramine removal with activated carbon: Stoichiometric analysis with isotopically labeled trichloramine and theoretical analysis with a diffusion-reaction model

Miki Sakuma, Taku Matsushita*, Yoshihiko Matsui, Tomoko Aki, Masahito Isaka, Nobutaka Shirasaki

Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form

20 October 2014

Accepted 21 October 2014

Available online 13 November 2014

Keywords:

Chlorinous odor

Trichloramine

Super powder activated carbon

Drinking water treatment

ABSTRACT

This study investigated the mechanism by which activated carbon removes trichloramine, a byproduct of water treatment that has a strongly offensive chlorinous odor. A stoichiometrical mass balance for ^{15}N before and after activated carbon treatment of laboratory-prepared ^{15}N -labeled trichloramine solutions clearly revealed that the mechanism of trichloramine removal with activated carbon was not adsorption but rather reductive decomposition to nitrogen gas. There was a weak positive correlation between the surface decomposition rate constant of trichloramine and the concentration of basic functional groups on the surface of the carbon particles, the suggestion being that the trichloramine may have been reduced by sulfhydryl groups ($-\text{SH}$) on the activated carbon surface. Efficient decomposition of trichloramine was achieved with super powdered activated carbon (SPAC), which was prepared by pulverization of commercially available PAC into very fine particles less than $1\ \mu\text{m}$ in diameter. SPAC could decompose trichloramine selectively, even when trichloramine and free chlorine were present simultaneously in water, the indication being that the strong disinfection capability of residual free chlorine could be retained even after trichloramine was effectively decomposed. The residual ratio of trichloramine after carbon contact increased somewhat at low water temperatures of $1\text{--}5\ ^\circ\text{C}$. At these low temperatures, biological treatment, the traditional method for control of a major trichloramine precursor (ammonium nitrogen), is inefficient. Even at these low temperatures, SPAC could reduce the trichloramine concentration to an acceptable level. A theoretical analysis with a diffusion-reaction model developed in the present study revealed that the increase in the trichloramine residual with decreasing water temperature was attributable to the temperature dependence of the rate of the reductive reaction rather than to the temperature dependence of the diffusive mass transfer rate.

© 2014 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel./fax: +81 11 706 7279.

E-mail address: taku-m@eng.hokudai.ac.jp (T. Matsushita).

<http://dx.doi.org/10.1016/j.watres.2014.10.051>

0043-1354/© 2014 Elsevier Ltd. All rights reserved.

Nomenclature

$c_i(t,R)$	liquid phase concentration on the outer surface of an adsorbent particle ($\mu\text{g/L}$)
$C(t)$	adsorbate concentration in bulk water phase as a function of time, t ($\mu\text{g/L}$)
C_c	adsorbent concentration in bulk water (g/L)
D_p	pore diffusion coefficient (cm^2/s)
$f(R)$	normalized particle size distribution function of adsorbent (cm^{-1})
k_F	liquid film mass transfer coefficient (cm/s)
k_{NCl_3}	surface decomposition rate constant of trichloramine (cm/s)
$c(t,r,R)$	liquid phase concentration in pore of an adsorbent having radius R , at radial distance r , and time t ($\mu\text{g/L}$)
r	radial distance from the center of an adsorbent particle (cm)
R	adsorbent particle radius (cm)
t	time (s)
ρ	adsorbent particle density (g/L)
ϵ	porosity of adsorbent (dimensionless)
a_p	surface area of pores per apparent volume of adsorbent ($1/\text{cm}$)

1. Introduction

Handling customers' complaints and dissatisfaction regarding the taste and odor of tap water are important issues that practitioners in drinking water treatment plants sometimes face. Chlorinous odor is the leading cause of dissatisfaction among persons who drink water in regions where chlorination or chloramination is employed for disinfection of drinking water (Piriou et al., 2004). Trichloramine (NCl_3) and dichloramine (NHCl_2) are recognized as the compounds that cause the chlorinous odor in tap water; trichloramine causes a much stronger chlorinous odor than dichloramine (Kranser and Barret, 1984). Trichloramine is formed mainly by the reaction between ammonium ions, which are present in raw sources of drinking water, and the chlorine used for disinfection. The removal of ammonium ions before the chlorination process is one strategy for mitigating the problem of trichloramine formation. Water treatment involving slow sand filtration (Stembal et al., 2005) or activated carbon (Andersson et al., 2001) are examples of biological methods used to remove ammonium ions. However, the activity of nitrifying microorganisms is reduced by low water temperatures, and in cold regions or during the winter nitrification becomes small to remove ammonium ions efficiently. To solve the trichloramine formation problem when the water temperature is low, treatment technologies that are independent of biological activity are required.

