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**The formation of haloacetamides and other disinfection by-products from non-nitrogenous
low-molecular weight organic acids during chloramination**

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ABSTRACT

Low-molecular weight organic acids (LMWOAs) are widespread in nature, and many are recalcitrant during conventional drinking water treatment, due to their LMW and hydrophilic character. This study assessed the formation of a range of disinfection by-products (DBPs) from the chloramination of seven non-nitrogenous LMWOA precursors, with an emphasis on the contribution of N-chloramine incorporation to haloacetamide (HAcAm) formation. The other DBPs comprised chlorinated halomethanes, haloacetonitriles and haloacetic acids. Citric acid generated higher yields of trichloromethane and two chloroacetic acids than the other LMWOAs. Further, the unsaturated acids (fumaric acid and itaconic acid) formed more chloroacetic acids than saturated acids (oxalic acid, succinic acid, adipic acid). Importantly, non-nitrogenous LMWOAs formed three nitrogenous DBPs (dichloroacetamide, trichloroacetamide, and small amounts of dichloroacetonitrile) during chloramination, firstly indicating the monochloramine can supply the nitrogen in nitrogenous DBPs, and the formation of haloacetamides at least in part is independent of the hydrolysis of haloacetonitriles. To the authors' knowledge, this is the first time formation of halogenated nitrogenous DBPs (N-DBPs) has been reported from chloramination of non-nitrogenous LMWOA precursors. This indicates that concentrations of dissolved organic nitrogen compounds in drinking water are not a reliable surrogate for formation of N-DBPs during chloramination. Bromine incorporation factor increased with increasing bromide during chloramination of citric acid, and bromine was easier to incorporate into di-HAcAms than mono- and tri-HAcAms during chloramination.

Keywords: Low-molecular mass organic acids (LMWOAs); Nitrogenous disinfection by-products (N-DBPs); Haloacetamides (HAcAms); Chloramination; Bromine substitution; Drinking water

1. Introduction

Since the discovery of disinfection by-products (DBPs) in chlorinated drinking water [1,2], there has been a considerable amount of research work exploring how DBPs are formed and how to control them [3-6]. Over the last 40 years, the number of DBP classes identified in drinking waters has grown from the trihalomethanes (THMs) and haloacetic acids (HAAs) to a long list of halogenated and non-halogenated organic and inorganic compounds, which are produced not only from chlorination, but also other disinfectants such as chloramines [3,7-10]. Most of the initial research focused on the currently regulated THMs and HAAs, which are two most abundant classes of DBPs on a mass basis in chlorinated drinking water [7]. However, in recent years, halogenated nitrogenous DBPs (N-DBPs), including halonitromethanes (HNMs), haloacetonitriles (HANs), and haloacetamides (HAcAms), have received increased attention, since toxicological studies suggest that they have higher toxicity than the currently regulated halogenated carbonaceous DBPs (C-DBPs) [3,11-13]. In particular, the HAcAms, an emerging class of halogenated N-DBPs, have been found to be highly cytotoxic and genotoxic in mammalian cell assays, i.e. 142× more cytotoxic and 12× more genotoxic than regulated HAAs [3,13]. Their elevated toxicity was also observed in a recent study based on metabonomics [14].

It is established that dissolved organic nitrogen (DON) precursors, for example, the amino acids, can react with chlorine to form halogenated N-DBPs [4,6,15-17]. Nonetheless, recent studies have reported that chloramines may provide the nitrogen in HANs and HNMs, during reactions with organic nitrogen precursors [18,19]. And, it was found that non-nitrogenous lignin phenols and chloroacetaldehyde could react with chloramines to form dichloroacetonitrile (DCAN) and chloroacetonitrile, respectively [20,21]. However, knowledge gaps remain regarding whether

chloramine may also contribute the nitrogen in HAcAms, and more broadly whether chloramine can also react with non-nitrogenous precursors to produce nitrogenous HAcAms.

