Formation of Halogenated C-, N-DBPs from Chlor(am)ination and UV Irradiation of Tyrosine in Drinking Water

Wenhai Chu [a], Naiyun Gao[a,*], Stuart W. Krasner [b], Michael R Templeton [c], Daqiang Yin[a]

[a]State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China
[b]Metropolitan Water District of Southern California, 700 Moreno Avenue, La Verne, California 91750-3399, USA
[c]Department of Civil and Environmental Engineering, Imperial College London, London, SW7 2AZ, UK

*Corresponding author.
Address: State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Mingjing Building No. 601, 1239 Siping Road, Yangpu District, Shanghai, 200092, China
Tel: +86 21 65982691
Fax: +86 21 65986839
E-mail: feedwater@yahoo.cn, feedwater@126.com.

Abbreviations:

Alanine –Ala; aspartic acid –Asp; carbonaceous disinfection by-products –C-DBPs; chloroform –CF; chloral hydrate –CH; 4-chlorophenol –4-CP; cyanogen chloride –CNCl; 1,1-dichloropropanone –1,1-DCP; disinfection by-products –DBPs; dichloroacetic acid –DCAA; dichloroacetamide –DCAcAm; dichloroacetonitrile –DCAN; dichloromethane –DCM; 2,4-dichlorophenol –2,4-DCP; dissolved organic carbon – DOC; dissolved organic nitrogen – DON; gas chromatography/mass spectrometry -GC/MS; haloacetic acids – HAAs; haloacetamides –HAcAms; haloacetonitriles –HANs; halonitromethanes –HNMs; 4-hydroxy-benzyl-cyanide –4-HBC; nitrogenous disinfection by-products- N-DBPs; natural organic matter – NOM; purge & trap- P&T; trichloroacetic acid –TCAA; trichloroacetyl chloride –TCAC; trichloroacetamide –TCAcAm; trichloroacetonitrile –TCAN; trichloronitromethane –TCNM; 2,4,6-trichlorophenol –2,4,6-TCP; 1,1,1-trichloropropanone –1,1,1-TCP; trihalomethanes –THMs; tyrosine –Tyr; U.S. Environmental Protection Agency –USEPA; water treatment plants–WTPs.

Abstract

The formation of regulated and emerging halogenated carbonaceous (C-) and nitrogenous disinfection by-products (N-DBPs) from the chlor(am)ination, UV irradiation of tyrosine (Tyr) was investigated. Increased chlorine contact time and/or Cl_2/Tyr ratio increased the formation of most C-DBPs. In contrast, 4-chlorophenol, dichloroacetonitrile, and dichloroacetamide had their greatest yields at particular conditions. 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 most C-DBPs formation but increased 4-chlorophenol, dichloroacetonitrile, dichloroacetamide, and trichloroacetonitrile yields for short pre-chlorination contact times before dosing ammonia. When UV irradiation and chlorination were performed simultaneously, the relatively stable C-DBPs increased, and 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 endproducts from the interaction of disinfectants with tyrosine.

Capsule abstract

Exploring the integrated formation mechanism of regulated and emerging highly toxic DBPs, which is expected to preferably reduce their occurrence in drinking water.

Keywords: Drinking water; Nitrogenous disinfection by-products; Tyrosine; Haloacetamides; Halonitromethanes; Integrated formation pathway

1. Introduction

Currently, water resource shortages and growing water demands have spurred utilities to exploit source waters impaired by treated 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 et al., 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; Muellner et al., 2007; Richardson et al., 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), relatively little involved 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, with subsequent or concomitant chlorine substitution to form trichloroacetaldehyde (chloral hydrate [CH]) and dichloroacetonitrile (DCAN), respectively (Trehy et al., 1986), whereas other amino acids (e.g., glycine, alanine, serine) did not (Trehy and Bieber, 1981). Recently, selected amino acids were shown to react with chlorine to form other N-DBPs, such as cyanogen chloride (CNCl) in the case of glycine (Na and Olson, 2006) and trichloronitromethane (TCNM) in the case of Asp (Hu et al., 2010). For HAcAms, there is only one study that assessed the role of amino acids in the formation of dichloroacetamide (DCAcAm) (Chu 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.

