



Formation of disinfection by-products in the chlorination of ammonia-containing effluents: Significance of Cl_2/N ratios and the DOM fractions

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ABSTRACT

The presence of ammonia nitrogen ($\text{NH}_3\text{-N}$) in the effluent strongly affected the formation of disinfection by-products (DBPs) during its chlorination. The effect of chlorine (as mg/L Cl_2) to $\text{NH}_3\text{-N}$ (as mg/L N) mass ratios (Cl_2/N) and the chemical fractions of dissolved organic matter (DOM) in the effluent on the DBPs formation was investigated. Results indicated that the formation of DBPs increased with increasing Cl_2/N . The concentration and speciation of DBPs varied among different DOM fractions at different zones of chlorination breakpoint curves. The formation rate of total haloacetic acids (THAA) and total trihalomethanes (TTHM) was promoted after the chlorination breakpoint, whereas the reaction of monochloramine with HOCl to dichloramine may cause a decrease in the DBPs formation potential thereafter. Organic acids were found to be the dominant precursors of DBPs with or without the presence of $\text{NH}_3\text{-N}$, which indicated that the $\text{C}=\text{C}$, $\text{C}=\text{O}$ and $\text{C}-\text{O}$ structures contributed to the formation of DBPs significantly. In addition, the incorporation of bromine in THMs of the HiA fraction increased with the increasing of Cl_2/N mass ratios before the chlorination breakpoint, but decreased sharply after the breakpoint. ΔA_{280} (absorbance at 280 nm), defined as $A_{280,\text{initial}} - A_{280,\text{final}}$, was proved to be linearly related to the TTHM and THAA of wastewater without containing Br^- during chlorination or chloramination.

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1. Introduction

Chlorination is a well-developed and widely used process for wastewater disinfection because of its broad spectrum germicidal potency, low cost, and well-established practices. However, the reactions between chlorine and dissolved organic matter (DOM) produce numerous disinfection by-products (DBPs), of which trihalomethanes (THMs) and haloacetic acids (HAAs) are the most prevalent ones by weight [1,2], which is found in most wastewater effluents, could influence the disinfection process. First, $\text{NH}_3\text{-N}$ may result in the formation of highly toxic nitrogenous DBPs, which were reported to serve as intermediates to yield dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and chloroform [3–7]. Second, the chloramines formed by reactions of $\text{NH}_3\text{-N}$ and chlorine could interfere in the formation of THMs and HAAs. The formation of by-products will be affected by the ratios of Cl_2 and $\text{NH}_3\text{-N}$, resulting in different DBPs with different species and structure. In addition, the reactions between DOM fractions and chlorine at different Cl_2/N

ratios will also vary the DBP species and their formation conditions. Yang et al. [8] demonstrated that there existed breakpoint curves in chlorination of wastewater containing $\text{NH}_3\text{-N}$ and the THM and HAA formation showed significantly different inclination below and beyond the breakpoint dosing level.

DOM in effluents from sewage treatment plants (STPs) is composed of recalcitrant natural organic matter (NOM) due to surface runoff of rain water, synthetic organic chemicals added during anthropogenic use and soluble microbial products [9–12]. The complex composition of total DOM poses a great challenge in research of the mechanism of DOM reactions with chlorine. Therefore, the resin adsorption chromatography (RAC) technique [9,13] is quite useful for isolating DOM into different fractions. With the application of RAC, Wang et al. [14] demonstrated that $\text{NH}_3\text{-N}$ significantly influenced the genotoxicity of DOM fractions during chlorination. To our best knowledge, no report is available about the DBP speciation in chlorination at different Cl_2/N ratios, or about the effect of the chemical characteristics of DOM fractions on DBP formation.

The main objectives of this study were (1) to investigate the effect of $\text{NH}_3\text{-N}$ on the concentrations and species of DBPs during chlorination of DOM fractions; (2) to illuminate the relationship of the characteristics of DOM fractions and the DBP formation at different Cl_2/N ratios. This work should shed light on the removal

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of DBP precursors so as to minimize the potential harm that exists in the chlorination of $\text{NH}_3\text{-N}$ -containing effluents.