The non-nitrogenous low molecular weight organic acids (LMWOAs) are widely distributed in the natural environment, including water [22], soil [23] and atmosphere [24], and are also the end products of oxidation of many organic pollutants in drinking water treatment plants (DWTPs) [25,26]. Also, many non-nitrogenous LMWOAs, containing one or more carboxyl groups, are characterized by low molecular weight and hydrophilic behavior, and therefore likely to be poorly removed by conventional DWTPs using coagulation–sedimentation–filtration [27-30]. Thereby they have a chance to react with dosed disinfectants to form DBPs. The use of chloramines has gained popularity recently because it reduces formation of THMs and HAAs. Therefore, it is important to investigate DBP formation from the chloramination of non-nitrogenous LMWOAs.

The objective of this study was therefore to explore the formation of C-DBPs and N-DBPs upon chloramination of seven non-nitrogenous LMWOAs (Table 1), with an emphasis on the contribution of N-chloramine incorporation to HAcAm formation. Two HANs (DCAN and trichloroacetonitrile [TCAN]), two HAcAms (dichloroacetamide [DCAcAm] and trichloroacetamide [TCAcAm]), two HNMs (dichloronitromethanes [DCNM] and trichloronitromethanes [TCNM]), two halomethanes (dichloromethane [DCM] and trichloromethane [TCM]), and two HAAs (dichloroacetic acid [DCAA] and trichloroacetic acid [TCAA]) were evaluated in this study. Bromine substitution for HAcAms were also considered, with particular emphasis on the extent of bromine incorporation, based on the analysis of all nine HAcAms (DCAcAm, TCAcAm, chloro- [CAcAm], bromo- [BAcAm], bromochloro- [BCAcAm], dibromo- [DBAcAm], bromodichloro- [BDCAcAm], dibromochloro- [DBCAcAm], and

tribromoacetamide [TBAcAm]). The seven non-nitrogenous LMWOAs were selected in the study because they have been frequently detected in natural waters [20,31,32] and they have a variety of chemical functionality (Table 1), which allowed us to evaluate the effect of LMWOA characteristics on HAcAm formation. The results of this study provide a preliminary indication of the potential involvement of LMWOAs in DBP formation, and specifically the contribution of chloramines to HAcAm formation.

[Table 1]

2. Materials and methods

2.1. Materials

The standard solutions of the studied DBPs were purchased from Sigma-Aldrich (St. Louis, USA), except DCaAm and TCaAm which were supplied from Alfa Aesar (Karlsruhe, Germany), and DBAcAm, BCaAm, BDCaAm, DBCaAm, and TBaAm standards which were all purchased from Orchid Cellmark (New Westminster, BC, Canada). All selected LMWOAs (>98.5%), including adipic acid [AA], benzoic acid [BA], citric acid [CA], fumaric acid [FA], itaconic acid [IA], oxalic acid [OA] and succinic acid [SA], were obtained from Aladdin Industrial Inc (Shanghai, China). Guaranteed reagent grade reagents—sodium hypochlorite, ammonium chloride, phosphate buffer salts, and sodium sulfite were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Monochloramine (NH_2Cl) solutions were prepared daily by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions at a weight ratio of 4 mg/L Cl_2 to 1 mg/L N-NH_4^+ . Other materials were at least analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) unless otherwise noted. The ultrapure

water was produced with a Millipore Milli-Q Gradient water purification system (Billerica, Massachusetts, USA).

2.2. Experimental procedure

The experimental materials are listed in supplementary material. Chloramination experiments were conducted by dosing the preformed monochloramine (NH_2Cl) to LMWOA solutions (0.1 mM) buffered at $\text{pH } 7.0 \pm 0.2$ with a phosphate buffer (10 mM), at a controlled room temperature (25.0 ± 0.2 °C) and under headspace-free conditions in 40-mL brown glass screw-cap vials with PTFE-lined septa, which were kept in the dark for 6, 24 and 72 h. NH_2Cl was dosed at a molar ratio (active Cl_2 /each C atom [Cl_2/C]) of 1:1 for each LMWOA (for example, CA has 6 carbon atoms per molecule, so the NH_2Cl dose as Cl_2 was 6 mol/mol CA). To investigate the effect of bromide on the formation and speciation of HAcAms, bromide was dosed at a molar ratio ($\text{Br}^-/\text{active } \text{Cl}_2$ [Br^-/Cl_2]) of 1:100 (0.01), 1:20 (0.05) and 1:10 (0.1) based on their practical concentrations [33,34], prior to chloramination. After chloramination reactions for a certain time, the disinfectant residual was quenched with a stoichiometric amount of sodium sulfite and the samples were analyzed immediately.

