



## Disinfection characteristics of the dissolved organic fractions at several stages of a conventional drinking water treatment plant in Southern China

Zhen-Ye Zhao<sup>a,c</sup>, Ji-Dong Gu<sup>a,b,\*</sup>, Hai-Bo Li<sup>c</sup>, Xiao-Yan Li<sup>d</sup>, Kenneth Mei-Yee Leung<sup>b,e</sup>

<sup>a</sup> Laboratory of Environmental Toxicology, School of Biological Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, Hong Kong, China

<sup>b</sup> The Swire Institute of Marine Science, The University of Hong Kong, Shek O, Cape d'Aguilar, Hong Kong SAR, Hong Kong, China

<sup>c</sup> Shenzhen Haina Water Co., Shenzhen, Guangdong Province, 518000, China

<sup>d</sup> Environmental Engineering Research Centre, Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, PR China

<sup>e</sup> Division of Ecology & Biodiversity, School of Biological Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, Hong Kong, China

### ARTICLE INFO

#### Article history:

Received 2 February 2009

Received in revised form 27 July 2009

Accepted 27 July 2009

Available online 3 August 2009

#### Keywords:

Drinking water

Dissolved organic matter (DOM)

Disinfection by-products

Reverse osmosis

Chlorine consumption

### ABSTRACT

Dissolved organic matter (DOM) influences many aspects of drinking water treatment, including the formation of harmful disinfection by-products (DBPs) when disinfectants are applied. DOM was isolated and fractionated using membrane ultra-filtration (UF) and reverse osmosis (RO) to eight individual fractions based on molecular weight cut-offs from a conventional surface water treatment plant (WTP) in Guangzhou of PR China. Molecular weights of these eight fractions were further calibrated using high performance size exclusion chromatography (HPSEC) and they ranged from 0.36 to 182.6 kDa. Fractions with molecular weight <0.80 kDa obtained by YC-05 UF membrane and RO were the major ones in all four stages of the water treatment processes; both ZM-500 and YM-100 membranes showed the highest removal efficiency when coupling with conventional coagulation and sedimentation processes. The elemental analysis showed that YC-05 fraction had greater polarity and aromaticity than any of the others. Furthermore, disinfection characteristics and trihalomethane formation potential (THMFP) were determined for all DOM fractions obtained in this study. YC-05 fraction was the major precursor for trihalomethane (THMs) formation among the samples tested and could be removed effectively by particulate activated carbon (PAC) adsorption. RO fraction could not be removed by PAC adsorption and, as a result, consumed more chlorine in the disinfection process. The results suggested that advanced drinking water treatment should focus on the removal of low molecular weight DOM in the source water.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

As soluble organic substances cannot be captured or removed easily using conventional water treatment techniques such as coagulation [1], they may enter the municipal drinking water treatment system and be distributed through the water supply network. Moreover, during the disinfection process using chlorine, the most common disinfectant used in the drinking water industry worldwide, soluble organic substances could be converted to harmful disinfection by-products (DBPs) including trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs) [2–6]. Because of this, utility industries need to implement additional organics removal processes such as enhanced coagulation [7,8], granular activated carbon (GAC) [9,10], membrane filtra-

tion [11], or advanced oxidation. All these are mainly focused on removal of specific molecular-weight fractions or sizes of the dissolved organic matter (DOM). The distribution patterns of molecular weight or size of DOM and its molecular structure in water system have been reported recently [12–15], but information on the relationship between the formation potential of THMs and the different molecular weights of DOM is not readily available.

It is very important to address whether the reactivity of the isolated fractions represent those of the DOM molecules in the source water after concentration and fractionation procedures. Gjessing et al. [16] showed that reverse osmosis (RO) isolation did not significantly alter the color (i.e., within 10–15%), the color to UV-absorbance ratio (i.e., absorbance at 430/UV-absorbance at 254 nm), the specific Ultra-violet absorbance ( $SUVA_{254} = UV_{254}/DOC$ ), conductivity, or the coagulation properties of the source waters based on color removal. Moreover, Kitis et al. [17] showed that RO isolation had no impact on the DOM reactivity and individual DBPs species for both THMs and HAAs did not show any significant change as a result of the isolation. Therefore, RO separation has been used in the pre-treatment process for

\* Corresponding author at: Laboratory of Environmental Toxicology, School of Biological Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, Hong Kong, China. Tel.: +852 2299 0605; fax: +852 2559 9114.

E-mail address: [jdgu@hkucc.hku.hk](mailto:jdgu@hkucc.hku.hk) (J.-D. Gu).

**Table 1**  
Characteristics of the water samples obtained from four stages of a conventional drinking water treatment plant in Guangzhou, PR China.

Water	Total alkalinity (mg/L)	Total hardness (mg/L)	DOC (mg/L)	UV <sub>254</sub> (m <sup>-1</sup> )
Raw water	157.1 ± 4.8 <sup>a</sup>	207.5 ± 5.6	4.30 ± 0.11	15.4 ± 0.52
PAC water	110 ± 3.6	179 ± 5.2	3.94 ± 0.12	10.1 ± 0.48
Clarified water	104.7 ± 3.8	165 ± 5.4	2.90 ± 0.09	5.96 ± 0.21
Filtered water	88.9 ± 4.2	129.1 ± 3.9	2.45 ± 0.09	4.75 ± 0.24

<sup>a</sup> Standard deviation of three samples.

concentration and isolation of DOM from source water with wide acceptance.

Understanding the role of DOM characteristics and DBP formation may provide insight to development of more effective solutions for their control during drinking water treatment operations. Although THMs removal [18,19] and control [20] methods have been widely investigated, regression models were developed in order to predict spatial and seasonal variations of THMs [21–23]. In order to effectively control THMs formation and remove the main molecular weight THMs precursors in the water treatment process, water samples were collected from a conventional drinking water treatment plant in Southern China for this investigation.

