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Molecular weight distribution for NOM in different drinking water treatment processes

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ABSTRACT

The purpose of this paper was to analyze molecular weight (MW) distribution in different drinking water treatment processes, and to find out the relationship between dissolved organic carbon (DOC) and disinfection by-products formation potential (DBPFP) in treated water. The results showed that in conventional water treatment, compared with similar methods, namely chlorination (Cl_2) and potassium permanganate ($KMnO_4$), pre-ozonation can reduce DOC concentration for larger MW fractions (>30k, 10k–30k and 3k–10 kDalton (Da)), while the smaller MW fraction portion increased. Coagulation, sedimentation and sand-filtration were effective to remove DOC in the larger MW fractions. Quantitative data were statistically explained. In combination with post-ozonation, biological activated carbon (BAC) can eliminate a large amount of DOC in the <1 kDa MW fraction. BAC with a 3-month service life had the optimal absorption and biodegradation effects. The treatment process was better at removing trihalomethane formation potential (THMFP) than haloacetic acid formation potential (HAAFP), though HAAFP concentration was reduced as well. In finished water, larger MW fraction had higher haloacetic acid (HAA) reactivity, and the part with lower than 1k and 1k–3k Da led to THMs formation.

Keywords: Ozone; DOC; Molecular weight; Organic matter; Drinking water

1. Introduction

Natural organic matter (NOM) is a complex matrix of organic compounds present in natural surface water sources. Not only does it affect the odor, color and taste of water but it also affects several processes in drinking water treatment [1]. The removal of NOM from drinking water by various processes has been extensively studied, mainly as a strategy to reduce disinfection by product (DBP) formation, which occurs when water containing NOM is chlorinated. Alum coagulation and clarification have been shown to be effective in removing large molecular components of NOM [2–4]. The application of advanced oxidation processes (O_3-BAC) for the removal of organics from water is gaining importance in water treatment [5,6]. Due to its capability of transforming contaminants into innocuous substances within a short period, ozone has been identified as a potentially effective means to treat source water. Unlike chlorination, ozonation does not produce any secondary pollutant in the environment since the ozonation of organic matter in water leads to the formation of low molecular weight compounds such as acetic acid [7]. In contrast, smaller size components area removed preferentially by microporous activated carbons [8,9]. A combination of ozonation and

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BAC adsorption has emerged as one of the most promising options for the treatment of advanced water treatment. Ozone is capable of oxidizing complicated organic substances to little molecular weight matters and their highest stable oxidation states and then, produces CO_2 and H_2O, while BAC can accelerate the kinetic rate of the ozone decomposition through the formation of •OH radicals in the solution. Adsorption and biodegradation occurred simultaneously onto BAC [10,11].

It is generally accepted that a major problem occurring from natural organic matter (NOM) is the production of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). NOM including humic substances is widely known as a precursor of DBPs [12,13]. Kim and Symons [14] measured THM formation in NOM size fractions prepared by ultrafiltration and found that the smallest fraction (0.5 kDa apparent MW) had the highest THM reactivity in terms of THM/dissolved organic carbon (DOC) although it comprised only 15% of the total dissolved organic carbon (TOC). All DBPs are suspected to be carcinogenic, mutagenic and teratogenic [15–17]. Among them, THMs and HAAs have been the center of particular attention because of their dominant occurrence in many chlorinated waters and potential carcinogenic effects. While these two groups contribute to about 50–75% of the total halogenated DBPs; they only account for 25–50% of the total organic halides (TOX) [18–20].

Molecular weight distribution in drinking water can be detected by many means. High performance size-exclusion chromatography (HPSEC) can be used to analyze the molecular weight of organic macromolecules [21]. During the process, the molecules larger than the gel pores move rapidly through the column with the eluent but smaller molecules penetrate into the pores of the gel in relation to both their size and shape as well as the pore size distribution of the gel. Also the molecular weight distribution by ultrafiltration membrane is effective and cost saving. The sample is filtrated by different pore size membrane, respectively. The TOC in different filtrated samples can represent the concentration of organic matters for certain molecular weight.

