

Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments

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Abstract

River water sample was collected from Guangzhou section of the Pearl River to investigate soluble organic fractions and formation of trihalomethane (THMs) after chlorine and chlorine dioxide treatments. The water sample was passed through Amicon[®] YC-05, YM-1, YM-3, YM-10, YM-30, YM-100 and ZM-500 series membranes after a pre-treatment. The molecular weight distribution and the specific ultra-violet absorbance (SUVA₂₅₄) of each fraction obtained from membrane were analyzed, and these fractions were further disinfected with chlorine and chlorine dioxide. The results showed that reverse osmosis (RO) fraction contained mainly dissolved organic matter (DOM) from the water sample, suggesting that the water has been highly contaminated by anthropogenic activities. Meanwhile, the THMs concentration and SUVA₂₅₄ increased gradually as the molecular weight of the obtained fractions reduced, indicating that the low molecular weight DOM was the major THMs precursor in the disinfection process with chlorine and chlorine dioxide. The results suggest that THMs in source water of Pearl River could be effectively reduced when pollution of human activity is greatly controlled. Between the two disinfection processes tested, chlorine dioxide produced less THMs than chlorine in this study.

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Keywords: Disinfection by-products (DBPs); Dissolved organic matter (DOM); Drinking water; Chlorine; Chlorine dioxide

1. Introduction

Most of the drinking water resources have various levels of contamination with chemicals and/or microorganisms, and water treatment often requires chlorination to eradicate microor-

ganisms and control their growth due to the presence of trace organics. A number of disinfection by-products (DBPs) has been detected as a result of chlorination in the water treatment processes [1,2]. This problem has prompted the researchers for an alternative disinfection strategy [3–5] to prevent or reduce the formation of trihalomethane (THMs) in the disinfection of drinking-water [6,7], removal of DBPs precursor, control of disinfection process [8,9] and degradation of DBPs [10].

Formation of THMs in drinking water is a result of the reaction between chlorine and dissolved organic matters (DOM), principally humic and fulvic acids. Aquatic humic substances are mostly responsible for 40–80% of the DOC in many surface waters and are especially reactive with a wide variety of oxidants and disinfectants commonly used in purification of drinking water, e.g., chlorine [11,12]. Therefore, the utility

Abbreviations: THMs, trihalomethanes; SUVA₂₅₄, specific ultraviolet absorbance; DOM, dissolved organic matter; UF, ultrafiltration; RO, reverse osmosis; DBPs, disinfection by-products; THMFP, trihalomethane formation potential; DOC, dissolved organic carbon; RAC, resin adsorption chromatography; GAC, granular activity carbon; AOC, assimilable organic carbon; TOC, total organic carbon; kDa, kilo-Dalton

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industries need to implement additional processes for removal of organics through enhanced coagulation [13,14], granule activated carbon (GAC) [15,16], membrane filtration [17], or advanced oxidation. All these processes are mainly focused on removal of specific molecular-weight fraction or size of DOM in the water. Meanwhile, different membrane filtration process such as microfiltration, ultrafiltration (UF), nanofiltration, and reverse osmosis (RO) are capable of removing different molecular weights and sizes of DOM in the source water. The distribution model of DOM molecular weight or size, and its molecular structure in water system has been studied in the recent years [18,19], but there has been few reports relating the formation of THMs to the different molecular weights of DOM.

Two techniques, resin adsorption chromatography (RAC) [20] and RO separation, are commonly used in isolating DOM from natural waters. Generally, DAX-8 resin is used to fractionate DOM into hydrophobic and hydrophilic fractions in the RAC separation process [21]. In contrast, RO separation has been shown to be a successful method for DOM isolation from natural waters [22–27]. Several important advantages of the latter method include: (i) absence of harsh chemical conditions such as extreme pH or contact with chemical solvents during isolation; (ii) very high recoveries of DOM with minimal fractionation; (iii) concentration of samples to high values; and (iv) processing of large volumes of water in a relatively short period of time.

Since concentration of DOM molecules from natural source waters is necessary for reactivity studies, it is important to address the question of whether the reactivity of the isolated fraction truly represents the reactivity of the source water. Gjessing et al. [25] showed that RO isolation did not significantly (i.e., within 10–15%) alter the color, the color to UV-absorbance ratio (i.e., absorbance at 430/UV-absorbance at 254), the specific UV absorbance ($SUVA_{254} = UV_{254}/DOC$), conductivity, or the coagulation properties (based on color removal) of the source waters. As a result, RO separation has been used in the sample pre-treatment process with wide acceptance.

