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Formation of disinfection by-products from the monochloramination of chironomid larvae metabolite solution

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ABSTRACT

In this study, the formation of disinfection by-products (DBPs) was investigated during the monochloramination of chironomid larvae metabolite solution under different conditions, to find out how the metabolites produced by organisms to affect the water safety and the production of DBPs. Longer reaction time and higher monochloramine dosage resulted in an increase of the most DBPs in bulk solution, where the concentrations of dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) appeared to be much higher than those of the trichloronitromethane (TCNM) and trichloroacetonitrile (TCAN), and chloral hydrate (CH) formation which exhibited an initial increase with a following stable stage. The pH affected the formation of different DBPs in the distinct manner. The concentrations of TCAN, DCAA, TCAA, and CH became lower gradually as pH increasing from 5 to 10, and TCAN and CH could not be detected when the pH exceeded 8–9. And as to the trichloromethane (TCM), dichloroacetonitrile (DCAN), and TCNM, their maximum concentrations are assumed in the pH range of 6–8. Higher temperature enhanced the formation of TCM, DCAA, and TCNM, but weakened that of TCAA and DCAN. Additionally, Cl/N mass ratio has effects on the formation of the DPBs, and as a whole, lower Cl/N ratio would lead to a decline in the concentrations of the four most common DBPs.

Keywords: Chironomid larvae metabolite solution; Monochloramination; Disinfection by-products

1. Introduction

Since trihalomethanes (THMs) were discovered in chlorinated water in the 1970s, disinfection by-products (DBPs) have become a focus of attention in water treatment. Till now more than 700 species of DBPs have been confirmed, such as THMs and haloacetic acids (HAAs), which have been identified as cancer-causing reagents in the last three decades [1]. Natural organic matter (NOM), defined as the complex matrix of naturally occurring organic materials present in natural waters, is usually considered to be a precursor of DBPs, and most researches on DBPs are based on NOM-containing natural bodies of water [2,3].

The recent studies [4,5] otherwise revealed that, besides the humic acid and organic matter, certain bacteria and algae cells with their extracellular organic matter (EOM) could also be the precursors of DBPs.

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Fang et al. [6] observed the formation of DBPs during the chlorination of *Microcystis aeruginosa*, and the results showed that most DBPs increased as the growth period of algal cells increased. The complex organic substances contained in bacteria, including fatty acids, proteins, and DNA, also resulted in the production of nitrogenous DBPs (N-DBPs), such as halogenated acetonitriles (HANs). Zhang et al. [5] additionally noted that three species of bacteria were the possible precursors of HANs, where the bromide ions played a vital role in N-DBPs generation.

In the 1920s, chironomid larvae were detected in urban water supply systems [7]. Although there are no indications that these organisms pose a threat to public health, their presence is still not desirable for the associated poor hygiene [8]. Many researchers have paid attention to chironomid larvae recently, with the aims for controlling the presence of chironomid larvae during the water purification process by strengthening the water treatment process [9,10]. And the studies concerned about the effects of chironomid larvae on water quality and safety during disinfection are lacking. Chironomid larvae are large in size compared with algae and bacteria, and it therefore suggests the contained biomass of amino acids, protein, fat, and other organic matter have a higher potential to form the DBPs. So, it is interesting to find out how the metabolites produced by these organisms to affect the water safety and the production of DBPs.

Many factors, such as the reaction time, pH, temperature, disinfectant concentration, and precursor properties, have been reported and extensively studied in DBPs generation [1,2,6]. The formation of stable THMs and HAAs could be enhanced when increasing chlorination time and increasing chlorine concentration [11]. However, increase in reaction time and chlorine concentration did not lead to the increasing formation of unstable DBPs, such as dichloroacetonitrile (DCAN). Higher pH led to an increase in THM formation but a reduction of DCAN [6]. The differences in these formation trends have been partially explained by the hydrolysis and oxidative decomposition of unstable DBPs at alkaline pH and by chloramine, respectively [12].

