NOM reactivity with chlorine in low SUVA water

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ABSTRACT

Natural organic matter (NOM) in surface water with low specific UV absorbance in Tianjin, China, was fractionated using XAD resins and ultra-filtration membranes into different groups based on hydrophobicity and molecular weight (MW), respectively. The effects of the pre-chlorination process on each fraction were also studied. The hydrophilic acid (HPIA) fraction was the main organic component of NOM and the most significant precursor of trihalomethanes (THMs) and haloacetic acids (HAAs) formation among the other two fractions (hydrophobic acid, HPOA and transphilic acid, TPHA). HPIA was the most reactive precursor to the formation of THMs, while the HPOA was the most reactive precursor to the formation of HAAs. Pre-chlorination tests were carried out at different contact times. Some of the HPOA and TPHA fractions transformed into HPIA fraction after oxidation of 180 min as deduced from the increase of HPIA and the decreases of HPOA and TPHA fractions. On the other hand, the MW <2 kDa fraction was predominant in source water (approximately 60%) and played the most important role in the formation of THMs and HAAs. Pre-chlorination caused the cleavage of large molecules and altered the MW distribution towards smaller molecules.

Key words | disinfection by-product, molecular weight distribution, natural organic matter, pre-chlorination, XAD resin

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INTRODUCTION

The relevance of natural organic matter (NOM) to water treatment is significant. It influences many aspects of water treatment, including the formation of undesirable disinfection by-products (DBPs), when pre-oxidation or intermediate oxidation with chlorine and chloramines is applied. It is critical to understand the characteristics of NOM, such as the reactivity with chlorine and the change during water treatment, in order to best control the formation of potentially hazardous DBPs. Since aquatic NOM is a complex mixture of heterogeneous organic compounds, which are generated by physical, chemical and biological activities related to its origin (e.g. vegetation, soil, wastewater), there is no single analytical method that can reveal the actual concentrations of these compounds (Richardson et al. 2002). However, it is desirable to isolate NOM into more homogeneous groups based on different chemical or physical properties, such as hydrophobicity and molecular weight (MW), for the purposes of

characterization and reactivity studies. Understanding DBP formation as a function of hydrophobicity or MW of NOM fractions is important since DBPs are strictly regulated. Characterization of NOM in source waters and water treatment steps may help drinking water treatment facilities optimize treatment technology to remove fractions associated with high DBPs formation.

Physical and chemical fractionation of NOM at specific pH can be used to classify organic solutes into groups of differing hydrophobic behavior (e.g. hydrophobic, hydrophilic and transphilic) based on adsorption affinity for resins (e.g. XAD-8 and XAD-4) (Croué et al. 2002; Santos et al. 2009). Hydrophobic NOM is characterized by large amounts of aromatic carbons, high phenolic structures, conjugated double bonds and low nitrogen contents. Hydrophilic NOM contains large aliphatic carbons, nitrogenous compounds (carbohydrates, sugars and amino acids) and low aromatic carbon and phenolic

contents (Peuravuori & Pihlaja 1997; Kanokkantapong *et al.* 2006). This fractionation allows a thorough investigation of the formation of DBPs. In general, there was no consensus on the contributions of individual fractions to the formation of DBPs. For example, hydrophobic NOM was reported to be the main DBPs precursor in Chang-Hsin waterworks (Chang *et al.* 2001). Conversely, hydrophilic NOM contributed substantially to the formation of DBPs in Passaic valley (Marhaba & Van 2000) and Songhua River (Lu *et al.* 2009).

In addition, the estimation of MW is an important factor for understanding the physical and chemical properties of the NOM. Ultra-filtration (UF) has been widely used for isolation and fractionation of NOM into different MW fractions (Kitis *et al.* 2002). One of the advantages is that UF is easy to operate and can handle large volumes. Many investigators showed that the MW distribution (MWD) of NOM varied from source to source (Chiang *et al.* 2002; Kitis *et al.* 2002; Hua & Reckhow 2007). A wide range of MW from lower than 0.5 kDa to higher than 50 kDa has been found in different origins (Kitis *et al.* 2002; Świetlik *et al.* 2004). DBPs formation on chlorination has been reported for various MW fractions obtained by UF (Peuravuori & Pihlaja 1997; Kitis *et al.* 2002; Zhao *et al.* 2006; Hua & Reckhow 2007). While no consistent trend has been observed with respect to DBPs formation from individual MW, the MW <1 kDa fraction generally exhibited higher reactivity with chlorine in DBPs formation.

