

Article

## Characteristics of DOM and Removal of DBPs Precursors across O<sub>3</sub>-BAC Integrated Treatment for the Micro-Polluted Raw Water of the Huangpu River

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**Abstract:** The aim of this study is to determine the impact upon dissolved organic matter (DOM) and removal of disinfection by-product (DBP) precursors of adding an ozone-biological activated carbon (O<sub>3</sub>-BAC) process after the conventional treatment process (CTP) using water from the Huangpu River in Shanghai, east China. Several metrics, including size fractionation, dissolved organic carbon (DOC) and trihalomethane formation potential (THMFP), were employed to accomplish this goal. In the raw water collected from the Huangpu River, the low molecular weight (MW) molecules (MW <3 kDa) were absolutely dominant in DOM, accounting for more than 55% of total DOC, and the DOM resulted in a high THMFP level of  $472.91 \pm 4.63$  µg/L after an excessive chlorination. The CTP reduced high MW molecules (MW >10 kDa) by 61% and the low MW molecules (MW <3 kDa) by only 8%. The O<sub>3</sub>-BAC presented an accumulated DOC removal efficiency of approximately 50%, in particular, showing a high degree of the removal effectiveness of low MW molecules. Samplings from the CTP, ozone and BAC were subjected to excessive chlorination to determine the THMFP, and the measured concentrations were  $211.89 \pm 4.58$  µg/L,  $169.52 \pm 4.55$  µg/L, and  $124.42 \pm 4.27$  µg/L, respectively. Therefore, coupled with the THMFP removal rate of 74%, the addition of the O<sub>3</sub>-BAC process after an existing CTP improved the water quality of the effluent, particularly, in terms of the improved reduction in the precursors of DBPs.

**Keywords:** drinking water treatment; molecular weight fraction; disinfection by-product; ozone; biologically activated carbon

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## 1. Introduction

The presence of dissolved organic pollutants, particularly xenobiotic compounds, in drinking water can cause a significant threat to human health, due to their chronic toxicity, persistence and bioaccumulation [1–3]. During recent decades, reports have shown a continuing worldwide increase in dissolved organic matter (DOM) in drinking water sources, which has an adverse effect on drinking water purification [4]. In general, the DOM in drinking water sources usually consists of a large range of different compounds, from largely aliphatic compounds to highly colored aromatics. Among these compounds, hydrophobic organic pollutants and high molecular weight (MW) fractions can be efficiently removed through a conventional treatment process (CTP), which consists of multi-step unit processes of coagulation, sedimentation and sand filtration [5,6]. However, the hydrophilic organic pollutants and low MW fractions are removed less efficiently than the hydrophobic and high MW fractions [4]. Furthermore, most of the DOM can produce precursors of disinfection by-products (DBPs) during the chlorination treatment of drinking water. These DBPs are either carcinogenic or potentially carcinogenic, and their presence in drinking water is being increasingly regulated by water quality standards in many countries [7]. Therefore, increasing concerns have been focused on the reduction of the DOM levels and DPB generation during the treatment of drinking water, especially in the treatment of micro-polluted water sources [8].

The DOM in drinking water, particularly the precursor of halogenated DBPs, is often a mixture of autochthonous, allochthonous and anthropogenic compounds, such as micro-organism-associated products, wastewater effluent organic matters, amino acids and proteinaceous compounds, which are characterized by a low molecular weight, low hydrophobicity and poor removal efficiency during the CTP [5,9]. In generally, a properly designed CTP for drinking water can efficiently remove suspended solids and relatively high MW fractions. However, the removal of the precursors of DBPs and low MW fractions should be enhanced through additional methods following and/or prior to an existing CTP. Therefore, some advanced post-treatment technologies or the addition of pretreatment units to the existing water treatment plants, including magnetic ion exchange [10], UV/H<sub>2</sub>O<sub>2</sub> [11,12], peroxone (H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>) [13], the TiO<sub>2</sub> photocatalytic process [14,15], UV/H<sub>2</sub>O<sub>2</sub>-granulated activated carbon (GAC) [16], ultrafiltration and nanofiltration membranes [17], nutshell carbons filtration [18] and ozone-biological activated carbon [19,20], have been increasingly used in the treatment of drinking water prior to disinfection to enhance the DOM removal and to prevent the generation of DBPs. A treatment method employing a CTP followed by an ozonation integrated with a biologically activated carbon (O<sub>3</sub>-BAC) process has been reported to be effective in the removal of certain organic contaminants during drinking water treatment [21,22]. Although a significant amount of studies have been conducted on O<sub>3</sub>-BAC, the application of the research findings is still somewhat limited by the contradictory results obtained in the previous studies. It is also important to interpret the characteristics of the residual organics after treatment to evaluate how some of the final products affect the downstream

processes [19,20]. In addition, a more comprehensive understanding of the DOM removal using the O<sub>3</sub>-BAC process would potentially lead to a better design of the drinking water treatment process.

