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Formation of disinfection by-products: Effect of temperature and kinetic modeling

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HIGHLIGHTS

- ▶ Water temperature has significant impact on DBP formation.
- ▶ Both regulated and emerging DBPs are embraced by conducting UFC test.
- ▶ A kinetic model for simulating DBP formation is developed.
- ▶ Temperature effect on DBP formation and decomposition are quantified.

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ABSTRACT

The temperature of drinking water fluctuates naturally in water distribution systems as well as often deliberately heated for household or public uses. In this study, the temperature effect on the formation of disinfection by-products (DBPs) was investigated by monitoring the temporal variations of twenty-one DBPs during the chlorination of a humic precursors-containing water at different temperatures. It was found that chloroform, DCAA, TCAA, DCAN and CH were detected at the considerable level of tens of $\mu g\ L^{-1}$. The three regulated DBPs (chloroform, DCAA and TCAA) were found increasing with both contact time and water temperature, while the five typical emerging DBPs (DCAN, CH, TCNM 1,1-DCPN and 1,1,1-TCPN) revealed the significant auto-decomposition in addition to the initial growth in the first few hours. Increasing water temperature could enhance the formation rates of all the eight detected DBPs and the decomposition rates of the five emerging DBPs. Further, a kinetic model was developed for the simulation of DBP formation. The validity and universality of the model were verified by its excellent correlation with the detected values of each DBP species at various temperatures. The formation rates of 1,1-DCPN and 1,1,1-TCPN, and the decomposition rate of 1,1,1-TCPN were faster as compared to the other DBPs. And the formation reaction activation energies of CH, DCAN and 1,1-DCPN were relatively large, indicating that their occurrence levels in the finished water were more susceptible to temperature variations.

1. Introduction

Disinfection by-products (DBPs) in drinking water have drawn global attentions due to their considerable adverse health effects (Xie, 2003; Liviac et al., 2010). Currently, there have been over 600 DBPs detected in the disinfected drinking water (Richardson et al., 2007). An important and empirical factor that can significantly affect DBP formation is water temperature, which may change notably in the distribution system (fluctuates at 5–25 °C mainly for seasonal transition) and sequently in household usage (e.g. for shower or bath at 30–40 °C) or public usage (e.g. sport activities and spa relaxing at 25–45 °C). The significance of DBP seasonal fluctuations has caused an increased concern and awareness for regulation compliance (Brett and Calverley, 1979; Arora et al., 1997; Golfinopoulos and Arhonditsis, 2002), as well as the temperature effect on DBP alternations in household and public usage is also considerable (Wu et al., 2001; Zhang and Minear, 2002; Symanski et al., 2004). A few studies have included the temperature effect by depicting the DBP variations at different temperatures. For example, Wu et al. (2001) conducted a comprehensive investigation on the temporal variation of DBPs by boiling tap water, expanding the DBP occurrence database to high temperatures. Zhang and Minear (2002) studied the temperature effect at 4 and 23 °C on the trihaloacetic acids decomposition rates. And Yang et al. (2007) compared the different formation levels of both the currently regulated and emerging DBPs at 10–30 °C after 72-h incubation. However, no systematic study quantitatively analyzing the temperature effect on DBP formation has been conducted. Besides, most previous studies of the temperature effect on DBP temporal variations have targeted the regulated species (THMs and HAAs) instead of the emerging ones. In actuality, some emerging DBPs such as nitrogenous haloacetonitriles (HANs) and

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halonitromethanes (HNMs) could expose much higher potential health risks, and have been considered as candidates for future regulatory control (Woo et al., 2002; Krasner et al., 2009). Given the very limited efforts invested in the emerging DBP studies, their occurrence levels and variation patterns at different temperatures remain little understood (Weinberg et al., 2002; Krasner et al., 2006).

In addition to the experimental studies, much effort has been devoted in the recent decades to modeling DBP formation regarding the temporal variations or temperature effect. One large cluster of such models was obtained by regression or statistical techniques (Amy et al., 1987; Siddiqui et al., 1994; Rodriguez et al., 2000; Golfinopoulos and Arhonditsis, 2002). However, it would be more desirable and representative for the model to be derived from the kinetic mechanics. The alternative DBP evaluation approach requires massive field monitoring work calling for extraordinarily high technical and financial support. In this regard, Clark et al. (2001) established a kinetic model on DBP formation by assuming the formation following the second order reaction kinetics. This model was however relatively difficult to use in application because of its complex form and numerous variables.

Another model using a simplified format and developed by Gang et al. (2003) assumes that DBP formation follows parallel first order reaction mode. However, both the Clark and Gang models assume a proportional association between the DBP formation and chlorine consumption. This assumption might not be appropriate as total chlorine consumption may largely be a result of the auto-decomposition of hypochlorous acid as well as non-DBP-producing reductions (such as reactions with the reductive ions and biological uptake) (Kiene et al., 1998; Frateur et al., 1999). Further, a few studies have shown that the organic precursor was more influential compared with the overall chlorine consumption to the DBP formation reaction (Morrow and Minear, 1987; Rossman et al., 2001).