The objectives of this research were to investigate the mass distribution of dissolved organic fraction of the water samples taken from selective stages of drinking water treatment process; to analyze the average molecular weight of the DOM in the obtained fractions using high performance size exclusion chromatography (HPSEC); to determine the main disinfection characteristics of the

different fractions for each treatment stage; and to identify the main precursors of the disinfection by-products in different fractions and THMs concentration of different molecular weight or size DOM in the disinfection process using chlorine.

## 2. Materials and methods

### 2.1. Water samples collection

Water samples were collected at different treatment stages, specifically raw water, effluent of pre-sedimentation tank (powder activated carbon was added at the inlet of the pre-sedimentation tank with a distance about 2.5 km from pre-sedimentation to coagulation and flocculation tank), sedimentation tank, and filtration tank, from a waterworks of Guangzhou city in PR China. These water samples taken from the four stages of water treatment process were named as raw water, PAC water, clarified water, and filtered water; and characteristics of them are presented in Table 1.

### 2.2. Water treatment processes

Fractionation of water samples based on their molecular weights was carried out by ultra-filtration process using equipment from Amicon® (Beverly, Massachusetts, USA) with a series of membranes with molecular weight cut-offs of 500, 100, 30, 10, 3, 1 kDa, and 500 Da. The obtained fractionation samples were filtered through a 0.45 μm membrane to remove any particulate matter, and then transferred to a continuous flow system consisting of ultra-filtration (UF) membranes (all of the membranes had been cleaned with pure water until a residual DOC was less than 0.2 mg/L in the filtrate) in series with large pore-size membranes proceeding smaller pore-size ones in sequence (Fig. 1) [24]. The residual volume for each fraction of UF was about 500 ml.

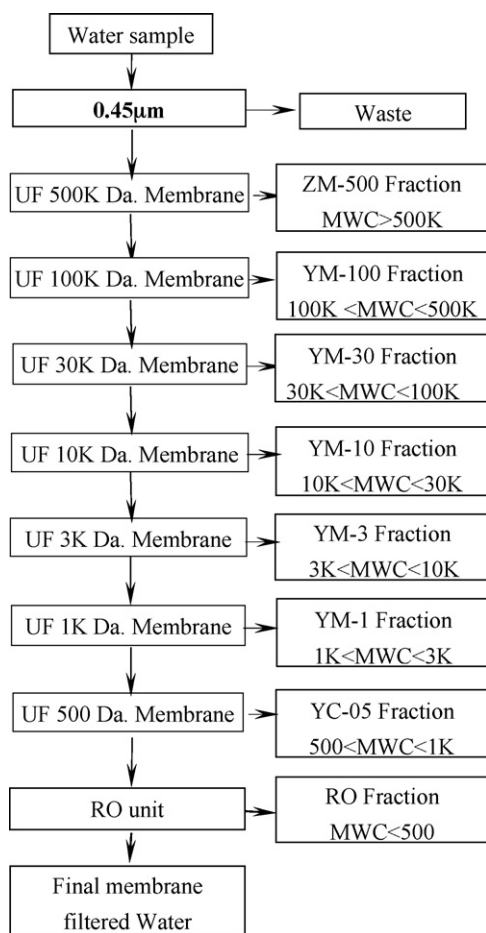
### 2.3. Analysis of water quality

#### 2.3.1. SUVA<sub>254</sub>

Panyapinyopol et al. [25] demonstrated that the specific Ultra-violet absorbance (SUVA<sub>254</sub>) related closely to the amount of removable dissolved aromatic organic substance, e.g., humic acid, in raw water. SUVA<sub>254</sub> is the UV absorbance at 254 nm per mass of carbon (DOC in mg/l). Total organic carbon analyzer (Dohrmann phoenix 8000) was used to determine the non-purgeable DOC in the water samples to quantify the concentration of DOC, which was filtered and adjusted to pH 7 prior to analysis.

#### 2.3.2. THMs analysis

THMs were analyzed using purge and trap Hewlett Packard GC-MS system (Tekmar, 5890 Gas Chromatography, and Hewlett Packard 5972 Mass selective detector) in accordance to the US standard Method 8260 [26]. High purity nitrogen gas was used as the purge gas at a flow rate of 40.0 ml/min under a pressure of 140 kPa. The purge time was 11 min and the dry purge time was 4 min, and the trap temperature was 45 °C. The trapped THM in Tenax adsorbent was desorbed at a temperature of 225 °C for 4 min, into a capillary column for the measurement of halomethane (CHCl<sub>3</sub>,



**Fig. 1.** Schematic diagram of the filtration and fractionation system for concentration and fractionation of dissolved organic substances from water samples taken from four stages of a water treatment plant.

CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl, CHBr<sub>3</sub>) concentration. The flow rate of the carrier gas (high purity helium) was 2.0 ml/min. The temperature was held at 40 °C for 5 min, and increased by 15 °C/min to 80 °C, then increased by 15 °C/min to 220 °C at which it was held for 5 min. Satisfactory analysis results were obtained at retention time of 7.44, 8.70, 9.95 and 11.24 min for CHCl<sub>3</sub>, CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl and CHBr<sub>3</sub>, respectively.

