Formation of halogenated C-, N-DBPs from chlor(am)ination and UV irradiation of tyrosine in drinking water

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Abstract

The formation of regulated and emerging halogenated carbonaceous (C-) and nitrogenous disinfection by-products (N-DBPs) from the chlor(am)ination and UV irradiation of tyrosine (Tyr) was investigated. Increased chlorine contact time and/or Cl\textsubscript{2}/Tyr ratio increased the formation of most C-DBPs, with the exception of 4-chlorophenol, dichloroacetonitrile, and dichloroacetamide. Chloroform and dichloroacetic acid increased with increasing pH, dichloroacetonitrile first increased and then decreased, and other DBPs had maximum yields at pH 7 or 8. The addition of ammonia significantly reduced the formation of most C-DBPs but increased 4-chlorophenol, dichloroacetonitrile, dichloroacetamide, and trichloroacetonitrile yields for short prechlorination contact times before dosing ammonia. When UV irradiation and chlorination were performed simultaneously, the concentrations of the relatively stable C-DBPs increased, and the concentrations of dichloroacetonitrile, dichloroacetamide, and 4-chlorophenol decreased with increasing UV dose. This information was used to develop a mechanistic model for the formation of intermediate DBPs and end products from the interaction of disinfectants with tyrosine.

1. Introduction

Water resource shortages and growing water demands have spurred utilities to exploit source waters influenced by wastewater effluents and/or algal blooms. Such source waters are typically characterized by higher dissolved organic nitrogen (DON) levels, where amino acids constitute an important class of the DON pool and may account for 15% and 35% of the DON (Westerhoff and Mash, 2002). During chlorination or chloramination, components of the DON in water can react with the disinfectant to form halogenated nitrogenous disinfection by-products (N-DBPs), such as haloacetamides (HAcAms), halonitromethanes (HNMs) and haloacetonitriles (HANs) (Richardson et al., 2007), which represent an emerging concern due to their cytotoxicity and genotoxicity (Plewa et al., 2004; Mueller et al., 2007; Richardson and Ternes, 2011). In particular, haloacetamides (HAcAms), an emerging class of halogenated N-DBPs that have been measured in tap waters (Krasner et al., 2006), exhibited much higher genotoxicity and cytotoxicity than many C-DBPs (e.g., trihalomethanes [THMs] and haloacetic acids [HAAs]) (Plewa et al., 2008).

Most formation studies, based on model compounds such as free amino acids, focus on C-DBPs (e.g., THMs and HAAs) and certain N-DBPs (HANs), while few have considered HAcAms and HNMs. Some laboratory studies reported that aromatic amino acids (e.g., tyrosine [Tyr]) generally produced more chloroform (CF) and other THMs than non-aromatic ones, and amino acids with a ring structure (e.g., Tyr) resulted in higher yields of dichloro- (DCAA) and trichloroacetic acid (TCAA) during chlorination (Hong et al., 2009). Chlorination (oxidation) of certain amino acids (e.g., Tyr,
tryptophan, aspartic acid [Asp]) can result in the formation of aldehydes and nitriles upon subsequent or concomitant chlorine substitution to form trichloroacetaldehyde (chloral hydrate [CH]) and dichloroacetonic acid (DCAN), respectively (Trehy et al., 1986), whereas other studied amino acids (e.g., glycine, alanine, serine) do not cause this result (Trehy and Bieber, 1981). Recently, selected amino acids were shown to react with chlorine to form other N-DBPs, such as cyanogen chloride (CNCI) in the case of glycine (Na and Olson, 2006) and trichloronitromethane (TCNM) in the case of Asp (Hu et al., 2010). For HACAs, there is only one study that assessed the role of amino acids in the formation of dichloroacetamide (DCACAm) (Cu et al., 2010b), the most common HACAm formed in chlorinated and chloraminated drinking water (Krasner et al., 2006), and found that Asp, histidine, and Tyr had the highest DCACAm yields among 20 free amino acids.

Ytr is a naturally occurring amino acid present in many peptides, proteins, and algae (Ram, 1985; Szajdak and Österberg, 1996). Mitch et al. (2009) investigated the occurrence of amino acids, peptides, proteins, and algae (Ram, 1985; Szajdak and Österberg, 1996). Mitch et al. (2009) investigated the occurrence of amino acids, peptides, proteins, and algae (Ram, 1985; Szajdak and Österberg, 1996) and found that Asp, histidine, and Tyr had the highest DCACAm yields among 20 free amino acids.

