Relationship of chlorine decay and THMs formation to NOM size

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Abstract

Because of increasing concern about balancing health risks for pathogen control and disinfection by-product (DBP) formation in water supplies, utilities are forced to closely examine and optimize their disinfection practices. A better understanding of the relationship between the molecular weights of the natural organic matter (NOM), chlorine decay kinetics and THMs formation can help the utilities to minimize the DBP concentrations, providing healthier and microbially safer water. The authors present data on chlorine decay kinetics and total trihalomethanes (TTHM) formation kinetics and modeling with different molecular weights NOM fractions of Mississippi River water. TTHM modeling results indicated that the TTHM formation in fractionated NOM was a function of chlorine consumption. TTHM yield coefficients ranged from 31 to 42 μg-TTHM/mg-Cl_2. As the molecular weight of the fractions decreased, TTHM yield coefficients increased.
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1. Introduction

Extensive research has been conducted over the last three decades regarding chlorine reactivity with natural organic matter (NOM) and the resultant formation of various chlorinated by-products since the discovery of THMs in 1974 [1]. It has been shown that the humic fraction within NOM is a likely precursor material for THM formation [2]. Thus,

Nomenclature

C_0	the initial chlorine concentration (dose) to give the chlorine residual of approximately 1 mg/l after 5 days of reaction
$C(t)$	the chlorine concentration at any time t (mg/l)
f	fraction of the chlorine demand attributed to rapid reactions
k_R	the first-order rate constant for rapid reactions (h^{-1})
k_S	the first-order rate constant for slow reactions (h^{-1})
M_W	molecular weight

Greek letter

α	TTHM yield coefficient, defined as the ratio of the concentration (μg/l) of TTHM formed to the concentration of chlorine consumed (mg/l)

most of the research until now has been focused only on one fraction of the NOM; the humic portion that has been considered to be the primary precursor to all chlorinated DBPs. Meanwhile, the non-humic portion of the NOM has generally been ignored and regarded to be less important in DBP formation.

The most common method to obtain humic portion of NOM is by chemical fractionation method using XAD-8 and -4 resins for sorption and desorption. These two types of resin are chosen because of certain advantages associated with their use. Larger, more hydrophobic fractions can be effectively adsorbed by the XAD-8 resin because of its larger pore size and smaller surface area. On the other hand, XAD-4 has smaller pore size and greater surface area and thus more effective for hydrophilic, smaller molecular weight fractions. However, the disadvantage of this procedure is the possible incorporation of organic matter from the adsorbent. Therefore, careful resin clean-up is required. In addition, 20–30% of DOC in natural waters did not adsorbed onto XAD-4 or -8 resins. Using this method only about 80% of the NOM is recovered, and the lower recovery efficiency of carbon from the resin indicates that the desorption portion does not represent the entire composition of the NOM. Recent studies have indicated that all fractions of NOM contributed to the formation of DBPs [3]. Marhaba and Van [4] concluded that the hydrophilic acid fraction was the most reactive precursor to the THMs formation, and the hydrophobic neutral fraction was found to relate to the formation of HAAs. Liang and Singer [5] reported that hydrophilic carbon also plays an important role in DBP formation, especially for waters with low humic content.

Since NOM is a heterogeneous mixture of compounds, a better understanding of the DBP formation from NOMs may be achieved by investigating different NOM fractions characterized by molecular size. Ultrafiltration (UF) is a method to fractionate NOM into different molecular size ranges based on the molecular weight, not on the chemical properties. UF membranes with different molecular weight cut-offs (MWCO), such as 500, 1000, 3000, 10,000, 30,000, and 100,000 Da, are commonly used. Leung [6] reported that the DOC mass recovery was more than 99% using the ultrafiltration fraction processes. This suggested that the fractionated waters could better represent the real composition of NOM. Although, Sinha [3] studied the DBP sensitivity to limited molecular weights ($M_W > 1$ k

and <1 k), little is known about the relationship of chlorine decay kinetics, THM modeling and THM yield coefficients to NOM molecular size. Many investigators [7–10] have reported the relationship between the NOM molecular weight and UV adsorption (or SUVA), little research has been done in the THM formation kinetics, and THM modeling in the different molecular size NOM fractions. The specific research objectives of this study were: (1) fractionate the Mississippi River water and establish carbon mass and UVA balance of the ultrafiltration processes; (2) evaluate the formation potential of THMs for different NOM fractions; (3) investigate the formation kinetics of THMs in the fraction having the highest total trihalomethanes (TTHM) formation potential; (4) model TTHM formation in the different NOM fractions and obtain the TTHM yield coefficients.