2.3. Analysis

Total organic nitrogen (TON) was measured by a total organic carbon analyzer equipped with a total nitrogen detection unit (Shimadzu TOC-VCPH, Japan). Inorganic nitrogen and residual total chlorine were measured with a HACH spectrophotometer (DR6000, USA) and special HACH reagent packages. A range of volatile DBPs (DCM, TCM, DCAN, TCAN, DCNM, and TCNM) were all analyzed with a purge & trap sample concentrator (eclipse4660, OI, USA) and gas chromatography/mass spectrometry (GC/MS) (QP2010, Shimadzu, Japan) according to US EPA

method 524.2 [35]. Two HAAs (DCAA and TCAA) were analyzed by a GC (Shimadzu - QP2010, Japan) coupled with an electron capture detector according to US EPA method 552.2 [17,36]. Two HAcAms (DCAcAm and TCACAm) were analyzed by liquid-liquid extraction and GC/MS detection [37]. In order to examine the effect of bromide on the formation and speciation of HAcAms, nine chlorine and bromine-containing HAcAms were determined by solid-phase extraction enrichment, high-performance liquid chromatography, and triple quadrupole MS with atmospheric pressure chemical ionization, using selective reaction monitoring (SRM) in the positive mode. The details of the HAcAm analyses are presented elsewhere [17], and are summarized in the supplementary material (Table S1). The detection limits for DCM, TCM, DCAN, TCAN, DCAcAm, TCACAm, and other selected HAcAms were $\leq 0.10 \mu\text{g/L}$, except DCAA ($0.5 \mu\text{g/L}$) and TCAA ($0.5 \mu\text{g/L}$). The each DBP yield was the molar ratio of the formed DBP to the initial concentration of selected precursor (equation 1). In the presence of excess NH_2Cl , the LMWOAs could be consumed completely before 6 h, based on the determination of the LMWOAs [31] before and after chloramination, thereby the initial LMWOA molar concentration can be regarded as the consumed LMWOA molar concentration.

$$\text{DBP yield} = \frac{\text{Formed DBP molar concentration}}{\text{Initial LMWOA molar concentration}} \times 100\% \quad (1)$$

3. Results and discussion

3.1. C-DBP formation

Figure 1 shows the yields of four C-DBPs (DCM, TCM, DCAA, and TCAA) formed from the chloramination of the seven LMWOAs (Table 1). As can be seen, the yields of TCM, DCAA and

TCAA increased with increasing the contact time from 6 h to 72 h, while the formation of DCM increased from 6 h to 24 h, before subsequently decreasing from 24 h to 72 h. Thus DCM was not the end product of these seven LMWOAs during chloramination, whereas TCM, DCAA and TCAA were relatively stable under the experimental conditions used, which is in agreement with the previous studies [7,38].

[Fig. 1]

DCM formation did not vary significantly with the changes in molecular structure of LMWOAs, and a good linear relationship between the carbon atom numbers in seven LMWOAs and the DCM yields of seven LMWOAs at 24-h was found (Figure S1). Conversely, the molecular structure characteristics of seven LMWOAs presented a significant influence on the formation of the stable products (TCM, DCAA, and TCAA) among the seven LMWOAs. Especially, CA presented the highest formation yields of TCM, DCAA and TCAA (1.56%, 1.54% and 0.23% at 72 h) during chloramination. Likewise, some previous studies also found THM formation of CA during chlorination is very high [39]. However, AA has the same carbon atom number with CA, but formed significantly less TCM, DCAA and TCAA than CA. This is because CA contains a beta-dicarbonyl acid structure, which can be converted to THMs and HAAs in high yields [40]. Additionally, it was also found that the unsaturated acids (FA and IA) formed more HAAs (DCAA and TCAA) than the saturated acids (OA, SA, and AA). A previous study reported that organic acid fraction isolated from wastewater, containing C=C and C=O structures, were the dominant precursors of THMs and HAAs during chlorination [41,42]. Additionally, FA and IA (two unsaturated dicarboxylic acids) also presented higher formation yields of DCAA (0.66% and 0.88% respectively) than TCM (0.54% and 0.80%) at 72 h, which is in agreement with

chloramination of authentic drinking water samples, where DCAA concentrations exceeded those of TCM [7,43]. Other selected LMWOAs (the four saturated carboxylic acids and one aromatic acid) formed more TCM than DCAA during chloramination, indicating the molecular characteristics of LMWOAs impacted the formation of TCM and DCAA.