The aim of this work was to investigate the following:

1. the MW distribution of NOM in different drinking water treatment processes such as pre-oxidation, coagulation, filtration and advanced water treatment (O_3-BAC); and
2. the relation between DOC and DBPFP in different drinking water treatment processes.

2. Materials and methods

An ultrafiltration (UF) membrane unit was used under 0.1 bar nitrogen pressure to detect the molecular weight for pre-treated samples. The membrane with certain pore diameters corresponding to molecular weight was fixed in the stirred tank. The water samples were collected after ultrafiltration. A series of membrane (1–30 kDa) were used to separate the samples. The detailed processes are shown in Fig. 1:

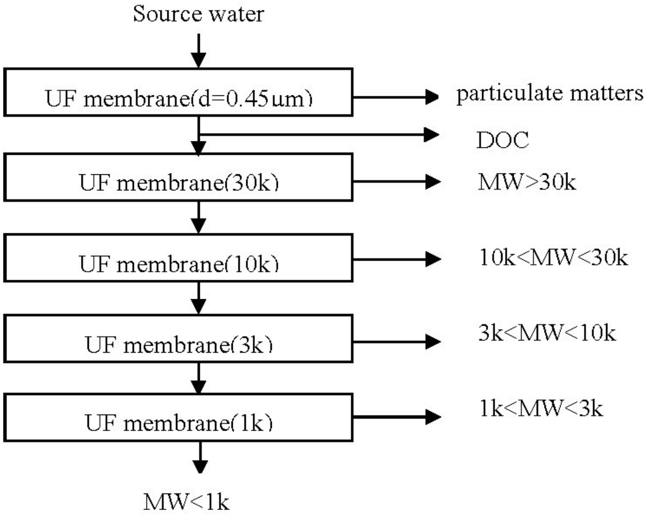


Fig. 1. Sample treatment processes.

- Step 1: The source water samples were filtrated by ultrafiltration membrane with a 0.45 μm pore diameter.
- Step 2: The outlet water was then treated by four kinds of UF membranes (1–30 kDa) in turn.
- Step 3: TOC was determined for the collecting outlets, e.g., DOC concentration, respectively. After that their percentages were calculated.

2.1. Retention characteristics for UF membrane

This is based on Rothschild's [22] theory:

$$P = \frac{C_P}{C_r} \tag{1}$$

where C_P and C_r are permeated and retentate solution concentration, and P is the retention coefficient.

Suppose the UF retention coefficient P was constant during the separation process, the balance is given as:

$$C_p = P \cdot C_{r0} \cdot \left(1 - \frac{V_p}{V_0}\right)^{P-1} \tag{2}$$

where V_0 and V_p are the initial and permeated solution volume and C_{r0} is the initial concentration of certain matter in samples.

Table 1
Membrane retention coefficient

Membrane	$PC_{r0}F^{P-1}$	R^2	P
PAN30000	$0.1242F^{-0.019}$	0.76	0.975
PES10000	$0.0872F^{-0.0778}$	0.91	0.920
PES3000	$0.0782F^{-0.0512}$	0.85	0.944
SPES1000	$0.0678F^{-0.0518}$	0.86	0.921
SPES500	$0.0613F^{-0.0724}$	0.90	0.957

Table 2
Upstream source water quality for the Huangpu River in 2007

Parameters	Values (average)
Turbidity (NTU)	16–25.9 (23.2)
pH	7.0–7.2 (7.1)
COD_{Mn} ($KMnO_4$, mg/L)	3.74–6.39 (5.27)
TOC (mg/L)	6.01–10.94 (8.52)
DOC (mg/L)	4.32–7.04 (6.2)
Conductivity (μs/cm)	600–824 (681)
UV_{254} (cm^{-1})	0.134–0.164 (0.152)

Rothschild demonstrated that when P was greater than 0.9, the separation concentration can be considered as the real concentration. During the separation process V_P/V_0 should be kept constant for reducing error. Eq. (2) can be expressed as Eq. (3) as well:

$$C_p = P\cdot C_{r0}\cdot F^{P-1} \tag{3}$$

where $F = 1 - V_P/V_0$.

