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CONTENTS

Aquatic environment

Atmospheric environment

Terrestrial environment

Environmental biology

Environmental health and toxicology

Environmental catalysis and materials

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Influencing factors of disinfection byproducts formation during chloramination of Cyclops metabolite solutions

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ABSTRACT

Effects of reaction time, chlorine dosage, pH and temperature on the formation of disinfection byproducts (DBPs), were investigated during the chloramination of Cyclops metabolite solutions. The results showed that some species of DBPs like trichloromethane (TCM), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) could accumulate to their respective stable values with a progressive elevation in reaction time and monochloramine concentration. And 1,1,1-2-trichloropropanone (1,1,1-TCP) content decreased correspondingly with a continuous increase of reaction time. The amounts of chloral hydrate (CH), chloropicrin (TCNM), 1,1,1-TCP and DCAA firstly increased and then decreased with increasing monochloramine doses. Higher temperature resulted in a decrease of CH, dichloroacetonitrile (DCAN), 1,1-dichloropropanone (1,1-DCP), 1,1,1-TCP, DCAA and TCAA concentration. pH affected the formation of the different DBPs distinctly. TCM accumulateded with the increase of pH under 9, and DCAA, TCAA, CH and 1,1-DCP decreased continuously with increasing pH from 5 to 10, and other DBPs had the maximum concentrations at pH 6–7.

Introduction

Cyclops of zooplankton excessively propagates in waters due to the eutrophication, especially in reservoirs and lakes for drinking water source in recent years. Cyclops overgrowth causes problems in drinking water treatment, such as clogging filters and easily penetrating sand filters. Cyclops also causes water quality problems in water supply, it may transmits disease as the host of pathogenic parasite, like schistosome and eelworm, to threaten human health (Cui et al., 2002; Lin et al., 2007).

Natural organic matter, defined as the complex matrix of naturally occurring organic materials present in natural waters, is usually considered to be a precursor of disinfection byproducts (DBPs) (Yang et al., 2007; Bougeard et al., 2010). Recent studies (Plummer and Edzwald, 2001; Zhang et al., 2009) otherwise revealed that, besides the humic acid and organic matter, certain bacteria and algae cells with their extracellular organic matter could also be the precursors of DBPs. Algal cells are known to be enriched in organic nitrogen in the forms of proteins, amino acids, and amines, and have established to the formation of carbonaceous and nitrogenous disinfection byproducts from the chlorination (Fang et al., 2010). It has been proved that trihalomethanes (THMs), haloacetonitriles (HANs) and chloral hydrate (CH) formation were detected after chlorination of the five kinds of bacteria cultures, and a great impact on the formation of HANs was bromide (Zhang et al., 2010). Compared to the algae, bacteria and other microorganisms, Cyclops is large in size, and it therefore suggests the contained biomass of amino acids, protein, fat and other organic matter, those all have a higher potential to form the DBPs (Liu and Fu, 2010). Therefore, it is interesting to find out how the metabolites produced by these organisms to affect the water safety and contribute to the production of DBPs.

Many factors have been extensively studied and reported to affect the formation of DBPs during disinfection, such as

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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., 2010). However, increasing in reaction time and chlorine dosage have little effect on the formation of unstable DBPs, such as HANs and haloketones (HKs). Higher pH led to an increase of THMs formation but a reduction of HAAs, dichloroacetonitrile (DCAN) and 1,1,1-trichloropropanone (1,1,1-TCP) (Reckhow et al., 2001; Yang et al., 2007).

Consistent efforts have been made to determine the identities and toxicities of various DBPs 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 chloramination of Cyclops metabolite solutions is unknown. The objective of this research is to evaluate the formation of selected DBPs during chloramination of Cyclops metabolite solutions under various conditions.

1 Materials and methods

1.1 Reagents and solutions

All chemical solutions were prepared from reagent grade chemicals or stock solutions. Methanol, acetone and methyl-tert-butyl ether were all HPLC grade. 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 and measured by DPD/FAS titration (APHA Standard Methods 4500-Cl). Phosphate buffers (0.2 mol/L) 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. Standard samples for THMs, HAAs, HANs, HKs, CH and chloropicrin (TCNM) analyses were obtained from Supelco.