It is evident that monochloramine can be used as a disinfectant without generating high levels of most DBPs. However, it has been proved that the nitrogenous DBPs formed when using monochloramine. The objectives of this study are to evaluate the formation of DBPs during monochloramine treatment of chironomid larvae metabolite dissolution under various conditions. The test parameters included the monochloramine concentration, reaction time, pH, temperature, and Cl/N ratio. The chironomid larvae metabolite dissolution concentrations were represented by the total organic carbon (TOC) content.

2. Materials and methods

2.1. Chemicals and materials

Solutions were prepared from reagent-grade chemicals or stock solutions. Deionized water was used in preparing all solutions. The monochloramine solution (500 mg/L) was freshly prepared by mixing a free chlorine solution with an ammonium chloride (NH_4Cl) solution at an initial Cl/N mass ratio of 4/1. Buffer solutions at pH 5, 6, 7, 8, 9, and 10 were prepared with phosphate salts (Tianjin Chemical Plant, China). Calibration standards, internal standards, and surrogate standards for the analyses of THM, nine HAAs (HAA9), HAN, chloral hydrate (CH), and trichloronitromethane (TCNM) were obtained from Supelco.

2.2. Chironomid larvae

Chironomid larvae were obtained from adult chironomids that were bred in our laboratory. Chironomid larvae, initially collected from temporary water bodies in the vicinity of waterworks in Harbin, were cultured in an aerated 25 L glass aquaria filled with tap water. A 5 cm thick artificial sediment layer consisting of washed siliceous sand and cellulose was introduced at the bottom of the aquarium. Adult midges were confined using wooden cages covered with 1 mm mesh metal net. Aquaria were kept at a constant temperature (20°C) and exposed to a consistent photoperiod (14 h light/10 h dark). To obtain homogenous samples (with respect to both size and age), egg masses were transferred from rearing aquaria into 2 L glass experimental tanks filled with aerated tap water. Egg masses were left for 24 h in these tanks, and nonhatched eggs were then removed. The fourth instar larvae were therefore used in the following study.

2.3. Preparation of the chironomid larvae metabolite solution

Five hundred active chironomid larvae of similar size were placed into a beaker containing 1 L of deionized water. The dead larvae were removed after 24 h, and the rest larvae were left for an additional 24 h. The water was filtered using a 0.45 μm membrane, and then standard samples were prepared by diluting reagents to 2 mg/L with deionized water at 50°C.

2.4. Analytical methods

The monochloramine concentration was measured by DPD/FAS titration [13]. Analyses of selected DBPs were carried out by gas chromatography (GC) (Agilent 7890) with an electron capture detector (ECD) [14,15]. For HAA9 analysis, the samples were pretreated using an extraction/derivatization procedure with methyl tert-butyl ether (MTBE) and acid methanol according to USEPA method 552.3 [15]. The column used was an HP-5 fused silica capillary column (30 mm × 0.25 mm I. D. with 0.25 mm film thickness). The injector, ECD, and GC oven temperature program for compounds other than HAA9 are as follows: injector temperature: 200℃; ECD temperature: 290℃; and oven temperature: 35℃ for 9 min, ramp to 40℃ at 2℃/min, hold for 8 min, ramp to 80℃ at 20℃/min, ramp to 160℃ at 40℃/min and hold for 4 min. The temperature program for the HAAs is as follows: injector temperature: 210℃; ECD temperature: 290℃; and oven temperature: 30℃ for 20 min, ramp to 40℃ at 1℃/min, ramp to 205℃ at 20℃/min and hold for 4 min. The limit of detection of DCAA and TCAA, respectively, was 0.020 and 0.019 μg/L. The THM, CH, TCNM, and HAN concentrations were measured by a liquid–liquid extraction procedure using MTBE and acid methanol according to USEPA Method 551.1 [14]. A HP-5 fused silica capillary column (30 mm × 0.25 mm I.D. with 0.25 mm film thickness) was used. The GC-ECD operating conditions are as follows: detector, 290℃; injector, 200℃; injection volume, 1 mL; and temperature program, 35℃ for 5 min, ramped to 75° C at 10℃/min, held for 5 min, ramped to 100℃ at 10℃/min, and then held for 2 min. The limit of detection of TCM, CH, TCNM, DCAN, and trichloroacetonitrile (TCAN) was 0.055, 0.005, 0.002, 0.001, and 0.002 μg/L.