Although the mass distribution and concentration (e.g. dissolved organic carbon, DOC) of NOM and their relationship with DBP have been well established, especially in waters with relatively high specific UV absorbance (SUVA) (UV_{254} absorbance divided by the DOC concentration) values (>2–3 L/mg/m), there is limited information in the literature on the chemistry of NOM for waters with low SUVA values. These waters may be characterized by having NOM of hydrophilic character and less aromaticity. In addition, there is little information available so far about the effects of each water treatment step, such as the pre-chlorination process, on the changes in NOM. Characterization of NOM in source waters and water treatment steps can provide designers and operators with additional understanding of process selection and operation, also confirming the process performance.

Pre-chlorination is a general process in conventional water treatment to control taste and odor-causing materials and facilitate the removal of some contaminants during the subsequent treatment steps (Korshin *et al.* 1997). As a high concentration of DBPs was reported during the pre-chlorination process (Zhou *et al.* 2004), pre-chlorination was not recommended in drinking water plants (Chen *et al.* 2007). However, chlorine, as an economical and effective disinfectant, is widely used in developing countries and the pre-chlorination process as a water treatment unit is common in water treatment plant in most developing countries (China, India and in Africa) and some developed countries (Spain and Korea). In China, the source water is high in micro-contamination (Yan *et al.* 2006) and commonly contaminated not only by NOM but also by anthropogenic pollutants. Therefore, water purification is more difficult than in countries with well-protected water sources, and over 90% of water treatment plants choose the pre-chlorination process to control the growth of microorganisms and algae. The aim of this work is to investigate the mass distribution of NOM fractions and their relationship with DBPs using the resin adsorption and UF techniques. The effects of pre-chlorination on NOM, especially on the comparison of separated fractions, were evaluated and their reactivity towards chlorine was also examined.

MATERIALS AND METHODS

Source water

The surface water in this work was collected from the influent (raw water) of a water treatment plant in Tianjin, China, in August 2009. Tianjin is the third largest metropolis in China and has suffered water shortage for many years. The source water comes from the Luan River in summer and autumn and the Yellow River in the other seasons. The Luan River is a local river running through industrial estates and residential areas in northern China. Major characteristics of the water are listed in Table 1. Although the DOC level was rather high (5.08–5.12 mg/L), the SUVA value was <2 L/mg/m and the water may be regarded as low SUVA water. The SUVA value is more than four in most well-protected water sources (Yan *et al.* 2006). This indicates

Table 1 | Characteristics of source water in this study in Tianjin, China

Parameters	Raw water
DOC (mg/L)	5.08–5.12
UV_{254} (cm^{-1})	0.0499–0.0513
SUVA (L/mg/m)	0.98–1.02
NH_3-N (mg/L)	0.12–0.14
pH	8.04–8.11
Conductivity (μS/cm)	498–523
Turbidity (NTU)	2.99–3.23
Alkalinity (mg $CaCO_3$/L)	97–104
Algae (million/L)	18.3–19.0
THMFP (μg/L)[a]	421–439
HAAFP (μg/L)[b]	194–196

[a]THMFP, trihalomethane formation potential.
[b]HAAFP, haloacetic acid formation potential.

that the source water for the test is seriously polluted by NOM, with a low SUVA value.

Fractionation procedure

Two different procedures were applied to these waters. A portion of filtered water was fractionated using UF membranes with nominal MW cut-off of 2, 6, 10 and 30 kDa. Each membrane procedure was performed with a stirred 300 mL UF cell. The applied pressure of nitrogen was maintained at 0.1 MPa. When the volume of the retained solution was reduced to 90% of the initial solution volume the filtration was stopped. This UF method resulted in five fractions with nominal MW of >30, 10–30, 6–10, 2–6 and <2 kDa. The concentrated permeation was diluted by deionized water (Milli-Q) and then analyzed for DOC and DBPs.