In these studies on DBP formation during chlorination of amino acids, Tyr was a typical precursor for certain C- and N-DBPs. Moreover, Tyr 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 in some US water treatment plants (WTPs)influent samples, and found the maximum concentration of hydrolyzable Tyr reached 27.4 μg/L (average=9.0 μg/L). In practical WTPs, pre- or post-chlor(am)ination may caused the formation of multiple DBPs from Tyr and other compounds (e.g., proteins, algae, humics) containing Tyr. Pre-chlor(am)ination is a common practice in China now to reduce tastes, odors, and algal growths. Although the above-mentioned studies reported the formation of individual DBP species from the chlorination of Tyr, a comprehensive reaction scheme, which includes key intermediates resulting in multiple DBP formation, is

lacking to date. Also, a novel possible pathway for the emerging HAcAms formation was proposed in the present study, which updated the previous speculation that HAcAms was from the hydrolysis of HANs. Besides, chloramination in practice often does not involve adding preformed chloramines, but rather adding ammonia and chlorine. The order of addition and/or free chlorine contact time can impact DBP formation during post-chloramination (Schreiber and Mitch 2009). Especially, the results for the formation of some emerging N-DBPs (e.g., DCAcAm, trichloroacetamide [TCAcAm]) during certain free chlorine contact times before adding ammonia were still lacking. Moreover, UV treatment is an emerging disinfection process for drinking water, and transformation of the NOM by UV irradiation could change the formation of some DBPs during post-chlorination (Liu et al., 2006; Dotson et al., 2010; Reckhow et al., 2010). At present, the contribution of UV irradiation on multiple DBP (esp. HAcAms) formation from selected individual amino acids is unknown.

A better understanding of the comprehensive formation mechanism of C- and N-DBPs during disinfection may improve the accuracy of predicting DBP occurrence and make it possible to optimize disinfection practices that minimize the formation of C- and N-DBPs. The objective of this study was to assess the role of Tyr in the formation of multiple chlorinated C- and N-DBPs: CF, DCAA, TCAA, 1,1-dichloro-2-propanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), CH, DCAN, trichloroacetonitrile (TCAN), TCNM, DCAcAm, TCAcAm, CNCl, and 4-chlorophenol (4-CP). This was evaluated for chlorination with and without UV irradiation and for chloramination under various conditions. Moreover, an important goal was to explore 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 (Billerica, 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 6% 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

149 temperature (23.0 ± 0.2ºC) and under headspace-free conditions in 200-mL brown glass
150 volumetric flasks, which were kept in the dark. During chlorination experiments, a typical
151 run involved applying a certain chlorine dose (0.5, 1.5, 2.5 mM) to a Tyr solution (0.1 mM)
152 for the designated reaction time. To stop the chlorination reaction, the disinfectant residual
153 was quenched with ascorbic acid with a normality twice as high as the initial normality of
154 the chlorine added, because ascorbic acid has little effect in the stability and analysis of
155 these investigated halogenated N-DBPs and C-DBPs (Joo and Mitch, 2007; Chu et al.,
156 2009a). NaOH and HCl were used to adjust the solution pH value (pH=5~9). Buffer
157 solutions were prepared from phosphate and carbonate salts. For comparing the effect of
158 chloramination on DBP formation, certain amounts of ammonium chloride were added to
159 provide ammonia at the desired level. By adjusting the free chlorine contact time before
160 dosing ammonia, three chloramination schemes were examined: I. Chloramination with
161 preformed monochloramine, where ammonia and chlorine with the same molar
162 concentration were dosed to the Tyr solution. II. Prechlorination (1-h), where ammonium
163 chloride with the same molar concentration as the residual chlorine after 1 h was added to
164 a Tyr solution pre-chlorinated for 1 h. III. Prechlorination (6-h), where ammonium chloride
165 with the same molar concentration as the residual chlorine after 6 h was added to a Tyr
166 solution pre-chlorinated for 6 h. In order to examine the effect of UV irradiation on the
167 formation of DBPs during chlorination of Tyr, before chlorination disinfection or at the
168 same time, some water samples were irradiated in a low pressure UV reactor with
169 different UV doses from 19.5 to 585 mJ/cm^2, as shown in Supplementary Information (SI)
170 (Figure SI 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 spectrophotometer (HACH DR2800) based on HACH method 8021. Prior to DBP analysis, glacial acetic acid was used to lower the pH to 4.8-5.5 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) (OI 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 of 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 CNCl or dichloromethane (DCM), but they were examined qualitatively by P&T and GC/MS (Figure 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.1]

