



# Effects of different secondary biological treatment processes followed by flocculation and sand-filtration on subsequent DBPs control from sewage treatment plants



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## ABSTRACT

The nature and chlorine reactivity of dissolved organic matter (DOM) in reclaimed water from sewage treatment plants (STPs) are quite important for assessing the risk of wastewater reuse. Elucidating relation between DOM and its fractions characterization with different treatment processes is quite important for selection of treatment processes focusing on disinfection by-products (DBPs) control. In this study, four classical STPs in Beijing (A ~ D) with different secondary biological treatment processes but all with flocculation and sand-filtration as advanced treatment process were selected to investigate DBPs formation potentials and DOM characterization variation during these processes and their relation. Chloroform, trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA) dominated among four trihalomethanes (THMs) and nine haloacetic acids (HAAs) formation potentials respectively during chlorination of both secondary and sand-filtration effluents with the order of TCAA > chloroform > DCAA. Both THMs and HAAs formation potentials were positively related with DOC percentage for the hydrophobic fractions in the DOM. The bromine incorporation in THMs was obviously higher than that in HAAs. The especially higher bromine incorporation in D STP was probably due to the higher SUVA value in this STP with SBR as secondary biological treatment process comparing to those in the other three STPs. DOC and bromide removal, SUVA decrease were important elements for selecting secondary treatment process considering DBPs control. Flocculation and sand-filtration performed not well in removing DBPs precursors especially for chloroform and DCAA except for C STP, which had higher hydrophobic fraction percentage removal and molecular weight decreasing during the advanced treatment process. FTIR analysis revealed that flocculation and sand-filtration probably removed more aliphatic structures than aromatic or COO<sup>-</sup> structures. The absorption ratio of aromatic C=C, COO<sup>-</sup>/aliphatic CH<sub>3</sub> peaks in D STP was the highest among the four STPs, which was consistent with the highest bromine incorporation in this STP.

## 1. Introduction

Dissolved organic matter (DOM) in effluent water or reclaimed water from sewage treatment plants (STPs) is the central issue for wastewater reuse applications [1]. Considering a substantial portion of drinking water sources can be derived from reclaimed water source during de facto (unplanned) potable reuse [2], disinfection by-products (DBPs) formation potentials in reclaimed water and relating it with DOM characterization data is especially important.

DOM from sewage treatment plants is composed of a wide variety of

compounds including natural organic matter (NOM), synthetic organic chemicals from anthropogenic use, such as aromatic sulfonates from anionic surfactant degradation, endocrine-disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs), etc., and soluble microbial products produced during biological treatment processes, such as *N*-acetyl amino sugars and proteins, etc. [1–5]. By far, the DBPs generated from disinfection of reclaimed water included the known classes, such as trihalomethanes (THMs), haloacetic acids (HAAs), *N*-nitrosodimethylamine (NDMA), halonitromethanes (HNMs), haloacetonitriles (HANs), etc., and the unknown ones, such as ketones,

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aldehydes, and alcohols, etc. [4,6–9]. It has been reported that DOM from wastewater effluent had higher proportions of brominated DBP formation potential implying greater health risks [10].

The compositions of DOM changed with physicochemical reactions during sewage treatment processes [4]. Elucidating relation between DOM and its different fractions removal with different treatment processes is quite important for selection of treatment processes focusing on DBPs control. There have been lots of studies about this in drinking water plants [6,11–14], while less in sewage treatment plants as the design of sewage treatment plants usually focus more on nutrients and common organic matters [5]. It has been noted among the sewage treatment processes, PAC adsorption, granular activated carbon (GAC) biofiltration, nanofiltration (NF) resulted in high dissolved organic carbons (DOC) removal of DOM compared to that of flocculation, ion exchange, advanced oxidation process, and ultrafiltration (UF) [5]. We could expect DBPs formation potentials decrease along with the decrease of DOC of DOM. However, as DOC is only a quite comprehensive surrogate parameter, further information about different DOM fractions removal, aromaticity characterization, molecular weight (MW) distribution, functional groups and even molecular characterization variation, and their relation with DBPs formation potentials of reclaimed water during common sewage treatment processes are still needed.

In China, most sewage treatment plants have been using flocculation and sand-filtration as the advanced treatment for reclaimed water prior to disinfection. In this study, we selected four classical STPs in Beijing with different biological treatment process but with flocculation and sand-filtration as advanced treatment process to investigate DBPs formation potentials variation during these processes and its relation with DOM characterization. The purpose of this study is to elucidate the influence of different biological treatment and flocculation and sand-filtration on variation of DOM characteristics and DBPs formation potential, and to point out their relation so as to giving suggestions on selection of treatment processes or conditions.

## 2. Materials and methods

### 2.1. Sample collection and analysis

Wastewater samples from the secondary effluents and the following advanced treatment effluents before disinfection were collected from different domestic sewage treatment plants A ~ D, in which conventional activated sludge process, oxidation ditch, anaerobic-anoxic-oxic process (AAO) and SBR were respectively used as the secondary treatment methods, and flocculation/sand filtration was used as the advanced treatment process (Table 1).

Water samples for this study were collected in glass bottles and filtered immediately through a pre-rinsed 0.45  $\mu\text{m}$  cellulose filter. The filtered water samples were then stored in the dark at 4 °C until analysis.