2.5. Experimental procedures

Experiments were carried out in aluminum-foil-wrapped glass vials with Teflon-faced septa. A baseline monochloramine concentration of 10 mg/L was applied to chironomid larvae metabolite dissolution solutions (2 mg/L TOC) in the absence of bromide at buffered pH of 7.5, and room temperature of 20 ± 1℃. An orthogonal matrix experimental design was employed with reaction time, monochloramine concentration, pH, temperature, and Cl/N ratio as the multiple factors, and the respective levels are as follows: reaction time (6, 12, 24, 36, 48, and 72 h), monochloramine concentrations (1, 2, 4, 6, 8, 10, and 20 mg/L as Cl_2), pH values (5, 6, 7, 8, 9, and 10), temperature (10, 20, and 30℃), and Cl/N ratio (1/0, 25/1, 10/1, 5/1, 4/1, 3/1, and 2/1).

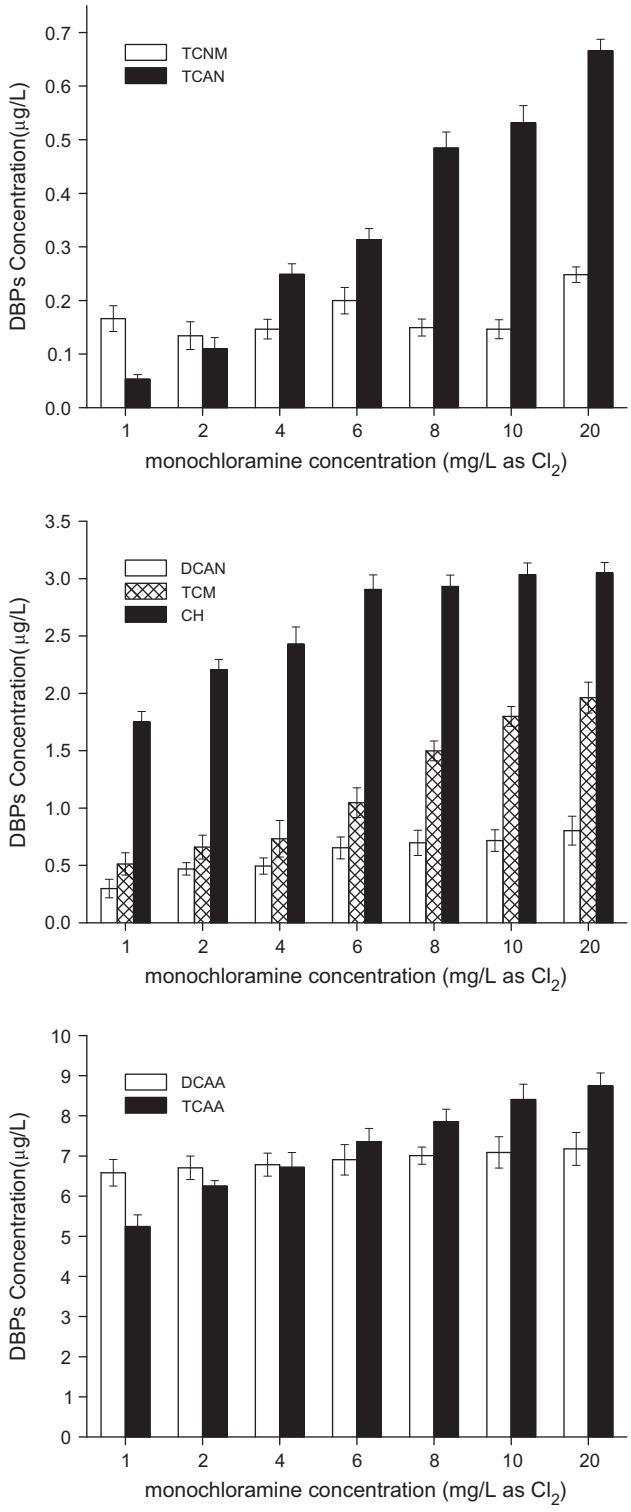

Fig. 1. Formation of DBPs as a function of the monochloramine concentration after 48 h chloramination of chironomid larvae metabolite solution (2 mg/L as TOC) at pH 7.5 and a temperature of 20 ± 1℃. The error bars represent the standard deviation of replicate measurements ($n = 2$).