According to Table 1, all the UF retention coefficients P were greater than 0.9, so the four UF membranes can be used to detect MW distribution. The percentage of different MW fractionation was expressed by $\eta_i (i = 1–5)$ and calculated by Eq. (4):

$$\eta_i(\%) = \frac{c_i}{\sum_{i=1}^{5} c_i}\times 100 \tag{4}$$

where c_i represents TOC concentration of permeate sample i.

2.2. Analysis

DOC was analyzed for each MW size fraction of dissolved organic matters (DOM) after filtrating by different pore size UF membranes, and the quantity was calculated based on DOC concentration and corresponding volume. The DOC was measured by a TOC analyzer (Phoenix 8000, America). More than 50 water samples were collected at different times in 2007. Every experiment was repeated for three times and the average value was then calculated.

The water samples were stirred by a magnetic force unit (BYJ45, China) with a rotation of 200–300 rpm. The nitrogen pressure was adjusted for less than 0.1 bar; the UF unit (UF-8200) was purchased from Amicon. The membranes were provided by Amicon (PAN30000, PES10000, 3000 and macromolecule alloy polymerizing membrane SPES1000).

DBPFP was measured by a standard method for EPA. THMFP was analyzed by a gas chromatograph (GC-2010, Shimadzu, Japan) equipped with an electron capture detector (ECD) and a 30 m × 0.25 mm ID, 1 m HP-5 ms column. HAAFP samples were measured by the slightly modified GC/ECD EPA method 552.2 [23].

The UF membranes were boiled with de-ionized water for more than 30 min and were rinsed for three times; they were refrigerated at 4°C.

2.3. Source water quality

The source water comes upstream from the Huangpu River, Shanghai, China. The water quality falls into category III–IV established by local regulation, which does not meet source water standards. Typical characteristics of the source water in 2007 are given in Table 2.

2.4. Experiment

Fig. 2 shows the pilot-scale experiment process composed of pre-oxidation(O_3, Cl_2 and $KMnO_4$), rapid mixing, flocculation, sedimentation, sand-filtration, post-O_3, BAC filtration and chlorine disinfection. The three different pre-oxidations for testing MW distribution were compared plus the latter water treatment processes. The whole capacity of the pilot plant for this study was 10 m^3/d. The ozonation contactor was built by stainless-steel column for 2 m height and 100 mm diameter operating in a counter-current mode with the dosage about 1.2 mg/L. Ozone gas was continuously bubbled into the water through a multi-porous titanium plate. The chlorine and potassium permanganate were directly injected into the source water transporting pipe with 2.5 mg/L and 1.2 mg/L dosage based on local water plants. The contact time of rapid mixing was about 1.5 min, sedimentation time 1.5 h and sand filtration velocity 8 m/h. For the advanced water treatment, the post-O_3 tank was divided into three chambers with total dosage 2.0 mg/L and the contact time was 12 min. The empty bed contact time (EBCT) for BAC tank was 12 min as well and granular activated carbon (Calgon Filtrasorb400, particle diameter 1.0–1.6 mm) was used as an adsorbent in this study.

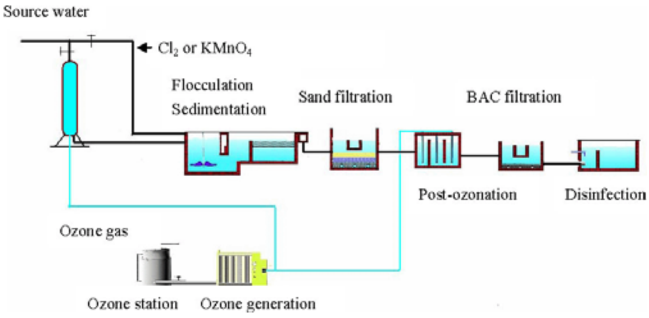


Fig. 2. Pilot-scale water treatment process.