Chloramination in practice often does not involve adding pre-formed chloramines, but rather adding ammonia and chlorine separately to form chloramines (e.g., DCAcAm, trichloroacetamide [TCAcAm]) from free chlorine and DCAN, dichloroacetonitrile (TCAN), TCNM, DCACAm, TCACAm, CNI, and 4-chlorophenol (4-CP). This was evaluated for chlorination with and without UV irradiation and for chloramination under various conditions. In addition, this study explored the formation pathways of these C- and N-DBPs, which is expected to contribute to a better understanding and prediction of the control and formation of these DBPs.

2. Materials and methods

2.1. Materials

THMs (Supelco 47904), HAAs (Supelco 49107-U), 4-CP (Supelco 48689), and CH (47335-U) chemical standards, and EPA 551B standard mixture (Supelco 48046) containing DCAN, TCAN, 1,1-DCP, 1,1,1-TCP, and TCNM were purchased from Sigma–Aldrich (St. Louis, Missouri, USA). Tyr (98.5%) was obtained from Wako (Osaka, Japan). DCACAm (98.5%) and TCAcAm (99%) were obtained from Alfa Aesar (Karlsruhe, Germany). The extraction solvent ethyl acetate was obtained from Fisher Scientific (Waltham, Massachusetts, USA). Guaranteed reagent (GR) grade reagents—sodium hypochlorite (NaOCl), sodium hydroxide (NaOH), hydrochloric acid (HCl), ammonium chloride, sodium nitrite, sodium nitrate, buffer salts, glacial acetic acid, ascorbic acid, and anhydrous sodium sulfate—were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared using ultrapure water produced with a Millipore Milli-Q Gradient water purification system (Billerca, Massachusetts, USA). All bottles were prewashed with phosphate-free detergent, rinsed with ultrapure water, and dried in an oven at 105 °C for 24 h. Chlorine solutions were prepared by diluting a 5% NaOCl solution with ultrapure water, which was standardized daily prior to use.

2.2. Disinfection experiments

Chlorination and chloramination experiments were conducted at a controlled room temperature (23.0 ± 0.2 °C) and under headspace-free conditions in 200-mL brown glass volumetric flasks, which were kept in the dark. During chlorination experiments, a typical run involved applying a certain chlorine dose (0.5, 1.5, 2.5 mM) to a Tyr solution (0.1 mM) for the designated reaction time. To stop the chlorination reaction, the disinfectant residual was quenched with ascorbic acid with a normality twice as high as the initial normality of the chlorine added; ascorbic acid has little effect on the stability and analysis of the investigated halo- genated N-DBPs and C-DBPs (Joo and Mitch, 2007; Chu et al., 2009a). NaOH and HCl were used to adjust the pH (pH = 5 ± 1). Buffer solutions were prepared from phosphate and carbonate salts. For comparing the effect of chloramination on DBP formation, ammonium chloride was added to provide ammonia at the desired level. By adjusting the free chlorine residual time before dosing ammonia, three chlor- amination schemes were examined: I. Chloramination with preformed mono- chloramine, where ammonia and chlorine with the same molar concentration were dosed to the Tyr solution. II. Prechlorination (1-h), where ammonium chloride with the same molar concentration was added to the residual chlorine after 1 h was added to a Tyr solution pre-chlorinated for 1 h. III. Prechlorination (6-h), where ammonium chloride with the same molar concentration as the residual chlorine after 6 h was added to a Tyr solution pre-chlorinated for 6 h. In order to examine the effect of UV irra- diation on the formation of DBPs during chlorination of Tyr, before chloramination or at the same time, some water samples were irradiated in a low pressure UV reactor with different UV doses from 15.5 to 585 mJ/cm², as shown in Supplementary Information (SI) (Fig. S1 and Table S1).