3.2. *N*-DBP formation

[Fig. 2]

As shown in Figure 2, after the chloramination of seven LMWOAs, three *N*-DBPs (DCAN [0.001%~0.006%], DCAcAm [0.001%~0.080%], and TCAcAm [0.020%~0.047%]) were formed from the specific LMWOAs. However, TCAN and two HNMs (DCNM and TCNM) were below the detection limits (detection limits were 0.10 µg/L for these species). This results indicated a portion of nitrogen atoms in NH_2Cl were transferred to the three formed *N*-DBPs because only NH_2Cl contains N atom in the reaction system. The recent studies found the N atom in NH_2Cl can enter into DCAN during the chloramination of several amino acids, lignin phenols and chloroacetaldehyde [18,20,21]. It is known that DCAN and TCAN can hydrolyze to form DCAcAm and TCAcAm respectively, which can themselves further hydrolyze to form DCAA and TCAA, respectively (Figure S2) [44]. However, DCAcAm and TCAcAm are both relatively stable at pH 7.0 upon 72-h chloramination even at a higher NH_2Cl dose (> 1.0 mM) than this study (< 0.6 mM) [33,45,46], thereby this probably resulted in DCAN gradually decreasing and two HAcAms continuously increasing (Figure 2). However, of note, LMWOAs formed relatively little DCAN (<0.01%) and undetectable levels of TCAN during chloramination, compared to formation of DCAcAm and TCAcAm. In particular, CA formed significantly more DCAcAm (0.08% at 72 h)

and TCAN (0.047% at 72 h), relative to DCAN (0.001% was only detected at 72 h) and TCAN (undetectable). Also, we found that a short period (1-60 min) of chloramination of CA solutions did not form substantial quantities of HANs. Together this indicates the incremental increase in DCACAm and TCACAm was not solely due to the hydrolysis of DCAN and TCAN, which has been the most studied pathway. More research is needed to confirm this hypothesis.

[Scheme 1]

In the study, dichloroacetyl chloride (DCAC) and trichloroacetyl chloride (TCAC) were both detected qualitatively by P&T and GC/MS (Table S2) during chloramination of CA, which is in agreement with the previous study which found the formation of DCAC during chlorination of CA [47]. As noted previously, DCAC and TCAC can react with ammonia quickly to form DCACAm and TCACAm (Scheme 1) [48]. These observations indicate there are some other HAcAm formation pathways during the chloramination of LMWOAs, besides for the hydrolysis of HANs. This is in agreement with the recent study which found DCAN and DCACAm could form independently from the nitrogenous precursors [49]. However, it should be noted that the proposed formation pathway of HAcAms via DCAC and TCAC during chloramination of CA was a speculative side reaction pathway. More research is needed to confirm the hypothesis. Anyway, to our knowledge, this is the first time formation of halogenated nitrogenous DBPs (N-DBPs) has been reported from chloramination of non-nitrogenous LMWOA precursors.

Additionally, the aromatic acid BA did not formed any of the measured N-DBPs, probably because the NH_2Cl cannot facilitate the rapid opening of the benzene ring in BA [50]. For other nonaromatic acids, it seems that the increasing number of carbon atom (higher chloramine dosages, due to the fixed $\text{Cl}_2/\text{C} = 1:1$) facilitate the formation of DCACAm and TCACAm. However, CA

and AA have the same carbon atom number, but have the different N-DBP formation yields. And, by comparing the formation of HAcAms (DCAcAm and TCACAm) from each carbon atom in LMWOAs (Figure 2d), it was also found the carbon atom in CA still has the greatest contribution in HAcAm formation, followed by IA and AA. This indicates that chemical functionality is more important than carbon content for HAcAm formation from LMWOAs.