### 2.3.3. Apparent average molecular weight analysis

Apparent average molecular weight was quantified for the eight UF fractions of the raw water using high performance size exclusion chromatography (HPSEC). A Biosep-Sec-S2000 column (300 × 7.8 mm, Phenomenex Torrance, California, USA) with a guard column of the same packing materials (30 × 7.8 mm, Phenomenex, Torrance, California, USA) was used. The mobile phase consisted of 2 mM phosphate at pH 6.8 with an ionic strength of 0.1 M adjusted with NaCl. The system was calibrated against polystyrene sulfonates (PSS) sodium standards (Scientific Polymer Products Inc., New York, USA) with molecular weights of 5, 8, 16, 35, 60, 127 and 500 kDa. In addition, blue dextran (2000 kDa, Sigma) and acetone (58 Da, HPLC grade, Fisher Scientific, Pittsburgh, Pennsylvania, USA) were also used as probes for the void volume ( $V_0 = 5.72$  ml) and total permeation volume ( $V_t = 12.35$  ml), respectively. All water fraction samples were filtered through a 0.22 μm membrane before test. The system was operated at 1.5 ml/min at 25 °C and the injected volume of sample was set at 20 μl. The wavelength of the UV detector was set at 224 nm for standards and 254 nm for water fraction samples. A calibration equation,  $\log M_w = -0.6941t + 9.3208$  ( $R^2 = 0.94$ ), was obtained based on the chromatograms of the seven PSS standards and acetone, in which  $t$  is the retention time. The apparent  $M_w$  value was determined for the DOM in each sample using the equations given by Yau et al. [27]. The term “apparent” was used here because the  $M_w$  measured for DOM macromolecules in these samples by this technique may differ variously from their actual  $M_w$  due to both the effect of solution chemistry on the configuration and polydispersity of molecules of the DOM in the samples and the difference in chemical, structural and molecular properties between the standards and DOM in these samples.

### 2.3.4. Elemental composition analysis

The elemental composition (C, H, N and O) of the different fractions was determined with a CHN-O-RAPID Elemental Analyzer (Heraeus) following a standard high-temperature combustion procedure [28].

### 2.4. Disinfection characteristics

In the experiments, the DOC concentration of each molecular weight fractions of the different treatment process was 3 mg/l, and the UV<sub>254</sub> of each DOM solution was then determined. After adding chlorine at a ratio of chlorine/DOC 20:1 into the DOM solution, the residual chlorine in the solution was measured after a reaction time of 196 h.

### 2.5. Trihalomethane formation potential

A 7-day trihalomethane formation potential (THM FP) test for chlorine was carried out in accordance with standard methods 5710B [27] at a chlorine dosage of 100 mg/l using each fraction water. Chlorine solution was prepared from calcium hypochlorite in powder form with 69.7% available chlorine. The chlorine dosage of 100 mg/l was selected to ensure maximum oxidation of the organic carbon in the sample. This condition meeting the maximum demand of the DOM involved in the THM FP test was verified at the end by measuring the residual chlorine in each sample. When no

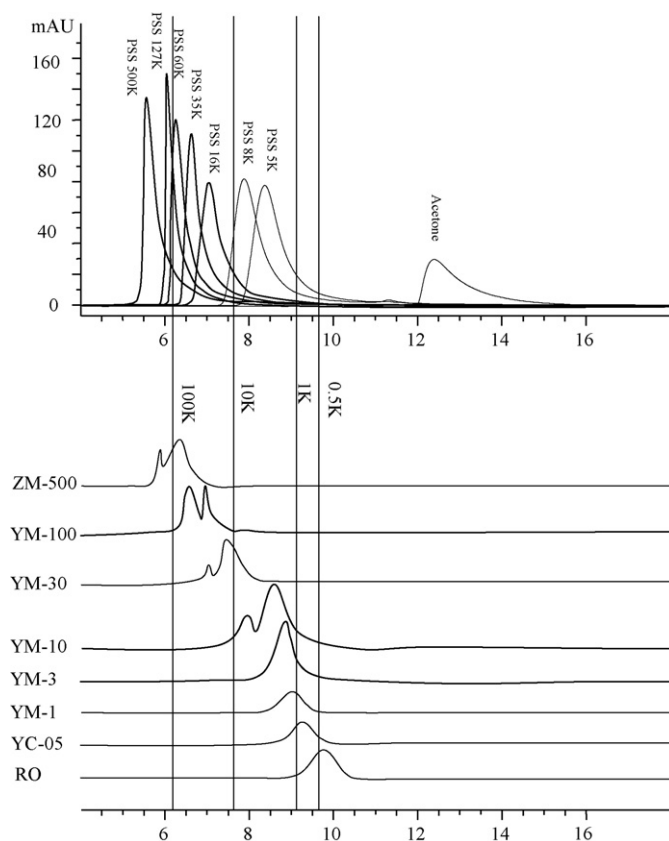


Fig. 2. Size distribution of different fractions of dissolved organic substances in raw water and the standard polystyrene sulfonate (PSS).

or very low residual chlorine was detected (<2 mg/l), the test was repeated. Post THM FP test data, between 4 and 6 mg/l of residual chlorine was detected. All samples were adjusted to a pH of  $7 \pm 0.2$  using 1 M HCl and 1 M NaOH. The neutralized solution was then buffered with a phosphate solution prior to be incubated at  $25 \pm 2$  °C in amber bottles for 7 days. All bottles were capped without any head-space. Sample solutions were prepared using Milli-Q Millipore water system (Billerica, Massachusetts, USA). At the end of 7-day chlorine contact time, samples were dechlorinated using ammonium chloride (NH<sub>4</sub>Cl) as the sole dechlorinating agent. This was a slight modification from the above standard methods 5710B [26] to be in compliance with the applicable EPA methods 551.1 and 551.2.

## 3. Results and discussion

### 3.1. Molecular weight distribution of the DOM in water samples and the fractionated DOM

The HPSEC chromatograms for the eight UF DOM fractions from the source water showed characteristic molecular sizes of 0.5, 1, 3, 10, 30, 100 and 500 kDa (Fig. 2). The apparent  $M_w$  values calculated from the HPSEC chromatograms are also listed in Table 2. The UF DOM fractions showed apparent  $M_w$  ranging from 0.36 to 182.1 kDa.

In this study, one major feature was that the apparent  $M_w$  values measured by HPSEC were apparently lower than those indicated by the nominal molecular weight cut-offs of the ultra-filtration membranes. This is consistent with several prior studies on DOM from several freshwater sources [29], aquatic humic substances [30–33] and soil humic substances [33,34]. Polystyrene sulfonates (PSS) are thought to be suitable standards for calibration of molecular

**Table 2**  
Molecular weight ( $M_w$ ) of different fractions of source water and mass distribution of different fractions and the TOC for each fraction of the four types of water samples.