Dissolved organic carbon (DOC) was measured with a TOC analyzer (Multi N/C 3000, Analytik Jena AG, Germany).  $UV_{254}$  (absorbance of UV at 254 nm) was measured with a spectrophotometer (U-3010, HACHI, Japan).  $SUVA_{254}$  was calculated as ratio of  $UV_{254}$  to DOC.

**Table 1**

Secondary treatment processes and the water quality of influent and effluent in A ~ D STPs.

STPs	Secondary treatment process	Daily capacity (* $10^4$ m <sup>3</sup> )	BOD <sub>5</sub> (mg/L)		COD (mg/L)		SS (mg/L)	
			Influent	Effluent	Influent	Effluent	Influent	Effluent
A	Conventional activated sludge process	100	126.5 ± 11.0	6.9 ± 0.5	264.1 ± 15.4	32.6 ± 5.6	201.4 ± 18.5	9.3 ± 0.8
B	Oxidation ditch	35	124.3 ± 10.8	7.5 ± 0.6	265.3 ± 14.7	36 ± 6.4	169.4 ± 14.1	9.4 ± 0.7
C	A <sup>2</sup> O	4	218.2 ± 12.4	7.8 ± 0.7	479 ± 24.2	38.2 ± 6.7	291.7 ± 19.4	9.4 ± 1.0
D	SBR	8	134.9 ± 10.6	8 ± 0.6	277.6 ± 16.7	40.6 ± 7.5	167.6 ± 11.2	9.9 ± 0.4

**Table 2**

Characteristics of wastewater samples from A ~ D STPs.

STP	Water sample	pH	$UV_{254}$	SUVA	DOC (mg/L)	DOC Removal (%)
A	Secondary effluent	7.01	0.095	1.32	7.22	–
	Sand-filtration effluent	7.14	0.068	1.31	5.2	27.98
B	Secondary effluent	7.47	0.114	1.63	6.98	–
	Sand-filtration effluent	7.85	0.098	1.45	6.76	3.15
C	Secondary effluent	7.62	0.183	2	9.17	–
	Sand-filtration effluent	7.63	0.13	1.9	6.86	25.19
D	Secondary effluent	7.24	0.209	2.61	8.02	–
	Sand-filtration effluent	7.34	0.165	2.15	7.66	4.49

### 2.2. Chemicals and materials

Solutions were prepared with ultra-pure water (18.2 M $\Omega$ -cm, Millipore). A free chlorine (HClO) stock solution (about 5 g/L) was prepared from 7% sodium hypochlorite (NaClO) and its concentration was measured prior to use according to DPD colorimetric method (EPA method 330.5). 50 mM sodium phosphate buffer solution was used to maintain solutions at pH 7.

Hexane and methyl *tert*-butyl ether (HPLC grade) used to extract DBPs were obtained from Fisher and J.T. Baker, respectively. Four THMs standards, i.e. chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHCl<sub>2</sub>Br), dibromochloromethane (CHClBr<sub>2</sub>) and bromoform (CHBr<sub>3</sub>), and nine HAAs standards, i.e. monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromo monochloroacetic acid (DBCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), tribromoacetic acid (TBAA), and dalapon were purchased from Sigma-Aldrich (Germany).

### 2.3. Fractionation and collection of DOM fractions

The fractionation of DOM was performed following the procedure modified from Imai [15]. Three resin adsorbents, i.e. Amberlite XAD-8 resin (20–60 mesh), Dowex Marathon MSC resin (20–50 mesh) and Duolite A-7 (free base), were used to isolate effluent organic matter (EfOM) into six fractions: hydrophobic acids (HoA), hydrophobic neutrals (HoN), hydrophobic bases (HoB), hydrophilic acids (HiA), hydrophilic neutrals (HiN), and hydrophilic bases (HiB). The fractionation procedure was described in detail in our previous study [16].

### 2.4. Fourier transform infra-red (FTIR) analysis

The powder of DOM from secondary and sand-filtration effluents obtained through freeze-drying from 1L water sample was analyzed for the structural and chemical characteristics of DOM. KBr (1 mg) was mixed with the DOM powder (100 mg) and the IR spectra of the mixture were obtained by scanning it with IR spectrometer (Thermo Nicolet

