



Evaluation of disinfection by-products formation during chlorination and chloramination of dissolved natural organic matter fractions isolated from a filtered river water

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ABSTRACT

Dissolved natural organic matter (DOM) in a filtered river water was isolated and fractionated into six different fractions. Trihalomethanes (THMs) and haloacetic acids (HAAs) formed from these isolated DOM fractions during chlorination and chloramination were determined. Results show that the hydrophobic acid, hydrophilic acid, hydrophilic base and hydrophobic neutral are major precursors of THMs and HAAs. There exist good correlations between the values of specific ultraviolet absorbance at 254 nm of the individual DOM fractions and their disinfection by-products formation potential, indicating that aromatic moieties are responsible for disinfection by-products formation for both hydrophobic and hydrophilic DOM fractions. Chloramination of the DOM fractions yields much less THMs and HAAs than chlorination. For the dominant DOM fraction (i.e. hydrophobic acid) in the water, the yields of THMs and HAAs increase more significantly in chlorination than those in chloramination with the increase of disinfectant dosage, contact time and dissolved organic carbon content.

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1. Introduction

Dissolved natural organic matter (DOM) is a complex mixture of various compounds with widely different chemical properties, and a major contributor to dissolved organic carbon (DOC) of the water. It is well known that DOM is the main precursor of disinfection by-products (DBPs) [1,2]. To date, many efforts have been made to characterize DOM in order to improve its removal and reduce DBPs formation during water treatment [3–5]. Among these works, isolation and fractionation of the DOM from water with XAD-resins and ion-exchange resins is most commonly used [6,7]. Many researchers examined DBPs formation potential of the isolated DOM fractions during chlorination. However, there are contradictory results on the DBPs formation potential of the DOM fractions from different water sources [8–10].

Chloramine has a significant advantage over chlorine in DBPs formation control [11]. The proportion of the preferred chloramine species, monochloramine, depends on chlorine to ammonia-nitrogen ratio and water pH. It is generally accepted that

monochloramine dominates at the chlorine to ammonia-nitrogen ratio about 4 in the pH range of 7.0–8.5 [12]. Only very limited amount of free chlorine can be formed from chloramine hydrolysis. There is even less free chlorine that will react with DOM forming DBPs, because the free chlorine from monochloramine hydrolysis can react with both ammonia and DOM [13]. To the authors' knowledge, very few researches have been carried out to evaluate DBPs formation of various DOM fractions with different chemical properties during chloramination.

DBPs formation is generally affected by disinfectant concentration, contact time, pH, DOM property and concentration, temperature and bromide concentration. Since these parameters are related with water qualities and water treatment efficiencies, the variation of water sources and treatment processes affects DBPs production significantly. Therefore, the influence of these parameters should be taken into account in investigating DBPs formation of the DOM fractions during chlorination and chloramination.

This work is to investigate trihalomethanes (THMs) and haloacetic acids (HAAs) formation from individual DOM fractions isolated from the filtered Songhua river water (at Harbin) during chlorination and chloramination. Since hydrophobic acid accounted for the largest proportion of the total DOC of the water among the isolated DOM fractions, the effect of disinfectant dose, reaction time, DOC and pH on DBPs formation from hydrophobic

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Table 1
Major characteristics of the filtered river water

Parameter (unit)	Average value
DOC (mg/L)	3.28
UV ₂₅₄ (cm ⁻¹)	0.074
pH	7.2
Br ⁻ (μg/L)	52

acid during chlorination and chloramination were further investigated in detail.

2. Material and methods

2.1. DOM isolation and fractionation

Since disinfection is generally applied after filtration in water treatment plant, the filtered water of a drinking water treatment plant in Harbin was used for DOM fractions isolation. The source water from Songhua River at the upstream of Harbin was successively aluminum coagulated, sand filtered and membrane filtered with molecular size cut-off of 50 kDa in this plant. Major characteristics of the filtered water are listed in Table 1.

The isolation and fractionation procedure was described in a former work [14]. Hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base were isolated by XAD-8, XAD-4, AG-MP-50 and Duolite A-7 resins. The fractions contained in the eluents were concentrated with vacuum evaporation at 40 °C. All isolated fractions were adjusted to pH 7 with diluted NaOH and HClO₄ and stored at 4 °C.

The obtained DOM fractions accounted for 75% of the original DOC. Hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base occupied 43.8, 34.0, 1.3, 15.6, 3.1 and 2.2% of the isolated DOM in terms of DOC, respectively.