Shanghai is one of the largest cities and the most developed regions in China, but, unfortunately, under its accelerating development, large amounts of anthropogenic organic pollutants have been detected in the Huangpu River, which is one of the major potable water sources for this large city. Over the past few decades, the water quality of the river has been significantly degraded as a result of industrial discharge and non-point pollution [23,24]. Most of the organic pollutants in the Huangpu River are characterized by low MW molecules that often lead to the formation of DBPs if chlorine and/or chloramine are used as a disinfectant unit [19,25]. With several references being made to the drinking water quality standards of the EU, US and World Health Organization (WHO), as well as to developing in line with the international standard, a new Chinese National Standard (GB 5749-2006) [26] for drinking water quality aimed at upgrading the quality of life and the protection of health was issued on 1 July 2007 and has been implemented throughout China from then on. This compulsory standard presented as much as 106 parameters of water quality and parametric values. In particular, some tougher controls on the generation of regulated DBPs than ever were exerted on drinking water treatment have been implemented to guarantee drinking water safety. With the dual goals of enhancing organic pollutant removal and improving drinking water quality, a pilot-scale water treatment plant was created using an integrated O<sub>3</sub>-BAC advanced treatment process after a CTP and prior to chlorination. The performance of the integrated drinking water treatment process was evaluated through investigation into the effects of each unit process on the characteristics of the MW fraction distribution and the removal rates of the trihalomethane formation potential (THMFP). This work also adds to the database of the performance of these technologies in micro-polluted surface water, thereby expanding the range of water matrices that have been evaluated using these treatment processes for the DOM and the precursors of DBP removal.

## 2. Materials and Methods

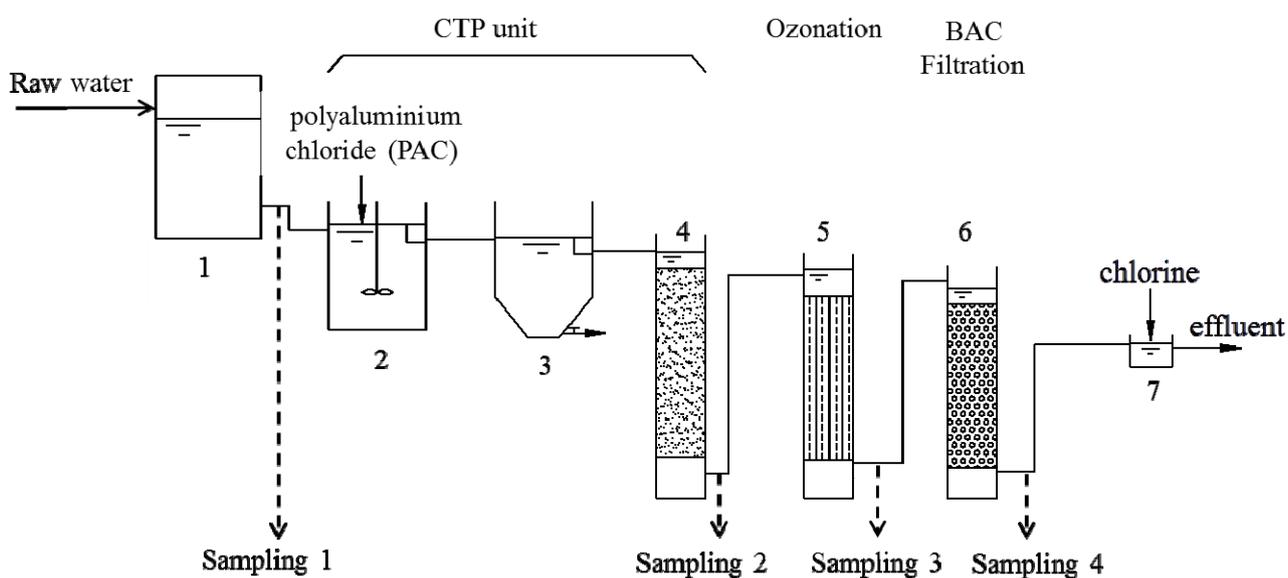
### 2.1. Experimental Set-up

The pilot-scale experiment was conducted in a drinking water treatment plant within the vicinity of the Huangpu River in Shanghai, China. Figure 1 shows the flow chart of the pilot-scale integrated drinking water treatment plant. Prior to the O<sub>3</sub>-BAC process, the CTP consisted of multi-step coagulation-flocculation-sedimentation-sand filtration reactors. Chlorination was employed in a subsequent disinfection unit. The pilot plant was operated at a design flow of 0.5 m<sup>3</sup>/h.