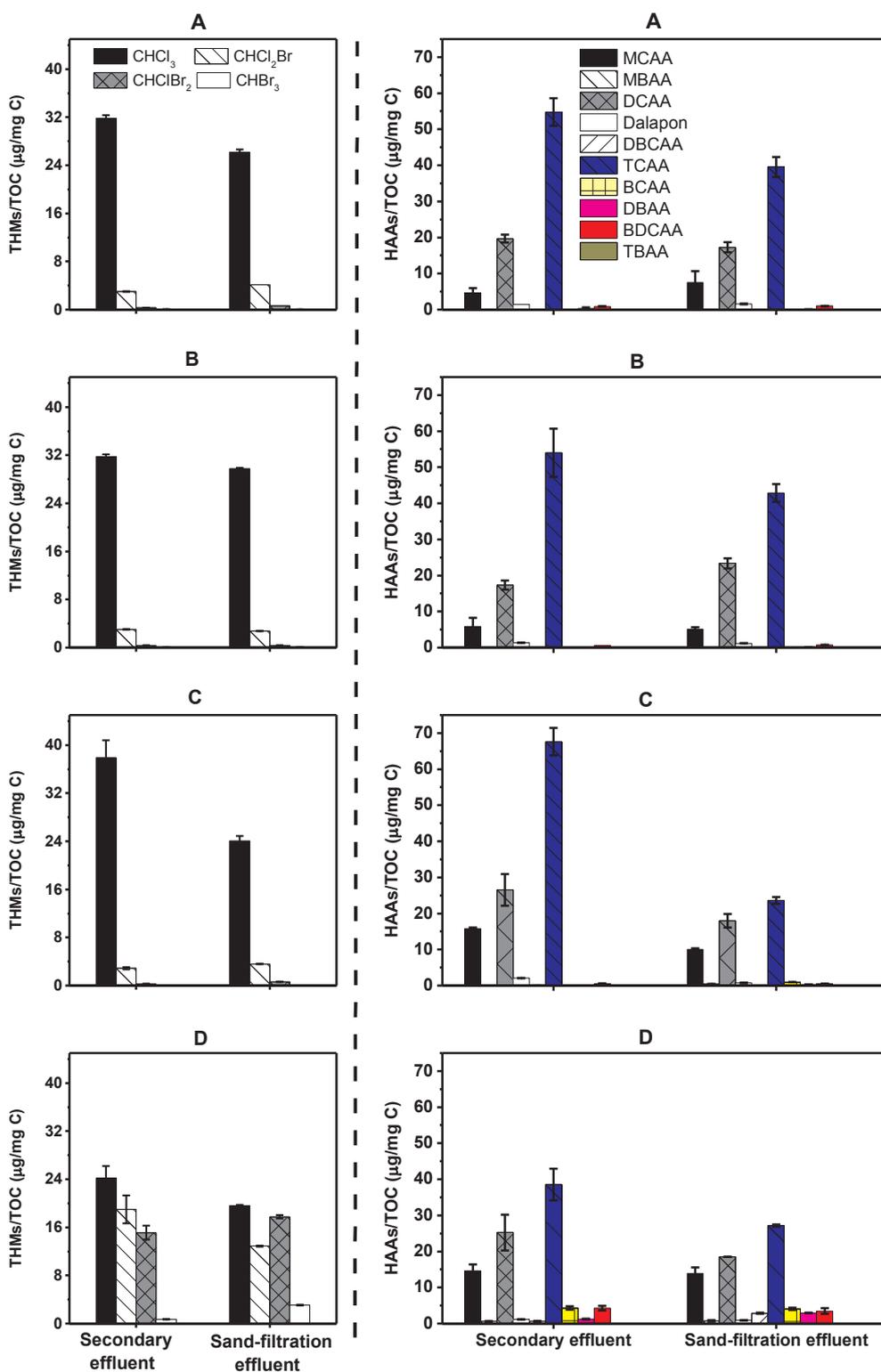


Fig. 1. The THMs and HAAs formation potential on a per carbon basis for the secondary effluent and sand-filtration effluent from A, B, C, and D, respectively.

5700, USA).

### 2.5. Molecular size distribution analysis

Chromatographic characterization and molecular weights distribution (MWD) of DOM were determined by HP-SEC with UV detection at 254 nm on a Hitachi L-2000 equipped with TSKgel G3000PW<sub>XL</sub> column. Sodium polystyrene sulfonate (PSS) (15650, 6400, 4600, AND 1370 Da)

and acetone were used as standards. Mobile phases were composed of Milli-Q water buffered with phosphate (0.0024 M NaH<sub>2</sub>PO<sub>4</sub> + 0.0016 M Na<sub>2</sub>HPO<sub>4</sub>) to a pH of 6.8 and 0.01 M sodium acetate (NaAc) to yield an ionic strength of 0.1 M.

Weight-average molecular weight (*M<sub>w</sub>*) and number-average molecular weight (*M<sub>n</sub>*) were calculated using the following equations [17].

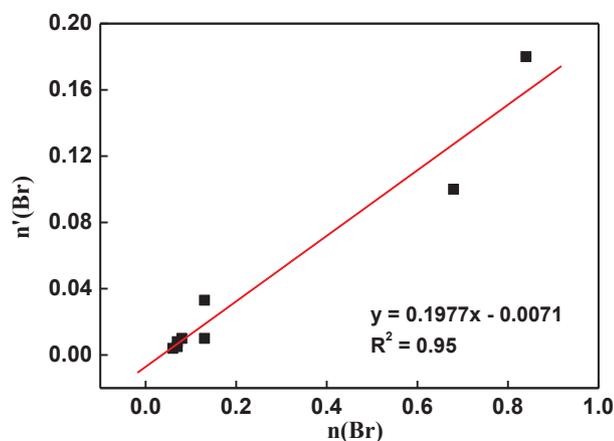


Fig. 2. The linear relationship between bromine incorporation in THMs ( $n(\text{Br})$ ) and in HAAs ( $n'(\text{Br})$ ).

$$Mw = \frac{\sum (hiMi)}{\sum hi} \quad (1)$$

$$Mn = \frac{\sum hi}{\sum \frac{hi}{Mi}} \quad (2)$$

where  $M_i$  is the molecular weight of each  $i$ th fraction of an analyte, and  $h_i$  is the height of the sample HPSEC curve eluted at volume “ $i$ ”.

### 2.6. Chlorination procedures and DBPs formation potential analysis

In order to compare the characteristics of DOM from different effluent, all samples were conditioned to similar DOC concentrations about 3 mg/L. A chlorine dose of 20 mg/L was applied to DOM solutions buffered at pH 7. Following incubation in the dark for three days, the solutions was quenched with sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), the amount of which was calculated according to chlorine residuals values measured with DPD spectrophotometric method. The experiments were repeated at least three times.