2. Materials and methods

2.1. Wastewater sampling and characterization

Undisinfected wastewater samples were collected at the sand-filtration site of secondary effluents from Gaobeidian sewage treatment plant (G STP), the largest sewage treatment plant in China with a treatment capacity of $1 \times 10^6 \text{ m}^3/\text{day}$. Though the anoxic-aerobic activated sludge process can biologically remove nitrogen to some extent, the secondary effluent has about 3 mg/L $\text{NH}_3\text{-N}$. Samples were carefully collected, transferred to the laboratory, then filtered immediately through a pre-rinsed $0.45\text{-}\mu\text{m}$ cellulose membrane, and stored at 4°C to minimize changes in the constituents. Dissolved organic carbon (DOC) and UV absorbance at 254 nm or 280 nm were measured with a TOC analyzer (Multi N/C 3000) and an ultraviolet-visible spectrophotometer (U-3010, Hitachi, Japan), respectively. The $\text{NH}_3\text{-N}$ concentration was obtained according to the salicylate method with an ultraviolet-visible spectrophotometer (U-3010, Hitachi, Japan). Bromide ion (Br^-) concentrations of effluents and DOM fractions were measured with an ionic chromatograph (Metrohm 761, Switzerland).

2.2. Chemicals and materials

Solutions were prepared with ultrapure water. Ammonia chloride (NH_4Cl) stock solution was 1 g/L . A free chlorine (HOCl) stock solution (about 5 g/L) was prepared from 7% sodium hypochlorite (NaClO) and its concentration was measured prior to use according to the DPD colorimetric method (EPA method 330.5). 50 mM sodium phosphate buffer solution was used to maintain solutions at pH 7.

Hexane and methyl tert-butyl ether used to extract DBPs were obtained from Fisher and J.T. Baker, respectively. Four THM standards, i.e., chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3), and five HAAs standards, i.e., monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA) were purchased from Aldrich.

2.3. Analytical methods

THM and HAA analyses were conducted according to EPA method 551.1 and EPA method 552.3, using an Agilent 6890N Gas Chromatograph (USA) that was equipped with a fused silica capillary column (HP-5, 30 m , $320 \mu\text{m} \times 0.25 \mu\text{m}$) and a linearized electron capture detector (ECD). For experiments involving THMs, a temperature program was used wherein the temperature was held at 35°C for 4 min and ramped to 60°C at $10^\circ\text{C}/\text{min}$. The following temperature program was used for HAAs: the temperature was held at 35°C for 4 min, ramped from 35°C to 70°C at $2^\circ\text{C}/\text{min}$ and held at 280°C for 3 min.

Standard curves were obtained by extracting standards from the aqueous solutions and a blank ($0 \mu\text{g/L}$ as DBPs) of ultrapure water was also included. In the study, the DBPs of samples without chlorination were measured as the controls.

DOM powder obtained through freeze-drying the fractions was analyzed for its structural and chemical characteristics. KBr was mixed with the DOM powder about the ratio of 100 to 1 and the Fourier transform infrared (FTIR) spectra of the mixture were obtained by scanning it with IR spectrometer (Thermo Nicolet 5700, USA).

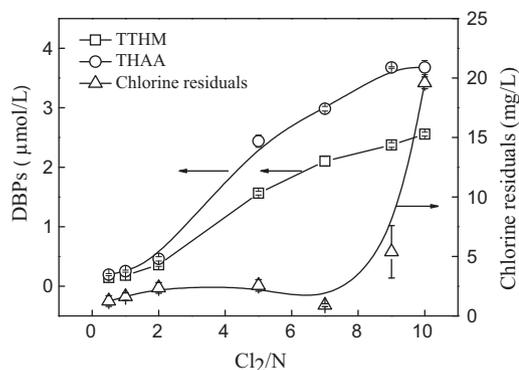


Fig. 1. Chlorine residuals and DBP formation of the effluent at different Cl_2/N mass ratios. Experimental conditions were $\text{DOC} = 7.2\text{--}8.2 \text{ mg/L}$; $\text{pH} = 7.0$; $\text{NH}_3\text{-N}$ concentration = 3.0 mg/L as N; temperature = 20°C ; and contact time = 3 days.

2.4. Fractionation of DOM

The fractionation of DOM was performed following the procedure modified from Imai et al. [13], Leenheer [15], and Chefetz et al. [16]. Three resin adsorbents, i.e., Amberlite XAD-8 resin (20–60 mesh), Dowex Marathon MSC resin (20–50 mesh), and Duolite A-7 (free base), were used to isolate DOM into six fractions: hydrophobic acids (HoA), hydrophobic neutrals (HoN), hydrophobic bases (HoB), hydrophilic acids (HiA), hydrophilic neutrals (HiN), and hydrophilic bases (HiB). The fractionation procedure is listed in supporting information.