2.2. Chlorination and chloramination

The DOM fractions were dissolved in MilliQ-water with a DOC concentration of about 2 mg/L. Specific ultraviolet absorbance at 254 nm (SUVA₂₅₄) of individual DOM fraction solution was detected before chlorination or chloramination. The SUVA₂₅₄ values of hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base were 2.61, 1.82, 0.77, 2.13, 0.80 and 1.96 m⁻¹ L⁻¹ mg C, respectively.

Monochloramine stock solution was prepared according to a detailed description elsewhere [15]. The available chlorine to ammonia-nitrogen ratio was 4:1. The chlorination/chloramination procedure was carried out following the Standard Method 5710 B with some modifications. The model water solutions (200 mL) of individual DOM fractions were phosphate buffered at pH 7.0. The stock solution of sodium hypochlorite or monochloramine was added into the samples. Then, the samples were incubated under dark condition at 25 °C for 48 h. Thereafter, the free chlorine or monochloramine residual was quenched with sodium sulfite for THMs analysis and ammonium chloride for HAAs analysis.

2.3. Analysis

Analysis of free chlorine and monochloramine followed the DPD-FAS titrimetric method (Standard Methods 4500-Cl F). DOC was analyzed with a Jena 3100 TOC analyzer with the analytical variance of ±0.01 mg/L (*n* = 3). UV-absorbance was measured with a spectrophotometer (Model UV-2550, Shimadzu) with the ana-

lytical variance of ±0.001 (*n* = 3). The bromide concentration was determined by an ion chromatography (Dionex ICS-3000, IonPac AS4-SC analytical column and conductivity detector). The eluent was 30 mM potassium hydroxide solution at a flow rate of 1.0 mL/min.

The determination of THMs followed US Environmental Protection Agency Method 551.1 with a GC/ECD (Agilent, 6890N; HP-5 30 m × 0.35 mm × 0.5 μm column). The detection limits were as follows: chloroform 0.020 μg/L, bromodichloromethane 0.006 μg/L, chlorodibromomethane 0.012 μg/L and bromoform 0.006 μg/L.

HAAs were determined according to US Environmental Protection Agency Method 552.3 with an Agilent GC-ECD (6890N; HP-5 30 m × 0.35 mm × 0.5 μm column). The detection limits were as follows: monochloroacetic acid 6.00 μg/L, dichloroacetic acid 0.10 μg/L, trichloroacetic acid 0.03 μg/L, monobromoacetic acid 0.20 μg/L and dibromoacetic acid 0.06 μg/L.

3. Results and discussion

3.1. THMs and HAAs formation potential of DOM fractions

It was reported that the distribution of chlorinated and brominated DBPs species has close relationship with bromide concentration of the water [16]. Bromide concentrations of the model water solutions were very low (under the detection limit of 20 μg/L) in this study. The THMs and HAAs species detected after chlorination and chloramination were only chloroform, bromodichloromethane, dichloroacetic acid and trichloroacetic acid. The specific yields of THMs and HAAs (expressed as μg/mg C) of each DOM fraction are shown in Figs. 1 and 2, respectively. Results indicate that hydrophobic acid, hydrophilic acid, hydrophilic base and hydrophobic neutral are the main DBPs precursors in chlorination and chloramination, while the other two fractions (hydrophobic base and hydrophilic neutral) yield very low concentrations of DBPs. According to Croué et al. [17], the differences of DBPs yields between the fractions are possibly due to their different characteristics of functional groups and structures. Former researches had showed that the active aromatic moieties of model compounds have high halogen consumption and DBPs production [18–20]. SUVA₂₅₄ was found to be a good surrogate of the aromatic carbon content of natural organic matter [17]. Good relationships between the SUVA₂₅₄ and THMs or total organic halides formation potential were also established [17,18]. Since the DOM fractions were isolated from the filtered water in this study, their SUVA₂₅₄ values are relatively lower than those isolated from untreated surface waters [17,21]. However, there are still good correlations between DBPs formation potential and SUVA₂₅₄ of these DOM fractions in chlorination and chloramination (Fig. 3). The corresponding linear regression coefficients (*R*²) in chlorination and chloramination were 0.99 and 0.92, respectively. The results also suggest that aromatic moieties of the DOM fractions play an important role in the formation of chlorinated DBPs regardless of their hydrophobic or hydrophilic nature.