Treatment with activated carbon is the traditional method used to remove dichloramine and monochloramine (NH_2Cl) in water treatment (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). However, sufficient removal requires a very long contact time with the carbon. For example, almost 2 d (45 h) is required to remove dichloramine by using powdered

activated carbon (PAC) with diameters of 149–177 μm (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). Therefore, although PAC treatment is a simple process, its slow removal rate detracts from its application as a technology for drinking water treatment. Decreasing the size of the activated carbon particles generally enhances the removal rate achieved with activated carbon, because size reduction increases the specific surface area (surface area per unit weight of activated carbon). However, the technology of pulverizing activated carbon particles has typically produced particles no smaller than 5 μm in diameter (Matsui et al., 2008). Recently, our research group developed a way to produce super fine activated carbon particles (SPAC) with diameters less than 1 μm by pulverizing conventionally sized PAC. We have reported highly improved adsorptive uptake rates of natural organic matter (NOM) (Matsui et al., 2005) and of compounds that produce earthy-musty odors (Matsui et al., 2007, 2009). We hypothesized that treatment with SPAC may also be an effective way to remove trichloramine efficiently. A preliminary study conducted by our research group actually found that SPAC was superior to PAC for removal of trichloramine and dichloramine (Matsui et al., 2008). However, sufficient studies have not been conducted on the effects of water temperature and SPAC characteristics on trichloramine and dichloramine removal.

In general, an important characteristic of activated carbon is its high adsorption affinity and high capacity to adsorb various target compounds to be removed from raw drinking water sources. Activated carbon has therefore been widely used in drinking water treatment plants for a long time to reduce contaminant levels of NOM (Çapar and Yetiş, 2002), earthy-musty odor compounds (Herzing et al., 1977), and pesticides (Robeck et al., 1965). In contrast to the adsorptive removal of these compounds, the removal of dichloramine and monochloramine by activated carbon has been reported to be due to reductive decomposition of these compounds on the surface of the carbon (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). It has been speculated that dichloramine reacts with functional groups located on the internal surfaces of activated carbon particles and is then reduced to nitrogen gas (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). However, no direct evidence for the reductive decomposition of dichloramine has been presented so far. The mechanism of trichloramine removal by activated carbon is also unclear.

The objectives of this study were 1) to provide direct evidence of the trichloramine removal mechanism involving reductive decomposition of trichloramine to nitrogen gas by activated carbon and 2) to model the effect of water temperature on trichloramine removal. The removal mechanism was investigated by 1) comparing the masses of ^{15}N before and after treatment of laboratory-prepared, ^{15}N -labeled trichloramine solutions, 2) comparing the trichloramine removal performances of activated carbon substrates with various surface characteristics, and 3) modeling the process of trichloramine removal at different temperatures in a diffusion-reaction system. Simulating the effect of water temperature enabled us to judge whether SPAC treatment could be a practical way to control chlorinous odors at low water temperatures.

Table 1 – Characteristics of SPACs used.

Name	Raw material	D ₅₀ μm	Pore surface area, m ² /g			Pore volume, mL/g		Functional group, μeq/g		Elemental composition, %				ZP mV	IEP	pHpzc
			BET	Micro	meso	Micro	meso	Basic	Acidic	C	N	S	O			
Wood-1	Wood	0.53	1174	918	88	0.405	0.136	780	351	81.9	0.2	0.2	8.2	−46	2.8	7.4
Wood-2	Wood	0.47	1111	953	131	0.450	0.252	711	193	84.6	0.2	0.1	9.1	−39	3.3	8.7
Wood-3	Wood	0.52	1145	919	138	0.395	0.223	790	350	85.3	0.1	0.1	8.9	−42	4.2	8.9
Wood-4	Wood	0.62	1130	922	116	0.388	0.392	696	553	83.3	0.2	0.1	8.9	−46	2.9	7.7
Coco-1	Coconut shell	0.57	978	824	103	0.302	0.310	329	425	88.1	0.2	0.1	6.1	−42	3.9	6.4
Coco-2	Coconut shell	0.50	1215	1023	79	0.432	0.133	582	433	89.1	0.2	0.1	6.1	−48	3.3	7.3
Coal	Coal	0.49	884	637	55	0.281	0.314	366	757	79.2	0.4	0.6	11.0	−38	4.2	6.3

D₅₀, median diameter; micro, micropore; meso, mesopores; ZP, zeta potential; IEP, isoelectric point; pHpzc, pH at point of zero charge.