Another portion of water was fractionated using absorption technology with XAD-8 and XAD-4 resins (Supelco, Bellefonte, PA). The isolation procedures were performed according to the descriptions of Leenheer (1981) and Croué *et al*. (2002). Both resins were purified by Soxhlet extraction prior to use in the process. The column distribution coefficient (k′) was kept at 100 for all samples. The samples were acidified to pH 2 by the addition of 18.4 mol/L H_2SO_4. After acidification, the samples were run on XAD-8 resin followed by XAD-4 resin. These samples were run through both columns at a rate of 4 mL/min. After all the

samples were run through the columns, each column was separately back eluted with 100 mL of 0.1 N NaOH at a rate of 2 mL/min. The eluate from XAD-8 is defined as hydrophobic acid (HPOA) and the eluate from XAD-4 is defined as transphilic acid (TPHA). The XAD-4 effluent was collected and defined as hydrophilic acid (HPIA). Hydrophobic neutral and transphilic neutral organics were adsorbed onto the XAD-8 and XAD-4 resins, respectively; however, they were not dissolved during back elution with NaOH. Therefore, they were not tested in this paper. The pH was adjusted to seven using 1 M H_2SO_4 or NaOH immediately after the extraction to avoid acid decomposition. The volumes of all fractions were adjusted to the initial sample volume with Milli-Q water and then the THMs formation potential (THMFP) and HAAs formation potential (HAAFP) of each of the three fractions, HPIA, HPOA and TPHA, were determined.

Pre-chlorination experiments

Experiments were performed using jar test devices to estimate the effects of pre-chlorination on the NOM. All samples were chlorinated in 2 L chlorine demand-free, gas-stopped bottles at room temperature. Chlorine was added as NaClO and reported here as the equivalent amount of Cl_2. The chlorine dose was 2.08 mg/L, calculated by the weight ratio of Cl_2 to DOC, which was 0.4. This is the typical dose used in the pre-chlorination process for drinking water treatment. At the end of contact time, the samples were quenched with NaS_2O_3 immediately. Parts of samples were used for DOC analyses and parts of them were fractionated before analyses.

DBPs formation potential

The THMFP and the HAAFP were determined according to *Standard Methods* 5710 B. All samples were adjusted to pH = 7 ± 0.2 by addition of 1 M H_2SO_4 or NaOH. Then a NaOCl solution (30 g/L, 200 μL) was added to ensure excess free chlorine with chlorine residue of 3–5 mg/L. The neutralized solutions were buffered by a phosphate solution prior to the incubation at 25 ± 2 °C in the space-free amber bottles with polytetrafluoroethylene (PTFE) liners. After the incubation period of 72 h, samples were quenched using

NaS$_2$O$_3$ (0.2 g), and the THMs and HAAs were analyzed by gas chromatography with electron capture detection (GC/ECD).

Analytical methods

The DOC was analyzed after filtration through a 0.45 μm membrane, acidified using 1 M HCl and bubbled to remove the inorganic matter in a Shimadzu Vcsh total organic carbon analyzer. The UV$_{254}$ was measured with a Hach DR/4000U spectrophotometer also after filtration through a 0.45 μm membrane. Turbidity was measured using a 2100 N Turbidimeter (Hach). Four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were measured by headspace-GC (Yan et al. 2006). Five HAAs (monochloro-, dichloro-, trichloro-, mono-bromo- and dibromoacetic acid) were analyzed by liquid-liquid extraction with methyl tert-butyl ether followed by derivation with acidic methanol according to Standard Method 552.3. The analysis was done with an Agilent 6890N instrument with HP-5 capillary column (30.0 m × 320 μm × 0.25 μm). The operating conditions for THMs and HAAs were as follows: injector temperature 150 °C, detector temperature 300 °C, injection volume 100 μL, temperature program: 30 °C for 2 min, 5 °C/min ramp to 70 °C; and injector temperature 220 °C, detector temperature 280 °C, injection volume 1 μL, temperature program 35 °C for 7 min, 5 °C/min ramp to 70 °C, 30 °C/min ramp to 250 °C, 5 min hold, respectively.

