Factors affecting formation of disinfection by-products during chlorination of Cyclops

Xing-bin Sun, Lei Sun, Ying Lu and Yi-feng Jiang

ABSTRACT

Effects of reaction time, chlorine dosages, pH, temperature and ammonia concentrations on the formation of disinfection by-products (DBPs), including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), chloral hydrate (CH), and chloropicrin (TCNM), were investigated during the chlorination of Cyclops metabolite solutions containing 4 mg/L (as total organic carbon). Increased reaction time, chlorine dosage, and temperature improved the formation of the relatively stable DBPs, such as trichloromethane (TCM), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and CH. Formation of nitrogenous DBPs (N-DBPs), including dichloroacetonitrile (DCAN) and TCNM, followed an increasing and then decreasing pattern with prolonged reaction time and increased chlorine dosages, and 1,1,1-2-trichloropropanone (1,1,1-TCP) decreased continuously with increasing reaction time. The amounts of N-DBPs and HKs decreased with increasing temperature. pH affected DBP formation differently, with TCM increasing, DCAA, TCAA, DCAN, and 1,1,1-TCP decreasing, and other DBPs having maximum concentrations at pH 6–7. The formation of most DBPs can be suppressed with increasing ammonia concentration. TCM, CH, TCNM, and 1,1,1-TCP concentrations were always low under all conditions at the level of 0.02–2.39 μg/L.

Key words | chlorination, Cyclops, disinfection by-products

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INTRODUCTION

Cyclops of zooplankton excessively propagates in water due to the eutrophication caused by water pollution, especially, in recent years, in reservoirs and fresh lakes which are a source for drinking water. Cyclops causes problems in drinking water treatment, such as clogging filters and easily penetrating sand filters. Cyclops also causes water quality problems in the water supply, as it may transmit disease as the host of pathogenic parasites, such as schistosome and eelworm, to threaten human health (Cui *et al.* 2002; Lin *et al.* 2007).

Chlorination remains the predominant disinfection means due to its broad-spectrum germicidal potency, low cost, and well-established practices. However, when water or wastewater is chlorinated, chlorine reacts readily with a wide variety of organics to form disinfection by-products (DBPs). DBPs detected in drinking water belong to the categories trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs) chloropicrin (TCNM), and chloral hydrate (CH), as described in a large number of reports (Nikolaou *et al.* 2000; Yang *et al.* 2007; Fang *et al.* 2010). These compounds are of great scientific interest due to the adverse health effects they may have on humans. These DBPs have been identified as cancer-causing reagents in the last three decades. Toxicology studies have shown that some of the HAAs (e.g., dichloroacetic acid (DCAA), BCAA, and trichloroacetic acid (TCAA)) are carcinogenic in laboratory animals (Li 2007). Also, recent studies have suggested links between adverse reproductive outcomes and exposure to DBPs during pregnancy (Yao 2009).

Many factors have been extensively studied and reported to affect the formation of DBPs during disinfection; these factors include the reaction time, pH, temperature, disinfectant concentration, and precursor properties. The formation of stable THMs and HAAs was increased with increasing reaction time and chlorine dosage (Fang *et al.*

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2010). However, increasing reaction time and chlorine dosage has little effect on the formation of unstable DBPs, such as HANs and HKs. Higher pH reduced HAAs, dichloroacetonitrile (DCAN), and 1,1,1-trichloropropanone (1,1,1-TCP) formation but increased the formation of THMs (Reckhow *et al.* 2001; Yang *et al.* 2007).

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. Examples of NOM include humic acid and fulvic acid. Most research on DBPs is based on NOM-containing natural bodies of water. Yang *et al.* (2007) and Bougeard *et al.* (2010) used Suwannee River water and water from England and Wales, respectively, as experimental water to research DBPs. More and more studies have discovered that humic acid and organic matter are not the only sources of DBP precursors; algae cells and their extracellular organic matter (EOM) and certain bacteria can also be precursors of DBPs (Plummer & Edzwald 2001; Zhang *et al.* 2009). Algal cells are known to be enriched in organic nitrogen in the form of proteins, amino acids, and amines, and have established the formation of carbonaceous and nitrogenous DBPs (N-DBPs) from chlorination (Fang *et al.* 2010). It has been reported that THMs, HANs, and CH formation were detected after chlorination of the five kinds of common bacteria cultures, and a great impact on the formation of HANs was bromide (Zhang *et al.* 2010). Compared to algae, bacteria, and other microorganisms, Cyclops are large in size and quantity, which therefore suggests the contained biomass of amino acids, protein, fat, and other organic matter have a higher potential to form the DBPs (Liu & Fu 2010). Thus, it is interesting to find out how the metabolites produced by these organisms affect water safety and contribute to the production of DBPs.