2. Materials and methods

2.1. Activated carbon

Seven commercially available PACs (four wood-based, two coconut-shell-based, and one coal-based PAC) were obtained from manufacturers (Table 1). These were pulverized to superfine particles (SPAC) with a wet bead mill (Metawater Co., Tokyo, Japan). The carbons were stored as slurries at 4 °C prior to use.

2.2. Preparation of trichloramine and ¹⁵N-labeled trichloramine solutions

Trichloramine was prepared according to the method reported by Kosaka et al. (2010). Phosphate buffer (pH 7.0, 5 mM sodium phosphate) was prepared with Milli-Q water (Milli-Q Advantage, Millipore Co., Bedford, MA, USA) and then supplemented with 0.25 mg-N/L ammonium chloride at room temperature. The solution was further supplemented with 4 mg-Cl₂/L of sodium hypochlorite and mixed at 400 rpm for 30 min with a magnetic stirrer. The solution was allowed to stand for 1.5 h at a room temperature of about 20 °C and then stored overnight at 4 °C in the dark. The resulting solution contained approximately 0.2–0.4 and 1.5–2.0 mg-Cl₂/L of trichloramine and residual free chlorine, respectively, the

trichloramine concentrations being one order larger than those reported in tap waters (<0.015–0.046 mg-Cl₂/L) (Kosaka et al., 2010). A ¹⁵N-labeled trichloramine solution was prepared in the same manner as described above with a ¹⁵N-labeled ammonium chloride solution containing 0.3 mg-N/L and a sodium hypochlorite solution containing 4.8 mg-Cl₂/L. In addition to the ¹⁵N-labeled trichloramine, the solution contained dissolved ¹⁵N₂ gas that had been generated during the chlorination of ¹⁵N-labeled ammonium chloride (Bauer and Snoeyink, 1973).

2.3. ¹⁵N mass balance experiments

The laboratory-prepared, ¹⁵N-labeled trichloramine solution, which contained ¹⁵N₂ as well as ¹⁵N-labeled trichloramine, was transferred to the lower chamber of a glass vessel with separable upper and lower chambers. The lower chamber was tightly sealed with a separator made of aluminum foil (Fig. 1A). The gas in the upper chamber of the vessel was replaced with Ar gas. The gas in the upper chamber of the vessel was replaced with Ar gas. To purge ¹⁵N₂ dissolved in the solution into the gas phase, the solution was intensely mixed for 20 min with the gas phase after the separator was removed and was then kept in a stationary mode for 30 min (Fig. 1B). An aliquot of the gas was withdrawn from the upper chamber to measure the ¹⁵N₂ concentration (Fig. 1C). The same steps corresponding to Fig. 1A–C were repeated (Fig. 1D–F) to purge ¹⁵N₂ completely from the solution. An aliquot of the solution

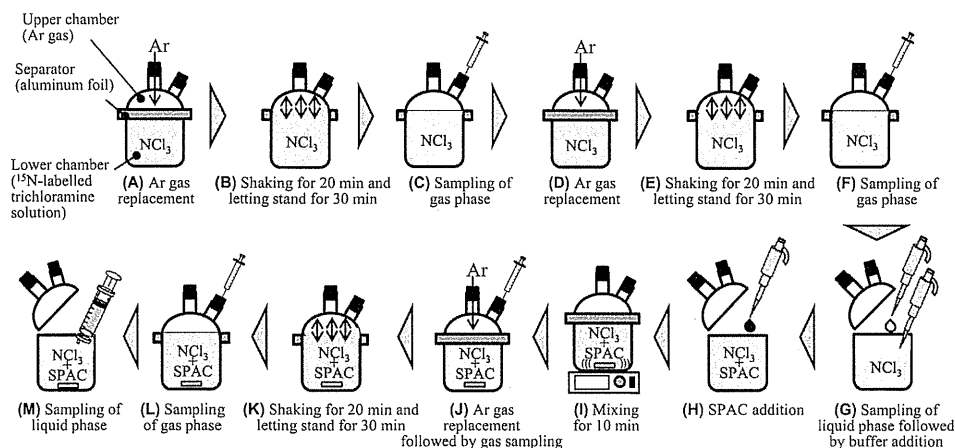


Fig. 1 – Protocol for ¹⁵N mass balance experiments.