The US Environmental Protection Agency (US EPA) has imposed more stringent regulations for DBPs in drinking water due to their suspected health impacts (e.g., toxic, carcinogenic, and mutagenic) to humans when ingested over an extended period of time [28–30]. Understanding the role of DOM characteristics in DBPs formation may provide insight to development of more effective solutions for their control during drinking water treatment and operations. In order to effectively control THMs formation and remove the mainly molecular weight fractions of THMs precursor in the water treatment process, a typical source water sample was collected from Guangzhou section of the Pearl River. The objectives of this research were (i) to provide information on the molecular weight distribution of the water sample, (ii) to determine THMs formation potential of different molecular weight or size fraction of DOM in the disinfection process using chlorine and chlorine dioxide, and (iii) identify the main precursor of the disinfection by-products among the different fractions of DOM.

2. Materials and methods

2.1. Chemical reagents

Trichloromethane (>99% purity) was obtained from Guangzhou Chemical Co. (Guangzhou, PR China), bromodichloromethane (>98% purity) was from Eastgate White (Lund, England), and chlorodibromomethane (98.6% purity) and bromoform (>99.5% purity) were obtained from Aldrich Chemical Co. (St. Louis, Missouri, USA). Primary standard solutions of THMs were made in methanol from Fisher Scientific, UK. The helium gas was UHP grade (99.999%). THMs stock solutions with concentrations of 1.0 mg/L were prepared in methanol first, and further diluted to prepare for standards calibration. A minimum of four standards was used to plot the calibration curve (peak area vs. concentration) for each THMs. Prior to analysis for THMs, it was necessary to make a series of dilutions of each chlorinated sample to ensure that the concentrations would fall in the linear range of the calibration curve.

Phosphate buffer was used for adjusting water pH by dissolving 68.1 g potassium dihydrogen phosphate (anhydrous), KH_2PO_4 , and 11.7 g sodium hydroxide, NaOH, in 1 L deionized water. After buffer is added to a sample, a pH of 7.0 should result.

2.2. Sample handling and DOM isolation

The natural river water used in this study was collected from Guangzhou section of Pearl River. Water samples after collection were analyzed immediately to determine selective physico-chemical characteristics at the time of sampling (Table 1). As reported by Gjessing et al. [25], water sample was pre-filtered by a sand column to remove large particulates, and passed through a Na^+ -cation exchange column to remove Ca^{2+} and Mg^{2+} , 200 L of water sample were concentrated to 20 L by reverse osmosis element (AQUA Safe Quality Product, USA). The method used was identical to those reported by Ma et al. [31]. Samples were further concentrated by RO membranes (Millipore, Bedford, Massachusetts, USA) and filtered through a 0.45 μm membrane to remove particulate matter, then was applied to a continuous flow system consisting of UF (Amicon[®] YC-05, YM-1, YM-3, YM-10, YM-30, YM-100 and ZM-500 series membranes, Beverly, Massachusetts, USA) in series with large pore-size membranes proceeding smaller pore-size ones in sequence (Fig. 1), and the molecular weight range for each fraction is listed in Table 2.

Table 1
Selected characteristics of raw waters

DOC (mg/L)	2.02 ± 0.06
$SUVA_{254}$ (L/mg m)	3.5 ± 0.6
Cl^- (mg/L)	19 ± 5
Ca + Mg hardness (mg/L as $CaCO_3$)	122 ± 15
Br^- (mg/L)	0.025 ± 0.006
pH	6.88