3. Results and discussion

3.1. Effect of the monochloramine concentration

Fig. 1 shows the formation of DBPs upon treatment with different concentrations of monochloramine at pH 7.5. Among the tested DBPs, the concentrations of dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were highest, and the other low DPBs of TCAN and TCNM were present in low concentrations. The concentrations of most DBPs, except CH and TCNM, monotonically increased as monochloramine concentration increased. DCAN accumulation could be attributed to its stable chemical structure in monochloramine solutions [2]. And as to the relatively stable CH [6], the concentration increased significantly from 1 to 6 mg/L and then remained almost unchanged with an increase in the monochloramine dosage. It means that CH precursors reacted with disinfectant completely at the certain higher dosage of oxidative chemical. The TCNM concentration was just at the level of 0.18 μg/L, and there was no obvious trend with an increase in monochloramine dosage, which indicates that the reaction to form TCNM is mainly controlled by the quantities of the precursors and not by the monochloramine dosage. In addition, there is competition between the hydrophobic organic and transition compounds in the chironomid larvae metabolite solution and the precursors of TCNM during disinfection, resulting in the production of other DBPs such as THMs and HAAs instead of TCNM [16].

3.2. Effect of reaction time

Fig. 2 shows the time dependence of the formation of DBPs after the monochloramination of chironomid larvae metabolite dissolution, with residual chlorine remaining at the end of the each test. The TCNM and TCAN concentrations were relatively low (namely, 0.2396, 0.7022 μg/L at 72 h, respectively), whereas the those of DCAA and TCAA were highest among the tested DBPs (namely, 7.9301 and 9.4273 μg/L at 72 h, respectively). In addition to TCNM, all other DBPs monotonically accumulated with the extension of time. In viewpoint of the formation rates, trichloromethane (TCM) accumulated significantly at 48 h and over 90% CH generated within 24 h, and DCAN concentration grew relatively slow in former 24 h but rapidly climbed up after 24 h. While the concentration of DCAA and TCAA increased steadily and that of TCNM changed only slightly (approximately 0.20 μg/L). THMs, HAAs, and CH were all stable products [6], so their