2. Material and methods

Mississippi River water (CH) was collected from the Mississippi River at Chester, IL, south of the Missouri River confluence in October 2000. When the samples were received at the laboratory, they were kept under dark conditions in a refrigerator at 4 °C throughout the 21 days holding time to retard biological activity prior to use.

In the membrane filtration process, an Amicon Model 8200 ultrafiltration membrane stirred cell system was used to fraction the molecular size of the NOM in the water. Table 1 lists the specifications of an UF stirred cell system [11]. The stir cell was attached to a 5 l stainless pressure vessel, which could be fractionated continuously. Fig. 1 presents the stirred cell ultrafiltration system. Molecular weight cut-off (MWCO) membranes including 460, 1000 (1 k) and 10,000 Da (10 k), or referred as BQ01 (part number: 1154241. Osmonics Inc., Minnetonka, MN), YM1, and YM10 membrane (Millipore) were used to generate the molecular size fractions (starting with the highest MWCO membrane). The transmembrane pressure was created using laboratory compressed air. Before air entered the pressure vessel, a dryer was used to remove the moisture and oil in the air. First, raw water was passed through several filters in series (starting with the largest pore size filter) to remove the particulates before using UF. These filters included 1.0 μm glass fiber filter (Pall Gelman Sciences, MI), and 0.2 μm nylon membrane filter (Whatman, England). Then, the water was placed in the pressure vessel and pressurized to the stir cell. Samples were prepared by using serial processing as listed in Table 2. A conceptual schematic of the samples' serial processing

Table 1
Specifications of stirred ultrafiltration cell system

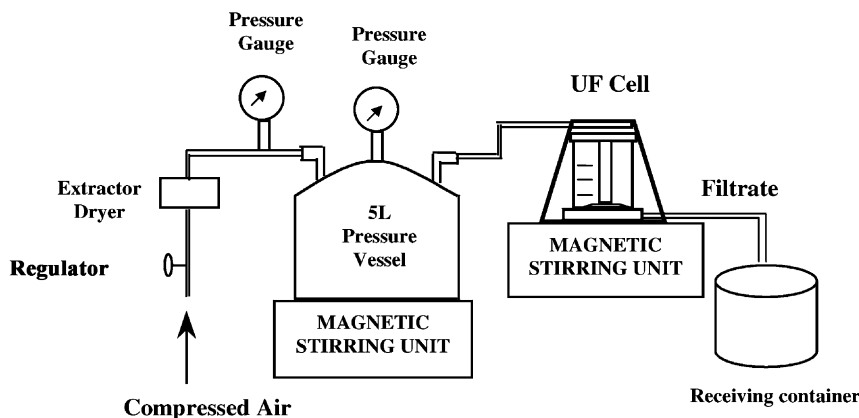|	Value	Unit
Model	8200	–
Cell capacity	200	ml
Minimum process volume	5.0	ml
Nominal membrane diameter	63.5	mm
Effective membrane area	28.7	cm^2
Hold-up volume	1.2	ml
Maximum operating pressure	75	psi

Fig. 1. Batch stirred cell ultrafiltration system.

Table 2
Ultrafiltration matrix for NOM fraction

Sample	Description	Preparation
CH1	$<1.0\,\mu m$	Filtrate from 47 mm, 1 μm glass fiber filter
CH2	$<0.2\,\mu m$	Filtrate from 47 mm, 0.2 μm nylon membrane filter
CH3	$>10\,k$	Retentate from the cell with 63.5 mm, YM10 (10 k) membrane disc
CH4	$10\,k > M_W > 1\,k$	Retentate from the cell with 63.5 mm, YM1 (1 k) membrane disc
CH5	$1\,k > M_W > 460$	Retentate from the cell with 63.5 mm, 460 NF membrane disc (BQ01)
CH6	$M_W < 460$	Filtrate from 460 NF membrane disc

is illustrated in Fig. 2. Organic compounds with molecular weight less than the nominal molecular weight cut-off of the ultrafiltration membrane permeated the membrane. The reminder of the water samples retained in the cell was suspended using deionized ultra filtered water (DIUF, obtained from Fisher Scientific) and collected as retentate.