	$M_w$ (kDa)	TOC (wt.%)			
		Filtered water	Clarified water	PAC water	Raw water
ZM-500 (>500 kDa)	182.10	3.19 ± 0.31 <sup>a</sup>	4.82 ± 0.79	14.56 ± 1.91	14.00 ± 1.37
YM-100 (100–500 kDa)	54.92	2.26 ± 0.06	2.50 ± 0.36	5.86 ± 0.27	5.44 ± 0.32
YM-30 (30–100 kDa)	24.70	3.28 ± 0.43	3.17 ± 0.46	4.11 ± 0.59	3.95 ± 0.23
YM-10 (10–30 kDa)	6.88	4.39 ± 1.08	4.82 ± 0.65	4.15 ± 0.12	4.25 ± 0.73
YM-3 (3–10 kDa)	2.07	4.18 ± 0.7	4.29 ± 0.48	4.43 ± 0.14	4.96 ± 1.77
YM-1 (1–3 kDa)	1.18	3.94 ± 0.51	3.91 ± 1.24	4.02 ± 0.19	4.71 ± 0.48
YC-05 (0.5–1 kDa)	0.80	6.72 ± 1.11	6.70 ± 1.08	4.90 ± 0.73	7.65 ± 0.38
RO (<500 Da)	0.36	72.05 ± 2.0	69.78 ± 1.23	57.96 ± 2.65	55.05 ± 0.47
TOC (mg/L)		2.04 ± 0.12	2.33 ± 0.09	3.29 ± 0.17	3.58 ± 0.28

<sup>a</sup> Standard deviation of three samples.

weights of NOM samples due to the assumed structural similarities between them. However, this approach can only provide approximate values, a fact which has been pointed out by Perminova et al. [35], Peuravuori and Pihlaja [32], and Pelekani et al. [36] previously. And the ultimate size of the fractionated DOM may be affected by the presence of metals and by configuration properties unique to the DOM phase [29]. Moreover, each UF membrane has a characteristic nominal molecular size cut-off, which is operationally defined as the mass of a molecule whose retention is 90% on a specific membrane selected. Globular proteins are often used as standards for testing macromolecule retention by a membrane, but the DOM is expected to have molecular configurations different from this protein of choice. It is likely that their polyelectrolytic nature may result in relatively larger apparent molecular sizes than their actual sizes during ultra-filtration.

In the HPSEC technique, the measured apparent molecular sizes are calculated against an external standard, and the specific operating conditions are different from ultra-filtration procedure. In this study, HPSEC was operated under the conditions of higher ionic strength and lower DOM concentration in order to minimize the interactions between DOM and the stationary phase materials of the column [31]. And the solution chemistry remains constant for HPSEC, the DOM concentration in the reservoir of an ultra-filtration apparatus changes over time during the concentration mode, causing the apparent DOM sizes to change over time. This suggests that the apparent molecular sizes measured with HPSEC are more reliable and accurate than the sizes given by the ultra-filtration technique.

### 3.2. Chemical compositions of the fractionated DOM

The elemental composition of the eight fractions of the source water is shown in Table 3. Different fractions of the raw water had variable elemental compositions. As the molecular cut-offs decreased from ZM-500 to RO fractions, hydrogen content displayed a gradual decrease from 5.4% for ZM-500 to 3.4% for YC-05 fraction and, similarly, carbon content decreased from 57.3% to

48.6%. The oxygen content increased from 32.1% to 38.6% for fractions from ZM-500 to YM-10, indicating that these components were mainly humic substances [37] and from natural sources but not synthetic ones. The corresponding carbon and oxygen contents for the lower molecular weight cut-off (<10 kDa) fractions (YM-3 to RO) were within a much narrow range of 48.6–49.9% and 42.3–44.5% (w/w), respectively. Nitrogen content showed a unique trend of decrease initially from 5.2% to 3.5% from ZM-500 to YC-05, then an increase from 3.5% to 4.0% from YC-05 to RO.

The change in elemental compositions was also well reflected by a decrease of H/C atomic ratio from 1.13 to 0.84 and an increase of O/C atomic ratio from 0.42 to 0.69 as the molecular weight cut-offs decreased from ZM-500 to YC-05 fraction. Such changes indicated that the DOM fractions of lower molecular weight cut-offs had higher polarity and aromaticity than those of higher molecular weight cut-offs. Furthermore, molar ratios such as H/C and O/C obtained by elemental analyses may provide valuable information on the composition and chemical characteristics of DOM. For example, H/C ratio was around 1.0, which is considered to indicate mature humic substance in water system. The ratios and the content of carbon in higher molecular weight cut-off fractions consisted of mature humic substances originated from soil and water [38]. Moreover, the materials possessing higher polarity and aromaticity were the major THMs precursors because of relatively high contents of carboxylic groups in the humic substances.

### 3.3. Mass distribution of the fractionated DOM

The yields of all UF fractions and the TOC calculated from all the fractions are listed in Table 2. The lower molecular weight fraction (<2.07 kDa,  $M_w$ ) of DOM was the dominant fraction in all source water samples from the four treatment stages and constituted >71% (w/w) of the total DOM recovered from the ultra-filtration process. The residual with molecular weight <0.36 kDa was 72.1%, 69.8%, 58.0% and 55.0% of the total organic carbon for filtered water, clarified water, PAC water, and raw water, respectively (Table 2). This result was consistent with Benner's [39] report in which 75%