1.2 Sample preparations

Cyclops, initially collected from the vicinity of Mopanshan reservoir in Harbin, and Mopanshan reservoir is an important drinking water sources for Harbin. Cyclops was cultured in an aerated 25 L glass aquaria filled with raw water from reservoir. Aquaria were kept at a constant temperature (15°C) and exposed to a consistent photoperiod (12 hr light/12 hr dark). Cyclops cultured for 10 days under this condition. Large numbers of Cyclops were added in a 1 L beaker with deionized water. Cyclops was removed after 24 hr, and Cyclops suspensions were filtered by a 0.45 μm membrane to eliminate suspended solids and stored in the dark at 4°C, to minimize changes in the constituents, and analyzed within one week. The total organic carbon (TOC) concentration was measured. Standards were prepared by diluting reagents to 4 mg/L.

1.3 Analytical methods

The chloramine concentration was measured by DPD/FAS titration (APHA Standard Methods 4500-Cl). 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) (US EPA, 1995, 2003). The THMs, HANs, HKs, CH and TCNM concentrations were measured by liquid-liquid extraction procedure by methyl tert-butyl ether and acid methanol according to US EPA Method 551.1. 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 methyl tert-butyl ether and acid methanol according to US EPA Method 552.3. 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; and 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.

1.4 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 monochloramine concentration of 10 mg/L was applied to Cyclops metabolite solutions buffered at pH 7.5 with deionized water in the 250 mL glass bottles, and incubated at 20 ± 1°C after 48 hr. Under the baseline conditions, the influencing factors of reaction time (2, 4, 6, 12, 24, 36, 48, 72 hr), monochloramine concentration (1, 2, 4, 6, 8, 10, 20 mg/L), pH (5, 6, 7, 8, 9, 10) and temperature (10°C, 20°C, 30°C) were investigated during the monochloramination of Cyclops metabolite solutions. After the reaction of monochloramination, solutions were quenched with sodium sulfite and extracted for subsequent DBPs analyses. For comparison, a study using deionized water was also conducted in the same manner under the baseline condition, and the following experimental results have been subtracted the blank. The DBPs detected in the present study were originated from the Cyclops metabolite solutions.

2 Results and discussion

2.1 Effect of reaction time

Figure 1 shows the effect of reaction time on formation of DBPs after chloramination of Cyclops metabolite solutions at pH 7.5. Cyclops metabolite solutions contain biomass of amino acids, protein, fat and other organic matter, it has been proved that those organic matter is the precursor of DBPs. Amino acids and protein are the precursor of N-DBPs (like HANs and TCNM) (Mitch and Schreiber, 2008). Aldehyde is the precursor of CH, it can produced during chlorination of amino acids and protein (Zhang et al., 2000). Therefore, chloramination of Cyclops metabolite solutions resulted in the formation of DBPs such as TCM, CH, TCNM, 1,1-DCP, 1,1,1-TCP, DCAN, DCAA and TCAA.

DCAA concentrations were the highest among the tested DBPs, followed by TCAA and 1,1-DCP. The concentrations of TCM, 1,1,1-TCP, CH, DCAN and TCNM were low and at the level of μg/L. In addition to 1,1,1-TCP, other DBPs all monotonically accumulated with the extension of time, but the progressiveness of increases of different DBPs was not the same. Over 90% of 1,1-DCP, DCAA and TCAA formed within 2 hr, compared to their formation on the next reaction, and the rate of formation of these DBPs increased slightly with reaction time from 2 to 36 hr. Formation of TCM, CH, DCAN and TCNM increased significantly with increasing reaction time. THMs, HAAs and CH were all stable products (Fang et al., 2010), so their concentrations increased with reaction time. DCAN accumulation in monochloramine solutions could be attributed to its stabe chemical structure (Yang et al., 2007). It has been reported that some volatile byproducts 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 TCM (Fang et al., 2010), therefore, 1,1,1-TCP decreased with increasing reaction time. 1,1-DCP was found to be very stable in the presence of monochloramine (Yang et al., 2007), therefore the concentration of 1,1-DCP changed slightly.

2.2 Effect of monochloramine concentration

Figure 2 shows the formation of DBPs after dosing with different concentrations of preformed monochloramine in solutions containing Cyclops buffered at pH 7.5. TCM, 1,1-DCP, DCAN and TCAA formation monotonously increased with higher monochloramine doses. 1,1-DCP was not detected when the monochloramine concentration below 10 mg/L. The amounts of CH, TCNM, 1,1,1-TCP and DCAA firstly increased and then decreased with increasing monochloramine doses. TCM is the common product from hydrolysis of 1,1,1-TCP and CH (Xie, 2004; Zhang and Minear, 2002). TCM formation increased with monochloramine doses, and 1,1,1-TCP, CH concentration decreased at higher monochloramine doses. Monochloramine contain nitrogen atoms in their molecular structures and may contribute to the formation of N-DBPs, including DCAN and TCNM (Yang et al., 2010). The trend of TCNM can be explained by their hydrolysis and oxidation when monochloramine concentration larger than 6 mg/L.