THMs and HAAs analyses were conducted according to USEPA method 551.1 and 552.3, respectively, using an Agilent 6890 N Gas Chromatograph (USA) that was equipped with a fused silica capillary column (HP-5, 30 m,  $320 \mu\text{m} \times 0.25 \mu\text{m}$ ) and a electron capture detector (ECD). The THMs and HAAs were extracted from water sample with hexane and methyl *tert*-butyl ether respectively. The extracts were dehydrated with anhydrous sodium sulfate before analysis.

A series of aqueous DBPs standards was generated by adding a range of volumes of the stock solutions to Milli-Q water. A blank (0  $\mu\text{g/L}$  as DBPs standards) of Milli-Q water was included in the development of all standards curves. Under the assumption of linear response behavior, regression analyses always yielded  $R^2 > 0.99$ . In the study, DBPs of samples without chlorination were measured as the controls.

Table 3  
Bromine incorporation in THMs ( $n(\text{Br})$ ) and bromine incorporation in HAAs ( $n'(\text{Br})$ ).

STPs	A		B		C		D	
	Secondary effluent	Sand-filtration effluent						
$n_{\text{Br}}$	0.08	0.13	0.07	0.07	0.06	0.13	0.68	0.84
$n'_{\text{Br}}$	0.01	0.01	0.005	0.008	0.004	0.033	0.1	0.18

## 3. Results and discussion

### 3.1. Characteristics of the wastewater samples used

DOC and SUVA were widely used as comprehensive surrogate parameters to quantify DOM concentration and characterize DOM aromaticity, respectively. The DOC content in secondary effluent and sand-filtration effluent from A ~ D STPs were between 6.98 and 9.17 mg/L and 5.2–7.66 mg/L, respectively (Table 2). The DOC content in secondary effluent from C and D STPs were slightly higher than those from A and B STPs. Generally, the DOC values in this study were similar to that in most reclaimed water source with median 7.5 mg/L [2]. The DOC levels were decreased by 3.15–27.98 % after sand-filtration process in A ~ D STPs. The secondary treatment process was conventional activated sludge and  $\text{A}^2\text{O}$  respectively for A and C STPs, which had higher DOC removal during sand-filtration process comparing with B and D STPs with oxidation ditch and SBR secondary treatment process. This implied the molecular weight distribution or structure of DOM in secondary effluent from A ~ D STPs were quite different as flocculation and sand-filtration usually removed the high molecular weight compounds [5]. There was no obvious difference in the SUVA values between secondary effluent and sand-filtration effluent. The SUVA was calculated as between 1.32 and 2.61 and 1.31–2.15 L/(mg-C·m) respectively for secondary and sand-filtration effluent. Similar to DOC content, the SUVA from C and D STPs were slightly higher than those from A and B STPs. The similar SUVA level in secondary and sand-filtration effluent indicated the sand-filtration process was not efficient for SUVA level decreasing. Additionally, this implied the samples had similar aromaticity which is closely related to reactivity with chlorine and ozone. It had been reported that DOM is mostly composed of non-humics and low hydrophobicity compounds when  $\text{SUVA} < 2 \text{ L}/(\text{mg-C}\cdot\text{m})$  [2]. This would be discussed further in the afterwards.

### 3.2. Effect of different treatment processes on the DBPs formation potentials

In order to investigate the reactivity with  $\text{NaClO}$  on a per carbon basis, all the DBPs data were normalized relative to the DOC concentrations to obtain the specific yields. The results of specific THMs and HAAs formation potential induced by the chlorination of secondary effluent and sand-filtration effluent from A, B, C, and D are shown in Fig. 1. The THMs formation potentials yielded from secondary and sand-filtration effluents from A ~ D STPs ranged from 35.2 ~ 59.0  $\mu\text{g}/\text{mg-C}$  to 28.3 ~ 53.3  $\mu\text{g}/\text{mg-C}$ , respectively. For HAAs, the level were 79.0 ~ 112.7  $\mu\text{g}/\text{mg-C}$  and 54.5 ~ 74.7  $\mu\text{g}/\text{mg-C}$ , respectively. The secondary effluents from C and D STPs with higher DOC and SUVA level yielded higher THMs and HAAs. After sand-filtration treatment, the DOC and SUVA level in D STP with SBR secondary treatment process was highest among the four STPs, and the DBPs formation potentials were also the highest (see Fig. 2).

It was obvious that both secondary effluent and sand-filtration effluent yielded remarkably high concentrations of  $\text{CHCl}_3$  among the four THMs species. The  $\text{CHCl}_3$  formation potentials of secondary effluents from A, B, C, and D STP were 31.8, 31.7, 37.9, and 24.2  $\mu\text{g}/\text{mg-C}$ , respectively, and were slightly higher than those of sand-filtration effluents (26.2, 29.8, 24.1, 19.6  $\mu\text{g}/\text{mg-C}$ ) except in C STP.  $\text{CHCl}_2\text{Br}$  formation potentials were less than 5  $\mu\text{g}/\text{mg-C}$  for both secondary and