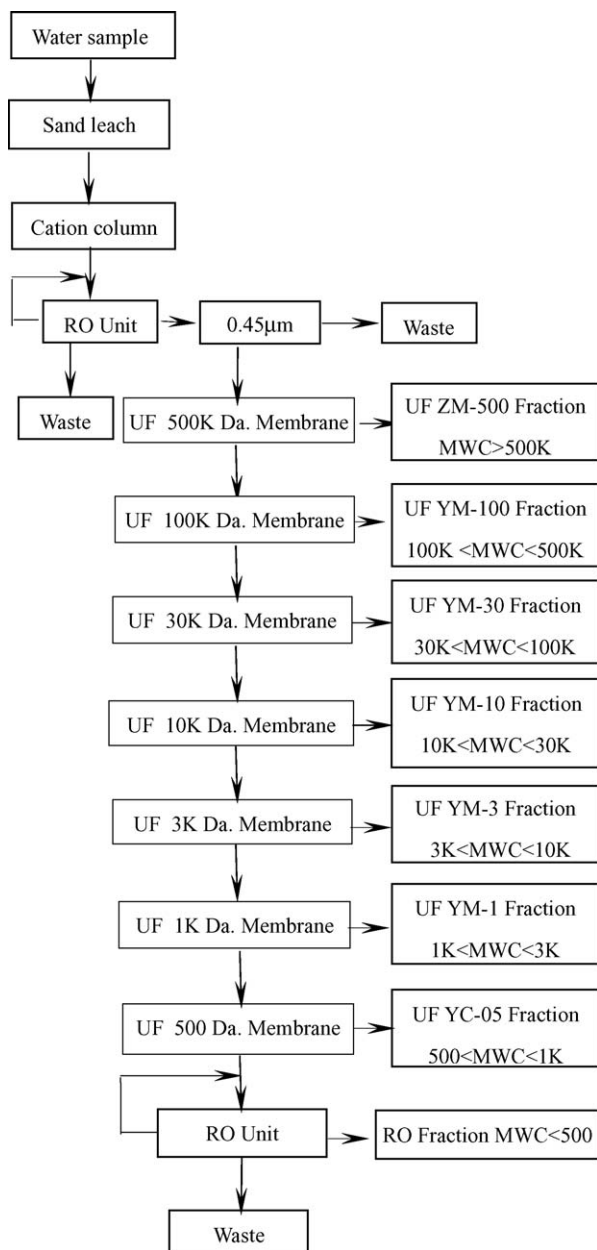


Fig. 1. A schematic flow chart showing ultrafiltration and reverse osmosis concentration system used in this study.

Table 2
The corresponding molecular weight cut-off range of each fraction using the method described

Fraction	Molecular weight range
UF ZM-500 fraction	>500000
UF YM-100 fraction	100000–500000
UF YM-30 fraction	30000–100000
UF YM-10 fraction	10000–30000
UF YM-3 fraction	3000–10000
UF YM-1 fraction	1000–3000
UF YC-05 fraction	500–1000
RO fraction	<500

2.3. Disinfection process

In the experiments, the concentration for each DOM fraction was chosen at 3 mg/L, the reaction time was 24 h, temperature was 20 °C, and the phosphate buffer was added to adjust pH to 7.0 for the reaction system in the process of disinfection, while chlorine or chlorine dioxide was 10 and 3 mg/L, respectively.

2.4. Analytical methods

DOC of water sample was analyzed using UV-persulfate technique and the infrared carbon dioxide analyzer (Phoenix 8000), and calibrated with potassium hydrogen phthalate as standard. Chlorine and chlorine dioxide were analyzed by iodometric method [32]. THMs were analyzed using purge and trap-GC/MS (Tekmar, Hewlett Packard 5890 Gas Chromatograph, and Hewlett Packard 5972 Mass selective detector) as detailed in US EPA Method 8260 [33], as purge and trap was most sensitive comparing with liquid–liquid extraction or head-space methods [34].

3. Results and discussion

3.1. DOM size distribution in the water sample

DOC was analyzed for each size fraction of DOM after filtering through different pore-size UF membranes, and the quantity was calculated from DOC concentration and corresponding volume. Mass distribution for different DOM fractions was obtained and compared. Fig. 2 shows the distribution of each size DOM.

The range of DOM molecular weights in natural river water of the Pear River generally covered several orders of magnitude with a mean value characteristically skewed toward lower molecular weight fractions, resulting in asymmetric distribution of DOM. Molecular weight of most DOM in the Pear River water sample was <500 Dalton (Da) and its percentage reached 58%. This is quite different from other water samples as reported by Schnoor et al. [35] and Amy et al. [36]. Natural organic matter consists of humic and fulvic acids and the latter is the majority of the DOM in the water sample according to Schnitzer [37] and its molecular weight is greater than 700. Based on this information, it is likely that Pear River has been polluted by human activities and most of the DOM resulted from anthropogenic sources.