3. Results and discussion

3.1. Comparison of MW distribution by different pre-oxidation processes

The oxidation of NOM as well as the formation of small molecular size organic matters during different oxidation processes were studied. As shown in Fig. 3, small molecular size fractions predominate in source water. There were more differences for the MW distribution in source water after pre-oxidation. The remaining percentage of larger MW (>30 k) in the ozonated sample was reduced from 12.9% to 3.4%, whereas the smallest MW fraction (<1 k) was increased from 59.2% to 71.7%. Statistics showed that pre-ozonation was effective to oxidize larger MW organic matter to smaller particles. In the middle fraction (1k–3k), the number was 14.26% compared with 7.3% in source water. Totally, after pre-ozonation the smaller part of MW (<3k) was up to 85.96% (71.7% + 14.26%) due to its oxidation potential (E_0) of 2.07 V as one of the most powerful oxidants. The sum of larger MW fractions was also decreased by Cl_2 and $KMnO_4$ though their oxidation potentials were less than that for ozone.

3.2. MW distribution in the drinking water treatment process

During the drinking water treatment process such as coagulation/sedimentation, filtration, post-ozonation and BAC filtration, the characteristics of NOM fractions were also more changeable as shown in Table 3.

3.2.1. Coagulation/sedimentation and filtration

There was evidence that the main part of NOM is removed in coagulation and sedimentation which remove better the larger molecular size hydrophobic, acidic molecules than the smaller molecules [24,25]. According to the results in Table 3, the smaller the MW fraction was the more difficult to remove by conventional processes would be. After coagulation and sedimentation an average of a 79% removal rate for the part of MW >30k can be removed, MW fraction from 10k to 30k was 40%, 3k–10k was 29.8%, 1k–3k was 20%, <1 kDa was 3.3%. The results confirmed the previous findings [26,27] that the removal of NOM deteriorated when the molecular size of NOM fractions became smaller. The removal percentage of the smallest molecular size NOM fractions was lowest (<1 k MW). The results were also affected by sand filtration, especially for the DOC removal rate (>30 k MW fraction) which was up to 83.9% and 10k–30k MW fraction was 60.11%, whereas the fraction <1k was lower (4.8%). In conventional water treatment (without ozone and BAC filtration), the removal of larger MW fractions occurred most efficiently. However, the differences for lower MW were statistically significant for the limitation by only chemical and physical processes (coagulation/sedimentation and filtration).

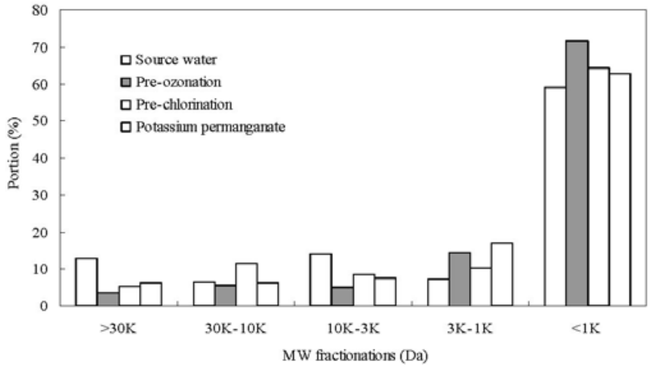


Fig. 3. MW distribution for source water by different preoxidation processes (O_3 dosage: 1.2 mg/L; Cl_2 dosage: 2.5 mg/L; $KMnO_4$ dosage: 1.2 mg/L).