2.3 Effect of pH

Figure 3 shows the concentrations of DBPs 48 hr after dosing with preformed monochloramine at 10 mg/L as Cl_2 in Cyclops metabolite solutions at different pH. The TCM concentration increased with pH ranging from 5 to 9 and then decreased as the pH elevated to 10. The amount of CH, 1,1-DCP, DCAA and TCAA decreased continuously with increasing pH from 5 to 10. The formation of 1,1,1-TCP, TCNM and DCAN varied significantly with pH from

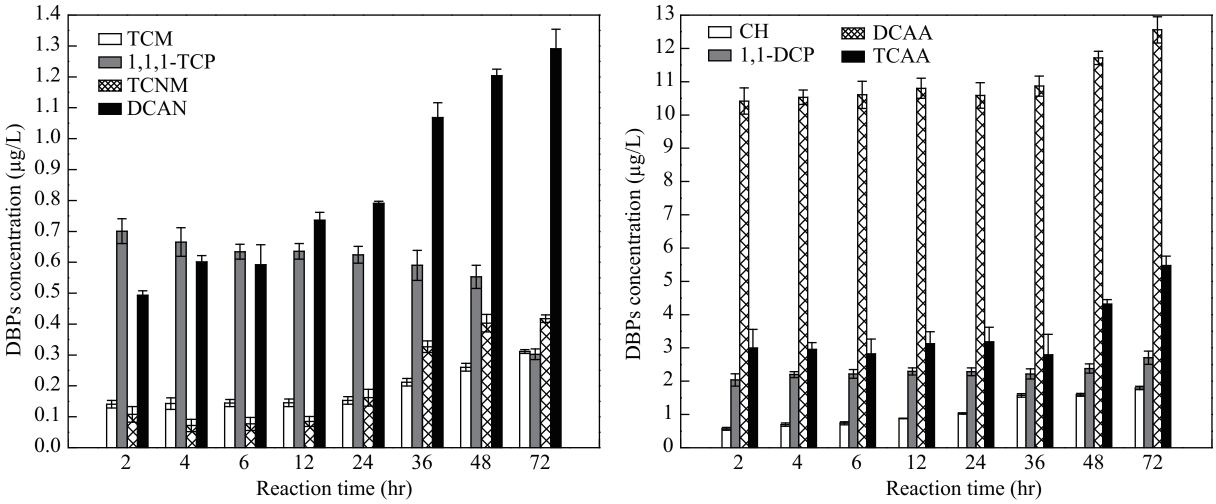

Fig. 1 Time-dependent formation of DBPs from the monochloramination of Cyclops metabolite solutions. Cyclops metabolite: 4 mg/L as TOC, pH: 7.5, monochloramine concentration: 10 mg/L (as Cl_2), temperature: 20 ± 2°C. The error bars represent the standard deviation of replicate measurements (n = 2).