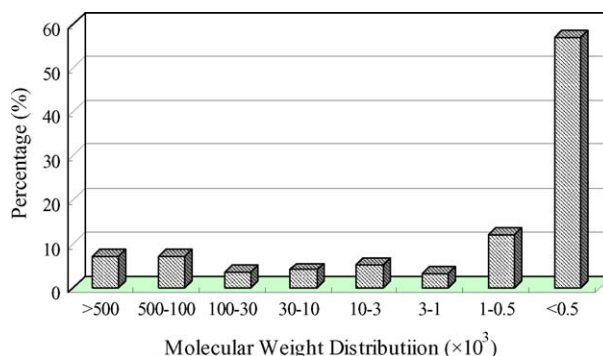


Fig. 2. Fraction mass distribution of the raw water from Pearl River.

A source water containing higher molecular weight of DOM, e.g., 5000–10,000 Da would require chemical coagulation in water treatment [13]. However, it may be difficult to treat such water by GAC adsorption because of a possible size exclusion phenomenon in which the large molecules are unable to enter the smaller pores of the carbon adsorbent. While material of medium molecular weight and size, e.g., 1000–5000 Da, can be effectively used in removing these molecules through adsorption. Molecules of low weight and size are relatively hydrophilic and not effectively removed by coagulation or adsorption, and such water source becomes a candidate for an oxidative process [36]. Furthermore, this fraction is the readily utilizable organic carbon by microorganisms [38]. Coagulation, flocculation and sedimentation can yield significant reduction in the active organic carbon (AOC) at high coagulant dosages (120 mg FeCl₃/L) [39]. As the molecular weight of most DOM in the Pearl River water was <500 Da, DOM in the source water would not be removed effectively by the traditional drinking-water treatment process.

3.2. Effect of disinfectants dosage

The RO isolate was the major fraction containing all the isolates of DOM in the water samples. Such fraction characteristics are valuable for studying the effect of disinfectant dosage during the disinfection process and for comparing with the raw water disinfection process, and can be used as a criterion for the disinfection of different DOM fractions.

In the experiments on the effects of disinfectants dosage, the reaction time was controlled in 24 h. THMs concentrations as a function of the ratio of disinfectant/TOC for the raw water and RO fractions were obtained (Fig. 3). There were visible differences between raw water and RO fractions during disinfection process. THMs concentration reached a peak as the ratio of disinfectant/TOC was between 2 and 2.5 with chlorine, then it decreased as the ratio increased for the raw water disinfection process. Reckhow and Singer [40] showed results of the average chlorine consumption of raw water from seven public drinking water systems in the USA with the consumed chlorine ranged from 1.58 to 2.41 mg Cl₂/mg TOC. Batterman et al. [9] reported that the THMs concentrations were virtually the

same for [Cl₂] = 4 mg/L and [Cl₂] = 6 mg/L with the TOC concentration of 2 mg/L in the synthetic water. However, the THMs concentrations could reach the highest value when the ratio of disinfectant/TOC was 3 for chlorine disinfection process with RO isolate of Pearl River water (Fig. 3A).

There was little difference in THMs concentration as the ratio of disinfectants/TOC increased for disinfection process with both the raw water and RO isolates using chlorine dioxide. When the ratio reached to 1, the average THMs concentrations were 2.5 and 3.5 μg/L for the raw water and RO isolate samples, respectively, bromoform was dominating in the disinfection process by chlorine dioxide for both samples (Table 3.). However, bromoform was observed when disinfected using chlorine dioxide, but not using chlorine. Li et al. [41] reported that when chlorine dioxide was used as the only disinfectant, no THMs were detected in bromide-free water, while only bromoform was formed in water containing bromide ion. Bromodichloromethane and chlorodibromomethane were formed except bromoform when the bromide-containing water was disinfected with chlorine [42], thus the bromoform was very low for the chlorine disinfection process [43,44].

3.3. Formation of THMs for each size DOM

In this work, a variety of experiments were performed to investigate the reactions characteristics of disinfectants including chlorine and chlorine dioxide, and DOM in each fractions under batch conditions. The focus was on comparison of THMs formation in the presence of different DOM fractions.