The sodium hypochlorite dosing solution was made from a 13% active chlorine (sodium hypochlorite) stock solution and buffered to pH 8.0 using a borate buffer [12]. Prior to chlorination, the strength of the dosing solution was measured three times to ensure accuracy. The average of the three analyses was used to calculate the dosing solution volume required for obtaining the desired chlorine dose in the test reactor. Chlorination was carried out at
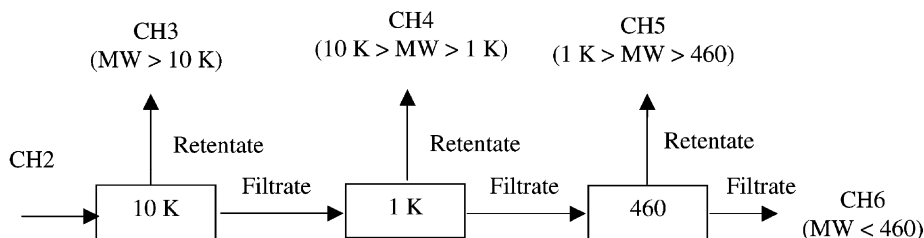

Fig. 2. Serial processing scheme in batch system.

pH 8.0 ($\pm$0.2). Before dosing, samples were buffered to pH 8.0 ± 0.2 with approximately 2 ml/l borate buffer (1.0 M boric acid (ACS grade) and 0.26 M sodium hydroxide (ACS grade) in DIUF water) [12]. Appropriate amounts from a concentrated sodium hypochlorite dosing solution (1–3 g/l) were added to the water samples to obtain the desired disinfectant doses. A blank was prepared using the same amount of DIUF water chlorinated under the same conditions as the samples. This blank was used as a reference to establish the initial chlorine concentration.

It is difficult to compare the chlorine decay kinetic behavior and DBP formation potential between water samples because the rate of chlorine decay and DBP formation is chlorine concentration (initial and residual) dependent [12–14]. In order to avoid the difficulty stated earlier, the chlorine dose in this study was selected to yield a 120 h residual of 1.0 ± 0.4 mg/l free chlorine. A 120 h chlorine demand preliminary study was performed using a series of three chlorine dosages based on Cl$_2$:TOC ratios of 1.2:1, 1.8:1, and 2.5:1 to determine the chlorine demand (120 h) of the water samples.

Samples were chlorinated in 2 gal glass bottles and then transferred into 150 ml amber glass bottles with Teflon-lined caps (making sure no air bubbles passed through the sample during the bottle filling operation, or were trapped in the sample when the bottle was sealed). A separate bottle was used for each reaction time investigated. Until analyzed, the samples were kept headspace free in the dark at room temperature (25 °C). Chlorine residual, and THMs concentration were measured at different times for each bottle.

Chlorine concentration was measured by DPD powder pillow photometric method (EPA approved HACH 8021) using HACH DR/2000 spectrophotometer. UV$_{254}$ analysis was conducted with a CARY 50 spectrophotometer (Varian, CA) with a 1-cm quartz cell. DOC concentrations were measured using a Dohrmann Phoenix 8000 TOC analyzer (Tekmar, OH). Potassium hydrogen phthalate was used as an external standard. THM concentrations were determined using a Varian Purge/Trap GC/MS (Varian, CA) according to US EPA 524 Methods. The sum of the four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) mass concentrations was reported as total TTHM in micrograms per liter (μg/l).

The following parallel first-order reaction model [15] was used to evaluate the chlorine decay:

$$C(t) = C_0 \left\{ f\, e^{-k_R t} + (1-f)\, e^{-k_S t} \right\} \tag{1}$$

where $C(t)$ is the chlorine concentration at any time t (mg/l); C_0 the initial chlorine concentration (dose) to give the chlorine residual of approximately 1 mg/l after 5 days of reaction; f the fraction of the chlorine demand attributed to rapid reactions; k_R the first-order rate constant for rapid reactions (h^{-1}); and, k_S the first-order rate constant for slow reactions (h^{-1}).

DBP formation model (2) [16] was used to fit the TTHM data of different fractions:

$$\text{TTHM} = \alpha C_0 \left\{ 1 - f\, e^{-k_R t} - (1-f)\, e^{-k_S t} \right\} \tag{2}$$

where $\alpha =$ TTHM yield coefficient, defined as the ratio of the concentration (mg/l) of TTHM formed to the concentration of chlorine consumed (mg/l).