Consistent efforts have been made to determine the identities and toxicities of various DBP species and their groups, especially those of THMs, HAAs, and HANs, and to model their formation and control their occurrence, but information about their relationship with chlorination of Cyclops metabolite solutions is unknown. The objectives of this research are to evaluate the formation of selected DBPs during chlorination of Cyclops metabolite solutions under various conditions, including reaction time, chlorine dosage, pH, temperature, and ammonia concentrations. Cyclops metabolite solution concentrations were measured as total organic carbon (TOC).

MATERIALS AND METHODS

Reagents and solutions

All chemical solutions were prepared from reagent grade chemicals or stock solutions. Methanol, acetone, and methyl-tert-butyl ether (MTBE) were all HPLC (high-performance liquid chromatography) grade. A free chlorine (HOCl) stock solution (2,500 mg/L as Cl_2) was prepared from a 4% sodium hypochlorite (NaOCl) solution and periodically standardized by N,N-diethyl-p-phenylenediamine and ferrous ammonium sulfate (DPD/FAS) titration, DPD/FAS titration method is from Part 4000 Inorganic Nonmetallic Constituents in *Standard Methods* (Standard Methods 1998). The disinfectant solutions were stored at 4 °C and brought to room temperature before use. The stock disinfectant solutions were standardized by DPD/FAS titration again before the test. 0.2 mol/L phosphate buffers at pH 5, 6, 7, 8, 9, and 10 were prepared with 0.2 mol/L NaH_2PO_4 and 0.2 mol/L Na_2HPO_4. Stock solutions of ammonia were prepared with analytical grade NH_4Cl and deionized water. Standard samples for THMs, HAAs, HANs, HKs, CH, and TCNM analyses were obtained from Supelco.

Sample preparations

Cyclops was initially collected from the vicinity of Mopanshan reservoir in Harbin, which is an important drinking water source for Harbin's population. Cyclops was cultured in aerated 25-L glass aquaria filled with raw water from the reservoir. Aquaria were kept at a constant temperature (15 °C) and exposed to a consistent photoperiod (12 h light/12 h dark). Cyclops was cultured for 10 days under this condition. Large numbers of Cyclops were added in a 1-L beaker with deionized water. After 1 day, Cyclops suspensions were filtered by a 0.45-μm membrane to eliminate suspended solids and stored in the dark at 4 °C, in order to minimize changes in the constituents, and then analyzed within a week. The TOC concentration was measured. Standards were prepared by diluting reagents to 4 mg/L.

Analytical methods

Available chlorine was measured by DPD/FAS titration (Standard Methods 4500-Cl 1998). Analyses of THMs, HAAs, HANs, HKs, CH, and TCNM were carried out on a gas chromatograph (GC) (Agilent 7890) with an electron capture detector (ECD), based on USEPA methods 551.1 (USEPA 1995) and 552.3 (USEPA 2003). The THMs, HANs, HKs, CH, and TCNM concentrations were measured by liquid–liquid extraction procedure by MTBE and acid methanol according to USEPA Method 551.1 (USEPA 1995). 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 GC-ECD operating conditions were: detector, 290 °C; injector, 200 °C; injection volume, 1 mL; and temperature program, 35 °C for 5 min, ramped to 75 °C at 10 °C/min, held for 5 min, then ramped to 100 °C at 10 °C/min, and then held for 2 min. For DCAA and TCAA analysis, the samples were pretreated with extraction/derivatization procedure by MTBE and acid methanol according to USEPA Method 552.3 (USEPA 2003). 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 programs for compounds other than HAA_9 were: injector of 200 °C; ECD of 290 °C; oven of an initial temperature of 35 °C for 9 min, ramping to 40 °C at 2 °C/min and holding for 8 min, ramping to 80 °C at 20 °C/min, ramping to 160 °C at 40 °C/min and holding for 4 min. Those for HAAs were: injector of 210 °C; ECD of 290 °C; oven of an initial temperature of 30 °C for 20 min, ramping to 40 °C at 1 °C/min, ramping to 205 °C at 20 °C/min and holding for 4 min.