Fig. 4 shows the SUVA₂₅₄ and THMs concentrations during the disinfection process with chlorine and chlorine dioxide for each fraction. It could be seen that the RO fraction was the major precursor for THMs, similar results were also obtained before [36] in which THMFP was the highest for the fraction with molecular size <500 for two raw water samples. Moreover, SUVA₂₅₄ and the THMs concentrations gradually reduced when the molecular weight increased for chlorine disinfecting process, indicating that the small size DOM was more reactive to form THMs in the disinfection process. As Gang et al. [45] reported that TTHM yield coefficients showed an increase as the molecular weight of the fractions decreased. Overall yields of

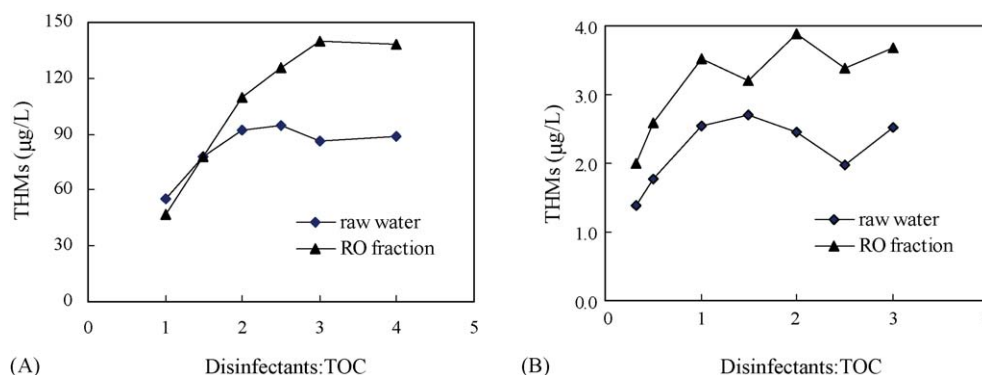


Fig. 3. The ratio of disinfectant to total organic chlorine vs. trihalomethane formation concentration of RO and raw source water: (A) chlorine disinfection and (B) chlorine dioxide disinfection.

Table 3

The major trihalomethane concentrations for the disinfecting process of two kind water sample using chlorine and chlorine dioxide ($\mu\text{g/L}$)

Disinfectant/TOC	Chlorine				Chlorine dioxide			
	RO fraction		Raw water		RO fraction		Raw water	
	CHCl_3	CHCl_2Br	CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	CHClBr_2	CHBr_3
0.33					0.2	1.2	0.2	1.9
0.50					0.2	1.6	0.2	2.4
1.00	51.4	4.1	41.5	5.6	0.1	2.4	0.2	3.4
1.50	74.7	3.5	73.7	4.5	0.3	2.5	0.2	3.0
2.00	88.5	4.0	106.3	3.9	0.1	2.4	0.4	3.5
2.50	91.3	3.2	121.5	3.9	0.2	1.8	0.2	3.2
3.00	83.9	2.7	136.5	3.8	0.1	2.4	0.2	3.5
4.00	86.3	2.7	135.3	2.9				

Note: CHClBr_2 and CHBr_3 were not detectable in chlorine disinfection process, and CHCl_3 and CHCl_2Br were not detectable in chlorine dioxide disinfection process. They are not listed in the table above.

total trihalomethanes (TTHMs) varied from 26.2 to 47.9 $\mu\text{g/L}$ per mg/L TOC in the disinfection process.

Shin et al. [18] reported the differences in structural characteristics and functional group contents between the fractions with molecular weight >100 kDa and the fractions with molecular weight <10 kDa. The fractions with larger size are more aliphatic in nature, while those with smaller size are more aromatic having a higher content of carboxyl groups. Singer [46] has reported that the production of halogenated disinfection by-products resulting from the chlorination of drinking water is directly proportional to the aromatic carbon content of organic constituents in the water. Similar findings relating aromatic carbon content to DBPs production have also been reported by other investigators [47]. Harrington et al. [48] compared DBP production and chlorine consumption to characteristics of the organic extracts as determined by ^{13}C NMR and chlorine pyrolysis gas chromatography/mass spectrometry (pyrolysis GC/MS) analysis. They found that the normalized peak area of the phenol pyrolysis fragment, which was presumed to be originated from activate aromatic structures, was the best indicator of chlorine consumption and CHCl_3 , Cl_2AA , and Cl_3AA production. The same results were obtained in the current experiments, and the variability of SUVA_{254} and TTHMs concentration was quite consistent in the chlorine disinfection process.