**Table 3**  
Elemental composition (%) and atomic ratio of different fractions of the raw water sample.

	Elemental composition (%)				Atomic ratio		
	C	H	O	N	H/C	O/C	N/C
ZM-500 (>500 kDa)	57.3 ± 0.90 <sup>a</sup>	5.4 ± 0.1	32.1 ± 2.82	5.2 ± 2.71	1.13 ± 0.03	0.42 ± 0.04	0.078 ± 0.04
YM-100 (100–500 kDa)	55.2 ± 0.6	4.8 ± 0.26	35.3 ± 0.62	4.7 ± 0.26	1.04 ± 0.06	0.48 ± 0.01	0.073 ± 0.01
YM-30 (30–100 kDa)	53.9 ± 0.82	4.5 ± 0.26	37.0 ± 1.14	4.6 ± 0.92	1.00 ± 0.06	0.51 ± 0.02	0.073 ± 0.02
YM-10 (10–30 kDa)	52.8 ± 0.78	4.2 ± 0.1	38.6 ± 0.72	4.4 ± 0.2	0.95 ± 0.04	0.55 ± 0.02	0.071 ± 0.01
YM-3 (3–10 kDa)	49.9 ± 1.21	3.7 ± 0.26	42.3 ± 3.48	4.1 ± 1.32	0.89 ± 0.07	0.64 ± 0.05	0.070 ± 0.04
YM-1 (1–3 kDa)	49.0 ± 0.66	3.6 ± 0.44	43.8 ± 1.32	3.6 ± 1.68	0.88 ± 0.11	0.67 ± 0.01	0.063 ± 0.03
YC-05 (0.5–1 kDa)	48.6 ± 0.5	3.4 ± 0.26	44.5 ± 1.23	3.5 ± 1.21	0.84 ± 0.06	0.69 ± 0.02	0.062 ± 0.02
RO (<500 Da)	48.9 ± 1.47	3.5 ± 0.1	43.6 ± 2.19	4.0 ± 1.23	0.86 ± 0.03	0.67 ± 0.05	0.070 ± 0.02

<sup>a</sup> Standard deviation of three samples.



of marine organic carbon were low-molecular weight DOM and 24% were high-molecular-weight DOM. However, Martin-Mousset and co-workers [40,41] showed that organics >1000 Da generally accounted for up to 70–80% of the total DOC in natural surface water, which was different from other water samples (Schnoor [42], Amy [43], Vuorio [12] and Chang [44]). In addition, soil humic acid fractions with >300 kDa and 30–100 kDa contained 52% and 34% of total carbon, respectively [33]. This indicated that most DOM in the natural water system was not originated from natural humic substances, but mainly from anthropogenic sources, specifically for DOM with molecular weight <500.

The DOC of the raw water was reduced by 43.5% after the full-scale treatment processes consisting of pre-sedimentation with amendment of the particle activated carbon, coagulation, flocculation, sedimentation, and sand filtration (Table 1). And the treatment processes were responsible for DOC removal, but the pre-sedimentation PAC adsorbent addition could only remove a small fraction of DOC. The full-scale treatment process, including the pre-sedimentation with the PAC adsorption process, could effectively remove the intermediate size of DOM for molecular weight 0.8–6.88 kDa, but performed poorly for both the smaller size (<0.36 kDa) and the large size (>6.88 kDa) (Table 2). Similar results were also reported by Amy [43] on PAC showed little removal effect on humic substance for molecular size <300 and >17,000 Da. Chemical treatment (coagulation and flocculation) with subsequent sedimentation could remove the higher molecular weight DOM (>182.10 kDa) efficiently, but had little effect for lower molecular weight <2.07 kDa. Matilainen [45] showed that high molecular weight matter was clearly easier to remove in coagulation and clarification than low molecular weight ones. Similarly, Rolando et al. [46] also identified that coagulation processes were not necessarily optimized for dissolved organic carbon (DOC) removal. The sand filtration removes a wide range of DOM, but the removal efficiency is not comparable to pre-sedimentation with PAC addition for intermediate molecular weight DOM and chemical treatment with subsequent sedimentation for higher molecular weight DOM.

The results on DOM removal of different molecular weights from the water treatment process showed that low molecular weight (<0.36 kDa) DOM could not be removed effectively by the treatment process employed at the waterworks of this conventional drinking water treatment plant, and majority of this DOM fraction was anthropogenic organic compounds. The sequential oxidation system of ozonation followed by photocatalytic oxidation using  $\text{TiO}_2$  [47] and biofilm reactors [48] could remove the lower molecular weight compounds. But, these processes have other issues to be addressed before any implementation.

### 3.4. Disinfection characteristics of different molecular weight DOM

Disinfection by-products formation during chlorination is correlated with several structural characteristics ( $UV_{254}$  and aromaticity) of humic substance [49,50] and the chlorine demand.  $SUVA_{254}$  can be used to infer the nature of the DOM and its consequent THMs formation, high  $SUVA_{254}$  values tend to indicate high humic content and also THMs formation [51].

YC-05 fraction showed the highest  $UV_{254}$  among all eight fractions of the source water samples obtained from the four stages of treatment process and it was higher than other fractions by at least 50% (Fig. 3). For the raw source water, the value of  $UV_{254}$  for the YC-05 fraction was twice that of the other fractions. Meanwhile, the results of the  $UV_{254}$  of YC-05 fraction for each of the treatment process indicated that the PAC could effectively remove the  $UV_{254}$  from the water. RO was the second after YC-05. Difference between different water samples was not significant for YM-1, YM-3, YM-10, YM-30, YM-100 and ZM-500. Hejzlar et al. [52] showed that

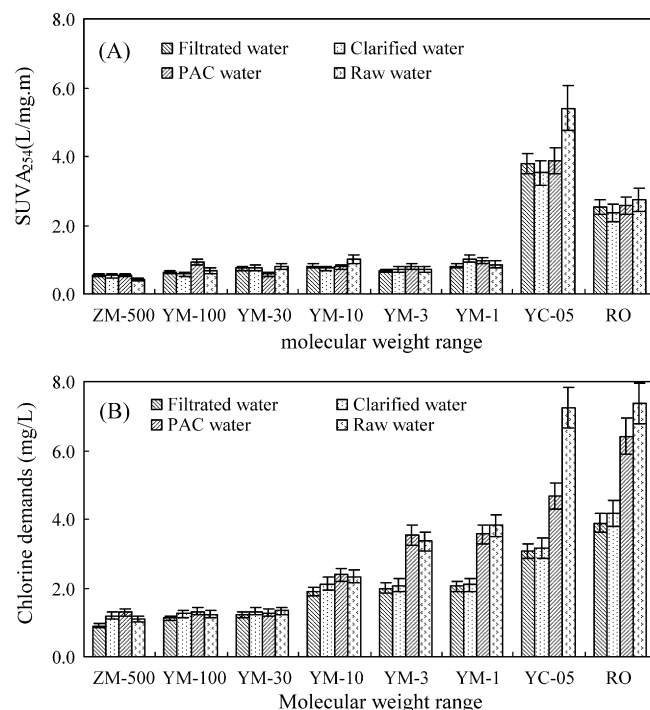


Fig. 3. Disinfection characteristics of different molecular weight fraction of DOM taken from water sample taken from different stages of treatment process (A:  $SUVA_{254}$ ; B: chlorine demands).