Experimental procedures

The stock solution with Cyclops metabolite solutions was diluted with deionized water to make testing solutions of 4 mg/L as TOC. A chlorine dosage of 20 mg-Cl_2/L was applied to Cyclops metabolite solutions (4 mg/L as TOC) buffered at pH 7.0 with deionized water in 250-mL glass bottles and incubated at 20 ± 1 °C after 48 h as the baseline condition. The influencing factors of chlorination are reaction time, chlorine dose, pH, temperature, and ammonia concentration in this research; each of the factors was varied one parameter at a time from the baseline condition: reaction time (1, 2, 4, 6, 12, 24, 36, 48, 72 h), chlorine dosages (1, 2, 4, 6, 8, 10, 20 mg-Cl_2/L), pH (5, 6, 7, 8, 9, 10), temperature (10, 20, 30 °C), ammonia concentration (0, 2, 4, 8, 16, 20, 32 mg/L as NH_4^+). After the reaction of chlorination, solutions were quenched with sodium sulfite and extracted for subsequent DBP analyses. For comparison, a study using deionized water was also conducted in the same manner under the baseline condition, and in the following experimental results that blank value, which is an unintentional carry-over of culture media to the chlorination experiments, has been subtracted. The DBPs detected in the present study originated from the Cyclops metabolite solutions.

RESULTS AND DISCUSSION

Effect of reaction time

Figure 1 shows the results of time-dependent formation of DBPs after chlorination of Cyclops metabolite solutions. There were free chlorine residuals in all the tested times (not shown). DCAA and TCAA concentrations were highest among the tested DBPs, followed by DCAN and 1,1-DCP. The concentrations of trichloromethane (TCM), CH, TCNM, and 1,1,1-TCP were low and at the level of several μg/L. The yields of TCM, DCAA, TCAA, CH, and 1,1-DCP increased with increasing time. DCAN and TCNM reached a maximum after 36 and 6 h, respectively, and then decreased with increasing reaction time, and 1,1,1-TCP decreased continuously with increasing reaction time. THMs and HAAs were stable in the presence of chlorine and they were the final product (Fang *et al*. 2010), so the concentrations of TCM, DCAA, and TCAA increased with reaction time when the chlorine residual was available. CH is relatively stable at pH 7.0 and as a result its concentration also increased with increasing reaction time. It has been reported that some volatile by-products, such as HKs, can decompose due to hydrolysis and reactions with residual chlorine (Nikolaou *et al*. 2000), and 1,1,1-TCP can be hydrolyzed to TCAA and TCM (Fang *et al*. 2010), therefore, 1,1,1-TCP decreased with increasing reaction time. The yields of N-DBPs, including DCAN and TCNM, can