2.5. Experimental procedures

In order to compare the characteristics of the DOM fractions, all samples were conditioned to similar DOC concentrations of about 3 mg/L . The reactants were added into the water samples in the following order: $\text{NH}_3\text{-N}$, buffer, and finally chlorine in the form of NaClO at a dosage of 20 mg/L (as Cl_2). Following incubation in the dark at 20°C for three days, the chlorination was quenched with sodium sulfite (Na_2SO_3) and the DBPs were analyzed by GC-ECD. A_{280} was determined before and after chlorination. A series of Cl_2/N ratios which were 4, 5, 6, 7, 8, 9, 10, and 11 was examined in this study, and control samples which did not contain $\text{NH}_3\text{-N}$ was also conducted for comparison. All experiments were performed at least 3 times.

3. Results and discussion

3.1. Effect of Cl_2/N mass ratios on the DBPs formation of DOM

The concentrations of $\text{NH}_3\text{-N}$ and Br^- of the effluents from G STP were measured, and the results showed a little variation for samples collected periodically, with $\text{NH}_3\text{-N}$ at about 3 mg/L and Br^- below 0.01 mg/L . Fig. 1 shows the total DBPs formation (TTHM and THAA) of the effluents and the chlorine residuals (either free chlorine or combined chlorine) at different Cl_2/N mass ratios. The breakpoint curve displayed a typical curved shape, as demonstrated by Yang et al. [8]. The Cl_2/N mass ratio to achieve the chlorination breakpoint was found to occur at 7. It was observed that the formation of DBPs increased sharply with increasing Cl_2/N mass ratios, which can be explained by the variation from monochloramination to chlorination. Monochloramine was the dominant species in the chlorinated system when the Cl_2/N mass ratio was less than 5 and the pH value was between 6.5 and 8.5 [17]. Although ammonia could quickly react with free chlorine and change to combined chlorines (chloramines) during chlorination [18–20], the reactivity of combined chlorines was much weaker than that of free chlorine,

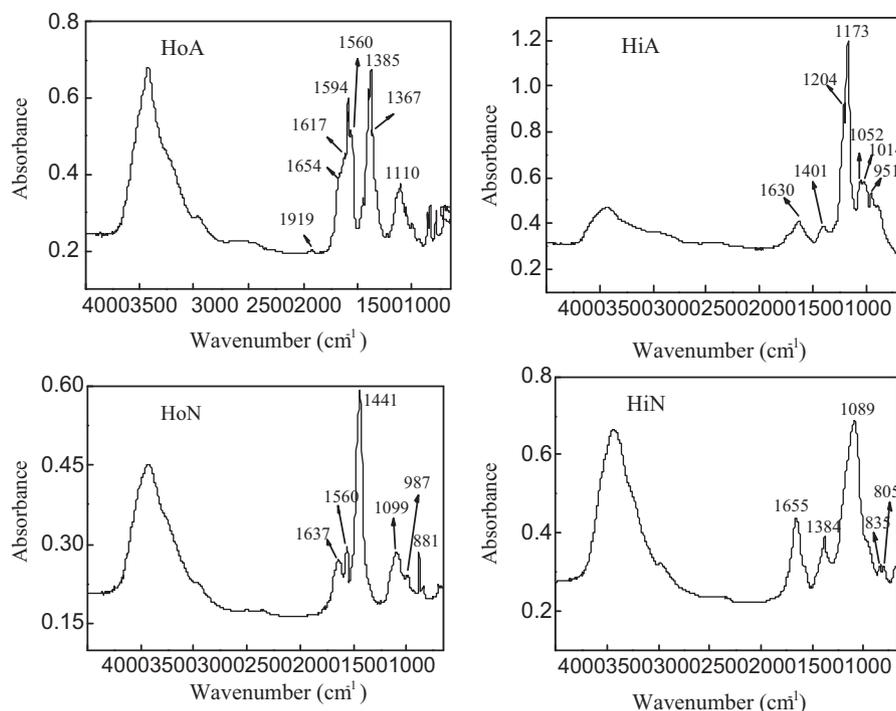


Fig. 2. Chemical structures of DOM fractions. HoA: hydrophobic acids; HiA: hydrophilic acids; HoN: hydrophobic neutrals; HiN: hydrophilic neutrals.

and the combined chlorines were more slowly to form DBPs during the reaction with DOM in wastewater.

3.2. Effect of Cl_2/N mass ratios on the DBPs formation of DOM fractions

In order to explore the effect of Cl_2/N mass ratios on the specific DBPs, DOM was isolated into six fractions using aforementioned fractionation techniques. The DOC concentrations of the effluent ranged from 7.2 to 8.2 mg/L, and the UV_{254} to DOC ratio (SUVA) was at 1.5–2.2 $\text{abs l cm}^{-1} \text{g}^{-1}$. Fractionation of DOM was conducted on water samples collected periodically. In general, hydrophobic organics were the dominant part, collectively accounting for more than 60% of their DOM as DOC. In particular, the HoA fraction was found to be the most abundant fraction, constituting about 40% of DOM. HiA was the second most dominant fraction, accounting for about 15%. The DOC percentages of HoN and HiN were similar, at about 10%. Hydrophobic bases, HoB and HiB, constituted less than 10%. The DOM was mainly composed of organic acids and neutrals. Therefore, organic bases were ignored in our study.