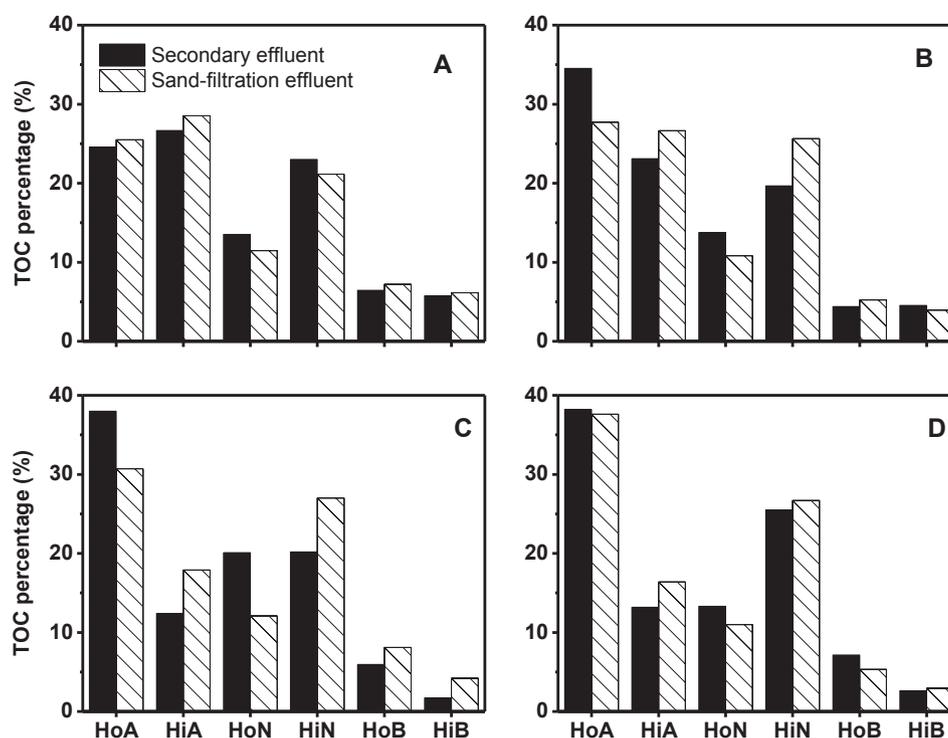


Fig. 3. TOC variation for DOM fractions of the secondary effluent and sand-filtration effluent from A, B, C, and D, respectively.

Table 4

The TOC percentage of hydrophobic organics and hydrophilic organics for DOM of the secondary effluent and sand-filtration effluent.

STPs	A		B		C		D	
	Secondary effluent	Sand-filtration effluent						
Hydrophobic organics (%)	44.57	44.17	52.69	43.78	64.04	50.9	58.65	53.94
Hydrophilic organics (%)	55.43	55.83	47.31	56.22	35.96	49.1	41.35	46.06

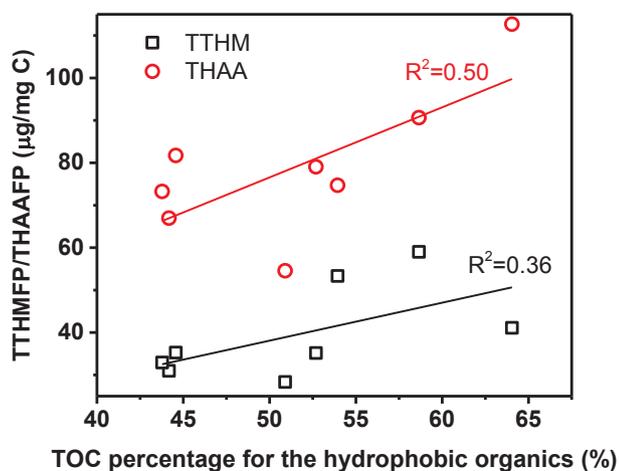


Fig. 4. The relationship between the TOC percentage for the hydrophobic organics and the total DBPs formation potential.

sand-filtration effluent from A, B, C STPs, while was 19.0 and 12.9 µg/mg-C for effluents from D STPs.  $\text{CHClBr}_2$  formation potential of effluent from D STP was also obviously higher than that from the other three STPs. Although bromide ions were  $< 0.01$  mg/L (detection limit of  $\text{Br}^-$  by ion chromatography) in all samples used in this study, bromide ions

in D STP was probably higher than that in the other three STPs. It has been mentioned above the SUVA from D STP was highest among the four STPs, which is closely related to reactivity with chlorine. On the other hand, it has been reported that hydrophilic DOM is more reactive with bromine toward the formation of THMs than the corresponding the hydrophobic organic structures [18]. The general TOC percentage of hydrophilic organics for DOM from D STP was similar and even slightly lower than those from A ~ B STPs (Table 4 in the next section). Therefore, the different DOM structure among D STP with the other three STPs was probably one important reason for the higher bromine THMs yields.

Comparing THMFP of secondary and sand-filtration effluent from all the four STPs studied in this study, we could conclude DOC removal and SUVA level decrease were important during secondary treatment process considering THMs control. On the other hand, sand-filtration performed not well on removing THM precursors from STPs effluent. For D STP,  $\text{CHClBr}_2$  and  $\text{CHBr}_3$  formation potential of sand-filtration effluent were not decreased but slightly increased comparing with those of secondary effluent indicating the specific  $\text{CHClBr}_2$  and  $\text{CHBr}_3$  precursor concentrations were increased after sand-filtration.