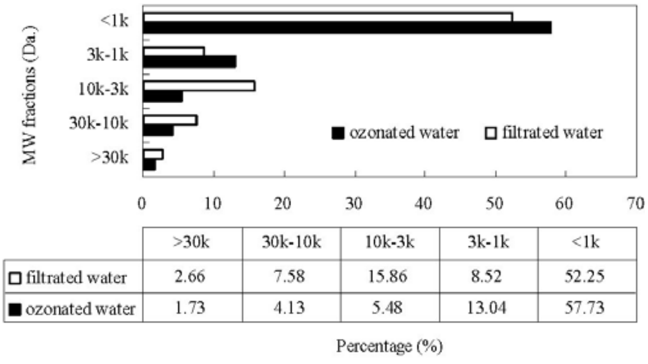
3.2.2. Advanced water treatment—O_3-BAC filtration

Post-ozonation — It was found that the DOC remained constant basically because a lower dosage of ozone (2.0 mg/L) was incapable of directly oxidizing organic substances to produce CO_2 and H_2O. But after ozonation alone, the percentages varied with the different MW fractions. Therefore, a study for post-ozonation was conducted to achieve the effectiveness on MW distribution, as indicated in Fig. 4. It was found that DOC with MW >30 k in ozonated water decreased to 1.73% compared with the 2.66% in filtrated water; 30k–10k was 4.13% and 10k–3k was 5.48% after ozonation. In contrast, DOC (MW <3k) was elevated to a total of 70.77% (13.04 + 57.73%). This could stem from the fact that as ozone oxidation occurred, the form of DOC with a larger MW was available to turn to a smaller one, which was difficult to break down continually. So there was no significant increase in DOC removal after applying post-ozonation, as shown in Table 3. It is noticeable that the DOC in ozonated water increased to 4.75 mg/L from an initial DOC of 4.66 mg/L which could be attributed to remaining oxidized algae dissolving into the sample.

Table 3
DOC removal during drinking water treatment processes for different MW fractions (water samples in 2007)

Item		MW fraction (Da)					
		>30k	30k–10k	10k–3k	3k–1k	<1k	Total
DOC (mg/L)	Pre-ozonation	0.77[a]	0.885	1.095	1.297	2.558	6.605
		0.34–0.99[b]	0.47–1.21	0.78–1.30	0.77–1.49	1.73–2.93	
	Sedimentation	0.162	0.529	0.769	1.037	2.473	4.97
		0.12–0.21	0.33–0.80	0.43–1.10	0.67–1.47	1.96–2.8	
	Filtration	0.124	0.353	0.739	1.009	2.435	4.66
		0.08–0.14	0.12–0.44	0.50–0.92	0.62–1.43	2.04–2.72	
	Post-ozonation	0.082	0.196	0.26	1.468	2.74	4.75
		0.04–0.12	0.12–0.3	0.17–0.41	1.12–1.73	2.33–2.9	
	BAC filtration	0.079	0.176	0.22	0.949	1.412	2.84
		0.03–0.10	0.14–0.24	0.14–0.31	0.76–1.24	0.96–1.82	
DOC removal (%)	Sedimentation	78.96	40.23	29.77	20.05	3.32	—
	Filtration	83.9	60.11	32.51	22.20	4.8	—
	Post-ozonation	33.87	44.48	64.82	−45.49	−12.53	—
	BAC filtration	3.66	10.20	15.38	35.35	48.47	—

[a]Average value; [b]Min. value–Max. value.



	>30k	30k-10k	10k-3k	3k-1k	<1k
□ filtrated water	2.66	7.58	15.86	8.52	52.25
■ ozonated water	1.73	4.13	5.48	13.04	57.73

Fig. 4. Effect of post-O_3 on MW distribution.

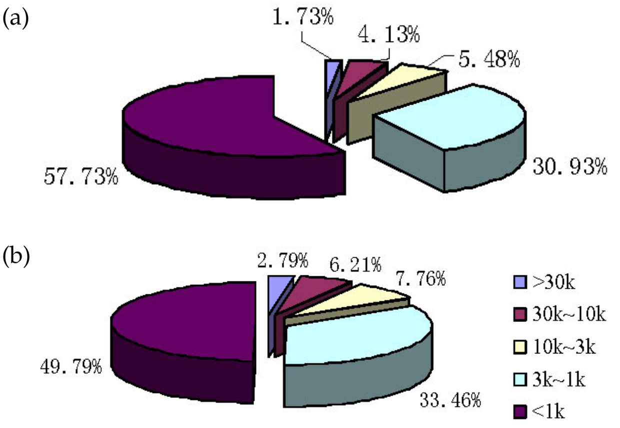


Fig. 5. MW distribution before (a) and after (b) BAC filtration.