The FTIR spectra of the four dominant fractions (HoA, HiA, HoN, HiN) are shown in Fig. 2. Interpretation of the absorption bands of DOM was done as described in the literature [9,21,22]. It was observed that the hydrophobic organics (HoA, HoN) were similar in spectra, which presented a distinctive absorption band at 1380–1450 cm^{-1} referring to aliphatic structures. Furthermore, the HoA fraction was found to contain more C=C or C=O structures at about 1600 cm^{-1} . Compared with HoA and HoN, the HiA and HiN fractions contained relatively high C–O content at about 1100 cm^{-1} .

The four DOM fractions were chlorinated with different Cl_2/N mass ratios at a chlorine dosage of 20 mg/L for 3 days. The chlorine residuals and the formation of total DBPs (TTHM and THAA) are shown in Fig. 3. In order to compare the reactivity of DOM fractions with chlorine, all TTHM and THAA data were normalized relative to the DOC concentrations to obtain the specific yields.

It was observed that the organic acids (HoA and HiA) exhibited a relatively high TTHM and THAA yield on a carbon basis and the spe-

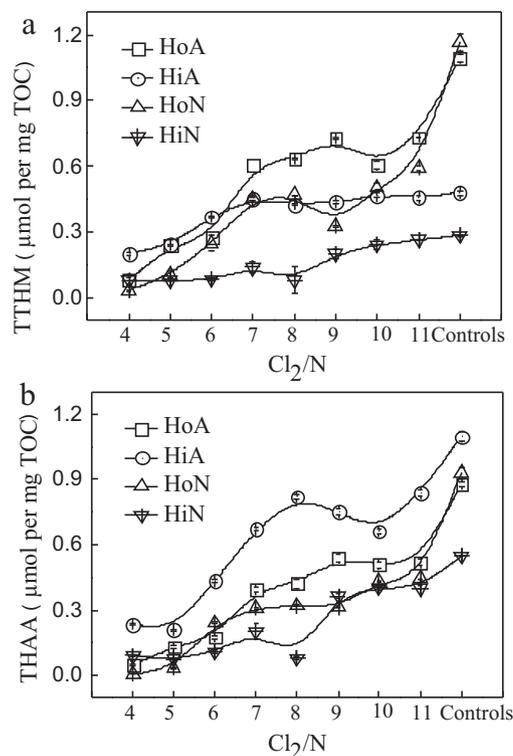


Fig. 3. Chlorine residuals and DBP formation of DOM fractions at various Cl_2/N ratios. HoA, hydrophobic acids; HiA, hydrophilic acids; HoN, hydrophobic neutrals; HiN, hydrophilic neutrals; Controls, samples without addition of $\text{NH}_3\text{-N}$. All samples were conditioned to similar DOC concentrations of about 3 mg/L. The experimental conditions were pH = 7.0; chlorine dosage = 20 mg/L as Cl_2 ; temperature = 20 °C; and contact time = 3 days.