was withdrawn from the lower chamber (Fig. 1G) to measure the initial concentrations of chloramines, and then an aliquot of phosphate buffer with the same volume as the aliquot that had been withdrawn was added to the solution to ensure that there was no head space between the surface of the solution and the separator. Trichloramine was quantified by head-space gas chromatography/mass spectrometry (HS-GC/MS) as described below. The solution was supplemented with 3 mg/L of SPAC (wood-1) (Fig. 1H), tightly sealed with the separator, and then mixed for 10 min with a magnetic stirrer (Fig. 1I). During the mixing, the gas in the upper chamber was replaced with Ar gas (Fig. 1J). An aliquot of the gas in the chamber was withdrawn to measure the initial concentration of $^{15}\text{N}_2$. After 10 min of mixing, the separator was removed. The liquid phase was intensely mixed with the gas phase for 20 min and then left in a stationary mode for 30 min to allow any $^{15}\text{N}_2$ gas generated by the reaction between trichloramine and the SPAC to transfer to the gas phase from the solution (Fig. 1K). An aliquot of the gas phase was withdrawn from the upper chamber to measure the $^{15}\text{N}_2$ concentrations (Fig. 1L). To measure the chloramine concentrations, an aliquot of the solution was withdrawn (Fig. 1M) and then filtered through a membrane filter ($\phi = 0.2 \mu\text{m}$, PTFE, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) to remove any SPAC particles. This experiment was conducted at 20 °C three times: these replicates are designated as Experiments 1, 2, and 3.

2.4. Batch decomposition of trichloramine with SPACs

The trichloramine solution was transferred to a 1-L glass beaker. The solution was supplemented with PAC at a concentration of 1 mg/L and then covered with a floating lid. The lid, made of a polystyrene form covered with aluminum foil, prevented volatilization of the chloramines. The solution was stirred with a magnetic stirrer, and samples were withdrawn from the beaker through a siphon at predetermined time intervals. The concentrations of chloramines and free chlorine were measured with the *N,N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method (American Public Health Association/American Water Works Association/Water Environment Federation, 2005) after the sample had been filtered through a membrane filter ($\phi = 0.2 \mu\text{m}$, PTFE, Toyo Roshi Kaisha, Ltd.). The experiments were conducted at water temperatures of 1, 5, or 20 °C.

2.5. Quantifications of trichloramine, ^{15}N -labeled trichloramine, other chloramines, and $^{15}\text{N}_2$ gas

The HS-GC/MS analysis of trichloramine (Kosaka et al., 2010) was carried out as follows: separation was performed using an Agilent 7890A gas chromatograph (Agilent Technologies, Inc., CA, USA) equipped with an HP-1MS capillary column (30 m \times 0.25 mm, 0.25 μm ; Agilent Technologies). The injection temperature was 40 °C, and the flow rate of He was 2.0 mL/min. The injection mode was pulsed-split, and the split ratio was 1:30. The oven temperature was constant at 30 °C. Detection was performed using an Agilent 5975C mass spectrometer (Agilent Technologies) in selected ion monitoring (SIM) mode. The auxiliary temperature, quadrupole temperature, and ion source temperature were controlled at 110, 150,

and 150 °C, respectively. The detected fragment ions of trichloramine, ^{15}N -labeled trichloramine, and d_3 -labeled 1,1,2-trichloroethane (internal standard) occurred at m/z of 84, 85, and 100, respectively. Dichloramine, monochloramine, and free chlorine were measured according to the DPD colorimetric method.

$^{15}\text{N}_2$ gas was quantified with a GC/MS equipped with a CP-Molsieve 5 Å capillary column (50 m \times 320 μm \times 30 μm ; Agilent Technologies). The temperatures of the ion source, injector, and transfer line were controlled at 230, 200 and 270 °C, respectively. The GC/MS was operated in the selected ion monitoring (SIM) mode with ^{38}Ar as an internal standard; the detected fragment ions of $^{15}\text{N}_2$ and ^{38}Ar occurred at m/z of 30 and 38, respectively.