BAC filtration — It can be observed from Table 3 that BAC filtration can reduce DOC from 4.75 mg/L to 2.84 mg/L, especially for the smaller MW fraction (<1k); 1.328 mg/L (2.74–1.412mg/L) DOC was removed from ozonated water. BAC filtration played an important role in the DOC removal since BAC served both as an adsorbent and a promoter [28]. Although BAC adsorption was more effective to remove DOC, the combination of post-ozonation and BAC methods was regarded as an integrated process to offer synergistic effects on the removal of many organic compounds [29]. Ozonation had decomposed organic compounds into smaller molecules which had been demonstrated previously through MW fractions analysis, the organic parts in ozonated water became more easily biodegradable, e.g. accumulated bacteria on the BAC may effectively degrade DOC, enabling BAC to easily adsorb the remaining organic materials which were unchanged during the ozonation [30]. Also, the increasing of DOC with the smaller MW fraction by ozonation before BAC treatment is very effective for prolonging BAC service life and the reduction of DOC loading in the BAC [31].

It is commonly believed that the small fraction of DOC can be removed by BAC filtration. The percentages of every fraction are calculated in Fig. 5(a) and (b). The smallest part (<1k) of MW fraction accounted for 49.79% compared with 57.73% in ozonated water, and simultaneously the relative proportions of >30k, 10k–30k and 3k–10k were increased to some extent.

In addition, the prolonged exposure to NOM loading water for BAC would lead to an extensive decreasing for DOC removal efficiency as shown in Fig. 6. As a whole, the DOC removals behaved well to BAC service life. For example, BAC 3 months removed maximum DOC in each

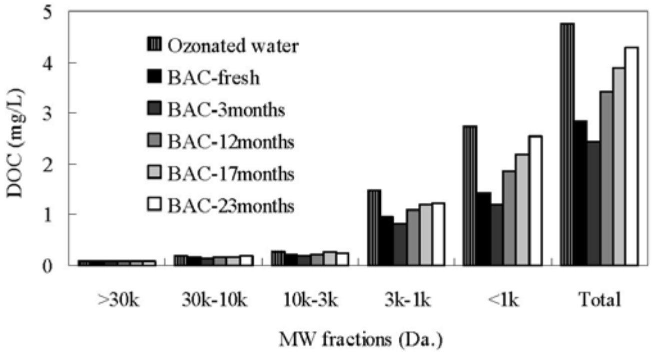


Fig. 6. DOC removal in different MW fractions for different BAC service periods.

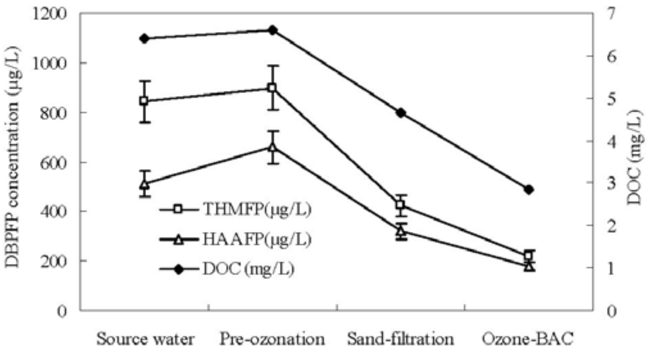


Fig. 7. DOC and DBPFP concentrations after different treatment processes.