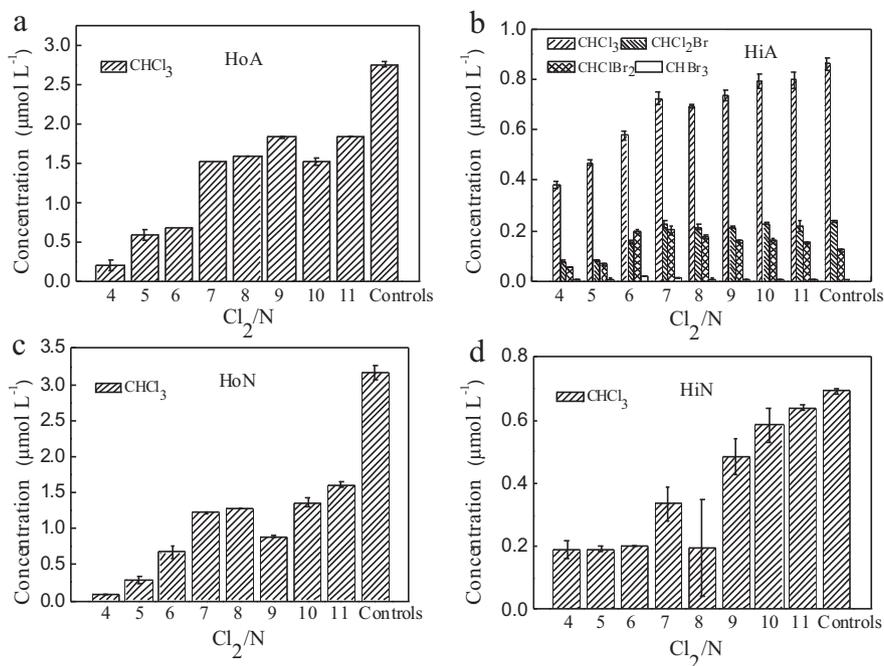


Fig. 4. Effect of Cl_2/N ratios on the formation of THMs. HoA, hydrophobic acids; HiA, hydrophilic acids; HoN, hydrophobic neutrals; HiN, hydrophilic neutrals; Controls, samples without addition of $\text{NH}_3\text{-N}$. All samples were conditioned to similar DOC concentrations of about 3 mg/L. The experimental conditions were pH = 7.0; chlorine dosage = 20 mg/L as Cl_2 ; temperature = 20 °C; and contact time = 3 days.

cific TTHM and THAA mostly presented an increasing trend as the Cl_2/N mass ratio increased. Furthermore, the chlorination breakpoint of all DOM fractions was found to occur at about Cl_2/N 6. The HiA fraction was found to have the highest specific TTHM before the breakpoint; however, the HoA fraction displayed the highest specific TTHM formation beyond the chlorination breakpoint. It can be inferred that the reactivity of HoA with chlorine was relatively high in comparison with that of HiA, but the THMs formation of HoA was significantly suppressed by chloramination. The reason might be explained by the variation in the reaction mechanism of HoA and HiA due to the difference in the chemical structures. According to the FTIR analysis, the HoA fraction contained more C=C or C=O and aliphatic structures, whereas the HiA fraction presented a high content of C–O structures. Yang et al. [7] demonstrated that chlorination of fulvic acids leads to the formation of intermediate by-products such as $\text{CHCl}_2\text{-CO-R}$ or $\text{CCl}_3\text{-CO-R}$, which can be hydrolyzed to form chloroform and DCAA. On the other hand, the HiA fraction formed the most specific THAA at various Cl_2/N mass

ratios and HoA produced the second most. It can be concluded that the C–O structures also contributed to the formation of DBPs, especially HAAs. In general, organic acids i.e., HoA and HiA were the dominant precursors of potential TTHM and THAA formation, though the HoN fraction showed higher TTHM formation than HiA at Cl_2/N ratios beyond 10.

When the Cl_2/N mass ratio reached or exceeded the chlorination breakpoint, substantial increases in the concentrations of TTHM and THAA were observed. Before the breakpoint, $\text{NH}_3\text{-N}$ was dominant in the chlorine–ammonia equilibrium; as the Cl_2/N mass ratio increased, monochloramine increased correspondingly and the formation of TTHM and THAA was enhanced. After the breakpoint, free chlorine was elevated as the Cl_2/N ratio increased, which caused the DBPs to increase faster than in the conditions of chloramination. Free chlorine produced a much higher level of total organic chlorine (DOCI) and bromine (TOBr) than chloramines [23]. The details of the species of DBPs at various Cl_2/N ratios are discussed in the subsequent sections.

3.2.1. THM speciation and concentration

Fig. 4 illustrates the formation of different THM species after 3-day chlorination of DOM fractions at various Cl_2/N ratios. The dominant fractions in the study were desorbed from the XAD-8 resin and Duolite A7 which did not adsorb ammonia nitrogen, and thus samples of the dominant fractions without $\text{NH}_3\text{-N}$ were used as control samples.

In the cases of HoA, HoN, and HiN fractions, only CHCl_3 was detected. As for the HiA fraction, four THM species were formed: CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 . The reason might lie in the fact that only HiA was desorbed from anionic resins. When the effluent samples were pumped through three sequential resins, Br^- was adsorbed onto the anionic resins. Thus, HiA was desorbed accompanied with Br^- .

