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Formaldehyde formation from tertiary amine derivatives during chlorination

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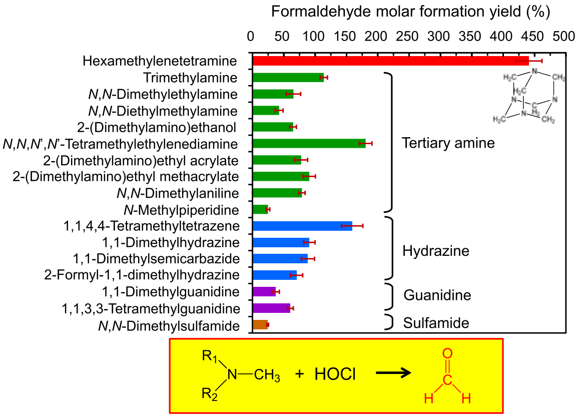
HIGHLIGHTS

- 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



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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.%.

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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 -CH_2- 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 (R_1, and R_2) 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 Cl_2/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.

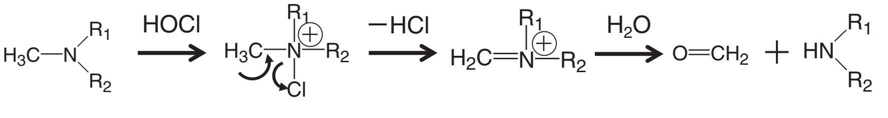

Fig. 1. Reaction scheme of FA formation from tertiary amines during the chlorination process (Ellis and Soper, 1954; Mitch and Schreiber, 2008).