RESULTS AND DISCUSSION

Fractionation of NOM

Figure 1 shows the composition of NOM and the characteristics of the NOM fractions. Based on the DOC measurement, the summation of fractions from the XAD resins fractionation procedure was approximately 5.5 mg/L, which was about 7% surplus compared with the original un-fractionated samples. That is most likely to be the release of organics or monomers from the resins during elution. Recoveries between 88% and 112% were previously
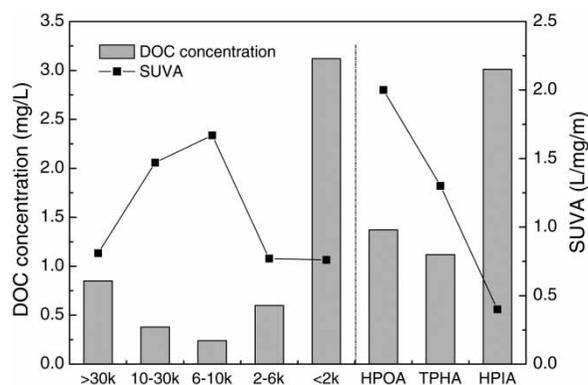

Figure 1 | Organic fractions of source water.

reported (Marhaba & Van 2000). The overwhelmingly dominant fraction of NOM of the Luan River in Tianjin was the HPIA fraction (58.8%) followed by the HPOA fraction (26.2%). This was lower than that found in well-protected water sources, in which the hydrophobic species were more than 70% (Yan et al. 2006). The relatively lower percentage of the HPOA fraction suggests contamination of the water source.

The source water for the drinking water treatment plant in Tianjin is transferred more than 100 km through a delivery pipe; hence, the water in this study is, unsurprisingly, contaminated by various types of point and non-point source pollutant generated by both residential and industrial activities upstream. This has potentially led to the accumulation of the hydrophilic species as detected from the fractionation procedure. This was in good agreement with the finding of Marhaba & Van (2000), who reported that the proportion of HPIA fraction was 53% in Passaic Valley Water. However, Croué et al. (2000) reported that the percentage of the HPIA fraction did not exceed 6% in South Platte River in Colorado; in fact, the total amount of hydrophilic species in South Platte River did not exceed 9% (Korshin et al. 1997). It should be noted that the distribution of each fraction in various source waters may vary significantly depending on the composition of NOM and the biogeochemical processes involved in the carbon cycle within the specific watershed. The HPOA fraction was slightly higher than the TPHA fraction in this work, while its SUVA value was consistently higher than the TPHA and HPIA fractions. The results support the belief that UV$_{254}$ was directly related to the hydrophobic content of NOM (Lu et al. 2009).

The MW <2 kDa fraction represented 60% of DOC in source water while the MW >30 kDa fraction accounts for 16%. The MW <2 kDa fraction was relatively hydrophilic and difficult to remove by coagulation or adsorption (Hua & Reckhow 2007). Furthermore, this fraction was the major portion of readily utilizable organic carbon by microorganisms. More attention should be paid to removing this fraction in water treatment plants. The SUVA of the MW <2 kDa fraction was lowest, while the highest SUVA value occurred in the fraction of MW 6–10 kDa. It appears that high MW NOM contains more aromatic content than low MW NOM. It is generally indicated in the literature that natural waters with high SUVA values (e.g. >4 L/mg/m), have relatively high contents of hydrophobic, aromatic and high MW NOM fractions, while waters with SUVA <3 L/mg/m contain mostly hydrophilic, non-humic and low MW fractions. The results obtained in this work verified this conclusion.