Figures 1A and B show the time-dependent formation of C- and N-DBPs during chlorination of tyrosine at a Cl_2/Tyr molar ratio of 15 at pH 7. There was a free chlorine residual at all times tested at Cl_2/Tyr = 15 (Figure S4) because the chlorine demand was approximately 13 mol Cl_2/mol Tyr. As shown in Table S2, at Cl_2/Tyr = 15 (as well as at 5 or 25), 1,1-DCP, 1,1,1-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 notable difference. From Figures 1A and B (Cl_2/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. (Their half-lives were >6 and <6 h, respectively.) 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% at 168 h. The yield of the relatively unstable N-DBP DCAcAm (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 endproducts 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;

214 Reckhow et al., 2001; Chu et al., 2009b; Chu et al., 2010a). Note that the loss of DCAN
215 cannot be fully accounted for by the increases in formation of DCAcAm or DCAA.

216 **3.2. Effect of chlorine dosage**

217 The yields of C- and N-DBPs after a 24-h chlorination of Tyr at different Cl_2/Tyr ratios
218 are shown in Figures 1C and D. Four relatively stable C-DBPs (CF, DCAA, TCAA, CH)
219 increased with increasing Cl_2/Tyr, whereas 4-CP decreased with increasing Cl_2/Tyr. The
220 yields of some N-DBPs (DCAN and DCAcAm) reached their highest levels at Cl_2/Tyr = 15.
221 At Cl_2/Tyr = 5, residual chlorine was barely detected at 0.02 mg/L detection limit (Figure
222 S4), which caused all DBPs except 4-CP to have lower yields (Table S2). At Cl_2/Tyr = 25,
223 the excess chlorine accelerated the decomposition rate of DCAN (Reckhow et al., 2001),
224 whereas DCAcAm was similar to what was present at Cl_2/Tyr = 15. CNCl and DCM were
225 detected at Cl_2/Tyr = 5. There was no significant change in CNCl level formed at different
226 chlorine contact times, whereas the DCM peak area gradually decreased with increasing
227 contact time (Figure S3). Na and Olson (2006) demonstrated that the chlorination of
228 glycine could form CNCl, where higher chlorine concentrations promoted its hydrolysis.
229 The absence of CNCl during chlorination of Tyr at Cl_2/Tyr = 15 or 25 was most likely due to
230 hydrolytic degradation of the CNCl by the free chlorine.

231 **3.3. Effect of pH**

232 **[Fig.2]**

233 The yields of C- and N-DBPs upon 24-h chlorination of Tyr at different pH levels are
234 summarized in Figures 2A and B, respectively. As shown, CF and DCAA yields kept
235 growing with increasing pH from 5 to 9. However, during the chlorination of humic acid,

236 increase in pH increases CF formation, but decreases DCAA formation (Babcock and
237 Singer, 1979). The impact of pH (e.g., from 7 to 9) was higher for CF (yield at pH 9 was
238 147% higher than yield at pH 7) than for DCAA (yield at pH 9 was 124% higher than yield
239 at pH 7). DCAN reached a maximum yield of 2.4% at pH = 6 and dropped substantially (to
240 a 0.35% yield) at pH 7. The highest formation of TCAA, CH, and DCAcAm occurred at pH
241 7 to 8, which had maximum yields of 0.76-0.78, 0.18-0.24, and 0.12-0.14%, respectively.
242 However, 4-CP yields (0.59 to 0.74%) were relatively insensitive to pH. At different pH
243 levels, chlorination of Tyr was not able to produce sufficient TCNM to make notable
244 differences. TCAN gave low yields at pH 5 to 8 and was not detected at pH 9, and
245 TCAcAm was not detected at all.