The parameters f, k_R, k_S, and yield coefficients α (mg-TTHM/mg-Cl$_2$ costumed) were determined by non-linear regression software (SigmaPlot Version 5.0, SPSS).

3. Results and discussion

3.1. Results of NOM fraction of Mississippi River water

In this study, a total of 201 Mississippi River water at Chester, IL (CH) was used for UF separation. Fractions CH3, CH4 and CH5 were obtained by resuspending the residuals from the membrane using DIUF water (Table 2). Fractions CH1, CH2 and CH6 were filtrate samples (Fig. 2).

Before doing the filtration experiments, carbon mass balances and UV$_{254}$ balances were performed to evaluate any loss or contamination during the filtration processes. Based on the DOC and UV$_{254}$ data of initial samples, permeate samples, and retentate samples, the amount of carbon mass and UV$_{254}$ recovery for each membrane size and overall sample fractionation processes were calculated and are listed in Table 3. It can be seen from Table 3 that overall UV$_{254}$ recovery was almost 100%, and the carbon recovery was more than 96%. Therefore, the effect of membrane adsorption or leaching organic matter was minimal and membrane preparation was adequate.

3.2. Chlorine decay and modeling

Fig. 3 shows the chlorine decay relationships for the three fractions (CH3, CH4, and CH5) at different initial chlorine concentrations to make the chlorine residual to be 1 ± 0.4 mg/l after 120 h. These data show that the chlorine consumption was very rapid during the initial part of the experiment followed by a more gradual decay after 10 h of reaction for all three fractionated water samples. After normalizing the difference in the initial chlorine dose (Fig. 4), the results showed that there is only about 15% difference among the three fractions. After 15 min, all water samples had a chlorine residual of about 75–85% of the initial dose; after 10 h, the residuals had been reduced to about 50–60% of the initial dose.

Attempts were made to fit the chlorine decay data to the parallel first-order reaction model (1) [15]. In Fig. 3, the lines are the model fit data. The chlorine data in Fig. 3 fit the model well, yielding the correlation coefficients of about 0.99. The reaction constants and other

Table 3
Carbon mass and UV$_{254}$ recovery of UF filtration

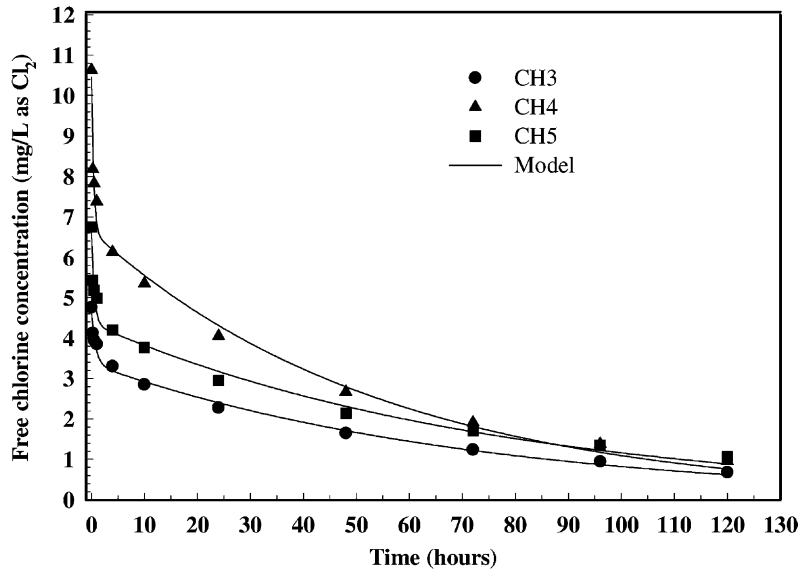| Membrane	Recovery (%)	
	Carbon	UV$_{254}$
YM10 (10 k)	101.5	98.6
YM1 (1 k)	97.7	107.0
450 (BQ01)	91.4	98.6
Overall processes	96.8	101.0

Fig. 3. Chlorine decay data of fractionated waters fitted to parallel first-order reaction model.