the value of  $SUVA_{254}$  represented the amount of phenolic hydroxyl and the ratio of H/C of the samples, the higher the  $UV_{254}$ , the more phenolic hydroxyl and the lower the ratio of H/C, and the aromatic characteristics for the samples, or the more unsaturated radical in the sample [51]. Thus, more THMs would be formed during the disinfection process by chlorine.

Moreover, there were differences between the chlorine demand and the  $UV_{254}$  of the DOM for each treatment process, the chlorine demand would decrease as the molecular weight increased for the DOM with molecular weight >0.80 kDa, and little difference was found for the molecular weight 0.8 kDa and 0.36 kDa of DOM. Chlorine could either replace some radical on the DOM or oxidize the DOM during the reaction process between chlorine and DOM. According to the mechanism of THMs formation, the amount of THMs was correlated with the substituted reaction, the low molecular weight DOM tends to be oxidized by the oxidant, both the oxidation process and substitution process would take place simultaneously when chlorine and DOM start to react, resulting in higher chlorine demand (Fig. 3b).

### 3.5. THMFP for different molecular weight DOM

Low molecular weight YC-05 fraction was the major precursor of THMFP for effluent of each of the four treatment processes in this water treatment plant in Guangzhou, China (Fig. 4). For source raw water, the THMFP formed in this fraction was higher than all other fractions by at least two folds, this fraction was most non-humic substances from anthropogenic sources for a net increase in THMs was observed for a water containing low level of humic substances [53]. A separate laboratory study was also conducted to quantitatively determine the contribution of fulvic acids and humic acids (natural organic matter in the Sea of Galilee) as precursor material to several of the DBPs identified. Results showed that fulvic acid plays a greater role in the formation of THMs [54] and its molecular weight range was between YC-05 and YM3. Meanwhile, as compare the quantity of all fractions for each treatment process,

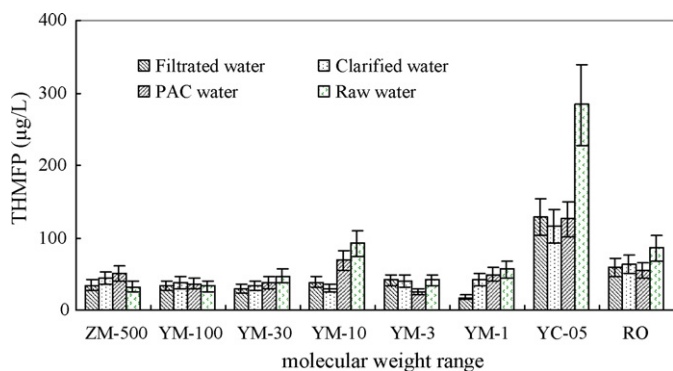


Fig. 4. THMFP for different molecular weight fractions of DOM taken from water sample taken from different stages of treatment process.

the major precursor of THMFP in the raw water was effectively removed by PAC though the regular coagulation and sedimentation could remove partial DOM from water system, but little effect for the remove of precursor for THMFP.

The data on chlorine decay kinetics and total trihalomethanes (TTHM) formation kinetics and modeling with different molecular weight NOM fractions of Mississippi River water indicated that the TTHM formation in fractionated NOM was a function of chlorine consumption. As the molecular weight of the fractions decreased, TTHM yield coefficients increased [55]. Similar results were also obtained by Chang et al. [44] in that the lower organic substances (5–1 kDa, average molecular mass <1 kD) contributed the most of disinfection by-products per unit organic carbon for per unit of chlorine dioxide oxidized.

At the same time,  $SUVA_{254}$  of the water and chlorine demand was correlated with THMFP, excepted RO fractions as some chlorine was contributed to oxidation process (Figs. 3 and 4). There was little THMs formation in the oxidation process for the chlorine and DOM, and THMs formation was correlated with the substituted reaction of chlorine and DOM.

#### 4. Conclusions

The water samples collected from the different stages of water treatment process from a waterworks in Guangzhou showed that the molecular weight of most DOM in each water treatment stage was less than 2.07 kDa. Fractions with molecular weight <0.80 kDa obtained by ultra-filtration and reverse osmosis were the major ones in the four stages of samples. This indicated that conventional water treatment process could not remove the lower molecular weight DOM. Moreover, the elemental composition and disinfection characteristics showed that these fractions were the major precursors of THMFP. Further analysis of DOM fraction from the conventional drinking water treatment process with amendment of PAC adsorption indicated that coagulation and sedimentation process could effectively remove the high molecular weight DOM, but had little effect for the low molecular weight DOM. Addition of PAC could effectively remove the middle range molecular weight DOM which was the major precursor of THMs.

#### Acknowledgements

This work was financially supported by Guangdong Natural Science Funds (021425) and additional support on Sustainable Water by the Faculty of Science, The University of Hong Kong. We thanks the comments of anonymous reviewers in improving this manuscript.