246 The effect of pH on the DBP yields is mainly attributable to their stability and formation
247 pathway from Tyr. Many of these results are consistent with previous research in bulk
248 water (e.g., conducted at pH levels of 5, 7, and 9.4) that has shown CF formation
249 increasing with pH; whereas CH formation increased over time at pH 5 and 7, and CH that
250 had formed within 4 h at pH 9.4 decayed over time at the elevated pH; and DCAN
251 formation only increased over time at pH 5, while DCAN formed within 4 h at pH 7
252 decayed over time at the neutral pH, and DCAN formed to a low extent at all reaction
253 times at pH 9.4 (Stevens et al., 1989). Relatively stable CH and TCAA, and relatively
254 unstable TCAN, DCAN, and DCAcAm are also all easily hydrolyzed to CF or DCAA under
255 alkaline conditions (Yang et al., 2007; Chu et al., 2009b). The incremental increase in
256 DCAA under alkaline conditions was due in part to the hydrolysis of DCAN and DCAcAm.
257 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 environment 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 1.8×10^{-5} s^{-1} (initial free chlorine was 10 mg/L, pH = 7.0) and 7.5×10^{-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 4.55×10^{-6} s^{-1} (initial free chlorine was 10 mg/L, pH = 7.0) and 2.37×10^{-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 level. 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 Figures 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 to 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 chloramination (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 before dosing ammonia. For these two chloramination schemes, the

302 formation of TCAC was tentatively identified (Figure S5). TCAC can react with ammonia to
303 form TCAcAm (Montalbetti and Falque, 2005) (Table S3, Eq. S3). No TCAC was detected
304 during 24-h chlorination or 6-h prechlorination, probably because the TCAC formed was
305 further oxidized by chlorine or hydrolyzed to TCAA (Table S3, Eq. S4).

306 **3.5. Effect of UV irradiation**

307 **[Fig.3]**

308 A significant increase of the studied DBPs during chlorination after UV exposure was
309 not detected by GC/MS. Moreover,. as shown in Figure S6, the optical spectra of Tyr were
310 similar or slightly larger with UV doses ranging from 19.5 to 585 mJ/cm^2, suggesting that
311 Tyr was relatively unchanged during UV irradiation. Previous studies have shown some
312 structural changes of NOM during UV irradiation, which resulted in an increase in some
313 DBPs (e.g., CF) after UV exposure and subsequent chlorination (Liu et al., 2006; Dotson
314 et al., 2010; Reckhow et al., 2010). However, in another recent study, there was an impact
315 from medium pressure UV whereas there was no impact from low pressure UV (Reckhow
316 et al., 2010), and it was a low pressure system that was used in this study.

317 The formation of various C- and N-DBPs was evaluated when both UV irradiation and
318 chlorination were conducted at the same time. This resulted in an increase in CF,
319 somewhat of an increase in DCAA and TCAA, and decreases in 4-CP, DCAN, and
320 DCAcAm.

321 As shown in Table S3, Eq. S5, the DCAN and DCAcAm formation pathway during
322 chlorination was proposed to include substitution, elimination, and decarboxylation
323 reactions, and a further substitution reaction to the methylene group (-CH_2-) in the main

chain of an amino acid (Reckhow et al.,2001; Chu et al., 2010b), where -CH_2- is an electron-donating group. The chlorine substitution reaction rate in -CH_2- 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 -CH_2- 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 -CH_2- in the main chain of Tyr and caused the decrease in DCAN and DCAcAm with increasing UV doses. 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 TCAA 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 TCAA.

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

[Scheme 1]

A possible integrated pathway of C- and N-DBP formation during Tyr chlorination is proposed in Scheme1. For the reactions A1 to A7, B6, C1 to C6, D1 to D2, and E1 to E4 in Scheme1, the possible formation pathways of DCAN, DCAcAm, DCAA, CH, and TCAN from chlorination of Tyr was modified from previous studies (Reckhow et al., 2001; Joo and Mitch, 2007; Hong et al., 2009; Chu et al., 2010b). From reaction C1 to C10 (secondary reaction), relatively small amounts of CF was formed from further chlorination

of Ala (Chu et al., 2009b). From reaction B1 to B5 (main reaction), 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 Figure 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 above-mentioned results of DBP yields.