2.3. Analytical methods

A UV/Vis double-beam spectrophotometer (Unico4802, Dayton, New Jersey, USA) was used to scan the spectrum of different samples from 220 to 500 nm at 10-nm intervals. Residual and total chlorine were detected by a portable spectropho- tometer (HACH DR2800) based on HACH method 8021. Prior to DBP analysis, glacial acetic acid was used to lower the pH to 4.8–5.3 for the THM, HAN, and TCNM samples, and to 5.0 ± 0.2 for the HACAm samples to prevent base-catalyzed hydrolysis of HANS or HAcAms (Chu et al., 2009a). CF, CH, DCAN, TCAN, TCNM, 1,1-DCP, and 1,1,1-TCP were measured using purge & trap (P&T) (O Analytical, Eclipse 4660, College Station, Texas, USA) and gas chromatography/mass spectrometry (GC/MS) (Shimadzu-QP2010, Kyoto, Japan), based on the U.S. Environmental Protection Agency (USEPA) Method 524.2. Two HAAs (DCAA and TCAA) were measured by GC (Shimadzu-QP2010 with an electron capture detector, based on USEPA Method 552.2 (Gao et al., 2009). DCACAm and TCACAm were analyzed using liquid–liquid extraction and GC/MS (Shimadzu-QP2010). The analysis details for DCAcAm and TCAcAm are available elsewhere (Chu et al., 2010b). Additionally, the details of the 4-CP analysis are briefly described in the SI. This study did not quantify the concentration of CNCI or dichloromethane (DCM), but they were examined qualitatively by P&T and GC/MS (Fig. S3). The same was done for trichloroacetyl chloride (TCAC). The yield of each DBP was calculated by the molar ratio of the formed DBP to the initial concentration of Tyr (Eq. S1).

3. Results and discussion

3.1. Time-dependent formation of DBPs from Tyr

Fig. 1A and B show the time-dependent formation of C- and N-DBPs during chlorination of tyrosine at a Cl₂/Tyr molar ratio of 15 at pH 7. There was a measurable free chlorine residual at all times tested at Cl₂/Tyr = 15 (Fig. S4) because the chlorine demand was approximately 13 mol Cl₂/mol Tyr. As shown in Table S2, at Cl₂/ Tyr = 15 (as well as at 5 or 25), 1,1,1-DCP, 1,1-TCP, and TCAcAm were not detected, and the yields of TCAN and TCNM were lower than.
0.02%, which were too low to distinguish a difference. From Fig. 1A and B (Cl₂/Tyr = 15), the yields of 4-CP (2.8%) and DCAN (1.6%) were much higher than other tested DBPs at the first 1 h, and they gradually decreased by 168 h to 0.05% and 0.11%, respectively. [The apparent first-order rate constant for hydrolysis of DCAN is 0.27 h⁻¹ at pH 7.5 (Yang et al., 2007); the hydrolysis of 4-CP does not occur in water at neutral pH.] The concentrations of four detected C-DBPs (CF, DCAA, TCAA, and CH) increased with increasing contact time and maximized at 4.0, 2.4, 2.9 and 0.46%, respectively, at 168 h. The yield of the relatively unstable N-DBP DCAcAm [The apparent first-order rate constant for hydrolysis of DCAcAm is 0.50 h⁻¹ at pH 7.0 (Chu et al., 2009a)] peaked at 0.16% at 6 h, and then declined at higher contact times (down to 0.05% at 168 h).

CF, DCAA, and TCAA were relatively stable in the presence of chlorine and generally were the end products of chlorination of Tyr in the absence of bromide. CH can form CF by base-catalyzed hydrolysis under alkaline conditions (Chu et al., 2009b), but the hydrolysis rate of CH is lower than the corresponding formation rate in neutral solution. The trends of DCAcAm formation and degradation can be explained by the hydrolysis of DCAN and DCAcAm. DCAN can hydrolyze to form DCAcAm (e.g., from 1 to 6 h), and DCAcAm can further hydrolyze to produce DCAA (e.g., after 6 h) (Table S3, Eq. S2) (Glezer et al., 1999; Reckhow et al., 2001; Chu et al., 2009a, 2010a). Note that the loss of DCAN cannot be fully accounted for by the increase in formation of DCAcAm or DCAA.