Fractions and DBPs precursors

Two types of DBPs formation potential (DBPFP), including THMFP and HAAFP, are introduced and used in the evaluation hereafter. One is the total DBPFP defined as the DBPs concentrations per unit mass DOC of the raw water. This was used to clarify the contributions of individual fractions to the DBPs formation in the water source. The other one is the specific DBPFP, which is normalized as the DBPs concentrations per unit mass DOC of each fraction. This is introduced in order to observe the reactivity of each fraction with chlorine in DBPs formation.

DBPs formation of XAD fractions

The raw water was found to contain more THMs precursors than HAAs precursors, as shown by the higher THMs concentration than HAAs concentration (Figure 2(a)). More THMs precursors were also observed by Marhaba & Van (2000). The HPIA fraction exhibited a greater contribution to DBPs formation than the HPOA and TPHA fractions as shown by the highest total DBPFP. Earlier work (Panyapinyopol *et al.* 2005) has shown that the HPIA fraction contains most of the bromide present in the raw water,
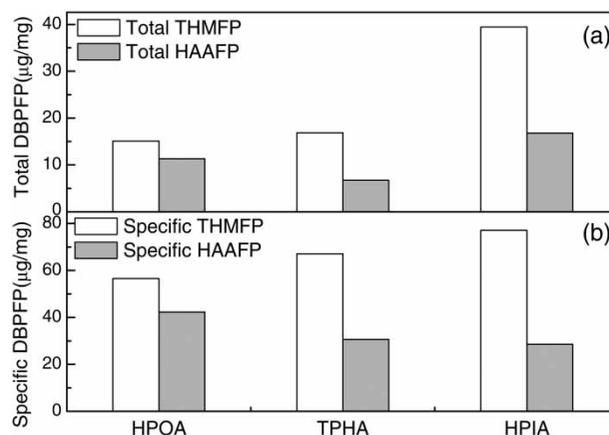
Figure 2 │ Total (a) and specific (b) DBPFP of each fraction with XAD resins (Cl_2 dose = 15 mg/L; pH = 7; temperature = 25 °C; contact time = 72 h).

and the bromide is known to boost formation of halogenated DBPs. Hua & Reckhow (2007) also suggested that bromine is relatively more reactive with hydrophilic than with hydrophobic fractions in the formation of DBPs. The fact that HPIA accounts for more than 58% of the DOC is another possible reason for the highest DBPs production among the isolated NOM fractions in source water. However, others (Chang *et al.* 2001; Kitis *et al.* 2002; Hua & Reckhow 2007) concluded that the hydrophobic organics with a greater aromatic content were the primary source of DBPs precursors. These waters were characterized as SUVA >3 L/mg/m. The results indicate that the organic species in water are location specific and should be investigated on a case-by-case basis.

The HPIA fraction exhibited the highest specific THMFP (Figure 2(b)), showing the highest reactivity with chlorine for THMs formation. This result further explains the above phenomenon that the THMs concentration was higher than that of HAAs in source water. Not only was the abundance of HPIA mass conducive to the competitive reaction with chlorine, but the high reactivity of HPIA also played an important role. Thus, removal of the HPIA fraction is the key to reducing the level of THMs for this water. The trend of relative reactivity for THMs formation among the fractions is HPIA > TPHA > HPOA. For HAAs, the HPOA fraction had the highest reactivity with chlorine as shown by the highest specific HAAFP. TPHA and HPIA had specific HAAFP of 31 and 29 μg HAAs/mg DOC, respectively. These results indicate that the mechanisms of THMs

and HAAs formation are different and relate to the chemistry of NOM.

Among the three fractions, the one with the greatest aromatic carbon content is the HPOA fraction (Croué *et al.* 2002). The aromatic organic contents, such as carbonyl and carboxyl groups, could be one of the target groups in forming HAAs (Kanokkantapong *et al.* 2006). The HPIA fraction has a lower concentration of aromatic carbon and greater heteroaliphatic, ketone and carboxyl content than the HPOA fraction (Aiken *et al.* 1992). It was reported (Marhaba & Van 2000) that chlorine species are electrophiles and, as such, have the tendency to react with electron-rich sites in organic structures. The results indicated that the HPIA fraction appeared to present such reactive sites. 'Transphilic' is a new operational adjective meaning intermediate or transitional polarity between hydrophobic and hydrophilic properties. TPHA has acetonitrile, pyrrole, phenol and carbohydrate contents (Croué *et al.* 2002). The fact that phenol was the precursor of DBPs has been confirmed. The data shown in Figure 2 confirm the principle that the HAAs precursors were more hydrophobic than THMs precursors as previously described (Hua & Reckhow 2007).