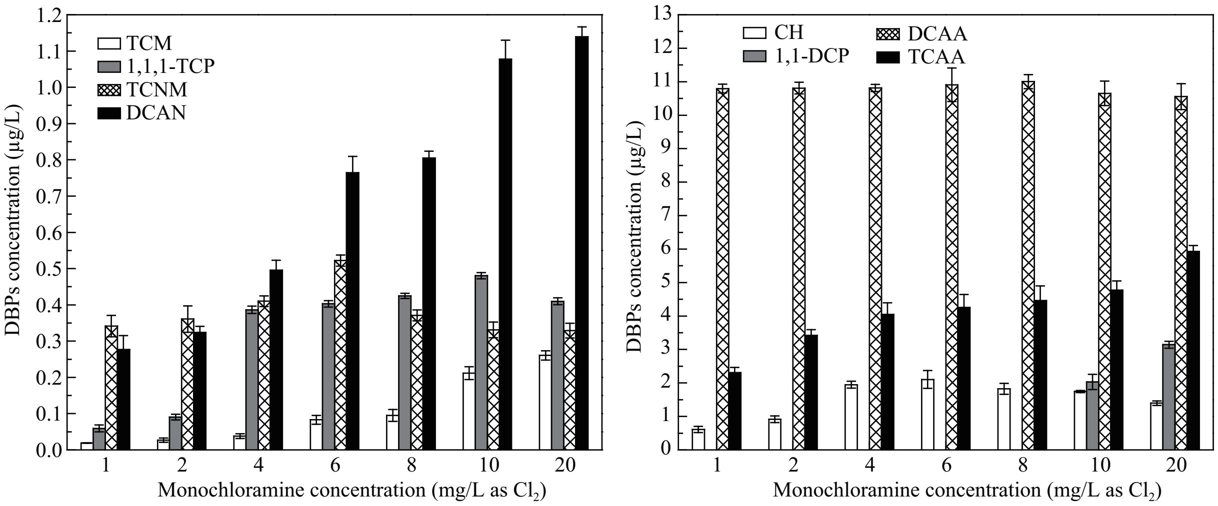

Fig. 2 Formation of DBPs as functions of monochloramine concentration after 48 hr chloramination of Cyclops metabolite solutions. Cyclops metabolite: 4 mg/L as TOC, pH: 7.5, temperature: 20 ± 2°C. The error bars represent the standard deviation of replicate measurements (*n* = 2).

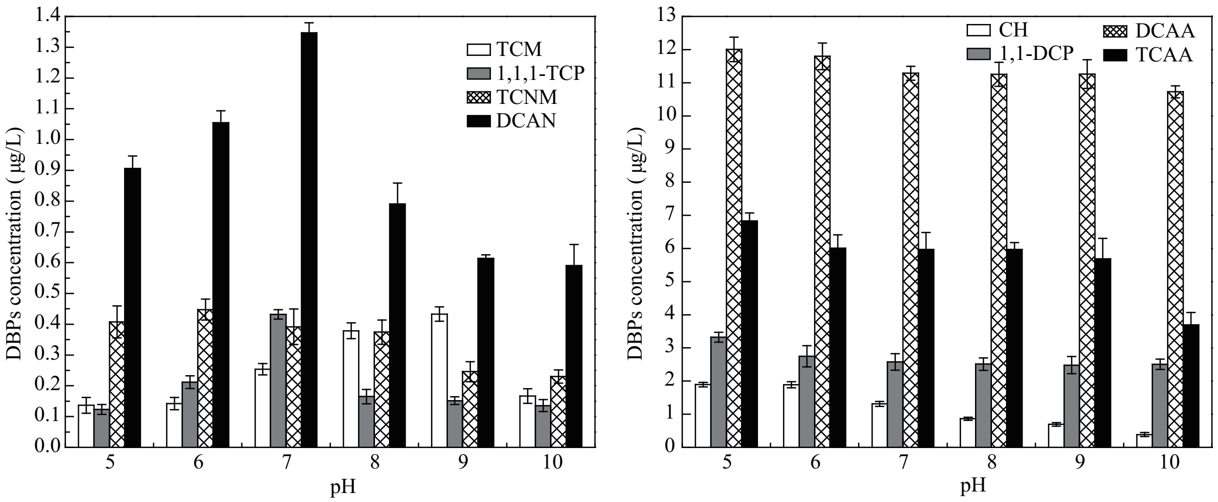

Fig. 3 Formation of DBPs as functions of pH after 48 hr chloramination of Cyclops metabolite solutions. Cyclops metabolite: 4 mg/L as TOC, monochloramine concentration: 10 mg/L (as Cl_2), temperature: 20 ± 2°C. The error bars represent the standard deviation of replicate measurements (*n* = 2).

5 to 10 and the maximum yields of these DBPs occurred at pH 6–7. Yang et al. (2007) showed monochloramine was the dominant specie at pH 7.5–9, pH affects hydrolysis of monochloramine to form free chlorine, and the hydrolysis rate at pH 7 is about three times higher than that at pH 8.5 for a monochloramine concentration of 10 mg/L (as Cl_2). $NHCl_2$ was dominant specie at pH 4–6. Therefore, the concentration of 1,1,1-TCP, TCNM and DCAN increased from 4 to 6, then decreased with pH from 7 to 10. Hydrolysis of monochloramine to form free chlorine was also affected by pH (Jolley and Carpenter, 1983), 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 10. The CH, 1,1-DCP, DCAA and TCAA concentrations decreased with increasing pH. These phenomena are consistent with the stabilities of these chloramines. Monochloramine is more stable at high pH value, the reaction between monochloramine and DBPs precursors were slow; therefore, a smaller amount of DBPs was generated.