### 3.2. Effect of chlorine dosage

The yields of C- and N-DBPs after a 24-h chlorination of Tyr at different Cl₂/Tyr molar ratios are shown in Fig. 1C and D. Four relatively stable C-DBPs (CF, DCAA, TCAA, and CH) increased with increasing Cl₂/Tyr, whereas 4-CP decreased with increasing Cl₂/Tyr. The yields of some N-DBPs (DCAN and DCAcAm) reached their highest levels at Cl₂/Tyr = 15. At Cl₂/Tyr = 5, residual chlorine was barely detected at 0.02 mg/L detection limit (Fig. S4), which caused all DBPs except 4-CP to have lower yields (Table S2). At Cl₂/Tyr = 25, the excess chlorine accelerated the decomposition rate of DCAN (Reckhow et al., 2001), whereas DCAcAm was similar to what was present at Cl₂/Tyr = 15. CNCl and DCM were detected at Cl₂/Tyr = 5. There was no significant change in CNCl level formed at different chlorine contact times, whereas the DCM peak area gradually decreased with increasing contact time (Fig. S3). Na and Olson (2006) demonstrated that the chlorination of glycine could form CNCl, where higher chlorine concentrations promoted its hydrolysis. The absence of CNCl during chlorination of Tyr at Cl₂/Tyr = 15 or 25 was most likely due to hydrolytic degradation of the CNCl by the free chlorine.

### 3.3. Effect of pH

The yields of C- and N-DBPs upon 24-h chlorination of Tyr at different pH levels are summarized in Fig. 2A and B, respectively. As shown, CF and DCAA yields kept growing with increasing pH from 5 to 9. However, during the chlorination of humic acid, an increase in pH increases CF formation, but decreases DCAA formation (Babcock and Singer, 1979). The impact of pH (e.g., from 7 to 9) was higher for CF (yield at pH 9 was 147% higher than yield at pH 7) than for DCAA (yield at pH 9 was 124% higher than yield at pH 7). DCAN reached a maximum yield of 2.4% at pH = 6 and dropped substantially (to a 0.35% yield) at pH 7. The highest formation of TCAA, CH, and DCAcAm occurred at pH 7 to 8, which had maximum yields of
0.76–0.78, 0.18–0.24, and 0.12–0.14%, respectively. However, 4-CP yields (0.59–0.74%) were relatively insensitive to pH. At different pH levels, chlorination of Tyr was not able to produce sufficient TCNM to make notable differences. TCAN gave low yields at pH 5 to 8 and was not detected at pH 9, and TCAcAm was not detected at all. The effect of pH on the DBP yields is mainly attributable to their stability and formation pathway from Tyr. Many of these results are consistent with previous research in bulk water (e.g., conducted at pH levels of 5, 7, and 9.4) that has shown CF formation increasing with pH; whereas CH formation increased over time at pH 5 and 7, and CH that had formed within 4 h at pH 9.4 decayed over time at the elevated pH. DCAN formation only increased over time at pH 5, while DCAN formed within 4 h at pH 7 decayed over time at the neutral pH, and DCAN formed to a low extent at all reaction times at pH 9.4 (Stevens et al., 1989). Relatively stable CH and TCAA, and relatively unstable TCAN, DCAN, and DCAcAm are also all easily hydrolyzed to CF or DCAA under alkaline conditions (Yang et al., 2007; Chu et al., 2009b). The incremental increase in DCAA under alkaline conditions was due in part to the hydrolysis of DCAN and DCAcAm. As shown in Table S4, with pH increasing from 7 to 9, the sum of the losses of DCAN and DCAcAm (0.41%) was greater than the increase in DCAA (0.17%). Alternatively, the sum of the losses of TCAA, CH, and TCAN (0.089%) was far lower than the increase in CF (0.52%). Therefore, there are other reasons to cause the incremental increase in CF rather than only the hydrolysis of TCAA, CH, and TCAN. For example, the alkaline condition can facilitate the rapid opening of the benzene ring, which can promote the formation of CF (Chu et al., 2009c).

Apparent first-order rate constants for the decomposition of DCAN in the presence or absence of chlorine were $1.8 \times 10^{-5}$ s$^{-1}$ (initial free chlorine was 10 mg/L, pH = 7.0) and $7.5 \times 10^{-7}$ s$^{-1}$ (pH = 7.5) (Reckhow et al., 2001; Yang et al., 2007). These were higher than the apparent first-order rate constants for the decomposition of DCAcAm, which were $4.55 \times 10^{-6}$ s$^{-1}$ (initial free chlorine was 10 mg/L, pH = 7.0) and $2.37 \times 10^{-7}$ s$^{-1}$ (pH = 7.5) (Chu et al., 2009a). At pH 7 to 8, the difference between the formation rate of DCAcAm from DCAN hydrolysis and the hydrolysis rate of DCAcAm was probably higher than that at other pH levels, as the net yield of DCAcAm was highest at pH 7 to 8. At pH 8 the maximum formation of CH, similar to that of DCAcAm, was probably due to a larger difference between CH formation and decomposition at this pH. TCNM was relatively stable at pH 5 to 9, in agreement with earlier studies (Joo and Mitch, 2007), and there was no observed effect of pH on the TCNM yield.