Additionally, 4-hydroxyl-benzyl cyanide (4-HBC) during chloramination of Tyr had a high peak (Figure 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 E1, E2, E3, and A4, where benzyl cyanide (Figure S7) was an important intermediate. TCAcAm was less likely to occur from the hydrolysis of TCAN, because TCAN yields were relatively low at all contact times tested. As involved in “3.4. Effect of chloramination”, TCAcAm was detected, and TCAC was also identified tentatively, during the same chloramination schemes. A novel possible formation pathway for TCAcAm was proposed; TCAC (Figure S5) could be produced by the ring opening (main reaction B7) and was also probably from chlorination of formaldehyde (secondary reaction C7). Also, it has been well known that TCAC could react quickly with ammonia to yield TCAcAm (reaction C8) (Montalbetti and Falque, 2005). We will confirm the novel possible formation pathway by quantifying TCAC and other intermediates at different experimental conditions in further studies.

4. Conclusion

Amino acids are an important component of the DON in water. Algal activity or treated wastewater discharges 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 regulated and emerging DBPs. It was found that factors that increased the formation of some by-products of Tyr decreased the formation of others. Moreover, the degradation of some DBPs resulted in the formation of other DBP. The information in this study was used to augment the 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. If a utility had low C-DBP formation potential but was experiencing halogenated N-DBPs (e.g., HAcAms, HANs), it is recommended to try to switch chlorination to chloramination, and chlorine should be dosed after ammonia, based on the results of this study. Meanwhile, it is necessary to monitor the concentration of non-halogenated N-DBPs (e.g., nitrosamines) because chloramines may increase their formation. Low-pressure UV before chlorination did not impact the formation of DBPs from Tyr, whereas with post-chlorination, increased levels of some DBPs were found with 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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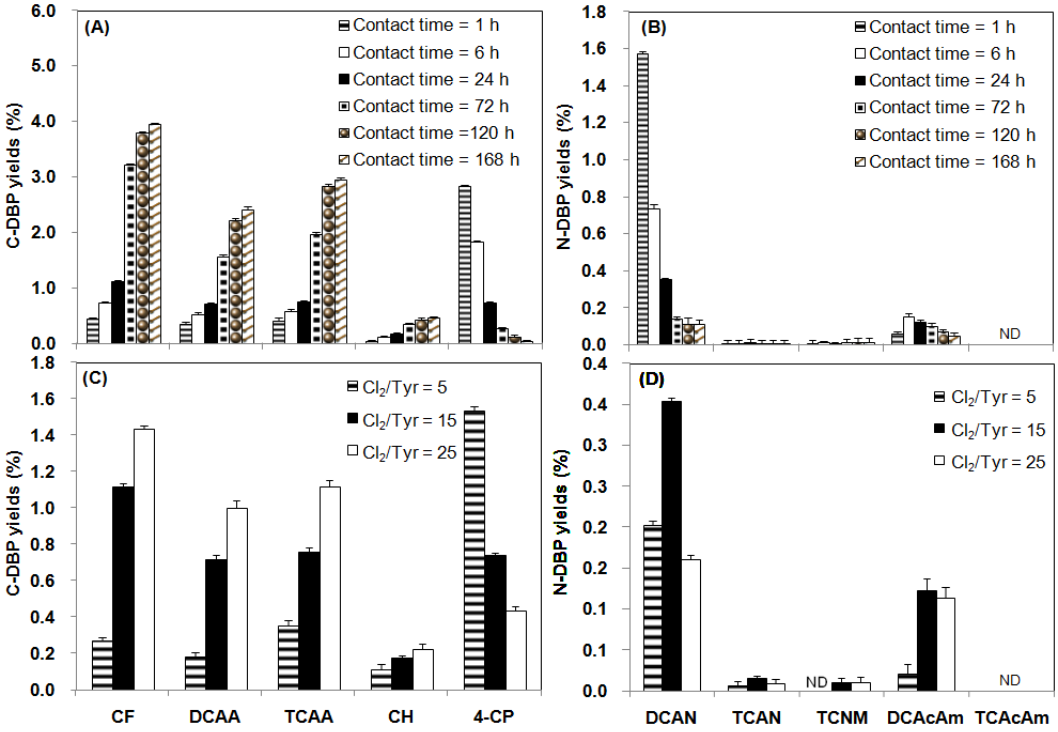