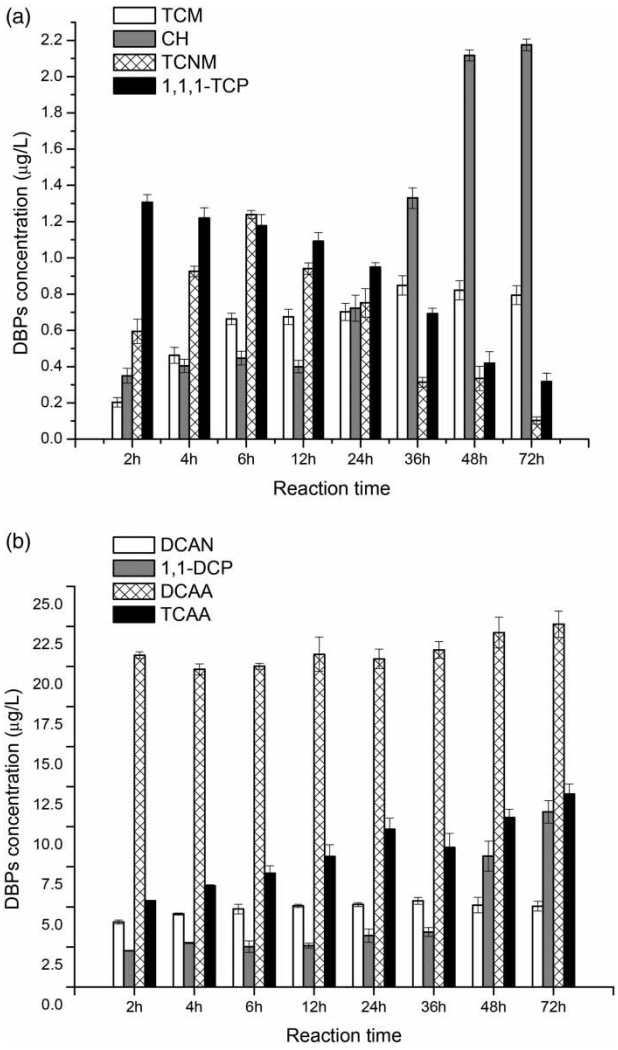

Figure 1 | Time-dependent formation of DBPs from chlorination of Cyclops metabolite solutions (4 mg/L as TOC) at pH 7.0, chlorine dosage 20 mg-Cl_2/L, temperature 20 ± 2 °C. The error bars represent the standard deviation of replicate measurements ($n = 2$).

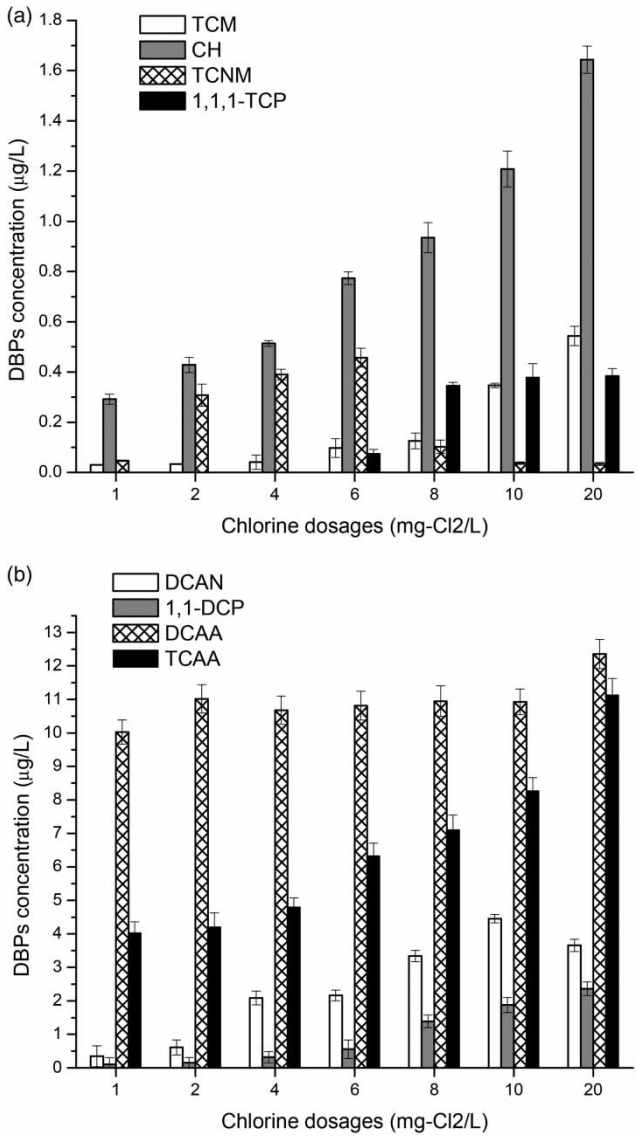

Figure 2 | Formation of DBPs as functions of chlorine dosage after 2 days' chlorination of Cyclops metabolite solutions (4 mg/L as TOC) at pH 7.0, temperature 20 ± 2 °C. The error bars represent the standard deviation of replicate measurements ($n = 2$).

be explained by their hydrolysis and oxidation by chlorine after a period of time, and the presence of chlorine increased the hydrolysis rates of DCAN (Yang *et al.* 2007).