All of the reactors employed in the CTP were composed of polymethyl methacrylate containers. The ozone contact reactor was composed of a stainless steel column with a diameter of 0.2 m and a height of 2.7 m, and six corundum fine bubble aerators were placed in the bottom of the reactor. The BAC filtration column was composed of a polymethyl methacrylate column with a diameter of 0.3 m and a height of 2.85 m. The cylindrical reactor was packed with a 30-cm supporting layer of cobblestone (5–10 mm in diameter). Then, activated carbon particles (ZJ-15, Zhuojun Chemical Ltd, Liyang, China) with diameters of 0.6–2.0 mm were added as the filter medium and microbial carrier on top of the supporting layer. The filling height of the activated carbon was 1.5 m.

The raw water, pumped from the Huangpu River, first entered an elevated storage tank and dropped by gravity into the subsequent treatment units. During recent years, the raw water quality, especially the level of the DOM, has been relatively stable, due to the exertion of excellent water source protection [23]. The raw water quality was monitored regularly and was summarized in Table 1. This study was carried out in September of 2012, and the DOC of raw water was  $6.712 \pm 0.055$  mg/L, which could be of the highest level of the DOM for the Huangpu River.

**Figure 1.** Flow chart of the pilot water treatment plant (the dotted arrows represent the sampling locations). 1: storage tank; 2: flocculation reactor; 3: sedimentation tank; 4: sand filter; 5: ozone contact reactor; 6: biologically activated carbon filtration (BAC); 7: disinfection reactor. (CTP: conventional treatment process).



**Table 1.** Raw water quality during the experimental course (NTU: nephelometric turbidity unit; TOC: total organic carbon; COD<sub>Mn</sub>: permanganate index).

Water quality	Minimum	Maximum	Mean
Temperature (°C)	4.0	27.5	16.2
Turbidity (NTU)	20	127	44
pH	7.1	7.7	7.4
UV <sub>254</sub> (cm <sup>-1</sup> )	0.143	0.193	0.159
DOC (mg/L)	5.64	7.29	6.78
TOC (mg/L)	8.10	11.52	9.16
COD <sub>Mn</sub> (mg/L)	4.6	9.0	6.5
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	0.26	2.53	1.72

The coagulant employed in this study was polyaluminum chloride (PAC) as AlCl<sub>3</sub>. The PAC dose ranged from 13 to 18 mg/L, depending on the raw water quality. The response time to flocculation was maintained at 20 min, and the precipitation time was 2 h. The filtration velocity in the sand filter column was approximately 8.0 m/h. Ozonation was carried out in an ozone contact reactor operated in concurrent flow mode. Ozone gas from an ozone generator (HMY-F, Huangming, Nanjing, China) was

continuously bubbled into the water through a fine bubble corundum plate. The ozone dose was maintained at 4.0 mg/L, and the ozone contact time was 10 min. The BAC filtration was generally operated with an empty bed contact time of 12 min, and the filtration rate of the BAC column was around 7.0 m/h. The chlorine dose was approximately 3.0 mg/L with a goal of more than 0.3 mg/L residual chlorine after 30 min of contact time, which was continually monitored with an online residual chlorine analyzer (YLG-2058, Boqu, Shanghai, China). The pilot experiment on the integrated water treatment plant was conducted in a consecutive flow model. The experimental set-up had been running for more than three months in a steady status since the system start-up. Due to laboratory constrains, the experiment was conducted under the appropriate running condition of the pilot water treatment plant as described above, which has been reported earlier in the literatures [27,28].

## 2.2. Water Sampling and Pretreatment

Once collected from several sampling locations shown in Figure 1, water samples were stored in 5.0 L brown glass bottles and immediately transported to the laboratory at Southeast University under a low ambient temperature of around 4 °C. All of the aqueous samples were filtered through polycarbonate filters (0.45- $\mu\text{m}$  pore size) to remove suspended solids and particles and to then determine the water quality metrics relative to the DOM, such as DOC, MW fractions and the THMFP. All microfiltration membranes (0.45- $\mu\text{m}$  pore size) were cleaned several times with pure water in sterile cleaned beakers until the DOC of the filter liquor was equal to that of pure water, and all membranes had been submerged in pure water before use. The water used in the test was prepared with ultrapure water obtained from an ultrapure water system (Yongjie, Hangzhou, China) under ambient temperature with a resistivity of more than 18  $\Omega\text{M}$ . All of the filtrates were maintained at refrigerator temperature (4 °C) to minimize sample degradation before analysis and were analyzed within 7 days.