Fig.1 – Formation of C- and N-DBPs during chlorination of Tyr at different contact times (A and B) and different Cl_2/Tyr molar ratios (C and D). Tyr concentration = 0.1 mM, pH = 7.0 ± 0.3. Cl_2/Tyr = 15 and contact time = 24 h, except as noted. The bars represent the standard deviation of replicate measurements (n = 3).

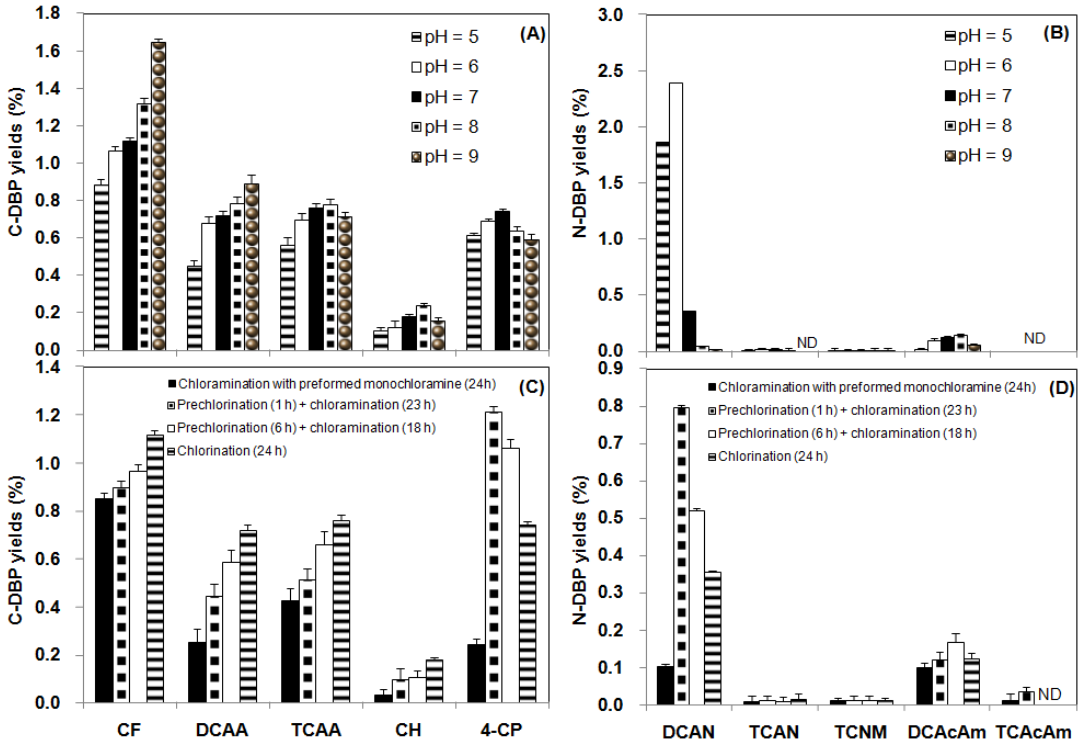


Fig.2 – Formation of C- and N-DBPs during chlorination of Tyr at different pH levels (A and B) and chloramination schemes (C and D). Tyr concentration = 0.1 mM, total disinfectant contact time = 24 h, pH = 7.0, Cl_2/Tyr = 15, and Cl_2/ammonia = 1, except as noted. The bars represent the standard deviation of replicate measurements (n = 3).