#### References

- [1] H. Humbert, H. Gallard, V. Jacquemet, J.-P. Croué, Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water, *Water Res.* 41 (2007) 3803–3811.
- [2] T.A. Bellar, J.J. Lichtenberg, R.C. Korner, The occurrence of organohalides in chlorinated drinking water, *J. Am. Water Work Assoc.* 66 (1974) 703–706.
- [3] A. Imai, K. Matsushige, T. Nagai, Trihalomethane formation potential of dissolved organic matter in a shallow eutrophic lake, *Water Res.* 37 (2003) 4284–4294.
- [4] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M.J. Scrimanti, G.D. Onstad, A.D. Thruston Jr., Occurrence of a new generation of disinfection byproducts, *Environ. Sci. Technol.* 40 (2006) 7175–7185.
- [5] J. Lu, T. Zhang, J. Ma, Z. Chen, Evaluation of disinfection by-products formation during chlorination and chloramination of dissolved natural organic matter fractions isolated from a filtered river water, *J. Hazard. Mater.* 162 (1) (2009) 140–145.
- [6] E.R.V. Dickenson, R.S. Summers, J.-P. Croué, H. Gallard, Haloacetic acid and trihalomethane formation from the chlorination and bromination of aliphatic beta-dicarbonyl acid model compounds, *Environ. Sci. Technol.* 42 (2008) 3226–3233.
- [7] W.P. Cheng, F.H. Chi, Influence of eutrophication on the coagulation efficiency in reservoir water, *Chemosphere* 53 (2003) 773–778.
- [8] J. Sohn, G. Amy, Y. Yoon, Bromide ion incorporation into brominated disinfection by-products, *Water Air Soil Pollut.* 174 (2006) 265–277.
- [9] R. Vahala, V.A. Långvik, R. Laukkanen, Controlling adsorbable organic halogens (AOX) and trihalomethanes (THMs) formation by ozonation and two-step granule activated carbon (GAC) filtration, *Water Sci. Technol.* 40 (9) (1999) 249–256.
- [10] T.K. Nissinen, I.T. Miettinen, P.J. Martikainen, T. Vartiainen, Disinfection by-products in Finnish drinking waters, *Chemosphere* 48 (2002) 9–20.
- [11] P. Fu, H. Ruiz, K. Thompson, C. Spangenberg, Selecting membranes for removing NOM and DBP precursors, *J. Am. Water Work Assoc.* 86 (1994) 55–78.
- [12] E. Vuorio, R. Vahala, J. Rintala, R. Laukkanen, The evaluation of drinking water treatment performed with HPSEC, *Environ. Int.* 24 (1998) 617–623.
- [13] H.S. Shin, J.M. Monsallier, G.R. Choppin, Spectroscopic and chemical characterization of molecular size fractionated humic acid, *Talanta* 50 (1999) 641–647.
- [14] C.J. Tadanier, D.F. Berry, W.R. Knocke, Dissolved organic matter apparent molecular weight distribution and number-average apparent molecular weight by batch ultrafiltration, *Environ. Sci. Technol.* 34 (2000) 2348–2353.
- [15] A.T. Chow, S. Gao, R.A. Dahlgren, Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: a review, *J. Water Supply: Res. Technol. – Aqua.* 54 (2005) 475–507.
- [16] E.T. Gjessing, P.K. Egeberg, J. Håkedal, Natural organic matter in drinking water—the “NOM-typing project”, background and basic characteristics of original water samples and NOM isolates, *Environ. Int.* 25 (1999) 145–159.
- [17] M. Kitis, J.E. Kilduff, T. Karanfil, Isolation of dissolved organic matter (DOM) from surface waters using reverse osmosis and its impact on the reactivity of DOM to formation and speciation of disinfection by-products, *Water Res.* 35 (2001) 2225–2234.
- [18] W.J. Cooper, E. Cadavid, M.G. Nickelsen, K.J. Lin, C.N. Kurucz, T.D. Waite, Removing THMs from Drinking-water Using High-energy Electron-beam Irradiation, *J. Am. Water Works Assoc.* 85 (1993) 106–112.
- [19] S. Nakano, T. Fukuhara, M. Hiasa, PTSA (pressure and thermal swing adsorption) method to remove trihalomethanes from drinking water, *Water Sci. Technol.* 35 (8) (1997) 243–250.
- [20] H. Gallard, U. von Gunten, Chlorination of natural organic matter: kinetics of chlorination and of THM formation, *Water Res.* 36 (2002) 65–74.
- [21] S.K. Goufopoulos, G.B. Arhonditis, Multiple regression models: a methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics, *Chemosphere* 47 (2002) 1007–1018.
- [22] J. Yoon, Y. Choi, S. Cho, D. Lee, Low trihalomethane formation in Korean drinking water, *Sci. Total Environ.* 302 (2003) 157–166.
- [23] A.D. Nikolaou, S.K. Goufopoulos, G.B. Arhonditis, V. Kolovoyiannis, T.D. Lekkas, Modeling the formation of chlorination by-products in river waters with different quality, *Chemosphere* 55 (2004) 409–420.
- [24] Z.-Y. Zhao, J.-D. Gu, X.-J. Fan, H.-B. Li, Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments, *J. Hazard. Mater.* B134 (2006) 60–66.
- [25] B. Panyapinyopon, T.F. Marhab, V. Kanokkantarapong, P. Pavasant, Characterization of precursors to trihalomethanes formation in Bangkok source water, *J. Hazard. Mater.* B120 (2005) 229–236.
- [26] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington DC, 1998.
- [27] W.W. Yau, J.J. Kirkland, D.D. Bly, Modern Size Exclusion Liquid Chromatography, John Wiley & Sons, New York, 1979.
- [28] D.W. Nelson, L.E. Sommers, Total carbon, organic carbon, and organic matter, in: *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*. SSSA Agronomy Monograph No. 9, SSSA and ASA, Madison, WI, 1982.
- [29] C.R. Everett, Y.P. Chin, G. Aiken, High pressure size exclusion chromatography analysis of dissolved organic matter isolated by tangential-flow ultrafiltration, *Limnol. Oceanogr.* 44 (1999) 1316–1322.
- [30] Y.P. Chin, P.M. Gschwend, The abundance, distribution, and configuration of porewater organic colloids in recent sediments, *Geochim. Cosmochim. Acta* 55 (1991) 1309–1317.