## 2.3. Determination of Distribution Ranges of the Molecular Weight Fraction

A series of ultrafiltration membranes with different MW cut-offs were employed to determine the MW fractions in the sampling water using a dead-end stirred ultrafilter (Amicon 8200, Millipore, Billerica, MA, USA); the analytical method had also been reported by Lee *et al.* [29] and Zhao *et al.* [30]. The DOM in water was fractionized into six groups with different MW ranges after filtration using these cellulose-derivative ultrafiltration membranes with five cut-offs of 100, 10, 3, 1 and 0.5 kDa. These membranes were also cleaned several times with pure water and submerged in pure water until use. The fractionation samples were transferred to a continuous flow system consisting of ultrafiltration membranes in series; note that the larger pore-size membranes preceded the smaller pore-size membranes in the sequence. High-purified nitrogen was used to pressurize the filtration process (held at 0.15 MPa). All the fraction permeates were analyzed with a TOC analyzer (TOC-V<sub>CSH</sub>, Shimadzu, Japan) to monitor the DOC/TOC according to the USA Standard Method 5310 [31]. The percentages of DOC in the different MW fraction ranges were calculated to determine the MW fraction distribution in the sampling water.

During the test procedure, blank samples and duplicate samples were analyzed simultaneously to provide rigorous quality controls. The accuracy of analysis was checked using duplicate samples. The quality control gave good precision (relative standard deviation, RSD <5%).

#### 2.4. Analysis of the Trihalomethane Formation Potential

For the determination of the THMFP, the chlorinated pretreatment of water samples was conducted according to methods reported by Hofmann *et al.* [20] and Xu *et al.* [21]. Before the THMFP was determined, sodium hypochlorite (NaClO) was added to each water sample, such that the initial weight ratio of NaClO (as Cl<sub>2</sub>) to DOC of each sample was 5.0. To avoid the effects of pH changes in the reaction process on the formation of trichloromethanes, a solution of KH<sub>2</sub>PO<sub>4</sub>/NaOH was used to buffer the pH (7.0 ± 0.2). Subsequently, 40 mL of the mixture was placed in an incubator chamber at 25 °C. After a 7-day incubation, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added to the vial to quench the residual chlorine. Then, the trichloromethane in the sampling water was extracted with n-pentane.

The extracts were analyzed using a gas chromatograph (GC-2010, Shimadzu, Japan) equipped with an electron capture detector (ECD) to determine the trichloromethane. The trichloromethane was separated with an Agilent DB-5 capillary (30-m length × 0.25-mm i.d., 0.25-µm film thickness). A 1.0-µL sample was injected by a syringe (GC-1.0 µL, Shimadzu, Japan) in a splitless mode, and the injection volume was exactly 1.0 µL. The GC conditions for the trichloromethane analysis were described by Wang *et al.* [32] as follows: the injection port temperature was maintained at 210 °C; the column temperature was programmed to 35 °C for 10 min to increase by 10 °C/min to 80 °C, then by 20 °C/min to 150 °C and remained at 150 °C for 1 min; the temperature of the ECD was maintained at 290 °C. All of the chemicals and reagents used for the sample processing and analyses were guaranteed to be of reagent or chromatographically pure grade.

During the test procedure, all analyses were submitted to rigorous quality control procedures. Blank samples, standard samples and duplicate samples were analyzed simultaneously in the experiment to provide quality controls. The blank samples were ultrapure water obtained from an ultrapure water system (Yongjie, Hangzhou, China) and were exposed to ambient conditions, while the water samples were collected from the experimental set-up. The accuracy of the analysis was checked using standard and duplicate samples. The quality control also gave good precision (RSD <5%).