In this study, HAAs formation potential was greater than THMs formation potential. TCAA, DCAA, and MCAA dominated among the nine HAAs species yielded from chlorination of effluent with the order of  $\text{TCAA} > \text{DCAA} > \text{MCAA}$  (Fig. 1). This is consistent with the results of previous studies on drinking water treatment plants [6], while a little

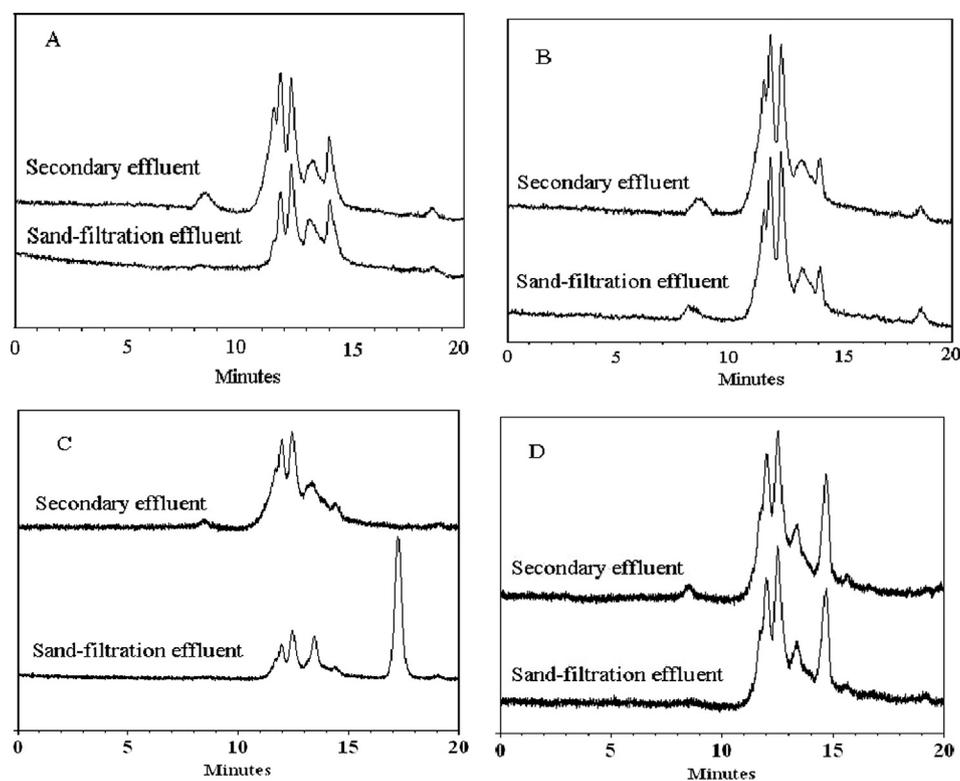


Fig. 5. Molecular weights distribution of DOM in secondary effluent and sand-filtration effluent from A, B, C, and D STPs, respectively.

Table 5

Molecular weights and polydispersity of DOM in the secondary effluent and sand-filtration effluent from A, B, C, and D STPs, respectively.

STPs	Water samples	Number-averaged molecular weight (Mn)	Weight-averaged molecular weight (Mw)	Polydispersity (Mw/Mn)
A	Secondary effluent	2021	3032	1.5
	Sand-filtration effluent	1708	2437	1.43
B	Secondary effluent	2369	3238	1.37
	Sand-filtration effluent	2655	3183	1.2
C	Secondary effluent	2394	3073	1.28
	Sand-filtration effluent	371	1383	3.73
D	Secondary effluent	1701	2622	1.54
	Sand-filtration effluent	1550	2412	1.56

different with previous study on STP with the order of DCAA > TCAA [10]. The TCAA formation potential of secondary effluent from A, B, C, and D STP was 54.8, 54.0, 67.6, and 38.5  $\mu\text{g}/\text{mg}\cdot\text{C}$ , respectively, and was removed by 28%, 21%, 65% and 29% by sand-filtration. The DCAA and MCAA formation potential was below 30 and 20  $\mu\text{g}/\text{mg}\cdot\text{C}$ , respectively, and were removed slightly and even none after sand-filtration process except in C STP, which suggested flocculation and sand-filtration process were inefficient in the removal of their precursors. BCAA, BDCAA, and DBAA were formed but in low level during chlorination of effluents from D STP, while were not found in the other three STPs. This indicated again bromide ions in D STP was probably higher than that in the other three STPs or the DOM structure in D STP was quite different with the other three STPs.

For THMs and HAAs, the bromine incorporation factors were calculated according to Zeng's study [19] and the results were shown in Table 3. The bromine incorporation factor ranged from 0.06 in C STP to 0.84 in D STP for THMs ( $n_{\text{Br}}$ ), which were obviously higher than those for HAAs ( $n_{\text{Br}}$ ) ranging from 0.004 in C STP to 0.18 in D STP. This indicated bromine trihalomethanes were more easily formed than bromine haloacetic acid. However, the bromine incorporation factors for THMs were significantly and positively related with those for HAAs. For both THMs and HAAs, the bromine incorporation factors in D STP

were highest among the four STPs as discussed above. It has been reported that the bromine incorporation into THMs and HAAs of the hydrophilic substances were higher than hydrophobic fraction [20] in a seawater reverse osmosis system. This would be further discussed in the next section. In all STPs, the bromine incorporation factors increased or remained unchanged after sand-filtration process probably due to bromide ion was difficult to be removed during this process. That is to say, removal of bromide with low content in the effluent was also important for bromine DBPs control.