Among these THM species, CHCl_3 was the most abundant and its concentration increased gradually with increasing Cl_2/N ratios before the breakpoint. A significant jump occurred at Cl_2/N 7. Subsequently, the CHCl_3 concentration kept increasing gradually until

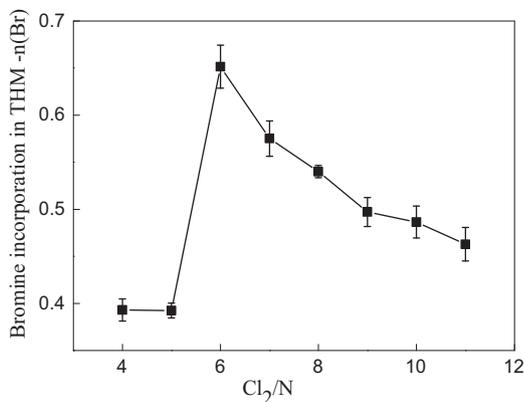


Fig. 5. Bromine incorporation in THMs as a function of Cl_2/N mass ratios of the HiA fraction. HiA, hydrophilic acids.

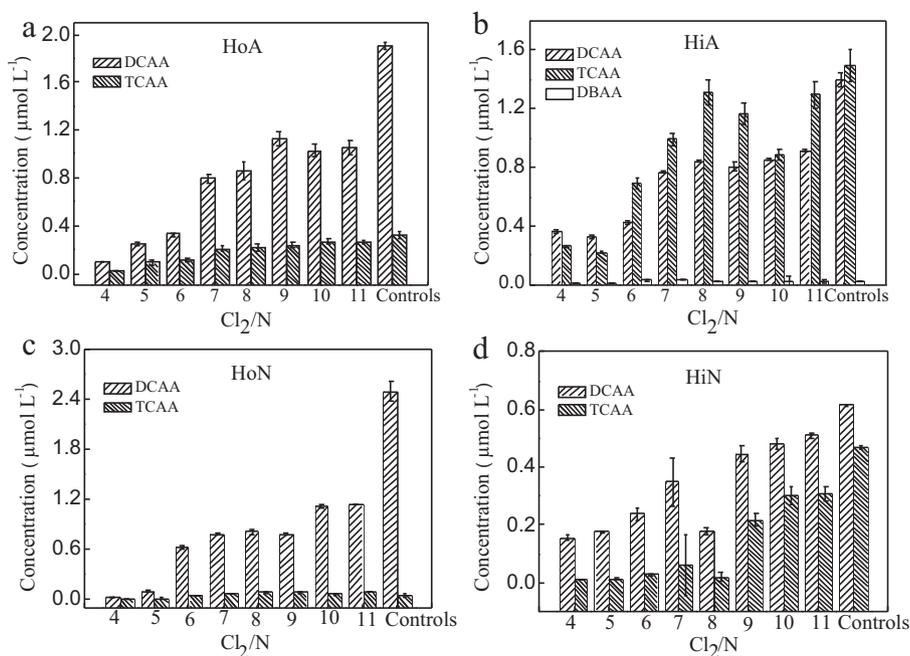


Fig. 6. Effect of Cl₂/N ratios on the formation of HAAs. HoA, hydrophobic acids; HiA, hydrophilic acids; HoN, hydrophobic neutrals; HiN, hydrophilic neutrals; Controls, samples without addition of NH₃-N. All samples were conditioned to similar DOC concentrations of about 3 mg/L. The experimental conditions were pH = 7.0; chlorine dosage = 20 mg/L as Cl₂; temperature = 20 °C; and contact time = 3 days.

a slight decrease occurred at a certain Cl₂/N ratio; however, the CHCl₃ concentration continued to rise to higher levels thereafter. Decreases in HoA and HoN occurred at Cl₂/N 10 and 9, respectively, whereas the decrease for hydrophilic organics was at Cl₂/N 8. In general, samples without NH₃-N produced the highest THMs. The decrease after the breakpoint suggested that the decrease of THMs was not always consistent with the increase of NH₃-N concentration. It seemed that at a certain high Cl₂/N mass ratio, free chlorine might react with NH₃-N to form some substances representing rather low reactivity with DOM, which caused the decrease in the formation of DBPs [24].

The presence of Br⁻ tended to shift THM species to bromine-containing ones. This can be clearly supported by comparing the formation of THMs in samples of HiA and the other three fractions. To assess bromine substitution in THM quantitatively, bromine incorporation factor *n*(Br) is often used. It can be calculated from the following equation [25]:

$$n(\text{Br}) = \frac{[\text{CHCl}_2\text{Br}] + 2[\text{CHClBr}_2] + 3[\text{CHBr}_3]}{\text{TTHM}} \quad (1)$$

where the concentration of each THM species is expressed in μmol/L, and TTHM refers to the total micromolar concentration of THMs. An increase in the *n*(Br) value indicates the formation of more bromine-substituted species.