fitting parameters are shown in Table 4. Values of k_R for the fractionated waters ranged from 1.26 to 2.48 h^{-1} and k_S ranged from 0.013 to 0.018. The constants of rapid first-order decay rate (k_R) were about 90–150 times larger than those of the slower first-order (k_S) for all fractions. However, Vasconcelos et al. [17] reported that this was not always true; sometimes
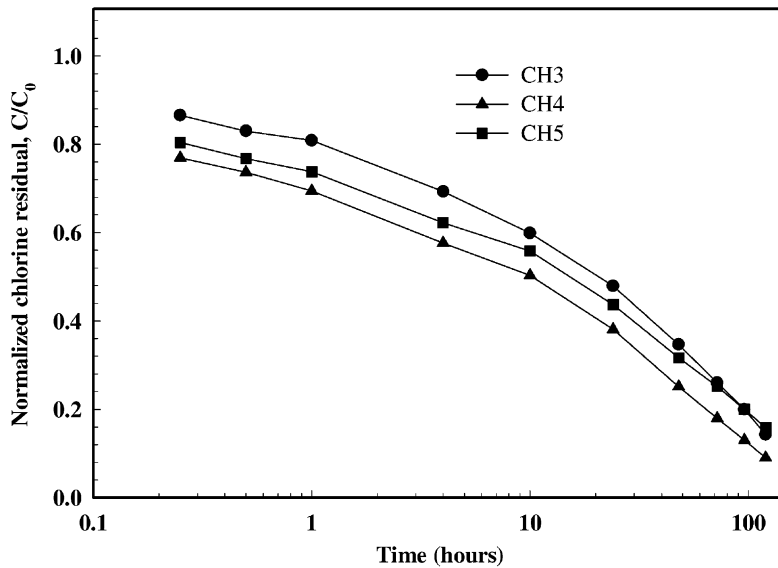

Fig. 4. Dose normalized chlorine decay curves of fractionated waters.

Table 4
Fractionated Mississippi River water chlorine decay constants for parallel first-order reaction

Sample ID	Description	k_R (h^{-1})	k_S (h^{-1})	f	R^2
CH3	$0.20\,\mu m > M_W > 10\,k$	1.26	0.014	0.28	0.994
CH4	$10\,k > M_W > 1\,k$	2.48	0.018	0.36	0.992
CH5	$1\,k > M_W > 460$	1.91	0.013	0.34	0.990

k_R values were bigger than k_S values in some water samples while in others k_R was smaller than k_S. This could be due to variable chlorine residual concentrations of water samples at the end of their study. Another possible reason could be the different characteristics of the water samples, because surface and well waters were used in their study. The k_R and k_S values of the CH4 were the largest among the fractionated water samples. Therefore, chlorine decay in CH4 fraction was the fastest. The f values of the fractionated water samples ranged from 0.28 to 0.36. Approximately 30% of the chlorine demands were attributed to the rapid reaction, which suggested that almost 70% of the NOM reactivity was attributed to the slow reaction. The f value of the CH4 was larger than the other fractions, which suggested that more chlorine followed the rapid first-order decay in the CH4 fraction.

3.3. Specific chlorine demand (SCD$_{24}$) and specific THMFP

The specific chlorine demand (SCD$_{24}$) in Fig. 5 was defined as the ratio of 24 h chlorine demand (mg/l) to the initial DOC concentration (mg/l). SCD$_{24}$ values decreased with the decreasing of NOM molecular. This may indicate that a larger number of conjugate bounds
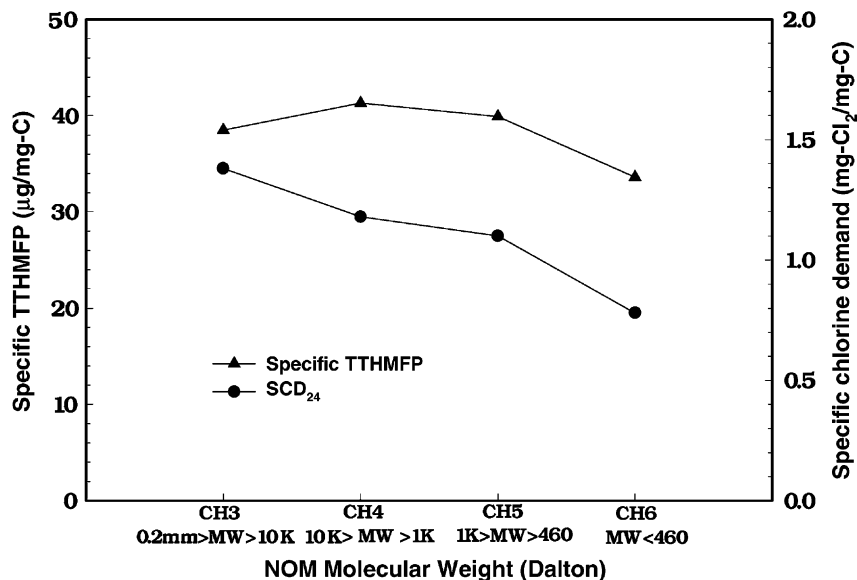