3.3. Bromine substitution

[Fig. 3]

Bromide naturally occurring in raw water can be rapidly oxidized by chlorine to form bromine during the drinking water chlorination process [51]. Bromine is usually more reactive than chlorine, and can react with organic matter to produce brominated DBPs [52]. As known, HAcAms that contain bromine generally are higher in cytotoxicity and genotoxicity than the chlorinated HAcAms [13]. To examine the effect of bromide on HAcAm formation, nine chlorine and bromine-containing HAcAms (HAcAm9) during chloramination of citric acid was determined. As shown in Figure 3, DCAcAm was the most abundant HAcAm species formed during chloramination, followed by TCACAm. In the presence of bromide, BCACAm was the most abundant species among the six bromine-containing HAcAms (Br-HAcAms), followed by DBACAm. TBACAm was undetectable in the whole study. There was no significant change in three chlorine-containing HAcAm (Cl-HAcAms: CACAm [0.0125%~0.0132%], DCAcAm [0.081%~0.093%] and TCACAm [0.047%~0.051%]) yields formed at different bromide levels, whereas the Br-HAcAms gradually increased with increasing bromide levels. Thereby, the total yields of 9 HAcAms (HAcAm9) also increased from 0.14% to 0.29% with increasing Br⁻/Cl₂

molar ratio from 0 to 0.1. In general, regardless of the presence and absence of bromide, the selected LMWOA (CA) formed primarily dihalogenated (di-) HAcAms, followed by trihalogenated (tri-) species and, to a much lesser extent, monohalogenated (mono-) HAcAms. These results were similar with the formation profile of 9 HAcAms from the chloramination of several selected natural waters [45].

To examine the effect of bromide on HAcAm speciation, the bromine incorporation factor (BIF) for HAcAms were calculated based on equations 2, 3 and 4, where all concentrations are on a molar basis. BIF is used as an index to describe the proportion of the HAcAms that can be partially or totally substituted with bromine atoms. As shown in Figure 4a, the BIF values of mono-, di-, and tri- HAcAms all gradually increased with increasing bromide levels. And, the BIFs (di-HAcAms) were significantly higher than BIFs of mono-HAcAms and tri-HAcAms, implying more bromine incorporation into di-HAcAms than in mono- and tri-HAcAms during chloramination of citric acid.

$$\text{BIF (mono-HAcAms)} = \frac{[\text{BAcAm}]}{[\text{CAcAm}] + [\text{BAcAm}]} \quad (2)$$

$$\text{BIF (di-HAcAms)} = \frac{[\text{BCAcAm}] + 2[\text{DBAcAm}]}{[\text{DCAcAm}] + [\text{BCAcAm}] + [\text{DBAcAm}]} \quad (3)$$

$$\text{BIF (tri-HAcAms)} = \frac{[\text{BDCAcAm}] + 2[\text{DBCACAm}] + 3[\text{TBACAm}]}{[\text{TCACAm}] + [\text{BDCAcAm}] + [\text{DBCACAm}] + [\text{TBACAm}]} \quad (4)$$

[Fig. 4]

From Figure 4a, it was also found that there is no significant difference between BIFs (tri-HAcAms) and BIFs (mono-HAcAms). BIFs for mono-HAcAms range from 0 (all CAcAm) to 1 (all BAcAm), BIFs for di-HAcAms range from 0 (all DCAcAm) to 2 (all DBAcAm), and BIFs for tri-HAcAms range from 0 (all TCAcAm) to 3 (all TBAcAm). To better compare BIFs, each was normalized by the number of halogens, where the normalized BIF (NBIF) for mono-HAcAms was its BIF divided by 1, the NBIF for di-HAcAms was its BIF divided by 2 and the NBIF for tri-HAcAms was its BIF divided by 3 (i.e., both NBIFs range from 0 to 1). As shown in Figure 4b, NBIFs for mono-, di- and tri- HAcAms kept increasing tendency, and it can be further found that bromine was easier to incorporate into di-HAcAms than mono- and tri- species. Compared to mono-HAcAms, tri-HAcAms were more difficult to be substituted by bromine, which was different with the recent study finding that bromine was easier to incorporate into tri-HAcAms during chloramination of several source waters [45]. Precursors of HAcAms in source waters are a mixture of autochthonous and allochthonous compounds, for example, the microorganism-associated (e.g. algae and bacteria) products, wastewater effluent organic matters, amino acids and proteinaceous compounds had been reported in the previous studies as nitrogenous organic precursors [6, 53-55]. The characteristics of different precursors might cause the difference of bromine substitution in mono-, di- and tri- HAcAms. Nevertheless, the results of this study indicated that citric acid was more likely to be brominated to di-HAcAms, followed by mono- HAcAms, during chloramination, rather than tri-HAcAms.