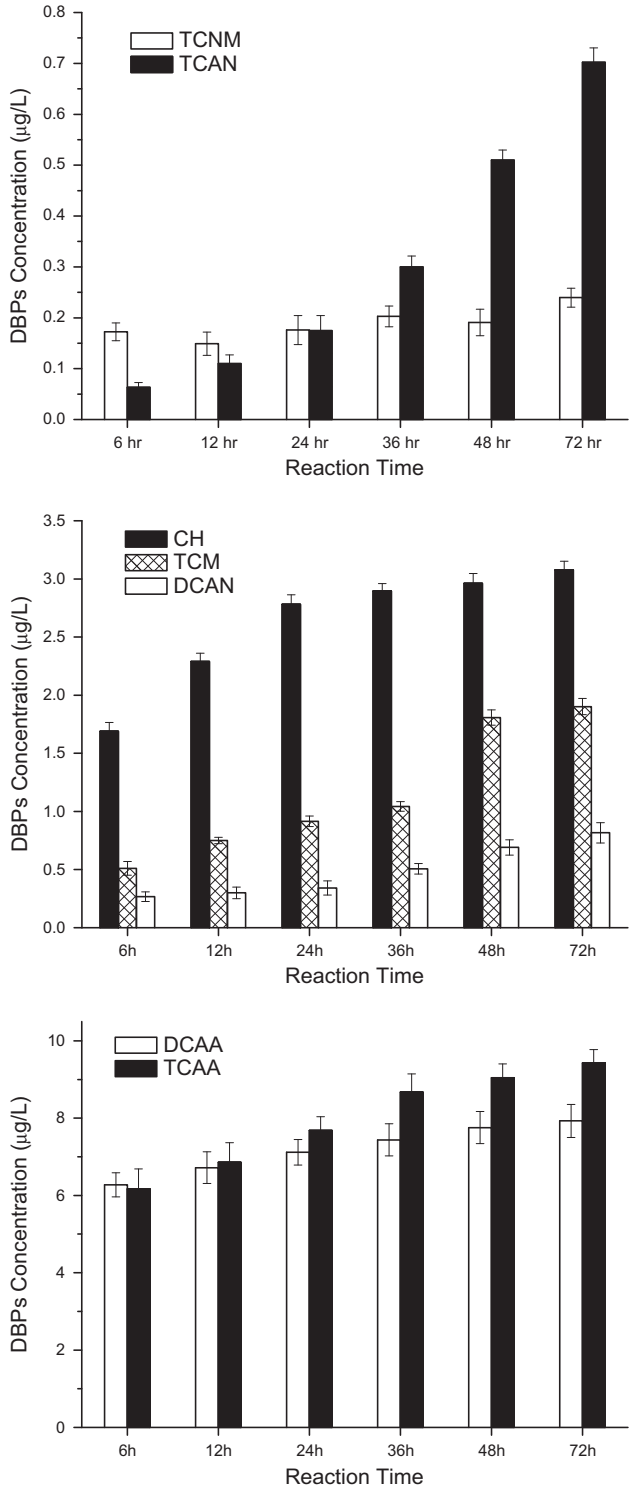

Fig. 2. Time-dependent formation of DBPs from the monochloramination of chironomid larvae metabolite solution (2 mg/L as TOC) at pH 7.5: monochloramine concentration: 10 mg/L (as Cl_2), temperature: 20 ± 1°C. The error bars represent the standard deviation of replicate measurements ($n = 2$).

concentrations increased with reaction time. DCAN concentration was observed to be increasing which could be due to the stability of DCAN in monochloramine solutions [2].

3.3. Effect of pH

Fig. 3 shows the concentrations of DBPs after 48 h treatment with monochloramine at 10 mg/L under different pH values. The TCM concentration increased with pH ranging from 5 to 8 and then decreased as the pH elevated to 10. The formation of DCAN increased with pH from 5 to 7, but the DCAN levels significantly decreased at a pH of 8 and then remained stable. It therefore deduced that pH played a role in the speciation of chloramines, monochloramine hydrolysis, and the stability of DCAN, during the monochloramination. Yang et al. [2] showed monochloramine was the dominant chloramine at pH 7.5 or above, and $NHCl_2$ was dominant chloramine at pH 5 or below, in which no chloroform was found and concentrations of DCAN were lower with $NHCl_2$ additions than that with NH_2Cl. Hydrolysis of monochloramine to form free chlorine was also affected by pH [17], and the hydrolysis rate was slow when pH ranges from 7.5 to 9. It therefore supplied the explanation for the lower TCM concentration at pH 9. On the other hand, pH affected the stability of unstable DBPs. DCAN underwent a base-catalyzed decomposition process [18]. The hydrolysis rates of unstable DBPs increased with pH increasing [12], and it made DCAN concentration much lower at high pH. That is to say that the maximum yield of TCM and DCAN came at pH 7–8. The rate of formation of TCNM also increased