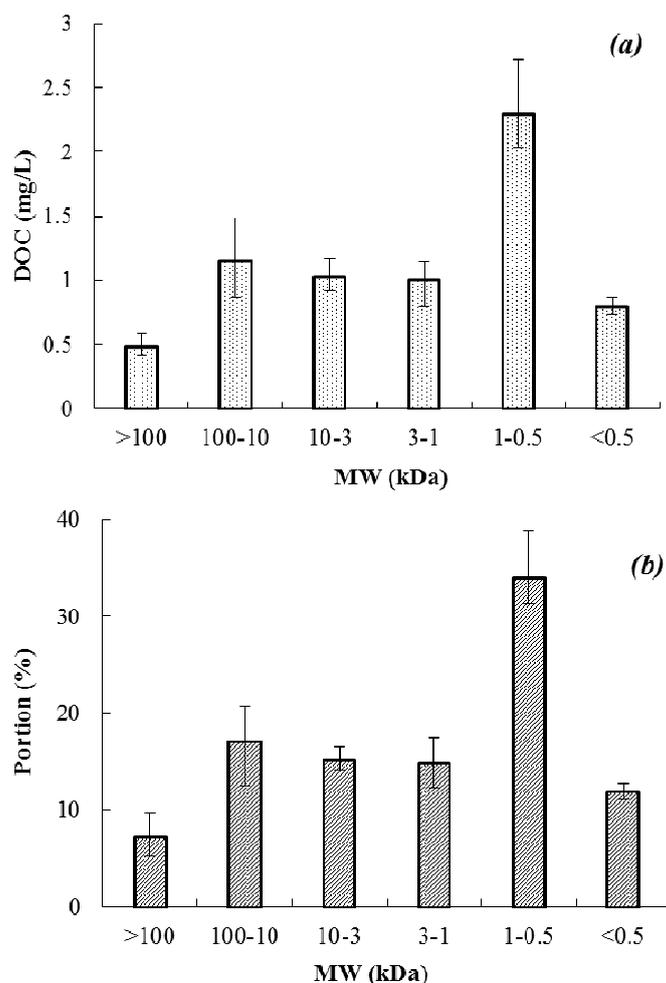
### 3. Results and Discussion

#### 3.1. DOM Size Fraction of Raw Water

The total DOC of the raw water collected from the Huangpu River (the water treatment plant monitoring point) ranged from 6.251 mg/L to 7.215 mg/L, with a mean value of 6.768 mg/L. In addition, the average concentration of the total organic carbon (TOC) in the raw water was 9.16 mg/L. Thus, the DOC dominated the total organic matters of the raw water, accounting for approximately 74% of the TOC. Figure 2 illustrates the DOC concentrations (a) of the different MW range groups and their portion (b) in raw water. The MW fractions were distributed over a wide range from less than 0.5 kDa to more than 100 kDa. The highest average DOC concentration was in the range of 0.5–3.0 kDa (accounting for approximately 42% of total DOC). The DOC concentration of high MW fractions (more than 10 kDa) were 1.707 mg/L and accounted for 20% of the total DOC. The low MW fractions (less than 3.0 kDa) contained 3.292 mg/L DOC, which likely originated in industrial discharge and non-point pollution sources of livestock farming, agriculture, towns, industrial parks and cities in the

vicinity [21,24], and accounted for 56% of the total DOC. The low MW fractions were also considered the dominant factor in the formation of regulated DBPs during exposure to chlorination.

**Figure 2.** The DOC concentration (a) at each molecular weight (MW) fraction group and their portion (b) in total DOC of the raw water (the presented data in the figure are the average of the observations for raw water in 2012).

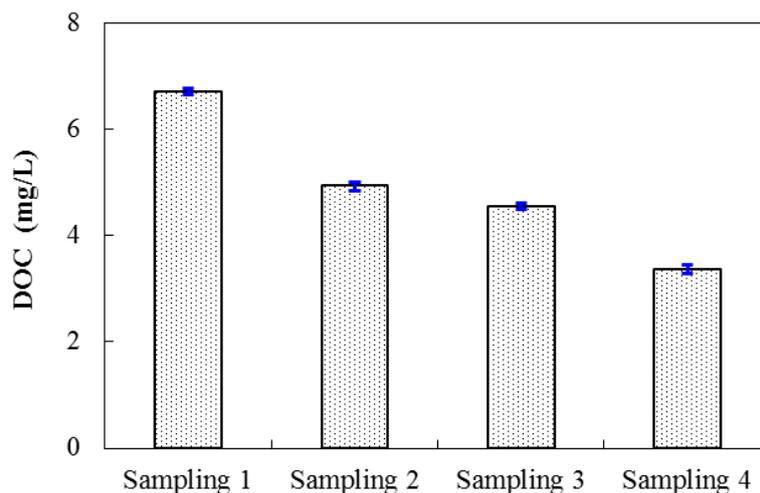


### 3.2. Overall DOC Removal

Figure 3 shows the effects of each unit process on the overall DOC removal across the entire water treatment process. The DOC concentration in the raw water (Sampling 1) was  $6.712 \pm 0.055$  mg/L. Compared to the raw water, the overall removal efficiency of DOC increased from 26% (CTP alone) to 50% (entire water treatment process). The CTP reduced DOC from  $6.712 \pm 0.055$  mg/L to  $4.929 \pm 0.082$  mg/L (Sampling 2) with a removal efficiency of 26%. Subsequently, the ozone presented a DOC removal efficiency of approximately 8%, because it was designed to decompose organic compounds and to change their biochemical properties, and the total DOC reduced to  $4.544 \pm 0.057$  mg/L (Sampling 3). What was more important for the ozone reactor within the water treatment process was that the ozonation could transform non-biodegradable organic compounds to biodegradable compounds to facilitate removal in the subsequent BAC treatment [33]. After further BAC treatment, the total DOC in the water was continually reduced to  $3.363 \pm 0.084$  mg/L (Sampling 4).

The introduction of the O<sub>3</sub>-BAC process significantly enhanced the DOM removal, and this finding was in agreement with previous studies [19,34,35].