### 3.3. Characterization of DOM before and after flocculation and sand-filtration treatment

#### 3.3.1. DOC variation for DOM fractions

In order to explore the main precursors for DBPs formation before and after flocculation and sand-filtration treatment, wastewater samples from A ~ D STPs were fractionated into six fractions including hydrophobic bases (HoB), hydrophobic acids (HoA), and hydrophobic neutrals (HoN), hydrophilic bases (HiB), hydrophilic acids (HiA) and hydrophilic neutrals (HiN). As shown in Fig. 3, the common dominant fractions of DOM in both secondary effluent and sand-filtration from all STPs were HoA and HiN, the percentage of which ranged from 24.6% in

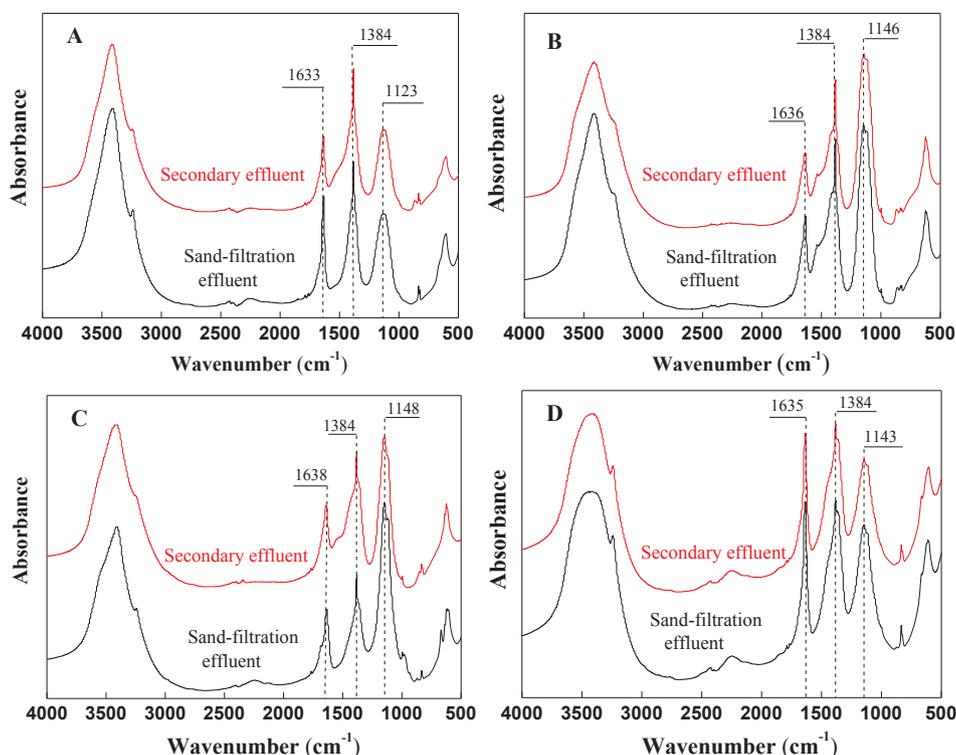


Fig. 6. FTIR analysis of DOM in the secondary effluent and sand-filtration effluent from A, B, C, and D STPs, respectively.

Table 6

Changes in the adsorption ratios of various peaks for DOM of the secondary effluent and sand-filtration effluent from A, B, C, and D STPs, respectively.

STPs	Water samples	1640/1384(C=C aromatic, COO-/CH <sub>3</sub> aliphatic)	1640/1143(C=C aromatic, COO-/C-O carbohydrates)
A	Secondary effluent	0.6	0.92
	Sand-filtration effluent	0.81	1.12
B	Secondary effluent	0.59	0.51
	Sand-filtration effluent	0.61	0.59
C	Secondary effluent	0.68	0.63
	Sand-filtration effluent	0.78	0.52
D	Secondary effluent	0.96	1.16
	Sand-filtration effluent	0.99	1.12

A STP to 38.2% in D STP, 19.7% in B STP to 27.0% in C STP, respectively. Additionally, HiA also dominated in DOM of A and B STPs with percentage higher than 20%. Generally, flocculation and sand-filtration didn't change the composition of organic matters in A and D STPs obviously, but decreased the percentage of HoA and HoN by about 20% or more and increased the percentage of HiA and HiN by 15 ~ 45% in B and C STPs. That is to say advanced treatment removed mainly hydrophobic fractions from B and C STPs. This is consistent with previous report that flocculation generally are used mainly to remove hydrophobic fractions [5]. The hydrophilic fractions percentage increased from 47.31% to 56.22% in B STP and from 35.96% to 49.10% in C STP (Table 4).

The positive relationships between the DOC percentage for the hydrophobic organics and the total DBPs formation potential (Fig. 4) revealed that the hydrophobic organics were substantially responsible for the formation of DBPs, especially the formation of THAA. However, according to our previous study [21], the main precursors for DCAA and TCAA respectively were hydrophobic and hydrophilic fractions. This was probably why the positive relationships between THAAs and TOC percentage for the hydrophobic organics were not strong. The TOC percentage for the hydrophobic organics in secondary effluent of C STP and in sand-filtration effluent of D STP was respectively highest among

all effluents in this study. This could explain the higher DBPs formation potential in these two STPs among the four STPs (Fig. 1).

### 3.3.2. HP-SEC analysis

In order to examine the changes in MWD of DOM caused by flocculation and sand-filtration process, HP-SEC analysis with UV detection was made in this study (Fig. 5). It can be seen that wastewater samples from the four sewage treatment plants exhibited relatively close chromatograms with a variety of shoulders and peaks occurring between 10 and 15 min. There were no obvious changes in peak heights between the samples before and after sand-filtrations process in STPs except C STP. Additionally, a rather low molecular weight peak at longer retention time was found for the sand-filtration sample from C STP.