Fig. 5. Relationship between specific TTHMFP, SCD$_{24}$, and molecular weight of NOM.
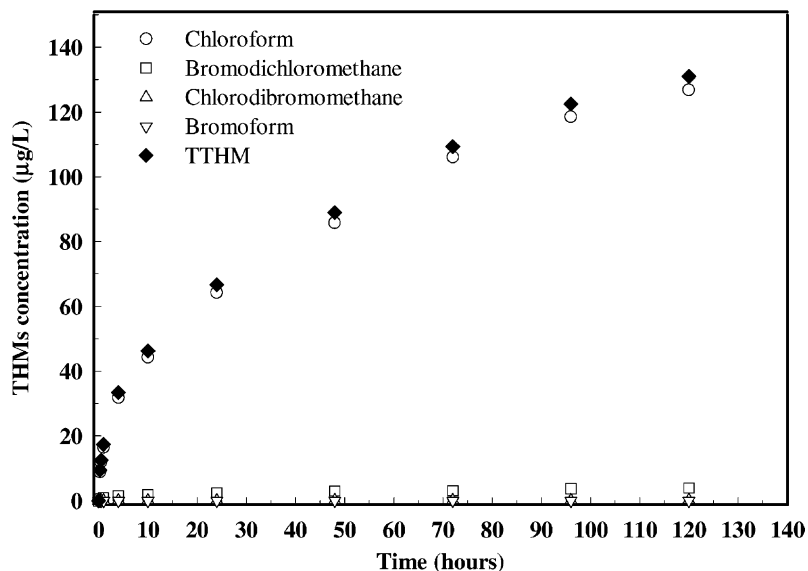
Fig. 6. TTHM and THM speciation with time of CH3 fraction.

in the higher molecular weight fraction lead to high chlorine demand (for oxidation and substitution). In order to represent the DOC reactivity directly associated with each of these fractions, normalized TTHM/DOC or specific THMFP was determined. The results are also shown in Fig. 5. Although, the specific chlorine demand (SCD_{24}) decreased with the decreasing of NOM molecular weight, no general relation between specific THMFP and NOM molecular weight fractions was observed based on the limited data collected. Sinha [3] reported that the larger molecular weight ($M_W > 1$ k) fraction had more or equal reactivity compared to the smaller molecular weight fraction ($M_W < 1$ k) in THM formation.

3.4. THMs formation kinetics, modeling and fitting parameters

THMs formation results showed that all of the samples had chloroform as the predominant species. About 95% of the TTHM was as chloroform. Fig. 6 shows the TTHM and THMs speciation with time for the CH3 fraction. This is typical of all fractions. This is in agreement with the findings of Krasner et al. [18] and Shorney [19]. It can also be seen from Fig. 6 that THM formation rates were initially rapid corresponding with the rapid consumption of chlorine, followed by a declining rate. Table 5 shows the specific TTHM formation kinetics of the fractionated waters. The formation kinetics among the various molecular weight fractions were similar based on the data collected. About 60% of TTHM was formed within the first 24 h. Sinha [3] had reported that THM formation was moderately sensitive to the molecular weight of the NOM fraction.

Attempts were made to fit the TTHM data to the DBP formation model Eq. (2) [16]. Fig. 7 shows that the data fit the DBP formation model well, yielding correlation coefficients of about 0.98. This indicated that the TTHM formation (in µg/l) was a function of