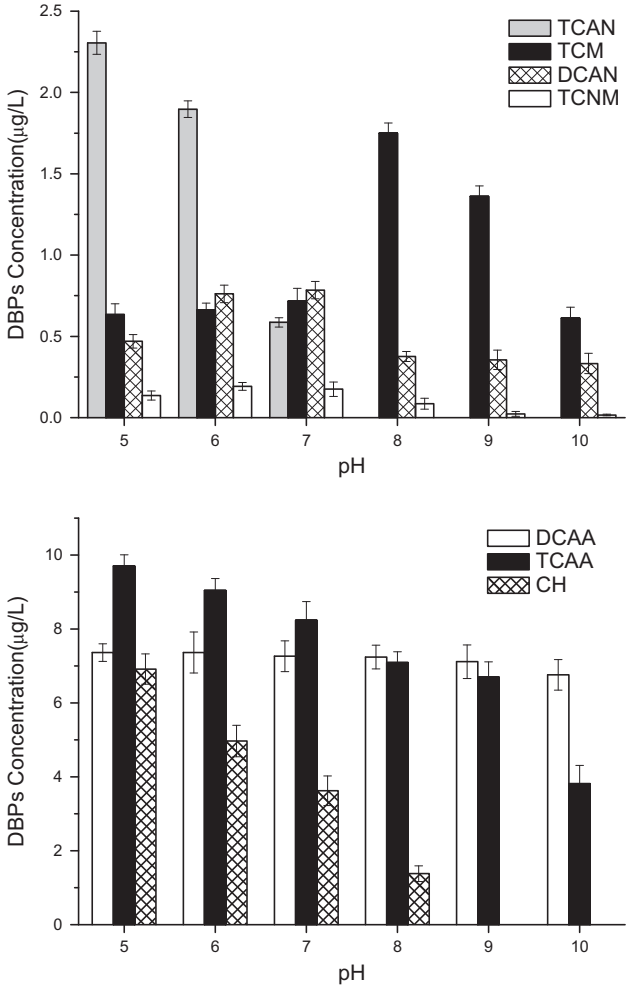

Fig. 3. The concentrations of DBPs and monochloramine using premixed monochloramine at 10 mg/L of Cl_2 in TOC solutions (2 mg/L) at different pH values after 48 h at 20 ± 1 °C.

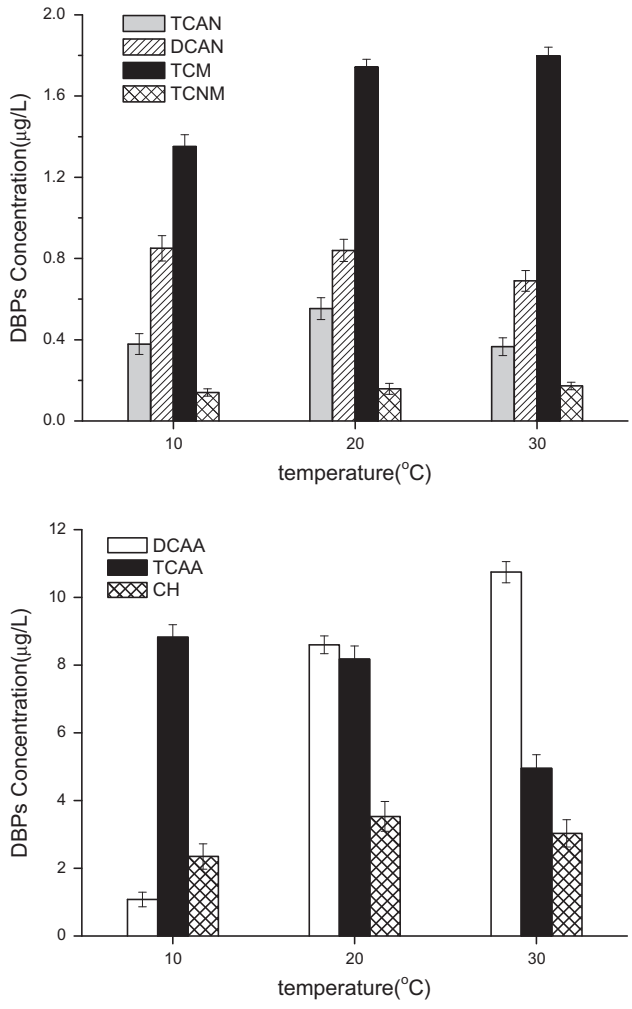

Fig. 4. DBP formation over 48 h due to chloramination as a function of temperature (adding 10 mg/L preformed monochloramine) of 2 mg/L TOC solutions at pH 7.5.

slightly with pH from 5 to 6 but varied significantly with pH from 7 to 10, with the maximum yields occurring at pH 6. The levels of other DBPs, such as TCAA, CH, and TCAN, decreased significantly with pH elevation after two days. TCAN concentrations were below the detection limits of 0.002 μgl/L at pH 8 and above. At pH 9 and above, CH was not detected (the detection limits was 0.005 μgl/L). The DCAA concentrations decreased slightly with increasing pH. These phenomena are consistent with the stabilities of these chloramines. Because monochloramine is more stable at high pH values, the reaction between monochloramine and DBPs precursors was slow; therefore, a smaller amount of DBPs was generated.