DBPs formation of UF fractions

The total and specific DBPFP of different MW fractions are given in Figure 3. The MW <2 kDa fraction had the highest THMs yields, while the MW >30 kDa fraction was also important for THMs formation (Figure 3(a)). A similar result was obtained by Chiang *et al.* (2002) who revealed the MW <1 kDa fraction contributed 46% of THMs in source water. On the other hand, the yields of HAAs generally increased with decreasing MW with the exception of MW >30 kDa fraction, which exhibited a slightly higher yield than MW 10–30 kDa fraction (Figure 3(b)). The general trend of DBPs with MWD suggests that most of the DBPs precursors are concentrated in the NOM fraction with low MW. Bromide, as part of the low MW fraction, had a critical contribution in the formation of DBPs. Hua & Reckhow (2007) also found that bromine is relatively more reactive with low MW than high MW NOM in the formation of DBPs. However, the main fraction of DBPs precursors (i.e. MW <2 kDa fraction) does not hold the
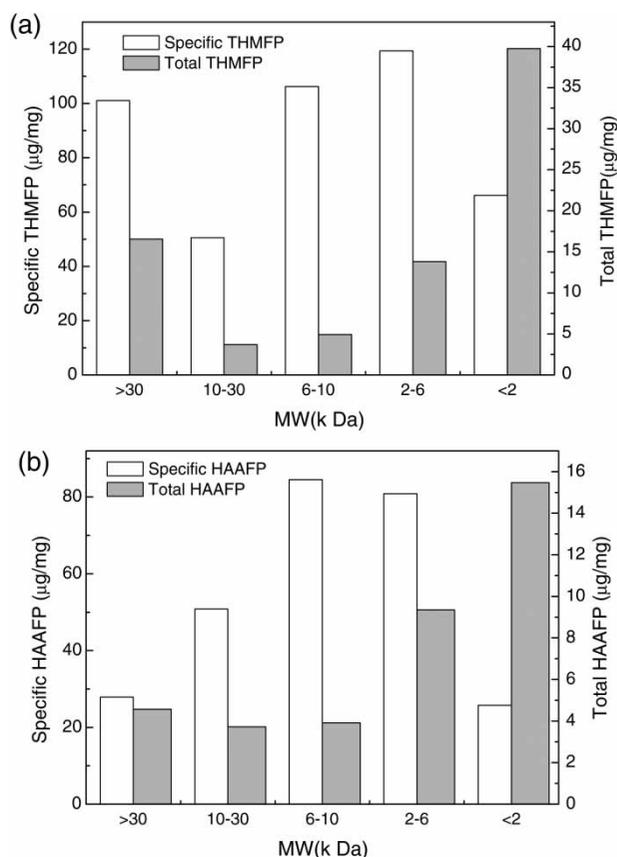
Figure 3 | Specific and total DBPFP of each fraction with UF: (a) THMs and (b) HAAs (Cl_2 dose = 15 mg/L; pH = 7; temperature = 25 °C; reaction time = 72 h).

highest reactivity with chlorine as expressed in specific DBPFP. The MW 2–6 kDa fraction showed the highest specific THMFP (Figure 3(a)), indicating that it is more active than the MW <2 kDa fraction, which contributed over 50% to the THMs formation in the water. The values of the specific HAAFP as illustrated in Figure 3(b) indicated that the MW 6–10 kDa fraction had the highest reactivity with chlorine, followed by the MW 2–6 kDa fraction. It is indicated that the NOM with high MW took priority in forming HAAs with chlorine, according to the values of the specific THMs and HAAs in Figure 3. The chemical structures of compounds in each fraction should be further studied to explain the reaction mechanism.