2.4 Effect of temperature

Figure 4 illustrates the resulting DBPs after 48 hr of chloramination at three temperatures (10, 20 and 30°C). Formation of TCM and TCNM increased continuously with increasing temperature. DCAN and TCAA formation decreased with increasing temperature from 10 to 30°C. The generation of 1,1-DCP, 1,1,1-TCP, CH and DCAA had maximum yields at 20°C. In general, reaction rates increase with increasing temperature, and it led to the higher relatively stable DBPs concentrations, like TCM. However, increasing the temperature also enhances the

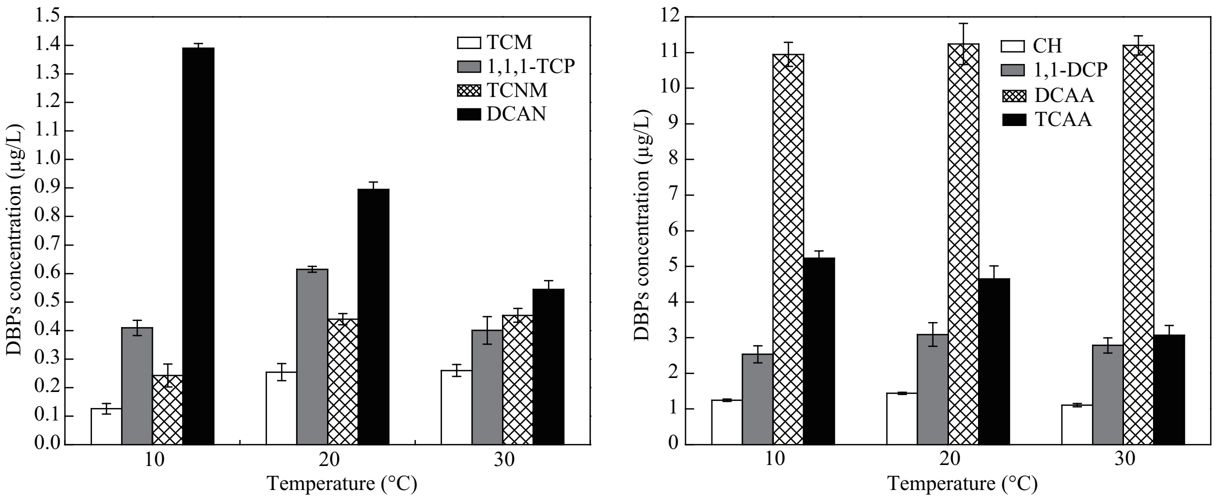

Fig. 4 Formation of DBPs as functions of temperature after 48 hr chloramination of Cyclops metabolite solutions. Cyclops metabolite: 4 mg/L as TOC, pH: 7.5, monochloramine concentration: 10 mg/L (as Cl_2). The error bars represent the standard deviation of replicate measurements (*n* = 2).

decomposition rates of DCAN (Nikolaou et al., 2000). Therefore, the concentrations of these unstable DBPs at different temperatures depend on the balance of their formation rates and decomposition rates.

3 Conclusions

Monochlamine disinfection of Cyclops metabolite solutions could bring DBPs, which effect water quality and safety. The key findings from the present research are listed as below:

Chloramination of Cyclops metabolite solutions resulted in the formation of DBPs such as TCM, CH, TCNM, 1,1-DCP, 1,1,1-TCP, DCAN, DCAA and TCAA. DCAA concentrations were the highest among the tested DBPs, followed by TCAA and 1,1-DCP. The concentrations of TCM, 1,1,1-TCP, CH, DCAN and TCNM were low and at the level of μg/L.

The results showed that some species of DBPs like TCM, DCAA and TCAA could accumulate to their respective stable values with a progressive elevation in reaction time and monochloramine concentration. And 1,1,1-TCP content decreased correspondingly with a continuous increase of reaction time. The amounts of CH, TCNM, 1,1,1-TCP and DCAA firstly increased and then decreased with increasing monochloramine doses. Higher temperature resulted in a decrease of CH, DCAN, 1,1-DCP, 1,1,1-TCP, DCAA and TCAA concentration, while pH affected the formation of the different DBPs distinctly, TCM accumulated with the increase of pH under 9, and DCAA, TCAA, CH and 1,1-DCP decreased continuously with increasing pH from 5 to 10, and other DBPs had the maximum concentrations at pH 6–7.

The study showed that it could achieve a better control of one kind of DBPs by adjusting the chloramination conditions. However, there is still a lot of work to be done to balance all kinds of DBPs.

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