### 3.4. Effect of chloramination

The yields of C- and N-DBPs after a 24-h disinfection of Tyr with different chloramination schemes are summarized in Fig. 2C and D, respectively. The use of chloramines with less free chlorine contact time reduced the yields of the C-DBPs, except for 4-CP, which is in agreement with studies with NOM or algae as the precursor (Zhang et al., 2000; Fang et al., 2010). With increasing free chlorine contact time, relatively stable C-DBPs (CF, DCAA, TCAA, and CH) increased, whereas 4-CP and N-DBP yields increased and then decreased. Yang et al. (2007) found that a short period (1–30 min) of chlorination of NOM solutions before switching to chloramination did not form substantial quantities of these DBPs, except for DCAcAm and TCAcAm. A similar phenomenon was also found in this study using Tyr as a precursor, whereas some significant differences in some DBP yields were found when the prechlorination time was increased to...
1 or 6 h before dosing ammonia. However, the typical prechlorination time is less than 6 h in water treatment plants.

Of note, the DCACAm yield was higher during 6-h prechlorination and 18-h chlorination (0.17%) than 24-h chlorination alone (0.12%), whereas its yield was similar to 6-h chlorination alone (0.16%). This was probably due to the stability and formation mechanism of DCACAm (Chu et al., 2010a). Although DCAN was relatively more stable in monochloramine solutions than in free chlorine solutions (Yang et al., 2007), some DCAN can still hydrolyze to DCACAm during chloramination. Moreover, the hydrolysis rate of DCACAm in monochloramine solutions was much lower than that in free chlorine solutions (Chu et al., 2009a), thus this probably resulted in the net yield of DCACAm to reach its highest level after 6 h of prechlorination and 18 h of chloramination.

The last detail of note is that TCACAm was first detected in this study during two chloramination schemes, which were chloramination with preformed monochloramine and 1-h prechlorination study during two chloramination schemes, which were chloramination with preformed monochloramine and 1-h prechlorination before dosing ammonia. For these two chloramination schemes, the formation of TCAC was tentatively identified (Fig. S5). TCAC can react with ammonia to form TCACAm (Montalbetti and Falque, 2005) (Table S3, Eq. S3). No TCAC was detected during 24-h chlorination or 6-h prechlorination, probably because the TCAC formed was further oxidized by chlorine or hydrolyzed to TCAA (Table S3, Eq. S4).

3.5. Effect of UV irradiation

No significant increase of the studied DBPs during chlorination after UV exposure was detected. Moreover, as shown in Fig. S6, the optical spectra of Tyr were similar or slightly larger with UV doses ranging from 19.5 to 585 mJ/cm², suggesting that Tyr was relatively unchanged during UV irradiation. Previous studies have shown some structural changes of NOM during UV irradiation, which resulted in an increase in some DBPs (e.g., CF) after UV exposure and subsequent chlorination (Liu et al., 2006; Dotson et al., 2010; Reckhow et al., 2010). However, in another recent study, while there was an impact from medium pressure UV, there was no impact from low pressure UV (Reckhow et al., 2010), and it was a low pressure UV system that was used in this study.