Hydrophobic acid has the highest DBPs formation potential (with specific yield of 270.7 μg/mg C) during chlorination. Similar result was obtained by Chang et al., who separated DOM of the Pan-Hsin raw water into four fractions and concluded that the hydrophobic acid showed the greatest ability to produce DBPs [22]. In addition, it is noted that the hydrophobic acid contributes almost half DOC of the filtered water. Therefore, the water in the plant will still have high DBPs formation potential upon chlorination after sand filtration.

Compared with chlorination, chloramination reduces THMs and HAAs production greatly. For the major DBPs precursors (i.e.,

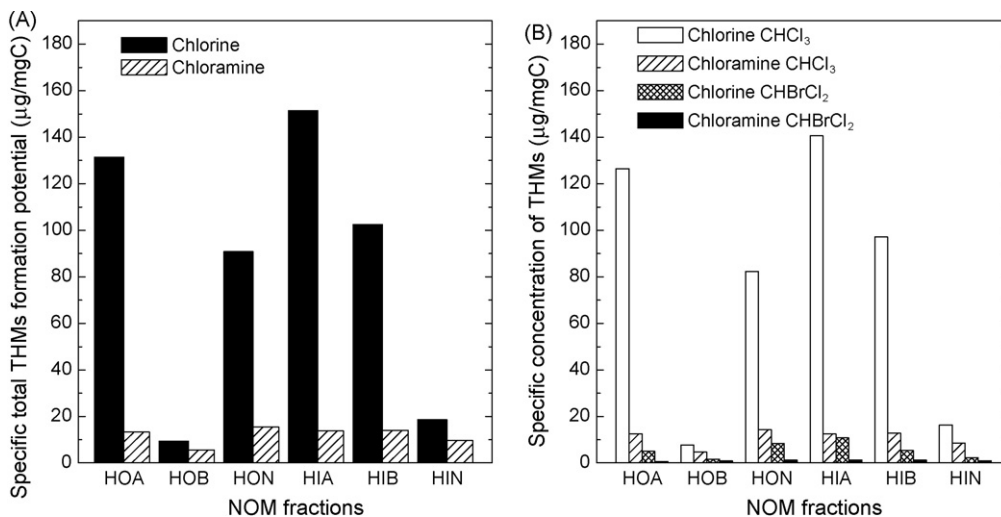


Fig. 1. Specific total THMs formation potential (A) and specific formation potential of chloroform and bromodichloromethane (B) of individual DOM fractions after chlorination and chloramination (DOC: 2 mg/L; disinfectant dosage: 20 mg/L; contact time: 48 h; pH 7.0; temperature: 25 °C).

hydrophobic acid, hydrophilic acid, hydrophilic base and hydrophobic neutral), the concentrations of DBPs formed in chloramination are just about 8.8–13.3% of those in chlorination. It is clear that chloramination can minimize the DBPs formation, which is consistent with the results of literatures [11,16,23]. The reason for low DBPs production in chloramination is not entirely clear. Cowman and Singer [16] proposed that chloramination might be a special case of chlorination with very low free chlorine formed from monochloramine hydrolysis.

It is also noted that chloroform is the major THMs species during chlorination/chloramination, while bromodichloromethane is the minor one (Fig. 1). Bromodichloromethane accounts for 3–17% and 4–15% of the total yield of THMs in chlorination and chloramination, respectively. The lower production of brominated THMs than that of chloroform is due to the low bromide concentration in the DOM fractions.

More dichloroacetic acid is formed than trichloroacetic acid for all the DOM fractions during chlorination and chloramination (Fig. 2B). It is reported that alum coagulation can remove more monohaloacetic acids and trihaloacetic acids precursors than

dihaloacetic acids precursors [24]. Reckhow and Singer observed that the high trichloroacetic acid formation potential in chlorination was related to the high SUVA_{254} of the water [18]. Therefore, the relatively high dichloroacetic acid concentrations of these DOM fractions in the filtered water are possibly due to their relatively low SUVA_{254} . Among these fractions, hydrophobic acid has a higher SUVA_{254} than other fractions. Its trichloroacetic acid yield is also higher than other DOM fractions in chlorination. In chloramination of these fractions, trichloroacetic acid is nearly not formed, and dichloroacetic acid is also the major HAAs species.