In contrast with the effluent, the HiA fraction contained concentrated Br⁻, which could not be easily removed from the solutions. In this study, the Br⁻ concentration of HiA (about 0.02–0.03 mg/L) was 2–3 times of that in the effluent, whereas its DOC concentration was only one half of that in the effluent. Thus, the HiA fraction showed a much higher Br⁻/DOC ratio. When a similar chlorine dosage was added to the effluent and the HiA fraction, the *n*(Br) values were much higher for the HiA fraction, whereas the highest *n*(Br) value for the effluent was below 0.18. The result was in accordance with the studies by Chellam and Krasner [26] and Yang et al. [8], in which an increase in *n*(Br) was observed with the increasing of the Br⁻/DOC ratio. In the case of HiA (Fig. 5), the *n*(Br) values remained relatively constant below the breakpoint, but a sharp increase occurred at the breakpoint. Subsequently, the *n*(Br) val-

ues decreased gradually after the breakpoint. In the reactions with HOCl, the rate constant of Br⁻ ($k = 2.95 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$) was lower than that of NH₃-N ($k = 6.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$) [27]. Furthermore, the Br⁻/N molar ratio was relatively low before the chlorination breakpoint, which limited the amount of Br⁻ available to react with chlorine and enhanced the formation of chloramines. With the increasing of the Cl₂/N ratio, the NH₃-N concentration decreased and the Br⁻/N ratio increased correspondingly. Thus, Br⁻ reacted with chlorine more easily to form bromo-species, thereby increasing the *n*(Br) value. After the breakpoint, the chlorine residuals increased and the formation of chloro-species was promoted, thus leading to the decrease of the *n*(Br) values.

3.2.2. HAA speciation and concentration

Fig. 6 displays the formation of different HAA species after 3 days chlorination of DOM fractions at various Cl₂/N mass ratios. As was shown, bromo-species such as MBAA and DBAA were not detected in the HoA, HoN, or HiN samples. Even for HiA, MBAA was below the detection limit and DBAA accounted for only a small fraction of the total HAAs.

With respect to HoA and HoN, DCAA was the dominant species and its yields increased with a gentle slope before the breakpoint, but jumped at or a little beyond the breakpoint. Generally, the increasing inclination of DCAA agreed with that of CHCl₃, as shown in Fig. 4. The distribution of HAA species for hydrophilic fractions was quite different from that for the hydrophobic fractions. As shown in Fig. 6, the proportion of TCAA for hydrophilic organics was just a little lower than DCAA. Even for the HiA fraction, DCAA was abundant at very lower Cl₂/N mass ratios, but thereafter TCAA became the dominant HAA species as the Cl₂/N mass ratio increased. In the case of the HiN fraction, TCAA occupied from 7.2% to 43.3% in THAA with the increase of Cl₂/N mass ratios. In general, TCAA occupied a larger proportion in THAA for hydrophilic organics, especially in conditions without the effect of chloramines. It can be concluded that the precursors of HAAs contained in hydrophilic organics were different from those in hydrophobic fractions, as shown in Fig. 2. Compared with bromo-THM species, HiA produced