Research has been carried out on the DBPs precursor from various MW fractions. Chiang *et al.* (2002) found that 53% of trichloromethane, 51% of trichloroacetic acid and 39% of dichloroacetic acid precursors were from the MW >30 kDa NOM in commercial humic substances, while

about 63% of the DBPs precursors were from the fraction with MW <1 kDa in surface water. Kitis *et al*. (2002) isolated NOM from Myrtle Beach, South Carolina, and Tomhannock, New York, and found that DBPs yields generally increased with increasing MW for Myrtle Beach, while the MW 1–3 kDa fraction produced the highest THMs and HAAs yields for Tomhannock. These results suggest that not only does the MWD vary from source to source but also the reactivity of MW fractions varies as well. The source-related environmental conditions may play important roles in the determination of MWD and reactivity with chlorine.

Effect of pre-chlorination on NOM fractions

In order to clarify the reactivity of NOM in raw water during pre-chlorination, this experiment investigated the mass and the composition of NOM before and after oxidation with chlorine at different contact times. Figure 4 gives the DOC concentration and the percentage of individual fractions of NOM obtained by XAD resin technology before and after pre-chlorination. Less change in NOM composition was noted after pre-chlorination within 30 min. It was reported (Zhao *et al*. 2006) that the average chlorine consumption of raw water in the USA ranged from 1.58 to 2.41 mg Cl_2/mg DOC. As the chlorine used in the pre-chlorination experiment was much less than 1.58 mg Cl_2/mg DOC, actually 0.4 mg Cl_2/mg DOC, the changes in NOM were not significant in a short contact time. After a contact time of 180 min, the DOC of source
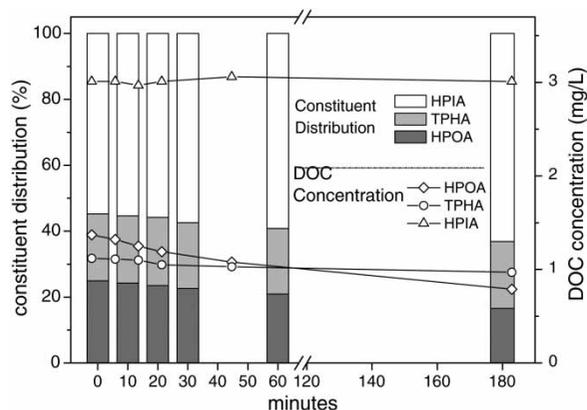

Figure 4 │ Concentration and constituent distribution of each fraction with XAD resins before and after pre-chlorination at different contact times.

water reduced with a reduction efficiency near 11%. The DOC concentration decreased from 1.37 to 0.79 mg/L of HPOA fraction and 1.12 to 0.97 mg/L of TPHA fraction. Some of the losses were compensated by an increase in HPIA fraction, from 3.01 to 3.11 mg/L. The results indicate that the HPOA and TPHA fractions transformed into HPIA fraction as deduced from the decreases in HPOA and TPHA fractions and the increase observed in the HPIA fraction.

A similar transformation trend was observed with ozone oxidation Galapate *et al*. (2001). Galapate and coworkers compared the hydrophilic and hydrophobic NOM in untreated and ozonated samples and found a great decrease in hydrophobic DOC and increase in hydrophilic DOC after oxidation. That is possibly because chlorine attacks the aromatic sites (Chiang *et al*. 2002; Kanokkantapong *et al*. 2006), which are found abundantly in the HPOA fraction (SUVA, 2 L/mg/m) and TPHA fraction (SUVA, 1.3 L/mg/m). As the SUVA of the HPIA fraction was 0.4 L/mg/m, indicating that a few aromatic contents were contained in this fraction, no significant effects were observed. This was an interesting finding because the HPIA fraction appeared to have the highest reactivity with chlorine to form THMs in this work (Figure 2). The possible explanation for this phenomenon is that the HPIA fraction has a slow reaction rate with chlorine. The pre-chlorination process was conducted only for 30 min while the reactivity with chlorine of the HPIA fraction was tested after 72 h. Contact time played an important role in analyzing the HPIA fraction. As the HPIA fraction showed the highest reactivity for THMs, the composition of NOM after pre-chlorination has contributed to the significant increase in THMs formation.