- [31] Y.P. Chin, G. Aiken, E. O'loughline, Molecular-weight, polydispersity, and spectroscopic properties of aquatic humic substances, *Environ. Sci. Technol.* 28 (1994) 1853–1858.
- [32] J. Peuravuori, K. Pihlaja, Molecular Size distribution and spectroscopic properties of aquatic humic substances, *Anal. Chim. Acta* 337 (1997) 133–149.
- [33] I. Christl, H. Knicker, I. Kogel-Knabner, R. Kretzschmar, Chemical heterogeneity of humic substances: characterization of size fractions obtained by hollow-fibre ultrafiltration, *Eur. J. Soil Sci.* 51 (2000) 617–625.
- [34] O. Francioso, S. Sanchez-Cortes, D. Casarini, J.V. Garcia-Ramos, C. Ciavatta, C. Gessa, Spectroscopic study of humic acids fractionated by means of tangential ultrafiltration, *J. Mol. Struct.* 609 (2002) 137–147.
- [35] I.V. Perminova, F.H. Frimmel, D.V. Kovalevskii, G. Abbt-Braun, A.V. Kudryavtsev, S. Hesse, Development of a predictive model for calculation of molecular weight of humic substances, *Water Res.* 32 (1998) 872–881.
- [36] C. Pelekani, G. Newcombe, V.L. Snoeyink, C. Hepplewhite, S. Assemi, R. Beckett, Characterization of natural organic matter using high performance size exclusion chromatography, *Environ. Sci. Technol.* 33 (1999) 2807–2813.
- [37] International Humic Substances Society (IHSS) Home page. <http://ihss.gatech.edu/> accessed March 2006.
- [38] H.-C. Kim, M.-J. Yu, Characterization of aquatic humic substances to DBPs formation in advanced treatment processes for conventionally treated water, *J. Hazard. Mater.* 143 (1–2) (2007) 486–493.
- [39] R. Benner, B. Biddanda, B. Black, M. McCarthy, Abundance, size distribution, and stable carbon and nitrogen isotopic compositions of marine organic matter isolated by tangential-flow ultrafiltration, *Mar. Chem.* 57 (1997) 243–263.
- [40] B. Martin-Mousset, J.P. Croue, E. Lefebvre, B. Legube, Distribution and characterization of dissolved organic matter of surface waters, *Water Res.* 31 (1997) 541–553.
- [41] Q.-S. Wei, C.-H. Feng, D.-S. Wang, B.-Y. Shi, L.-T. Zhang, Q. Wei, H.-X. Tang, Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study, *J. Hazard. Mater.* 150 (2) (2008) 257–264.
- [42] J.L. Schnoor, J.L. Nitzschke, R.D. Lucas, J.N. Veenstra, Trihalomethane yields as a function of precursor molecular weight, *Environ. Sci. Technol.* 13 (1979) 1134–1138.
- [43] G.L. Amy, R.A. Sierka, J. Bedessem, D. Price, L. Tan, Molecular size distributions of dissolved organic matter, *J. Am. Water Work Assoc.* 84 (1992) 67–75.
- [44] C.Y. Chang, Y.H. Hsieh, Y.M. Lin, P.Y. Hu, C.C. Liu, K.H. Wang, The effect of the molecular mass of the organic matter in raw water on the formation of disinfection by-products, *J. Water Supply Res. Technol. – Aqua* 50 (2001) 39–45.
- [45] A. Matilainen, N. Lindqvist, S. Korhonen, T. Tuula, Removal of NOM in the different stages of the water treatment process, *Environ. Int.* 28 (2002) 457–465.
- [46] R. Fabris, C.W.K. Chow, M. Drikas, B. Eikebrokk, Comparison of NOM character in selected Australian and Norwegian drinking waters, *Water Res.* 42 (2008) 4188–4196.
- [47] A. Kerc, M. Bekbolet, A.M. Saatci, Effects of oxidative treatment techniques on molecular size distribution of humic acids, *Water Sci. Technol.* 49 (4) (2004) 7–12.
- [48] B.E. Logan, G.A. Wagenseller, Molecular size distributions of dissolved organic matter in wastewater transformed by treatment in a full-scale trickling filter, *Water Environ. Res.* 72 (2000) 277–281.
- [49] D.A. Reckhow, P.C. Singer, R.L. Malcolm, Chlorination of humic material: byproduct formation and chemical interpretations, *Environ. Sci. Technol.* 24 (1990) 1655–1664.
- [50] W.W. Wu, P.A. Chadik, W.M. Davis, J.J. Delfino, D.H. Powell, The effect of structural characteristics of humic substances on disinfection by-product formation in chlorination, in: S.E. Barrett, S.W. Krasner, G.L. Amy (Eds.), *Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water.*, American Chemical Society, New York, NY, 2000, pp. 109–121.
- [51] S.W. Krasner, J.P. Croue, J. Buffle, E.M. Perdue, Three approaches for characterizing NOM, *J. Am. Water Work Assoc.* 88 (1996) 66–79.
- [52] J. Hejzlar, B. Szpakowska, R.L. Wershaw, Comparison of humic substances isolated from peatbog water by sorption on DEAE-cellulose and amberlite XAD-2, *Water Res.* 28 (1994) 1961–1970.
- [53] G.H. Hua, D.A. Reckhow, Comparison of disinfection byproduct formation from chlorine and alternative disinfectants, *Water Res.* 41 (8) (2007) 1667–1678.
- [54] S.D. Richardson, A.D. Thruston, C. Rav-Acha, L. Groisman, I. Popilevsky, O. Juraev, V. Glezer, A.B. McKague, M.J. Plewa, E.D. Wagner, Tribromopyrrole, brominated acids, and other disinfection byproducts produced by disinfection of drinking water rich in bromide, *Environ. Sci. Technol.* 37 (2003) 3782–3793.
- [55] D.C. Gang, T.E. Clevenger, S.K. Banerji, Relationship of chlorine decay and THMs formation to NOM size, *J. Hazard. Mater.* 96 (2003) 1–12.