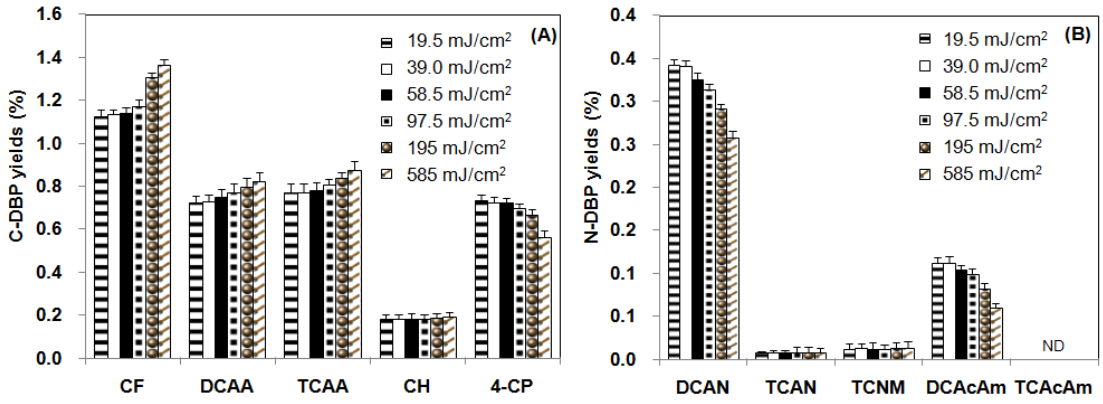
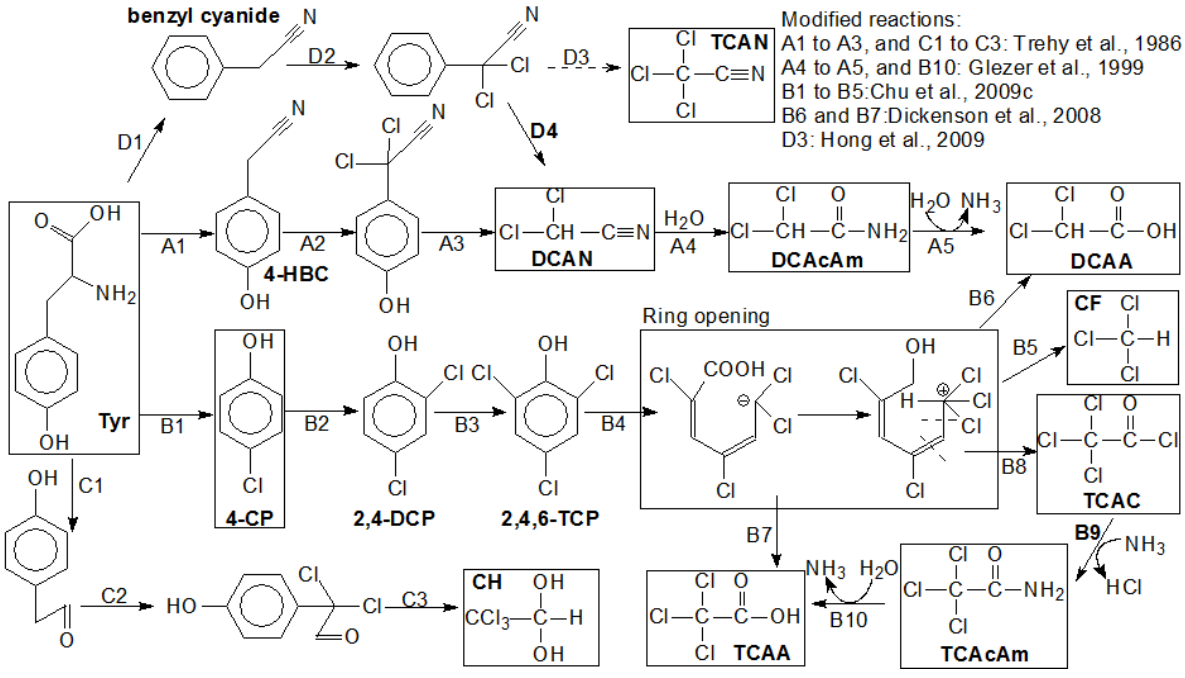


Fig.3 – Formation of C- and N-DBPs at different UV dosages (UV irradiation and chlorination were conducted at the same time). Tyr concentration = 0.1 mM, chlorination contact time = 24 h, pH = 7.0, and Cl_2/Tyr = 15. The bars represent the standard deviation of replicate measurements (n = 3).



Scheme 1 – Proposed formation pathway of C- and N-DBPs from Tyr (Ala = alanine).