The research done by Iriarte-Velasco *et al*. (2007) verified that 60% of THMs production in filtered water was caused by the HPIA fraction (obtained by ionic resin adsorption). The decreases in the HPOA fraction could be related to the reduction of HAAs formation as this fraction has the highest reactivity with chlorine to form HAAs. In conclusion, pre-chlorination caused the chemical transformation of NOM, leading to a decrease in HAAs precursors and an increase in THMs precursors. Optimum plant performance should assess bulk parameters such as DOC or turbidity removal as well as specific NOM removal, and some form of advanced treatment technology should be adopted by
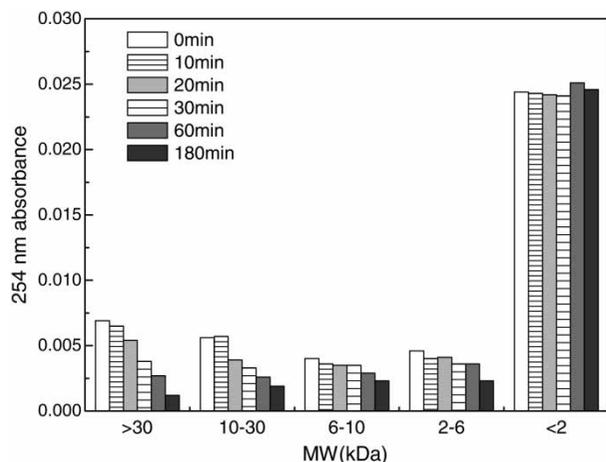
Figure 5 | MWD of each fraction with UF before and after pre-chlorination recorded at $\lambda = 254$ nm.

drinking water plants to further enhance the removal of the HPIA fraction.

The effect of pre-chlorination on MW of NOM is shown in Figure 5. The examination of MW with UV detection is one of the highly visual methods to analyze changes in the quality of water (Peuravuori & Pihlaja 1997), and it is used in this work. Pre-chlorination treatment led to a decrease of 27% of the UV_{254} in raw water. After the pre-chlorination process, significant decreases of UV_{254} were observed in all fractions except the fraction of MW <2 kDa, which had a slight increase. It was observed that the pre-chlorination process caused the cleavage of the large molecules and altered the MWD to smaller molecules deduced from the decreasing UV_{254}. The results reveal that the compounds with high MW are more reactive with chlorine, while low MW fractions are inactive with chlorine. It was reported (Kitis *et al*. 2002; Kanokkantapong *et al*. 2006) that the fractions with high MW were more aromatic and had a high content of carboxyl groups, which have more reactive sites with chlorine.

CONCLUSION

The HPIA fraction was the major component of the NOM of source water as well as the dominant DBPs precursor in Tianjin. The most active precursor for THMs in this water was the HPIA fraction, while the HPOA fraction was the most active precursor of HAAs. The THMs precursors seem to be more hydrophilic than the HAAs precursors. The pre-chlorination treatment caused a decrease of 11% of DOC and transformed the HPOA and TPHA fractions into HPIA fraction, leading to a decrease in HAAs formation and an increase in THMs formation.

The MW <2 kDa fraction occupied the largest proportion of DOC in source water followed by the MW >30 kDa fraction. The MW <2 kDa fraction had the greatest contribution to the formation of THMs and HAAs. The MW 2–6 kDa fraction had the highest reactivity with chlorine to form THMs, while the MW 6–10 kDa fraction had the highest reactivity with chlorine to form HAAs. The pre-chlorination process caused the break-up of large molecules and altered MWD towards smaller molecules. It was shown that the large molecules with high SUVA had the priority to react with chlorine.

Hydrophilic and low MW NOM played a significant role in DBPs formation for the water with low SUVA. Furthermore, these NOM fractions were very difficult to remove by coagulation and more attention should be paid to this when choosing water treatment processes. Pre-chlorination of surface water will not have a dramatic impact on NOM characteristics, and may play a positive role in the improvement of water quality.

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