3.2. Factors affecting the formation of THMs and HAAs from hydrophobic acid

Since hydrophobic acid accounts for more than 43% DOC of the filtered water and produces the highest DBPs yield among the isolated DOM fractions, it was selected for a further detailed study to investigate the effect of disinfectant dosage, contact time, DOC and pH on its DBPs production in chlorination and chloramination.

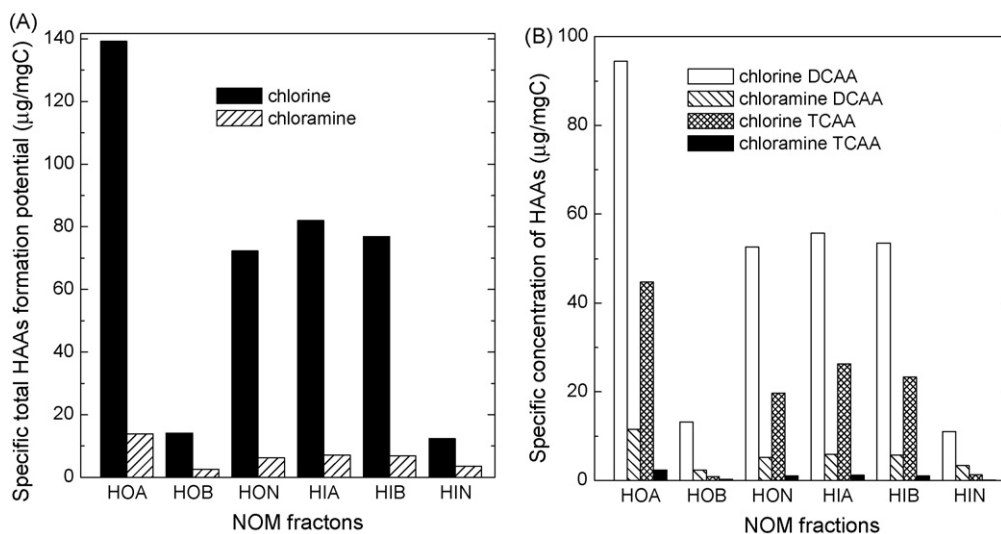


Fig. 2. Specific total HAAs formation potential (A) and specific formation potential of dichloroacetic acid and trichloroacetic acid (B) of individual DOM fractions after chlorination and chloramination (DOC: 2 mg/L; disinfectant dosage: 20 mg/L; contact time: 48 h; pH 7.0; temperature: 25 °C).

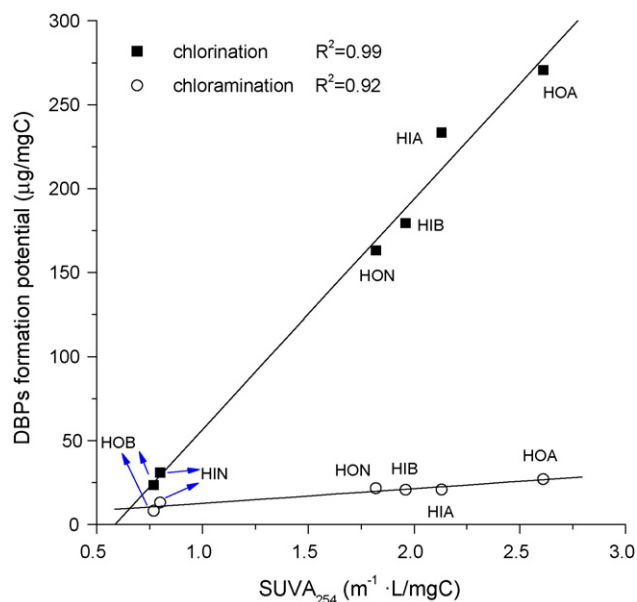


Fig. 3. Relationships between DBPs formation potential and SUVA₂₅₄ (m⁻¹ Lmg⁻¹ C) for individual DOM fractions in chlorination and chloramination.