There was not much difference for THMs during chlorine dioxide disinfection process. The overall yields of TTHMs var-

ied from 6.7 to 14.6 $\mu\text{g/L}$ TTHMs per mg/L TOC in the 24 h of disinfection process with chlorine dioxide for the water sample. No positive relationship was observed between the SUVA_{254} and TTHMs, illustrating that there were different reaction mechanism for the disinfection process involving chlorine and chlorine dioxide.

3.4. Contribution of each size DOM to THMs in the raw water

Contribution of each fraction to THMs could be calculated from the fraction mass distribution and the THMs formed during the disinfection process with difference disinfectants. Fig. 5 shows the concentration of THMs formed for each isolate fraction of DOM during the disinfection process of raw source water.

THMs concentration of the RO fraction was 37.9 $\mu\text{g/L}$, while UF YM-100 fraction was only 26.2 $\mu\text{g/L}$ for the chlorine disinfection process. Thus 65% of the THMs formed for chlorination by chlorine were converted from RO fraction of DOM, accumulation of THMs from fractions with molecular less than 1000 Da was more than 77%. Similar trends for chlorine dioxide disinfection process were also found and 64% of the THMs formed for chlorination by chlorine dioxide from RO fraction of DOM, accumulation of THMs from fractions with molecular less than 1000 Da were greater than 72%.

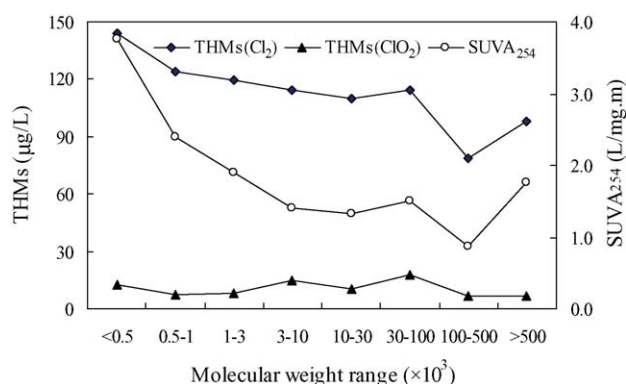


Fig. 4. Effect of DOM size on the formation of trihalometahne.

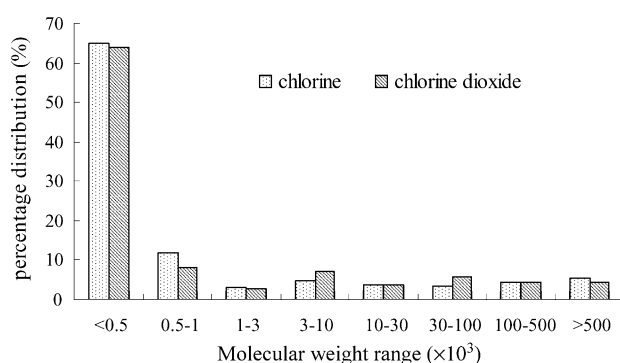


Fig. 5. Relationship between percentage of trihalometahne formed and molecular weights of organic substances concentrated.

The RO fraction was the majority for all isolates in the fraction mass distribution of raw water, accumulation of UF YC05 fraction were more than 65%. These results indicated that DOM with molecular weight <1000 Da was important in the formation of trihalomethanes during the disinfection process by both chlorine and chlorine dioxide in treating the raw source water samples. As compared from mass fraction distribution, the RO fraction was 58% among all the fractions, indicating that RO fraction was the major precursor as it was the major dominating fraction of all the isolates.

4. Conclusions

The water sample collected from Guangzhou section of the Pearl River was separated according to molecular weight cut-off using different UF membrane, and the RO fraction was the gathering majority for the DOM of the water sample. The RO fractions were the major precursor in the disinfection process for all the isolates. In order to efficiently control THMs formation in the disinfection process, it is necessary to remove DOM with molecular weight below 500, suggesting that THMs could be effectively controlled when the organic pollutants were removed. THMs concentration produced in the disinfection process by chlorine dioxide was lower than by chlorine for both water samples. A definition could be summarized that chlorine dioxide is better than chlorine on the basis of THMs formation in the disinfection process.

Acknowledgments

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