2.6. Measurement of physicochemical properties of SPACs

Particle size distributions of activated carbons were determined with a laser diffraction and scattering instrument (Microtrac MT3000 II, Nikkiso Co., Ltd., Tokyo, Japan). The median particle diameter (D_{50}) was calculated from the particle size distribution.

Specific surface areas and pore size distributions of the SPACs were analyzed by nitrogen gas adsorption at 77 K with an automated gas sorption analyzer (Autosorb-iQ-MP; Quantachrome Instruments, Boynton Beach, FL, USA). Specific surface area (S_{BET}) was determined by using the BET (Brunauer–Emmett–Teller) method. Pore size distributions were determined by a combination of two widely accepted models: the DFT (Density Functional Theory) model for the pore size distribution of micropores (<2 nm) and the BJH (Barrett–Joyner–Halenda) model for mesopores and macropores (>2 nm). Elemental analysis of the SPACs was carried out with an elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH, Hanau, Germany).

Surface acidity and basicity of the SPACs were determined by using the Boehm titration method (Boehm, 1994, 2002) with some modifications. SPACs were dried at 105 °C for 12 h in a drying oven. After cooling, an aliquot of 200 mg of the SPAC was transferred to a test tube, and 10 mL of 0.05 M sodium hydroxide (NaOH) or hydrogen chloride (HCl) was added. The suspension was placed under vacuum for 1 h to remove any air from the pores and then vortexed intensely for 24 h to allow the surface functional groups of the SPAC to react with the base or acid. After vortexing, the suspension was filtered through a membrane filter to remove any SPAC particles. Aliquots (5 mL) of the filtrate were transferred to beakers, and then an aliquot of 15 mL of 0.05 M HCl or NaOH was added to each filtrate of the NaOH-treated or HCl-treated SPACs, respectively. The acidic or basic filtrates were neutralized by back titrating with NaOH or HCl, respectively.

The zeta potential of the SPACs was measured with a dynamic, light-scattering, laser zeta potential analyzer (Zetasizer Nano ZS, Malvern Instruments Ltd., Malvern, UK) in the same phosphate buffer used for the preparation of the trichloramine solutions. The isoelectric point (IEP) was determined by measuring the zeta potential of the SPACs as the pH of the solution was changed.

The pH at the point of zero charge (pH_{pzc}) indicates the condition of the surface of the activated carbon when it has no net charge in solution. The initial pH was adjusted to the range 2–8 by adding 0.1 M HCl or NaOH to 50 mL of 0.01 M sodium chloride (NaCl). An aliquot of 150 mg of SPAC was added to each of the different pH solutions, and the solutions were agitated for 48 h. The equilibrium pH was plotted against the initial pH. The pH_{pzc} was the initial pH that was identical to the equilibrium pH (Noh and Schwarz, 1990).

2.7. Theoretical analysis

When the size distribution of adsorbent particles is taken into consideration, the mass balance for an adsorbate in a batch container is described by the following equation:

$$\frac{dC(t)}{dt} = \frac{3C_c k_F}{\rho} \int_0^{\infty} \frac{f(R)}{R} [C(t) - c_i(t, R)] dR \quad (1)$$

For highly adsorbent substrates, intraparticle migration of the adsorbate is mainly the result of surface diffusion, because most of the adsorbate particles adsorb onto the surface of the adsorbents, and the fraction of the adsorbate in the liquid phase of the pores is negligibly small. The large K_{ow} of trichloramine (–1.6 calculated with Estimation Programs Interface Suite software, United States Environmental Protection Agency), however, suggests that it is very unlikely to adsorb to activated carbon. Surface diffusion is therefore not expected to account for most intraparticle migration of trichloramine. Instead, radial mass transport of trichloramine molecules occurs in the liquid phase within the pores by pore diffusion. We have assumed that the trichloramine decomposition that occurs on the surface of pores in carbon particles follows first-order reaction kinetics. Finally, the rate of change of the liquid phase concentration of trichloramine in pores is described by the following equation:

$$\varepsilon \frac{\partial c(t, r, R)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ D_F r^2 \left[\frac{\partial c(t, r, R)}{\partial r} \right] \right\} - \varepsilon \cdot a_p k_{\text{NCl}_3} \cdot c(t, r, R) \quad (2)$$