3.2.1. Effect of disinfectant dose

As the chlorine dosage is increased from 2 to 12 mg/L, THMs and HAAs production increase significantly (Fig. 4). The increase of chloramine dosage shows a similar effect on THMs and HAAs production of hydrophobic acid. It is noticed that the HAAs yields of hydrophobic acid increase more significantly than those of THMs during chlorination as the chlorine dosage increases. According to the literatures, hydrophobic acid is composed of fulvic acids, aliphatic carboxylic acids of five to nine carbons, one and two-ring aromatic carboxylic acids, one and two-ring phenols and tannins [6,25,26], which would produce more HAAs (trichloroacetic acid and dichloroacetic acid) than THMs during chlorination [27]. Likewise, it is also reasonable that the hydrophobic acid produces slightly higher yields of HAAs than those of THMs during the increase of monochloramine dosage, because chloramination can

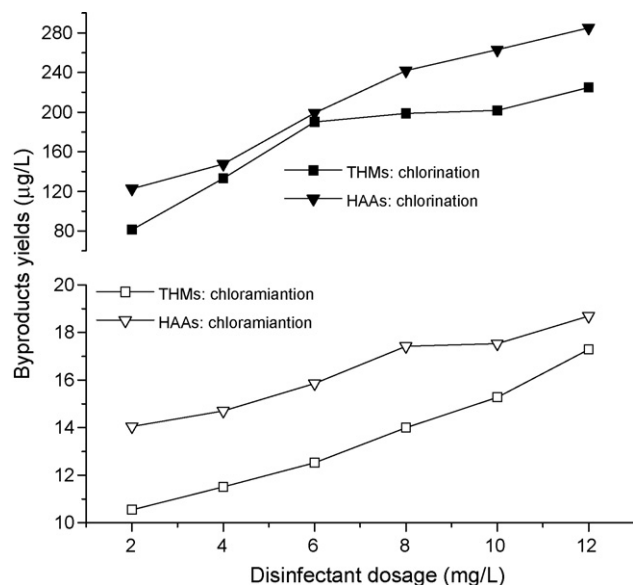


Fig. 4. Effect of disinfectant dosage on THMs and HAAs production from hydrophobic acid (DOC: 2 mg/L; contact time: 48 h; pH 7.0; temperature: 25 °C).

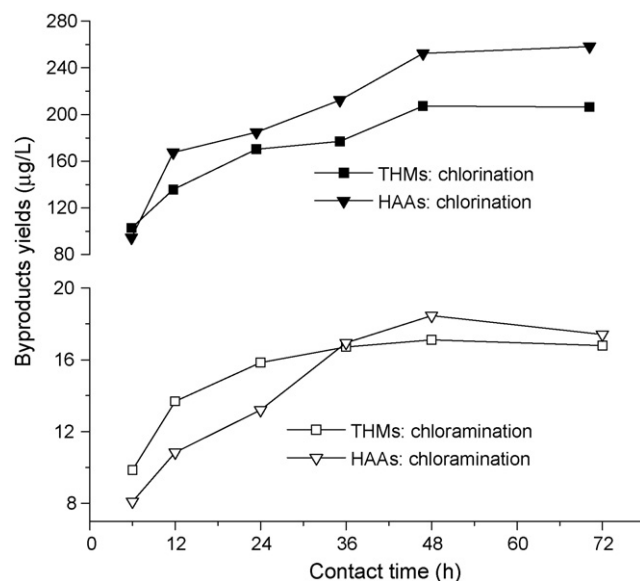


Fig. 5. Effect of contact time on THMs and HAAs production from hydrophobic acid (DOC: 2 mg/L; disinfectant dosage: 6 mg/L; pH 7.0; temperature: 25 °C).

be regarded as a special case of chlorination with a low concentration of free chlorine.

3.2.2. Effect of contact time

Fig. 5 shows the influence of disinfectant-hydrophobic acid contact time on THMs and HAAs production. As the chlorination time is extended, the THMs and HAAs yields of hydrophobic acid increase before 48 h, but keep steady between 48 and 72 h. Pourmoghaddas and Stevens [28] found a similar trend that DBPs concentrations increased with increasing reaction time, but significant differences were not observed between 48 and 168 h. The reason for this phenomenon may be that active DBPs precursor sites of the hydrophobic acid (2 mg/L) has been almost exhausted by free chlorine in 48 h reaction time. A similar trend is observed with the increase of contact time in chloramination. In addition, HAAs yields are higher than THMs when the contact time extended over 6 h during chlorination, which is possibly related to the formation mechanisms of these two classes of DBPs.

3.2.3. Effect of DOC

The effect of DOC of the hydrophobic acid on the formation of THMs and HAAs is investigated by keeping the chlorine/chloramine dose constant. The DOC of hydrophobic acid samples was 2, 4, 6, 8 mg/L, respectively. The THMs and HAAs yields increase substantially during chlorination and increase slightly during chloramination as the DOC increases (Fig. 6). Higher content of the hydrophobic acid provides more active aromatic carbon, leading to more DBPs production at a constant disinfectant dosage, which is consistent with a former report of Uyak et al. [29].