The average molecular weights and polydispersity were summarized in Table 5. The weight-averaged molecular weights for the secondary effluents ranged from 2622 Da (D) to 3238 Da (B), and decreased after flocculation and sand-filtration especially for C STP probably due to the removal of rather high MW molecules. This significant decrease in average molecular weight for C STP was consistent with its highest decrease in the DBPs formation potential (Fig. 1). This was probably because more DBPs precursors with high MW in water from C STP were removed during the flocculation and sand-filtration

process.

The MW distribution of a mixture of polymers is defined as polydispersity, which could be calculated by the weight-average dividing to number-average MW (i.e.,  $M_w/M_n$ ) [17].  $M_w/M_n = 1.0$  represented polymer has a single MW. The polydispersity of both secondary and sand-filtration effluent was less than 2.0 except that of sand-filtration effluent from C STP, indicating the molecules in most effluent samples occupied a relatively narrow MW distribution. The exception was sand-filtration effluent from C STP, the polydispersity of which was 3.73 due to the presence of rather low MW molecules in the effluent.

### 3.3.3. FTIR analysis

The functional groups characterization of DOM in secondary and sand-filtration effluent from A, B, C, and D STPs were performed with FTIR analysis in order to further examine the effect of advanced treatment on it. The FTIR spectra were shown in Fig. 6. Interpretation of the absorption bands of the spectra was done as described in the literature [1,22–24]. The band at around  $3400\text{ cm}^{-1}$  is generally attributed to H-bonded OH groups. It can be seen that the FTIR spectra for the four secondary effluents showed the locations of similar peaks: aromatic C=C or COO<sup>-</sup> band around  $1640\text{ cm}^{-1}$ , CH<sub>3</sub> aliphatic band around  $1384\text{ cm}^{-1}$  and C–O carbohydrate band around  $1143\text{ cm}^{-1}$ . However, the relative absorption intensities for the bands varied among different samples.

Monitoring structural transformations through a series of absorption ratios of various peaks (FTIR) i.e. 1385/1050 (CH<sub>3</sub>/C–O polysaccharides) and 1425/1050 (COO<sup>-</sup>, phenolic OH/C–O polysaccharides) has been done previously [24,25] to determine the degree of aromatic character and polycondensation of the fulvic acids. In this study, the results were obtained for the adsorption ratios of the three dominant peaks i.e. 1640/1384 (aromatic C=C, COO<sup>-</sup>/aliphatic CH<sub>3</sub>) and 1640/1143 (aromatic C=C, COO<sup>-</sup>/C–O carbohydrates) (Table 6). For the four sewage treatment plants, the ratios of 1640/1384 showed an increase more or less as a result of flocculation and sand-filtration treatment, suggesting that the aliphatic compounds were probably removed more than the aromatic or COO<sup>-</sup> compounds especially for A and C STPs after the advanced treatment. This was consistent with the increase in the TOC percentage of hydrophilic organics. Additionally, the ratio of 1640/1384 in samples from D STP was the highest among the four STPs indicating the relative abundance of aromatic structures was highest in this STP. This was consistent with the SUVA values trends that samples from D STP had the highest values (Table 2).

However, the impact of flocculation and sand-filtration on the ratios of 1640/1143 varied with water sources. It was noted that the ratios of 1640/1143 (aromatic C=C, COO<sup>-</sup>/C–O carbohydrates) for A and B increased but decreased for C and D after the flocculation and sand-filtration process. As shown in Table 4, the TOC percentage of hydrophilic organics in secondary effluents for C and D was rather lower than that for A and B. Even after the advanced treatment, the percentage of hydrophilic organics for C and D was below 50%. The ratio of 1640/1143 in samples from D STP was also the highest among the four STPs.

## 4. Conclusions

This study investigated the effects of different secondary biological treatment processes followed by flocculation and sand-filtration on DBPs formation potentials control in four classical STPs in Beijing (A ~ D), which had similar DOC values with most reclaimed water source in other studies and SUVA values ranging from 1.31 to 2.61 L/(mg-C·m). The THMs and HAAs production were higher in secondary effluent from C and D STPs with higher DOC and SUVA levels. No matter before and after flocculation and sand-filtration, CHCl<sub>3</sub>, TCAA and DCAA were the main THMs and HAAs species formed during chlorination with the order of TCAA > CHCl<sub>3</sub> > DCAA. The TCAA formation potential of secondary effluent from A, B, C, and D STP was 54.8, 54.0, 67.6, and 38.5 µg/mg-C, respectively, and was removed by

28%, 21%, 65% and 29% by sand-filtration. For the other DBPs species, flocculation and sand-filtration was inefficient on removing their precursors in the four STPs. The bromine incorporation in THMs was obviously higher than that in HAAs indicating bromine trihalomethanes were more easily formed than bromine haloacetic acids. Flocculation and sand-filtration removed mainly hydrophobic fractions and decreased the average molecular weight of DOM from C STP, which was consistent with the highest DBPs formation potentials removal in this STP among the four STPs. FTIR analysis showed that aromatic C=C or COO<sup>-</sup> band, aliphatic CH<sub>3</sub> band, and C–O carbohydrate band were the main structures but with different relative absorption intensities in all secondary and sand-filtration effluents. Flocculation and sand-filtration probably removed more aliphatic structures than aromatic or COO<sup>-</sup> structures.

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