The mass balance of trichloramine with respect to a carbon particle is described by equating the rate of change of the amount of trichloramine in a carbon particle, the rate of mass transfer from the external particle surface to the inside of the particle, and the rate of decomposition of trichloramine as follows:

$$\varepsilon \frac{d}{dt} \left\{ \int_0^R c(t, r, R) \cdot 4\pi r^2 dr \right\} = k_F [C(t) - C_{i,i}(t)] \cdot 4\pi R^2 - \varepsilon \cdot a_p k_{\text{NCl}_3} \int_0^R c(t, r, R) \cdot 4\pi r^2 dr \quad (3)$$

The particle size distribution was approximated by a discrete density function. The set of model equations was converted into a set of ordinary differential equations with respect to time t using the method of orthogonal collocation. The resulting equations were solved as a system of ordinary differential equations by the Gear's stiff method in the International Mathematics and Statistics Library (IMSL, Visual Numerics, Houston, TX, USA), after deriving the analytical

Jacobian of the equations. Details are presented in Supplementary content.

A single pore diffusion coefficient (D_p) at a given water temperature was used, irrespective of carbon particle size. Mass transfer across the liquid film external to the adsorbent particle surfaces cannot be the rate-determining step in well mixed reactors (Sontheimer et al., 1988), and resistance to such mass transfer was therefore neglected. For purposes of modeling mass transfer in the model simulations, the liquid film mass transfer coefficient (k_F) was set to 0.1 cm/s. Coefficients larger than this value produced the same simulated trichloramine concentrations, the indication being that the k_F value did not limit the rate of decomposition of trichloramine by PAC.

3. Results and discussion

3.1. ^{15}N mass balance experiments

After the ^{15}N -labeled trichloramine solution was intensely mixed with the gas phase in order to purge the $^{15}\text{N}_2$ gas that had been produced during the preparation of the ^{15}N -labeled trichloramine solution by the reaction of ^{15}N -labeled ammonium ions with chlorine, $^{15}\text{N}_2$ was detected in the gas phase (Fig. 1C) at 110–192 ppm. However, no $^{15}\text{N}_2$ gas was detected (<1.4 ppm) in the gas phase (Fig. 1F) after the solution was again intensely mixed with the gas phase. Therefore $^{15}\text{N}_2$ was almost completely removed from the ^{15}N -labeled trichloramine solution. Even if a small fraction of the $^{15}\text{N}_2$ remained in solution, the $^{15}\text{N}_2$ was not potentially transferrable to the gas phase. The ^{15}N -labeled trichloramine solutions contained 232, 243, and 370 $\mu\text{g}\text{-Cl}_2/\text{L}$ of trichloramine in Experiments 1–3, respectively. Neither dichloramine nor monochloramine was detected, the indication being that the ^{15}N -labeled trichloramine solution contained only trichloramine as a sole source of nitrogen before the reaction with the SPAC. The amount of ^{15}N from the ^{15}N -labeled trichloramine solution (600 mL) was calculated to be 10.3, 10.3, and 15.7 $\mu\text{g}\text{-}^{15}\text{N}$ in Experiments 1–3, respectively (white vertical bars in Fig. 2).

After addition of the SPAC and mixing of the trichloramine solution, none of chloramines was detected in the solution (Fig. 1M), the indication being that the ^{15}N -labeled trichloramine was completely removed by the SPAC. In contrast, $^{15}\text{N}_2$ gas was detected in the gas above the solution, which had been in contact with the solution (Fig. 1L). The $^{15}\text{N}_2$ concentrations in the gas phase were 51, 52, and 78 ppm, equivalent to 9.5, 9.6, and 14.4 $\mu\text{g}\text{-}^{15}\text{N}$, respectively (the volume of the gas phase was 150 mL), as shown in Fig. 2 (gray bars). Before addition of the SPAC, the amount of $^{15}\text{N}_2$ that was potentially transferrable to the gas phase from the ^{15}N -labeled trichloramine solution was undetectably small, as already noted. The solution therefore contained only trichloramine as a source of nitrogen. The $^{15}\text{N}_2$ in the gas phase must therefore have originated from the ^{15}N -labeled trichloramine that had been removed by the SPAC. Moreover, the amounts of nitrogen detected in the gas phase were almost the same as those previously present in the ^{15}N -labeled trichloramine solutions. This result clearly demonstrates that trichloramine was