3.2.4. Effect of pH

Fig. 7 shows the effect of solution pH on THMs and HAAs formation from hydrophobic acid. The yield of each THMs and HAAs species during chlorination (Fig. 8(A)) and chloramination (Fig. 8(B)) is also illustrated. Before chlorination/chloramination, the sample pH was adjusted using phosphate buffer to reach the values of 6, 7, 8 and 9, respectively. The solution pH has a significant impact on DBPs formation. The increase of pH leads to more THMs formation during chlorination in the pH range 6–9. As far as the HAAs formation is concerned, the yield of HAAs increases as

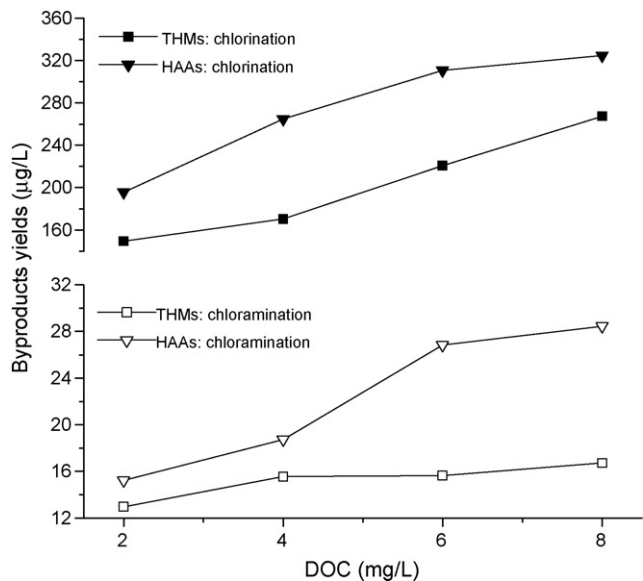


Fig. 6. Effect of DOC on THMs and HAAs production from hydrophobic acid (disinfectant dosage: 6 mg/L; contact time: 48 h; pH 7.0; temperature: 25 °C).

pH increases from 6 to 7, but decreases obviously when pH further increases.

In detail, the yield of chloroform increases while that of trichloroacetic acid decreases with the increase of pH during chlorination. The dependence of chloroform and trichloroacetic acid yields on pH during chlorination has been reported by previous researches [30,31]. According to Reckhow and Singer [32], the relatively high chloroform yield at high pH is due to the base-catalyzed hydrolysis of the THMs precursor structure (R-CO-CX₃), while the relatively high trichloroacetic acid yield at low pH can be ascribed to the readily oxidizable property of the R group in the precursor structure (R-CO-CX₃). In this work, chloroform

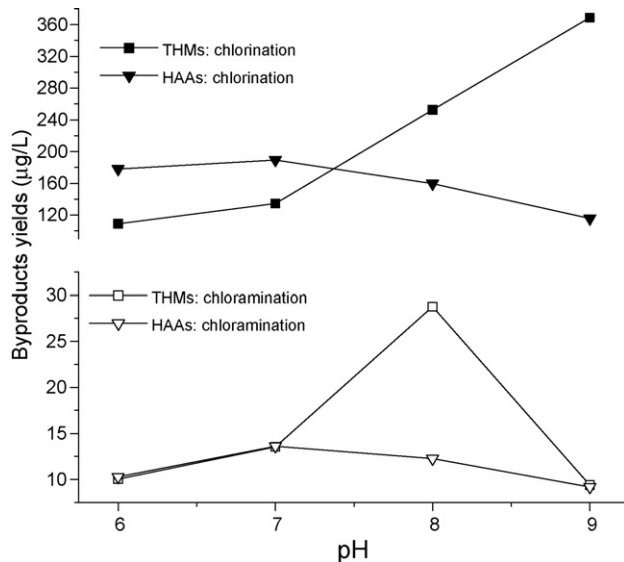


Fig. 7. Effect of pH on THMs and HAAs production from hydrophobic acid (DOC: 2 mg/L; disinfectant dosage: 6 mg/L; contact time: 48 h; temperature: 25 °C).