**Figure 3.** The removal of overall DOC across the water treatment process (from Figure 1, Samplings 1–4 represented the water sampling from raw water, after the CTP, ozone and BAC). The presented data in the figure are the average of the observations (n = 3); the error bars represent the standard deviation of replicate measurements, and their relative standard deviation (RSDs) are all below 5%.



### 3.3. Effects of Unit Process on MW Fraction Distribution

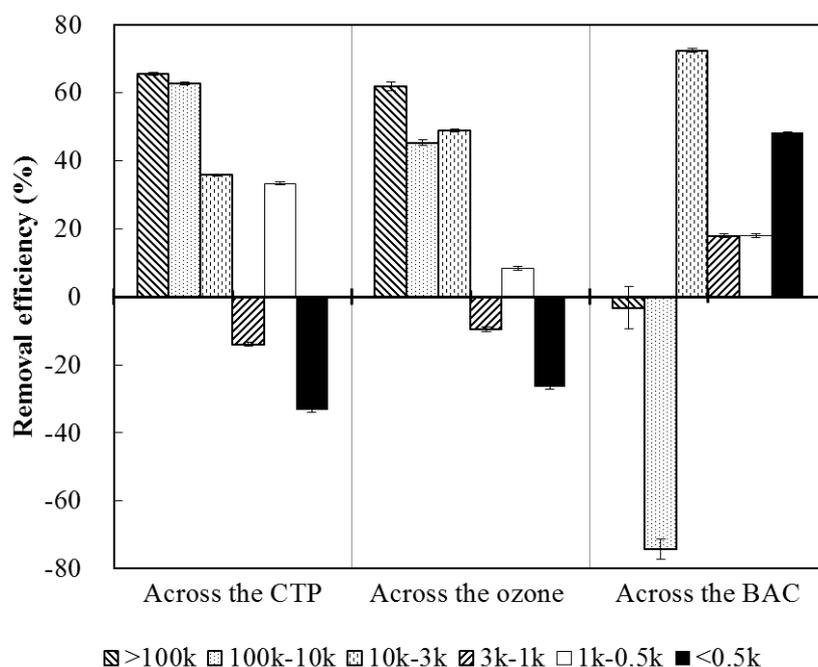
During the entire water treatment process, each treatment unit had impacts upon the distribution of MW fraction groups. Table 2 shows the effects of each unit water treatment process on the variation of DOC concentration at different MW fraction groups and their percentages. In addition, compared to the previous water treatment unit, the removal efficiencies of DOM at different MW fraction groups after the CTP, ozone and BAC are shown in Figure 4.

**Table 2.** The DOC concentration and percentage of different MW fraction groups in different stages of the water treatment process (from Figure 1, Samplings 1–4 represented the water sampling from raw water, after the CTP, ozone and BAC). The standard deviations of replicate measurements for DOC concentrations (n = 3) are shown with the average of the observations, and their RSDs are below 5%.

MW ranges (kDa)	Sampling 1		Sampling 2		Sampling 3		Sampling 4	
	DOC (mg/L)	Portion (%)						
>100	0.572 ± 0.003	8	0.197 ± 0.002	4	0.075 ± 0.002	2	0.078 ± 0.002	2
10–100	1.336 ± 0.006	20	0.496 ± 0.003	10	0.272 ± 0.003	6	0.473 ± 0.004	14
3–10	1.117 ± 0.004	17	0.717 ± 0.001	14	0.366 ± 0.003	8	0.101 ± 0.002	3
1–3	1.063 ± 0.003	16	1.212 ± 0.003	25	1.328 ± 0.005	29	1.088 ± 0.004	32
0.5–1	1.785 ± 0.007	26	1.189 ± 0.004	24	1.088 ± 0.003	24	0.892 ± 0.004	27
<0.5	0.839 ± 0.003	13	1.118 ± 0.003	23	1.415 ± 0.003	31	0.731 ± 0.002	22

After the first treatment of the CTP, the DOC percentages of the fractions containing compounds with MWs of >100, 100–10, 10–3, 3–1, 1–0.5 and <0.5 kDa were 4%, 10%, 14%, 25%, 24% and 23%, respectively. The fraction containing compounds with an MW less than 3 kDa accounted for approximately 72% of the total DOC. As shown in Figure 4, the removal efficiency of the fractions with an MW greater than 10 kDa was as high as 77%, whereas the removal efficiency of the fractions with an MW less than 3 kDa was only 4.5%. In addition, based on the MW distribution, the fractions with an MW greater than 3 kDa exhibited a reduction from 45% to 28%. In contrast, the fractions with an MW less than 3 kDa presented an increase from 55% to 72%. During the CTP, some of the high MW fractions were removed efficiently via coagulation and separation; meanwhile, others might have been converted into smaller compounds through a series of chemical reactions of coagulation-flocculation. In addition, some low MW molecules that were originally attached to the high MW fraction were released into the water [36,37]. Therefore, it could be inferred that the CTP exhibited poor performance for the removal of low MW molecules from the water. A previous study [33] had reported that a combined reaction between low MW biodegradable materials and humic substances could improve the removal of the low MW molecules by the subsequent O<sub>3</sub>-BAC process. Hence, after the CTP, the low MW fraction and hydrophilic natural organic matter were dominant in the residual organic matter.