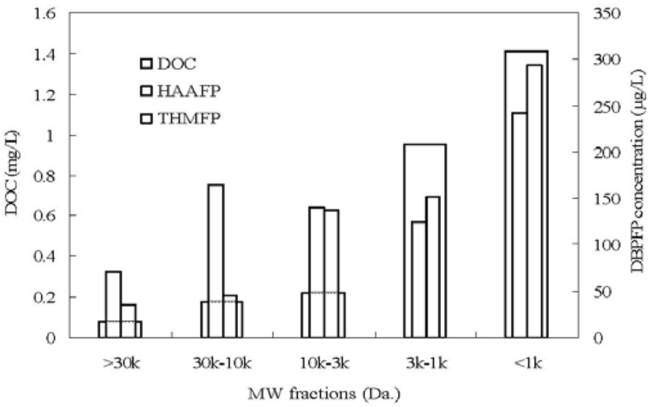


Fig. 8. DBPFP concentrations in different MW fractions for BAC filtrated water.

MW fraction from ozonated water since the adsorption capability for BAC decreased little with fresh BAC and the bacteria gradually accumulated on the surface of the adsorbent to enhancing biodegradation. For larger MW fractions (>30k and 10k–30k), there was hardly any DOC removal for ozonated water by whatever BAC age. This was necessary for the part of NOM to improve coagulation and sedimentation. But for the smaller parts 1k–3k and <1k, it was observed for DOC removal by different ages of BAC even if the adsorption capability weakened by gradual surface blockage. It still worked well for their biodegradation process so much as the BAC service period was up to 23 months.

3.3. Relation between DOC and DBPFP

The relation between DOC and DBPFP is shown in Fig. 7 for different drinking water treatment processes. The various DOCs and DBPFPs were similar during treatment processes. It was observed that THMFP was removed better than HAAFP after the whole process. About 74% THMFP was removed from the initial concentration 842 μg/L to 220 μg/L (relative error 10%); in contrast, only 65% HAAFP was removed for the final concentration of about 178 μg/L. The results showed sand filtration and O_3-BAC were the most effective methods to reduce THMFP and HAAFP, whereas pre-ozonation can increase their concentration more or less, especially for HAAFP most likely for the pre-ozonation transforming the part of NOM incapable of chlorination into THMFP and DBPFP [32–34].

Waterworks with advanced water treatment–BAC filtration reduced DOC, especially in smaller MW fractions. This was indicated previously in Table 3. Though DOC in treated water after BAC filtration can be very low (about 2.84 mg/L) compared with the source water (6.605 mg/L), DBPs (THMs and HAAs) after chlorine disinfection were still inevitable [35–37]. The DBPFP were available in every MW fraction as a part of DOC as shown in Fig. 8. An interesting result was that the larger the MW fraction, such as 10k–30k, the more the portion of HAAFP in DOC would be. In the smaller MW fractions (1k–3k or <1k), the THMFP was in the majority of DOC. Evidently, the larger MW organic material in BAC filtrated water was more likely to form HAAs and THMs than formed mainly by smaller organic matter during chlorination.

4. Conclusions

The MW distributions and conversion for organic matter in different water treatment processes have been investigated to determine whether conventional and advanced methods could effectively remove DOC in different MW fractions. In view of the risks of DBPs in finished water, the relationship between DOC and DBPFP was studied in addition as well.

- The larger MW fractions (>30k, 10k–30k and 3k–10k) in ozonated samples were reduced remarkably, whereas the smaller MW fractions (1k–3k and <1k) were increased. The varying trends for pre-Cl_2 and pre-$KMnO_4$ were similar with pre-O_3 for the MW distribution.

- As expected, the smaller MW fraction was more difficult to remove by a conventional process including coagulation, sedimentation and sand filtration. For example, the DOC removal in the >30k fraction (83.9%) was more effective than that in <3k (4.8%) by sand filtration.
- For O_3–BAC, BAC filtration played an important role in the DOC elimination in the <1k MW fraction and its removal capability for DOC was remarkably improved by post-O_3. Also the DOC removal rate by BAC was more relative to its service life. The best BAC service time was 3 months for both adsorption and biodegradation.
- The relationship between DOC and DBPFP (THMFP and HAAFP) was validated in this paper. Sand filtration and O_3–BAC were the most effective methods to reduce THMFP and HAAFP risks. It is demonstrated that the larger MW organic fractions were inclined to form HAAs and THMs were formed mainly by smaller organic matter during chlorination.

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