Effect of chlorine dosage

Figure 2 shows formation of DBPs after 2 days' chlorination of Cyclops metabolite solutions with different chlorine dosages buffered at pH 7. Most DBPs, except for TCNM and DCAN, monotonically increased with increasing chlorine dosages. The amounts of TCNM and DCAN first increased and then decreased with increasing chlorine dosage. Generally, when the chlorine dosage is lower, the reaction of chlorine consumption after a period of time during the reaction is not enough to provide chlorine. 1,1,1-TCP was not detected when the chlorine dosage was below 6 mg-Cl_2/L, and the concentrations were quite low and at the level of 0.07–0.38 μg/L. The yields of unstable DBPs depend on their formation and decomposition rates. DCAN is decomposed faster by oxidation or hydrolyzation than is

its formation at chlorine dosages larger than 10.2 mg-Cl_2/L (Fang *et al.* 2010). The same applies to TCNM, which is decomposed faster at 6 mg-Cl_2/L.

Effect of pH

Figure 3 shows the concentrations of DBPs after 2 days' chlorination of Cyclops metabolite solutions at various pH from 5 to 10. Formation of TCM increased with increasing pH value. The amount of DCAA, TCAA, 1,1,1-TCP, and DCAN decreased continuously with increasing pH from 5 to 10. The formation of CH, TCNM, and 1,1-DCP varied significantly with pH from 4 to 10 and the maximum yields of these DBPs occurred at pH 6–7. When pH was greater than 7.6, the dominant species of chlorine shifted from halogenating agent, hypochlorous acid (HOCl) to hypochlorite (OCl^-), of which, sterilization ability is poor (Chen *et al.* 2001); therefore a change in chlorine species retards DBP formation. The pH also affects the stability of unstable DBPs. DCAN, 1,1-DCP, 1,1,1-TCP, and CH can hydrolysis decomposition at alkaline pH (Yang *et al.* 2007), and the hydrolysis rates of these unstable DBPs increases with increasing pH (Xie 2004). In addition, 1,1-DCP can be oxidized to 1,1,1-TCP, and TCM is the common product from hydrolysis of 1,1,1-TCP, CH, and TCAA (Zhang & Minear 2002; Xie 2004; Yang *et al.* 2007), so only the concentrations of TCM increased with increasing pH, and those of the others decreased in the basic range.

Effect of temperature

Figure 4 shows the results of formation of DBPs after 2 days' chlorination of Cyclops metabolite solutions under the baseline conditions, at three different temperatures of 10, 20, and 30 °C. Formation of TCM, DCAA, and TCAA increased continuously with increasing temperature. The amounts of DCAN, 1,1-DCP, and 1,1,1-TCP decreased with increasing temperature from 10 to 30 °C. Concentrations of CH and TCNM showed maximum yields at 20 °C. At high temperature, the reaction rate with chlorine is enhanced, which results in an increase with relatively stable DBPs, like TCM, DCAA, and TCAA. However, increasing the temperature also enhances the decomposition rates of DCAN (Nikolaou *et al.* 2000). Therefore, the concentrations of these unstable