**Figure 4.** Removal efficiencies of the DOC at different molecular fraction groups across the CTP, ozone and BAC (the removal efficiencies of DOC at different MW fraction groups were compared to the previous treatment unit; the presented data in the figure are the average of the observations (n = 3), the error bars represent the standard deviation of replicate measurements).



Biodegradable materials have generally been considered to be carbohydrates and low MW compounds. Ozone generally reacts with macromolecules quickly and decomposes these into low MW molecules to improve the DOM removal through the subsequent BAC [21]. The effluent of the ozone

unit process contained  $4.544 \pm 0.057$  mg/L DOC with a limited removal efficiency of 8%. The fractions with an MW less than 3 kDa were dominant in the total DOC with an accumulated percentage of 84%, whereas the accumulated percentage of the fractions with an MW greater than 3 kDa was only 16%. Because the ozonation process significantly reduced the level of high MW fractions and converted them into low MW molecules, the process led to a slight increase in the DOC concentration of molecules with an MW less than 3 kDa from 3.519 mg/L to 3.831 mg/L and presented a negative mean removal efficiency value of approximately -9%. Therefore, low MW molecules were likely generated from the high MW fraction, and little impact of the oxidation process on the total DOC concentration was observed.

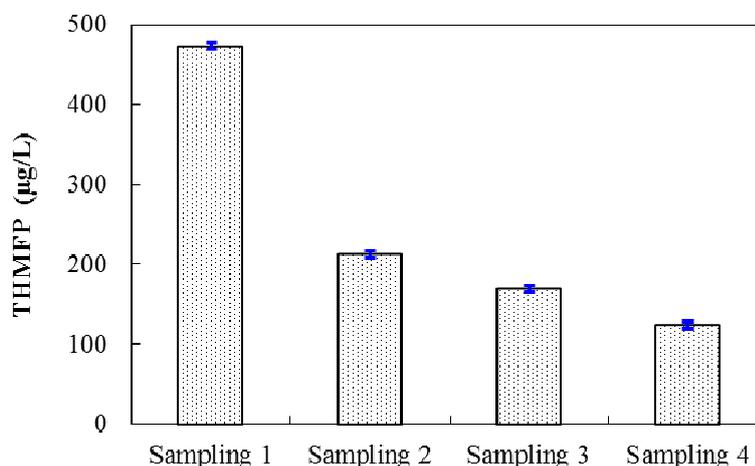
After further treatment of the BAC, the total DOC was reduced to  $3.363 \pm 0.084$  mg/L with the highest accumulated removal efficiency of 50%. In the BAC effluent, the DOC percentage of the fractions with MW fractions of >100, 100–10, 10–3, 3–1, 1–0.5 and <0.5 kDa were 2%, 14%, 3%, 32%, 27% and 22%, respectively. Based on the DOC data, the BAC effluent contained 0.652 mg/L DOC of the fraction with an MW greater than 3 kDa, and a removal efficiency of only 8% was obtained. In contrast, the DOC of the fractions with an MW less than 3 kDa decreased from 3.831 mg/L to 2.711 mg/L with a high removal efficiency of 29%. As observed in Figure 4, the DOC of the fractions with different MWs decreased, with the exception of the fraction with an MW 10–100 kDa, which increased from 6% to 14%. In general, the DOM removal through the BAC treatment is a two-step process. The activated carbon first adsorbed the low MW molecules, particularly those with an MW less than 3.0 kDa, due to the initiation of radical-type chain reactions [38]. Subsequently, these adsorbed low MW molecules were decomposed by the biomass attached to the carbon. In addition, some high MW compounds were also released into the water, likely due to microbe metabolism. Accordingly, the increase in the fraction with an MW of 10–100 kDa could be likely explained by the release of components of detached biofilm or other excretions, for instance, metabolites of microbiology, and this finding was also reported by a previous study [38].

In the raw water from the Huangpu River, low MW molecules, including estrogen, phthalate esters, atrazine and nonylphenol, contributed most of the DOC [21,37]. However, most of the low MW molecules cannot be efficiently removed across a CTP alone or directly utilized for metabolism [12,39]. The O<sub>3</sub>-BAC process after following the CTP significantly enhanced the DOC removal, especially for low MW molecules. Therefore, the addition of a combination of O<sub>3</sub>-BAC processes presented higher removal efficiencies for different MW fractions compared with the CTP alone.