3.4. Effect of temperature

Fig. 4 shows the results of DBP formation after 48 h of monochloramination at three designated temperatures of 10, 20, and 30 ℃. The formation rates of TCM, DCAA, and TCNM increased with temperature increasing from 10 to 30 ℃, while the DCAN and TCAA changed in an opposite way; the concentrations of TCAN and CH were highest at 20 ℃. Generally speaking, at the conditions of same reaction time and enough disinfectant dosage, the higher temperature, the greater formation reactivity, so it led to the higher DBPs concentrations. Stable DBPs such as TCM generally followed this trend. However, temperature affects not only the formation rate but also the decomposition rate, therefore, the concentrations of DBPs at different temperatures was depended on the balance of the DBP formation rate and the decomposition rate. As shown in Fig. 4, the DCAA concentration increased but that of TCAA decreased on the contrary. Indeed, DCAA was the precursor of TCAA, the concentration of TCAA decreased because of the increase in DCAA concentration.

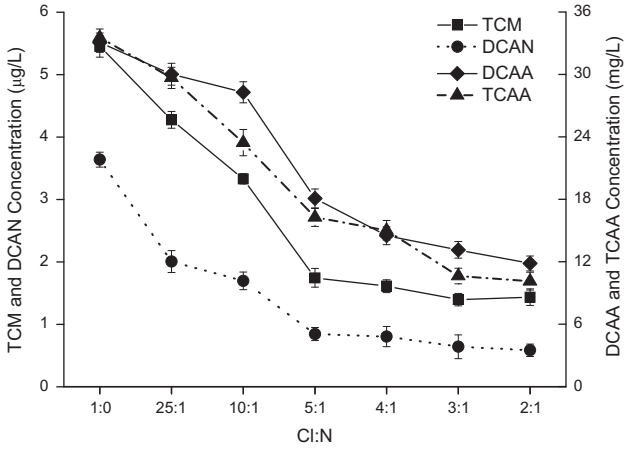

Fig. 5. Formation of DBPs as a function of the Cl/N ratio after the 2-day chloramination of chironomid larvae metabolite solution (2 mg/L as TOC) at pH 7.5 using a chlorine concentration of 10 mg/L at 20 ± 1 ℃. The error bars represent the standard deviation of replicate measurements ($n = 2$).

3.5. Effect of the Cl/N ratio

Fig. 5 shows the results from the formation of four typical DBPs after 48 h of chloramination under baseline conditions with varied Cl/N mass ratios of 1/0, 25/1, 10/1, 5/1, 4/1, 3/1, and 2/1. The concentrations of these four DBPs decreased as the mass ratio of Cl/N decreased. When the Cl/N ratio dropped to 5/1 or below, the TCM concentration remained almost unchanged. The larger quantity of HAAs formed at an initial Cl/N ratio of 5/1, and it was partially attributable to a higher free chlorine concentration at a higher Cl/N ratio [1], this follows breakpoint chlorination principle. The conversion of free chlorine into monochloramine decreased the formation rates of most DBPs, and the result is in agreement with the data reported by Zhang et al. [19].

4. Conclusions

Chironomid larvae metabolite solution could provide DBPs precursor during monochloramine disinfection, and then they would affect water quality and safety. The key findings from the present research are listed as below:

Most DBPs concentrations accumulated with reaction time extension and monochloramine dosage increase. CH formation initially increased and then remained stable. The concentrations of DCAA and TCAA were highest among all the DBPs (6–10 μg/L), and this should be given more attention.

The pH and temperature affected the formation of DBPs in the different mode. The formation rates of DCAA, TCAA, CH, and TCAN were faster at lower pH, but TCM, DCAN, and TCNM exhibited maximum concentrations at pH values between 6 and 8. Higher temperature enhanced TCM, DCAA, and TCNM formation but weakened TCAA and DCAN formation under our testing conditions. The CH and TCAN concentrations increased from 10 to 20 ℃ and then decreased from 20 to 30 ℃.

When the Cl/N mass ratio decreased, four common DBPs showed declining concentrations. This indicated that lower Cl/N mass ratio was benefit to control the amount of the four DBPs during monochloramination of chironomid larvae metabolite solution.