4. Conclusions

Four halogenated C-DBPs (DCM, TCM, DCAA and TCAA) and three halogenated N-DBPs

(DCAN, DCAcAm and TCACAm) were detected during the chloramination of seven LMWOAs.

Citric acid formed the highest yields of TCM, DCAA, TCAA, DCAcAm and TCACAm. Further, two unsaturated acids (fumaric acid and itaconic acid) formed more HAAs than three saturated acids (oxalic acid, succinic acid, adipic acid). Most importantly, the chloramine may supply the nitrogen for LMWOAs to form N-DBPs, and several LMWOAs can form HAcAms not only from the hydrolysis of HANs. To the authors' knowledge, this is the first time formation of N-DBPs has been reported from chloramination of non-nitrogenous LMWOA precursors. Moreover, this indicates that concentrations of DON compounds are not reliable predictors for formation of N-DBPs in chloraminated drinking water. In the presence of bromide, citric acid formed primarily di- HAcAms, followed by tri- species and, to a much lesser extent, mono- HAcAms during chloramination, and bromine was easier to incorporate into di-HAcAms than mono- and tri-HAcAms during chloramination.

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Figure captions

Fig. 1. The formation of C-DBPs from the chloramination of seven LMWOAs. Each LMWOA molar concentration = 0.1 mM. NH_2Cl was dosed at a molar ratio (active Cl_2 /each C atom [Cl_2/C]) of 1:1 for each LMWOA. The bars represent the standard deviation of replicate measurements ($n = 3$).

Fig. 2. The formation of N-DBPs from the chloramination of seven LMWOAs. Each LMWOA molar concentration = 0.1 mM. NH_2Cl was dosed at a molar ratio (active Cl_2 /each C atom [Cl_2/C]) of 1:1 for each LMWOA. The bars represent the standard deviation of replicate measurements ($n = 3$).

Scheme 1. A proposed pathway to form HAcAms from citric acid during chloramination

Fig. 3. The formation of HAcAms from the chloramination of citric acid. Citric acid molar concentration = 0.1 mM. NH_2Cl dosage = 0.6 mM. Contact time = 72 h. The bars represent the standard deviation of replicate measurements ($n = 3$).

Fig. 4. BIFs and NBIFs of mono-, di- and tri-HAcAms during chloramination of citric acid at different spiked bromide concentrations. Citric acid molar concentration = 0.1 mM. NH_2Cl dosage = 0.6 mM. Contact time = 72 h. Bromide was dosed at a molar ratio (Br^- ion/active Cl_2 [Br^-/Cl_2]) of 1:100 (0.01), 1:20 (0.05) and 1:10 (0.1) prior to chloramination.

Fig. 1

Fig. 2

Scheme 1

Fig. 3

Fig. 4

Table 1. Characteristics of seven selected LMWOAs.

Chemical name	Abbreviation	Molecular formula	Type	Molecular weight	Molecular structure
Oxalic acid	OA	$C_2H_2O_4$	Saturated dicarboxylic acid	90.03
Succinic acid	SA	$C_4H_6O_4$		118.09
Adipic acid	AA	$C_6H_{10}O_4$		146.14
Citric acid	CA	$C_6H_8O_7$	Tricarboxylic acid	192.12
Fumaric acid	FA	$C_4H_4O_4$	Unsaturated dicarboxylic acid	116.07
Itaconic acid	IA	$C_5H_6O_4$		130.1
Benzoic acid	BA	$C_7H_6O_2$	Aromatic acid	122.12

Highlights

- NH_2Cl supplied the nitrogen during N-DBP formation from non-nitrogenous precursors
- HAcAm yields from chloramination of LMWOAs were higher than those of HANs
- Yields of THMs, HAAs and HAcAms were highest from chloramination of citric acid
- DON concentration unlikely to be a good predictor of N-DBPs in chloramination
- The rank orders for normalized BIFs were di- HAcAms > mono- HAcAms > tri- HAcAms