### *3.4. The Removal of Trichloromethane Formation Potential*

Trichloromethane was one of the main halogenated DBPs formed during the drinking water treatment process, and the compounds were formed during the chlorination process, more or less depending on the characteristics of the type of organic components. The THMFP has been considered as an operational parameter to indicate the amount of trichloromethane generated during a chlorination process. Tests of the THMFP were undertaken on water samples collected from the effluents of the CTP, ozone and BAC, as well as raw water to better understand the DPBs precursor removal by the entire water treatment process. Figure 5 shows the effects of the unit water treatment process on the removal of the THMFP.

**Figure 5.** The removal of the trihalomethane formation potential (THMFP) across the water treatment process (from Figure 1, Samplings 1–4 represented the water sampling from raw water, after the CTP, ozone and BAC). The presented data in the figure are the average of the observations ( $n = 3$ ). The error bars represent the standard deviation of replicate measurements, and their RSDs are all below 5%.



The THMFP concentration of raw water (Sampling 1) was  $472.91 \pm 4.63 \mu\text{g/L}$  due to the high level of DOM in raw water. Compared to the raw water, the CTP was able to remove 28% of the DOC through mechanisms of coagulation, absorption and separation and led to a reduction in the THMFP concentration to  $211.89 \pm 4.58 \mu\text{g/L}$  (Sampling 2). The ozone only presented a removal efficiency of around 9% in the THMFP, likely due to the lower removal rate of DOM. The THMFP concentration of the ozone effluent (Sampling 3) was  $169.52 \pm 4.55 \mu\text{g/L}$ . Finally, the introduction of the BAC significantly enhanced the DOM removal, particularly the precursors and low MW molecules. Accordingly, the lowest level of the THMFP was observed in the BAC effluent (Sampling 4), which exhibited a concentration of  $124.54 \pm 4.27 \mu\text{g/L}$ . The BAC reduced the THMFP by approximately 27%, and the accumulated removal efficiency of the THMFP reached a maximum of 74%. These results were similar to those reported by Hofmann *et al.*, where water from coagulation/flocculation and sedimentation was subsequently treated by  $\text{O}_3$ -BAC, with an observed result of approximately 30% removal of the THMFP [20].

The reductions of the THMFP across the water treatment plant are somewhat higher than the DOC removal (Table 3) and were further enhanced by the subsequent  $\text{O}_3$ -BAC process. This suggested that the water treatment process may have been selectively removing dissolved organic matter, particularly THM precursors. In general, the high MW fractions in water could be more efficiently removed, whereas the low MW fractions (less than 0.2 kDa) were more reactive to the formation of chlorinated DBPs during the chlorination process [20,36]. Therefore, the low MW fractions played an important role in the formation of chlorinated DBPs during a disinfection process. This also suggested that the removal rate of the fraction with a low MW by the  $\text{O}_3$ -BAC combined process was a key factor in the reduction of the level of regulated DBPs in the drinking water treatment process.

**Table 3.** Percentage removal of the DOC and THMFP across treatment processes (the removal efficiencies of the DOC and THMFP were compared to the previous treatment unit).

parameters	Across the CTP (%)	Across the ozone (%)	Across the BAC (%)
DOC	27	8	26
THMFP	55	20	27

#### 4. Conclusions

The effects of unit processes on the characteristics of different MW fractions and the removal of the THMFP were investigated to evaluate the performance of an integrated drinking water treatment process, which consisted of an O<sub>3</sub>-BAC step after the CTP and prior to chlorination. In the raw water from the Huangpu River in Shanghai, China, the fraction with an MW less than 3 kDa was dominant in the DOM and accounted for 53% of the total DOC. The DOM in raw water could result in a high level, as high as  $472.91 \pm 4.63$  µg/L, of the THMFP after exposure to excessive chlorination. The CTP, which consisted of multi-step coagulation, flocculation, sedimentation and sand filtration reactors, efficiently removed the fraction with an MW greater than 10 kDa with a removal efficiency of 61%, whereas only 8% of the fraction with an MW less than 3 kDa was removed. The introduction of the O<sub>3</sub>-BAC step significantly enhanced the DOM removal, particularly the fraction with an MW less than 3 kDa. The removal efficiency of this fraction was 29%. The sampled waters from the CTP, ozone and BAC were subjected to excessive chlorination to determine the THMFP, and the measured concentrations were  $211.89 \pm 4.58$  µg/L,  $169.52 \pm 4.55$  µg/L and  $124.42 \pm 4.27$  µg/L, respectively. Coupled with the THMFP removal rate of 74%, the addition of the O<sub>3</sub>-BAC step after an existing CTP and prior to chlorination improved the quality of the effluent, particularly in terms of an improved reduction of the precursors of regulated DBPs.

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#### Conflicts of Interest

The authors declare no conflict of interest.

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