and bromodichloromethane yields both significantly increased as the pH increased from 6 to 9 during chlorination. The yields of dichloroacetic acid increased before pH 7 and decreased dramatically over that pH, while trichloroacetic acid concentration decreased with the increment of pH. The highest production of HAAs was observed at neutral pH in both chlorination and chloramination. The variation of dichloroacetic acid production as the pH increases in this work can be interpreted with the mechanism proposed by Reckhow and Singer [32]. They proposed that there are more precursor structures and pathways for dichloroacetic acid formation than that for trichloroacetic acid formation, thus making dichloroacetic acid formation exhibit a more complex behavior

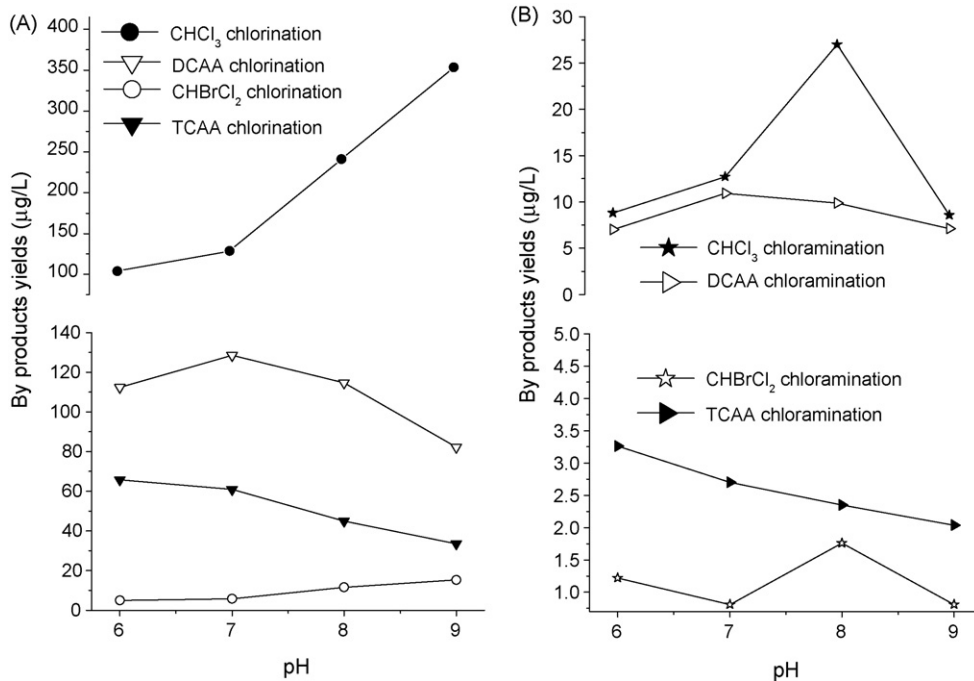


Fig. 8. Effect of pH on chloroform and bromodichloromethane yields (A) and dichloroacetic acid and trichloroacetic acid yields (B) from hydrophobic acid (DOC: 2 mg/L; disinfectant dosage: 6 mg/L; contact time: 48 h; temperature: 25 °C).

with respect to the variation of pH. No significant influence of pH on the production of THMs and HAAs species was observed during chloramination except an increase of chloroform production at pH 8. According to Diehl et al. [33], the high concentrations of chloroform at pH 8 during chloramination was possibly ascribed to the formation of some unknown active halogenating agents under this pH condition.

4. Conclusions

Six different kinds of DOM fractions (hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base) isolated from a filtered river water were chlorinated and chloraminated in this study. Chloroform, bromodichloromethane, dichloroacetic acid and trichloroacetic acid were detected during both chlorination and chloramination. Results show that chloroform and dichloroacetic acid are major DBPs species for each of the DOM fractions. Chloramination produces significantly low THMs and HAAs production for each of the DOM fractions in comparison to chlorination. Both chlorination and chloramination produce more dichloroacetic acid than trichloroacetic acid for all the fractions. Hydrophobic acid, hydrophilic acid, hydrophilic base and hydrophobic neutral are the dominant DBPs precursors.

DBPs yields of hydrophobic acid, the major component of the DOM of the water, increase considerably with the increase of chlorine dosage, DOC and contact time. However, the increase of these parameters has much less effect on DBPs formation during chloramination. The hydrophobic acid produces more HAAs than THMs during chlorination. Its THMs yield in chlorination increases significantly as the pH is increased from 6 to 9, while that in chloramination is relatively high at pH 8. Its HAAs yields at pH 7 are higher than those at other pHs in both chlorination and chloramination.

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