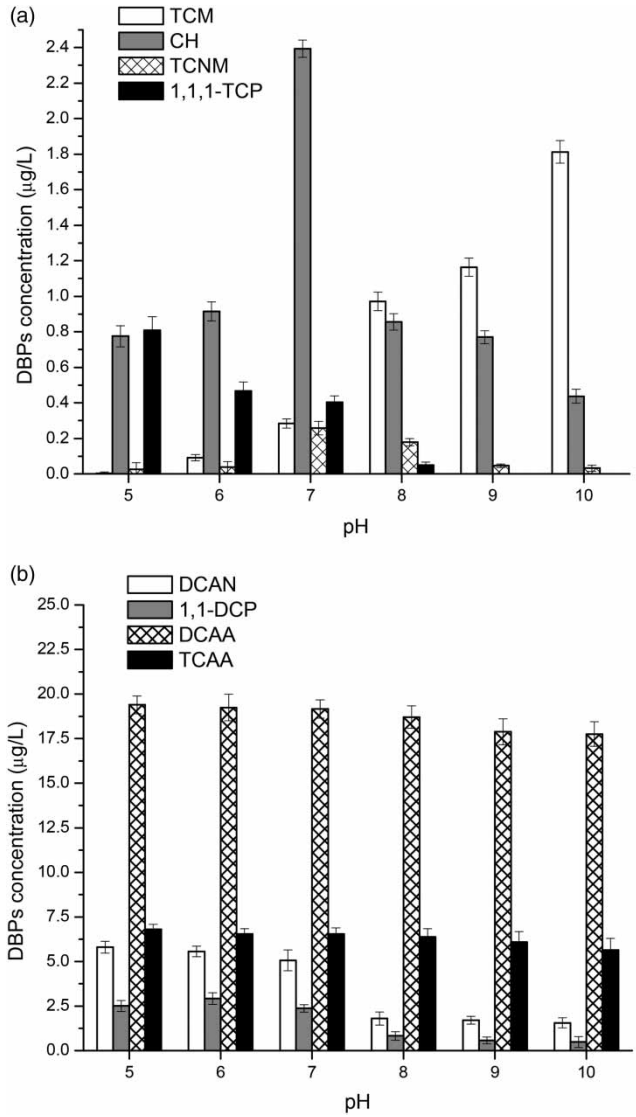

Figure 3 | Formation of DBPs as functions of pH after 2 days' chlorination of Cyclops metabolite solutions (4 mg/L as TOC), chlorine dosage 20 mg-Cl_2/L, temperature 20 ± 2 °C. The error bars represent the standard deviation of replicate measurements ($n = 2$).

DBPs at different temperatures were dependent on the balance of their formation rates and decomposition rates.

Effect of ammonia

Figure 5 shows the results of DBP formation after 2 days' chlorination of Cyclops metabolite solutions under baseline conditions with varied ammonia concentrations (0, 2, 4, 8, 16, 20, and 32 mg/L as NH_4^+). Concentrations of ammonia

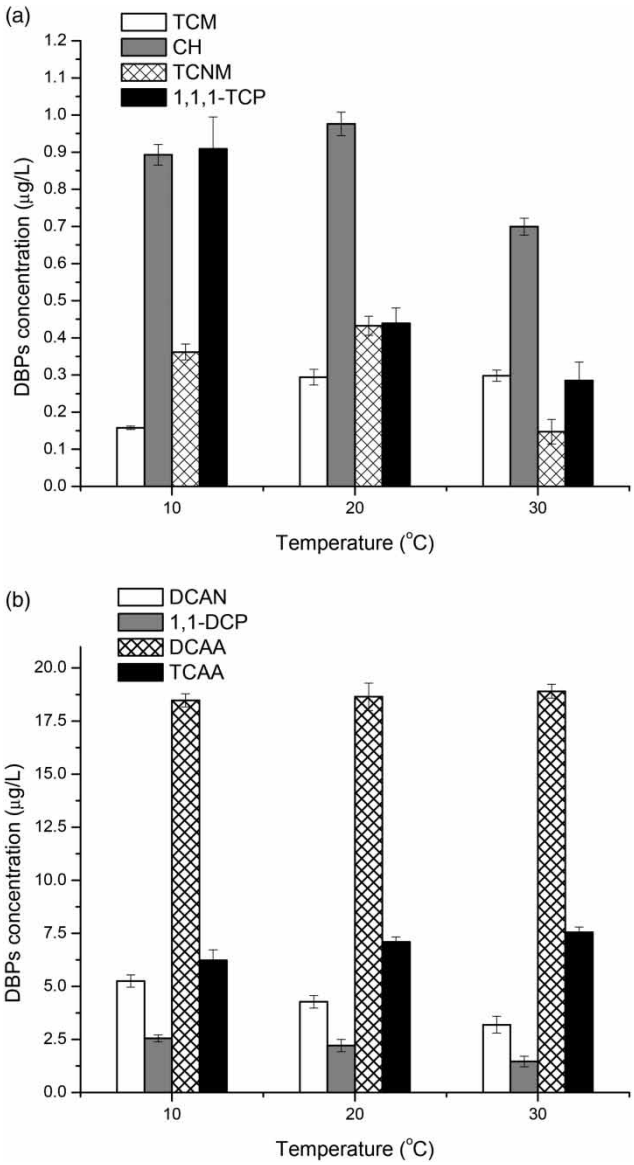

Figure 4 | Formation of DBPs as functions of temperature after 2 days' chlorination of Cyclops metabolite solutions (4 mg/L as TOC) at pH 7.0, chlorine dosage 20 mg-Cl_2/L. The error bars represent the standard deviation of replicate measurements ($n = 2$).