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References

[1] Y.N. Qi, C. Shang, I.M.C. Lo, Formation of haloacetic acids during monochloramination, Water Res. 38 (2004) 2375–2383.
[2] X. Yang, C. Shang, P. Westerhoffb, Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination, Water Res. 41 (2007) 1193–1200.
[3] C.M.M. Bougeard, E.H. Goslan, B. Jefferson, S.A. Parsons, Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine, Water Res. 44 (2010) 729–740.
[4] J.D. Plummer, J.K. Edzwald, Effect of ozone on algae as precursors for trihalomethane and haloacetic acid production, Environ. Sci. Technol. 35 (2001) 3661–3668.
[5] Q. Zhang, X.B. Yang, D.C. Zhou, Disinfection byproduct formation by bacterial cell materials during chlorination, Acta Scientiae Circumstantiae 30 (2010) 314–320.
[6] J.Y. Fang, J. Ma, X. Yang, C. Shang, Formation of carbonaceous and nitrogenous disinfection by-products from the chlorination of *Microcystis aeruginosa*, Water Res. 44 (2010) 1934–1940.
[7] M.K. Alexander, New strategies for the control of the parthenogenetic chironomed, J. Am. Mosq. Control Assoc. 13 (1997) 189–192.
[8] J.H.M. Van Lieverloo, D.W. Bosboom, G.L. Bakker, A.J. Brouwer, R. Voogt, J.E.M. De Roos, Sampling and quantifying invertebrates form drinking water distribution mains, Water Res. 38 (2004) 1101–1112.
[9] X.B. Sun, F.Y. Cui, J.S. Zhang, F. Xu, L.J. Liu, Inactivation of chironomid larvae with chlorine dioxide, J. Hazard. Mater. 142 (2007) 348–353.
[10] F.Y. Cui, D. An, X.B. Sun, J.S. Zhang, L.J. Liu, Y.Q. Chen, L.S. Yao, The reproduction rule and control of chironomus larva in water bodies, Tech. Equip. Environ. Pollut. Control 5 (2004) 1–4.
[11] Z.Z. Jiao, Z.L. Chen, J. Chen, L.J. Liu, W.Q. Lu, G.B. Li, Control of disinfection by-products in drinking water by monochloramine disinfectant, J. Harbin Inst. Technol. 37 (2005) 1486–1495.
[12] Y.F. Xie, Disinfection by products in drinking water: Formation, analysis and control, Recherche 67 (2003) 2–3.
[13] American Public Health Association, American Water Works Association and Water Environment Federation, Standard Methods. In: A.E. Greenberg, L.S. Clesceri, A.D. Eaton (Eds.), Standard Methods for the Examination of Water and Wastewater, twentieth ed., American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, 1998.
[14] J.W. Much, D.P. Hautman, U.S.EPA Method 551.1. Determination of Chlorination Disinfection by Products, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection (Revision 1.0). Office of Research and Development, Washington, DC, 1995.
[15] M.M. Domino, B.V. Pepich, D.J. Munch, P.S. Fair, Y. Xie, U.S. EPA Method 552.3. Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid–liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection (Revision 1.0). Office of Ground Water and Drinking Water, Cincinnati, OH, 2003.
[16] J.F. Lu, Y. Zhang, Y.F. Liu, L.X. Fu, X.Y. Guo, Q.S. Wang, The research of HNMs nitrogenous disinfection by-products formation and control, Technol. Water Treat. 36 (2010) 5–9.
[17] R.L. Jolley, J.H. Carpenter, A review of the chemistry and environmental fate of reactive oxidant species in chlorinated water, In: R.L. Jolley, J.H. Carpenter (Eds.), Water Chlorination: Chemistry, Environmental Impact and Health Effects, vol. 4, Ann Arbor Science, Ann Arbor, 1983, pp. 3–47.
[18] X. Yang, C. Shang, P. Westerhoff, Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination, Water Res. 41 (2007) 1193–1200.
[19] X.R. Zhang, S. Echigo, R.A. Minear, M.J. Plewa, Characterization and comparison of disinfection by-products of four major disinfectants, ACS Symp. Ser. 761 (2000) 229–314.