Table 5
Fractionated Mississippi River water specific TTHM formation kinetics

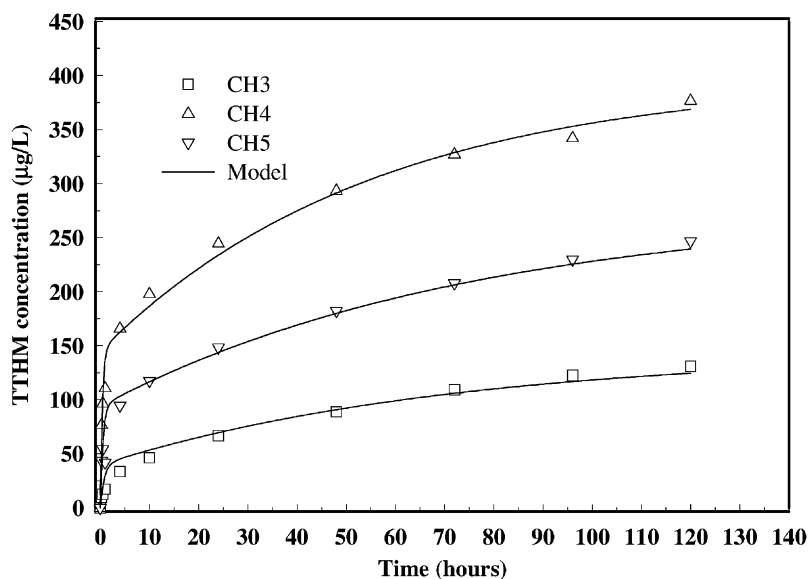| Sample ID	Description	Specific TTHMFP (μg/mg-C)					TTHMFP ratio (24/120 h)
		0.5 h	4.0 h	10.0 h	24.0 h	120.0 h	
CH3	$0.20\,\mu m > M_W > 10\,k$	7.9	20.9	28.9	41.7	81.8	0.51
CH4	$10\,k > M_W > 1\,k$	17.9	30.7	36.6	45.3	69.9	0.65
CH5	$1\,k > M_W > 460$	16.2	28.2	35.0	44.1	73.4	0.60

Fig. 7. TTHM data of various fractions fitted to the DBP formation model.

chlorine consumption in the fractionated waters. It can be concluded that any pretreatment in the water utilities reducing chlorine consumption would reduce the THM formation. For instance, ozone and chlorine dioxide pretreatments both can decrease chlorine demand; therefore, these pretreatment can reduce THM formation. Reckhow et al. [20] also found that the specific by-product formation was related to the activated aromatic content, while activated aromatic content was correlated with chlorine consumption. The results are shown in Table 6. TTHM yield coefficients ranged from 31 to 42 μg-TTHM/mg-Cl$_2$. As

Table 6
Fractionated Mississippi River water TTHM yield coefficient

Water samples	C_0 (Cl$_2$) (mg/l)	DOC (mg/l)	α (μg-TTHM/mg-Cl$_2$ consumed)
CH3	4.65	1.60	30.9 ($R^2 = 0.979$)
CH4	10.46	5.39	38.0 ($R^2 = 0.992$)
CH5	6.60	3.36	41.9 ($R^2 = 0.974$)

the molecular weight of the fractions decreased, TTHM yield coefficients increased. For example, CH5, the smallest molecular weight fraction, had the highest yield coefficient (41.9 μg-TTHM/mg-Cl$_2$ demand). On the other hand, CH3, the largest molecular weight fraction, had the lowest yield coefficient (30.9 μg-TTHM/mg-Cl$_2$ demand). One possible explanation may be that the halogenated intermediates formed from the smaller molecular weight DOCs decompose easily, which could favor formation of more THMs.

4. Conclusions

The results reported herein were based on a single sampling of Mississippi River water at Chester, IL. Specific chlorine demands decreased with the decreasing of NOM molecular weight. This may indicate that a larger number of conjugate bounds in the higher molecular weight fraction lead to high chlorine demand (for oxidation and substitution). TTHM yield coefficients ranged from 31 to 42 μg-TTHM/mg-Cl$_2$. As the molecular weight of the fractions decreased, TTHM yield coefficients increased. CH5, the smallest molecular weight fraction, had the highest yield coefficient (41.9 μg-TTHM/mg-Cl$_2$ demand). On the other hand, CH3, the largest molecular weight fraction, had the lowest yield coefficient (30.9 μg-TTHM/mg-Cl$_2$ demand). The possible reason is that the halogenated intermediates formed from the smaller molecular weight DOCs decompose easily, which could favor formation of more THMs. TTHM modeling results indicated that the TTHM formation was a function of chlorine consumption in the fractionated waters, yielding correlation coefficients of about 0.98. No strong correlation between molecular weight and chlorine decay kinetics was seen based on the limited data.

Acknowledgements

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