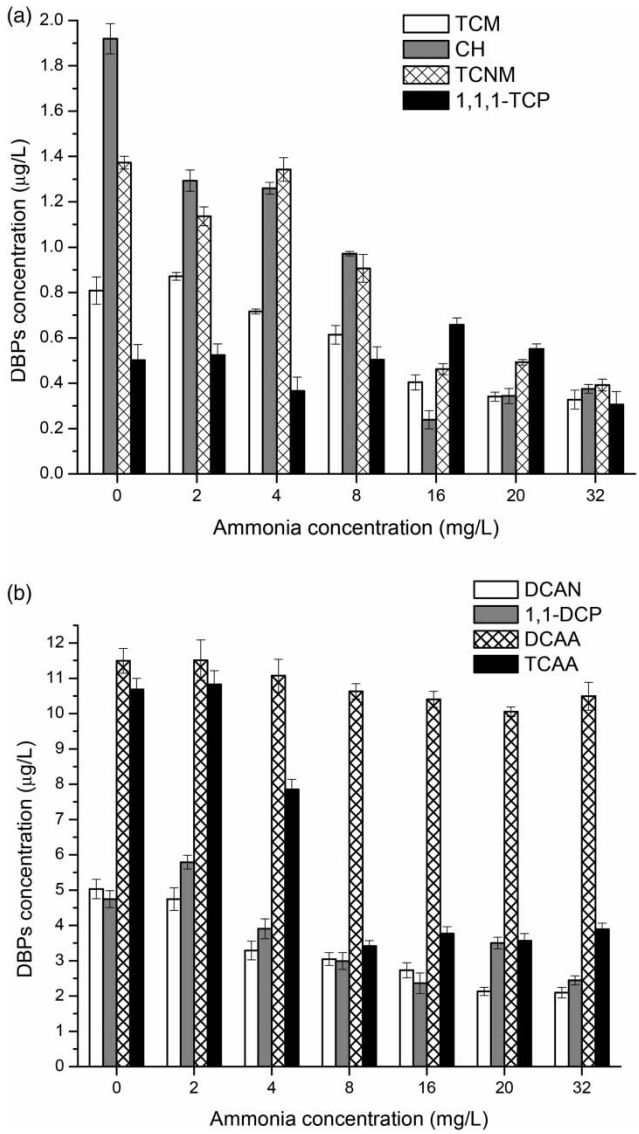

Figure 5 | Formation of DBPs as functions of ammonia after 2 days' chlorination of Cyclops metabolite solutions (4 mg/L as TOC) at pH 7.0, chlorine dosage 20 mg-Cl_2/L, temperature 20 ± 2 °C. The error bars represent the standard deviation of replicate measurements ($n = 2$).

were changed by adding NH_4Cl. This research shows the concentrations of DBPs decreased with increased ammonia concentrations. During chlorination, ammonia can quickly react with free chlorine and change to combined chlorine (Scully & Hartman 1996; Fayyad & Al-Sheikh 2001). Additionally, the reactivity of combined chlorines is much weaker than that of free chlorine, and the combined chlorines are more slow to form DBPs during the reaction with organic matter (Sun *et al*. 2009). It is possible that the transformation of free chlorine to chloramine by NH_4^+ in our study reduced the formation of DBPs.

CONCLUSIONS

The results of this study show that increased reaction time, chlorine dosage, and temperature improved the formation

of the relatively stable DBPs, like TCM, DCAA, TCAA, and CH. Formation of N-DBPs, including DCAN and TCNM, followed an increasing and then decreasing pattern with prolonged reaction time and increased chlorine dosages, and 1,1,1-TCP decreased continuously with increasing reaction time. The amounts of N-DBPs and HKs decreased with increasing temperature. pH affected DBP formation differently, with TCM increasing, DCAA, TCAA, DCAN, and 1,1,1-TCP decreasing, and CH, TCNM, and 1,1-DCP having maximum concentrations at pH 6–7. The formation of most DBPs can be suppressed with increasing ammonia concentration.

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