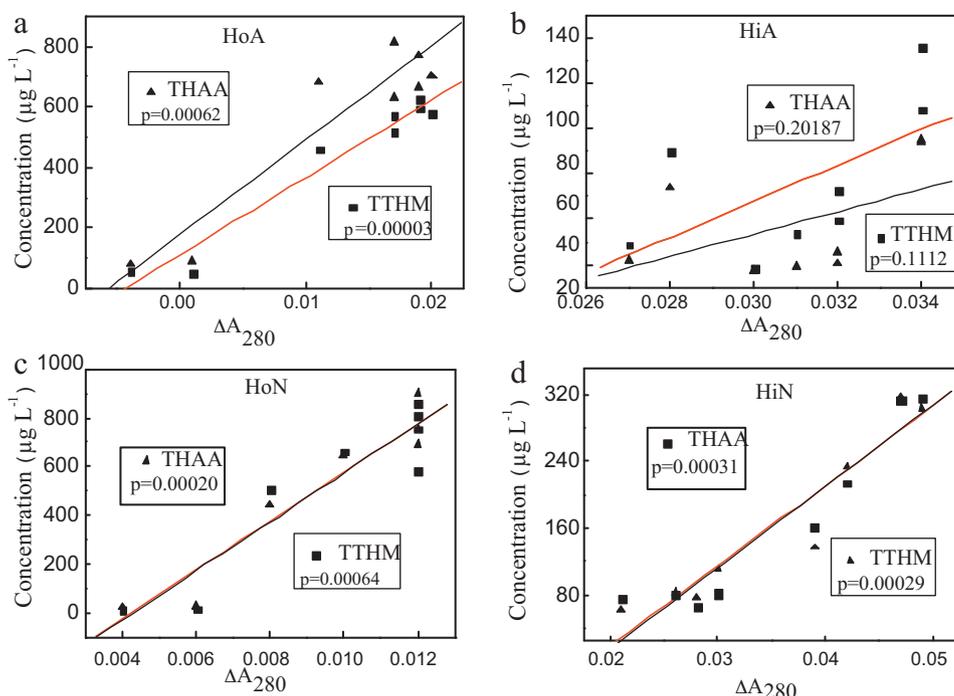


Fig. 7. The relationship between A_{280} loss (ΔA_{280}) and the formation of DBPs. HoA, hydrophobic acids; HiA, hydrophilic acids; HoN, hydrophobic neutrals; HiN, hydrophilic neutrals. All samples were conditioned to similar DOC concentrations of about 3 mg/L.

low concentrations of bromo-HAA species (MBAA and DBAA). The results were in accordance with the study by Yang et al. [8], which suggested that the brominated species comprised higher molar fractions in THMs than in HAAs.

It was interesting that a similar decrease at a certain Cl_2/N mass ratio was also found in HAAs. In general, the decrease in THMs or HAAs occurred a little beyond the chlorination breakpoint, where decomposition of the disinfectants i.e., HOCl or monochloramine seemed to occur. Since the reaction was buffered at pH 7, chloramines especially monochloramine were the dominant species before the chlorination breakpoint. However, more dichloramine may be produced with the increasing of Cl_2/N mass ratio as shown in the following reaction (2) [24], which finally caused a decrease in the reactivity of the reactions to form DBPs. Thereafter, the formation potential of DBPs was enhanced by higher Cl_2/N mass ratio.



3.3. A_{280} loss (ΔA_{280}) of DOM fractions

UV absorbance at a wavelength generally between 254 nm and 280 nm has been used to represent the aromatic characteristics of organic matter [28]. The change in absorbance at wavelength λ (ΔA_λ), defined as $A_{\lambda, \text{initial}} - A_{\lambda, \text{final}}$, has frequently been found to exhibit a relationship with the formation of DBPs in chlorination. Li et al. [29] demonstrated that ΔA_{272} was linearly related to the total organic halogen (TOX). However, different water sources may lead to various results. In our study, the DBPs formation of each DOM fraction varied according to the change in Cl_2/N mass ratios, which was attributed to the formation of chloramines during chlorination. In addition, correlations were observed between ΔA_{280} and DBP abundance for each DOM fraction (Fig. 7).

As shown in Fig. 7, TTHM and THAA showed good positive correlation results ($p < 0.001$) in samples of DOM fractions, with the exception of HiA ($p > 0.1$). The reason might lie in the formation of bromo-DBPs due to the presence of Br^- , as Yang et al. [8] demonstrated that the linear relationship between UV absorbance and

DBPs formation did not hold for bromo- and bromochloro-DBPs. The formation of THMs and HAAs in chlorination was affected by both UV absorbance values and Br^- concentrations [26].

Due to the presence of NH_3-N during chlorination, free chlorine and chloramines both existed and reacted with DOM to form DBPs. It was clear that DBPs showed positive linear relationship with ΔA_{280} during chlorination or chloramination [8]. The results allowed ΔA_{280} to monitor DBPs formation for DOM without containing bromide.

4. Conclusions

- (1) Organic acids were the dominant precursors of THMs and HAAs. In view of the FTIR analysis, the C=C, C=O and C-O structures contributed to the formation of DBPs significantly during chlorination.
- (2) Increasing of Cl_2/N mass ratios enhanced the formation of DBPs in wastewater chlorination. The DBPs formation potential of DOM fractions increased gently before the chlorination breakpoint, but a significant increasing trend was observed after the breakpoint. However, an unusual decrease in DBPs occurred a little beyond the chlorination breakpoint for each DOM fractions, which was caused by the formation of dichloramines at a certain Cl_2/N mass ratio.
- (3) The incorporation of bromine in DBPs was largely affected by Cl_2/N mass ratios. Generally speaking, the incorporation of bromine in THMs of the HiA fraction increased with the increasing of Cl_2/N mass ratio before the chlorination breakpoint, but decreased sharply after the breakpoint. The results indicated that high Cl_2/N mass ratios enhanced the formation of chloro-DBPs. In addition, the presence of Br^- affected the linear correlation between ΔA_{280} and the formation of DBPs, indicating that ΔA_{280} was linearly related to the TTHM and THAA of wastewater without containing Br^- during chlorination or chloramination.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.098.

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