The formation of various C- and N-DBPs was evaluated when both UV irradiation and chlorination were conducted at the same time (Fig. 3). This resulted in an increase in CF, somewhat of an increase in DCAA and TCAA, and decreases in 4-CP, DCAN, and DCACAm. As shown in Table S3, Eq. S5, the DCAN and DCACAm formation pathway during chlorination was proposed to include substitution, elimination, and decarboxylation reactions, and a further substitution reaction to the methylene group (−CH₂−) in the main chain of an amino acid (Reckhow et al., 2001; Chu et al., 2010b), where −CH₂− is an electron-donating group. The chlorine substitution reaction rate in −CH₂− of Tyr was faster than many other amino acids, probably because of the R—group including an aromatic ring in the side chain of Tyr, which enhanced the electron-donating ability of −CH₂− in the main chain of Tyr (Chu et al., 2010b). The aromatic ring in the R—group was probably broken by a strong oxidizer (e.g., hydroxyl radical, Table S3, Eq. S6) formed under the combined action of UV irradiation and chlorine (Nowell and Hoigne, 1992; Feng et al., 2007), and the extent of the damage to the R—group in the side chain of Tyr increased with increasing UV dose. This probably lessened the electron-donating ability of −CH₂− in the main chain of Tyr and caused the decrease in DCAN and DCACAm with increasing UV dose. The decrease in 4-CP was also likely caused by the damage of the aromatic ring in the side chain of Tyr. The increase in CF, DCAA, and TCACAm could have been caused by the strong oxidizer transforming the Tyr structure to a form that was more reactive with chlorine to form CF, DCAA, and TCACAm.

3.6. Preliminary hypothesis of C- and N-DBPs formation pathways from Tyr

A possible integrated pathway of C- and N-DBPs formation during Tyr chlorination is proposed in Scheme 1. For the reactions A1 to A5, B1 to B7, C1 to C3, and D1 to D3 in Scheme 1, the possible formation pathways of CH, DCAN (Trehy et al., 1986), DCAcAm (Reckhow et al., 2001; Chu et al., 2010b), TCAcAm (Hong et al., 2009), DCACAm and TCAA (Glezer et al., 1999; Dickinson et al., 2008) from chlorination of Tyr was modified from previous studies. From reaction B1 to B5, the formation of CF mainly goes through 4-CP, 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6- TCP), and a ring opening reaction, which has been confirmed in an earlier study (Chu et al., 2009c). As shown in Fig. S7 and Table S5, 4-CP, 2,4-CP, and 2,4,6-TCP were formed to much greater extents during chlorination, which was in agreement with the above-mentioned experimentally determined DBP yields.

Additionally, 4-hydroxyl-benzyl-cyanoamid (4-HBC) during chlorination of Tyr had a high peak (Fig. S7), it was likely the main intermediate to form DCACAm during chloramination by the reactions A1 to A4 (Scheme 1). During chlorination, the formation of DCACAm was probably from the reactions D1, D2, D4, and A4, where benzyl cyanide (Fig. S7) was an important intermediate. Hong et al. (2009) proposed the formation pathway of TCAN from Asp.

![Fig. 3.](image)
Nevertheless, TCAN yields were relatively low at all contact times tested in the study using Tyr as a model compound. Therefore, TCAcAm was less likely to occur from the hydrolysis of TCAN. TCAcAm was detected, and TCAC was also identified tentatively, during the same chloramination schemes. A novel possible formation pathway for TCAcAm was proposed; TCAC (Fig. S5) could be produced by the ring opening (reaction B8). Also, it has been well known that TCAC could react quickly with ammonia to yield TCA-cAm (reaction B9) (Montalbetti and Falque, 2005). We will confirm the novel possible formation pathway by quantifying TCAC and other intermediates under different experimental conditions in future studies.

4. Conclusions

Amino acids are an important component of the DON in water. Algae and wastewater effluents are important sources of DON in watersheds. Amino acids are precursors to certain C- and N-DBPs. Recent research has indicated that certain emerging DBPs (e.g., HANs, HAcAms, HNMs, haloacetaldehydes) are more toxic than regulated C-DBPs (THMs, HAAs). Thus, it is important to better understand the formation and control of both regulated and emerging DBPs. In this study it was found that the factors that increase the formation of some by-products of the reaction of water disinfectants with the amino acid tyrosine (Tyr) can simultaneously reduce the formation of other DBPs. Moreover, the degradation of some DBPs resulted in the formation of other DBPs. The new information obtained in this study was used to augment the reaction scheme proposed for the formation of DBPs from Tyr. Increased chlorine dose and pH could decrease the production of some N-DBPs, but increase the formation of the relatively stable C-DBPs. The pretreatment of low pressure UV before chlorination did not impact the formation of DBPs during post-chlorination of Tyr, whereas increased levels of some DBPs were found when UV was used together with chlorine for disinfection. In the future study on health effects and risk assessment in drinking water, the effect of some emerging DBPs may be considered more important than regulated DBPs because their concentration and toxic potency could be much greater than these regulated DBPs in certain disinfection conditions.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2011.09.037.

References