In this study, the temporal variations of both regulated and emerging DBPs were comprehensively investigated in a proper temperature span from 4 to 50 °C. Given the lack of the understanding of the DBP formation kinetics and of the kinetic modeling endeavor for DBP occurrence, a kinetic model was developed in which the DBP formation was associated with the consumption of the organic precursors. A simple model equation was derived containing only three physical variables. And the temperature effect was then quantitatively obtained by deducting the activation energy of each DBP's formation (decomposition for 1,1,1-TCPN). The primary objective of this study is to provide the occurrence information of various DBPs and facilitate the preliminary prediction on DBP levels with the practical temperature effect consideration.

2. Material and methods

2.1. Experiment procedure

The Uniform Formation Conditions (UFCs) test (Summers et al., 1996) was employed to evaluate the DBP formation. A humic acid stock solution of 1.0 g L^{-1} was prepared by dissolving the commercial humic acids (SCRC, Beijing, China) into an alkaline solution (NaOH, pH = 12), the pH of which was then adjusted to neutral by using a 1.0 M sulfuric acid solution. The diluted humic solution was freshly prepared by diluting the stock solution using reagent water (Millipore Super-Q system, Millipore, USA) until the total organic carbon (TOC) content was 4.0 ± 0.1 mg L^{-1}, which was then added with 2 mL L^{-1} borate buffer (1.0 M boric acid and 0.26 M sodium hydroxide, pH = 8.0) and finally adjusted to pH = 8.0 ± 0.2 by using a 1.0 M sulfuric acid solution. The buffered disinfectant (NaClO) solution (2700 mg L^{-1} free chlorine; pH = 8.0 ± 0.2) was prepared by mixing a sodium hypochlorite solution (3300 mg L^{-1} free chlorine) that was diluted from a commercial sodium hypochlorite solution (5% mass fraction for free chlorine; XDDF, Beijing, China) using reagent water with a borate buffer solution (1.0 M boric acid and 0.11 M sodium hydroxide, pH = 6.7) at an approximate 4:1 volume ratio.

To study the temperature effect, the UFC test was conducted under a number of temperatures (4, 15, 25, 35 and 50 °C). During the experiment at each temperature, 7 L of the buffered humic solution (TOC = 4.0 ± 0.1 mg/L; pH = 8.0 ± 0.2) was first stored in a biochemical incubator (SPX-310, Ningbo, China) for at least five hours to reach the preset water temperature (within 0.1 °C). Then the solution was quickly distributed into 24 brown glass bottles of 250 mL each equipped with PTFE-faced septa and screw cap. More specifically, the bottle was firstly filled with the buffered humic solution to about three quarters full, then dosed with the buffered NaClO solution (capped and inverted twice) and finally filled to top with the buffered humic solution and capped headspace-free. The bottle was then quickly inverted for at least ten times and transferred into the incubator to start sampling procedure. During the distribution of the buffered humic solution, the solution temperature was continuously monitored to ensure thermal consistency in the reaction system. Duplicate samples were collected at each preset sampling time until the incubation period reached 120 h.

2.2. Analytical methods

The four THMs, the nine HAAs, four species of HANs (including dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN)) and four of other concerned DBPs (including chloral hydrate (CH), trichloronitromethane (TCNM), 1,1-dichloropropanone (1,1-DCPN) and 1,1,1-trichloropropanone (1,1,1-TCPN)) were analyzed by using gas chromatography with an ECD detector (Agilent 7890A, Santa Clara, USA) after liquid–liquid extraction according to the standard analyzing methods of EPA 551.1 (US EPA, 1995) and 552.3 (US EPA, 2003). The detection limit of DBPs investigated was 0.1 μg L^{-1}. The TOC, pH and free chlorine were detected using a total organic carbon detector (TOC-V CPH, Kyoto, Japan), a pH meter (868, Orion, USA) and an electric chlorine analyzer (0.01 L, Loveland, USA), respectively.

2.3. Modeling

A universal and simple kinetic model was developed to model the formation of the concerned DBPs. It starts from mass balance, requiring that the accumulation rate (dC/dt) of the DBP is equal to the difference of its production rate and consumption rate, i.e.

$$\frac{dC}{dt} = kM_t - k_2C \tag{1}$$

In Eq. (1), the underlying assumptions are the DBP production rate is first order to the organic precursor concentration available at time t (M_t) and the consumption rate is first order to its own concentration, where k and k_2 are the respective apparent reaction rate constants of DBP formation and decomposition. M_t is the difference of its initial concentration (M_0) and the amount (in concentration unit) that has been consumed at time t (M_r). As such, Eq. (1) can be transformed to

$$\frac{dC}{dt} = k(M_0 - M_r) - k_2C \tag{2}$$

One additional assumption is that the DBP formed is stoichiometrically proportional to the organic precursor consumed. Therefore, Eq. (2) can be transformed to