Evaluation of drinking water treatment processes focusing on natural organic matter removal and on disinfection by-product formation

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Abstract The aim of this study was to characterize and compare natural organic matter (NOM) removal and disinfection by-product (DBP) formation in the drinking water treatment train that can give valuable information, while optimizing the treatment process. In this study, the determination of the hydrophobic (HPO), transphilic (THP) and hydrophilic (HPI) NOM distribution was used in parallel with more related drinking water parameters to compare the selected waters. High-performance size-exclusion chromatography (HPSEC) was applied to evaluate the relative changes of molecular size distribution of NOM in different treatment steps and source waters. This showed that the quantity, speciation and activated carbon adsorption of DBPs could vary not only by water quality, but also by the distribution and properties of the organic molecules that comprise NOM.
Keywords Disinfection by-products (DBPs); molecular weight; natural organic matter (NOM)

Introduction

Characterization of the physicochemical properties of NOM is an integral part of understanding the role of NOM in an array of environmentally important processes, such as fate and transport of micropollutants, and its impacts on potable water treatment unit operation.

Molecular weight and size distribution are two important bulk properties of NOM. The size of NOM is important in drinking water treatment processes. Numerous studies have shown that processes such as coagulation are effective in removing the high molecular weight components. The reactions of chlorine with organic material in water have been known for some time. Rook (1974) believed that NOM, as measured by color, was the precursor to the formation of THMs. Conventional alum coagulation caused the removal of most of the precursor material from the source water (Stevens *et al*., 1976). More recently, a similar effect has been demonstrated in another class of DBPs, the haloacetic acids (HAAs) (Pourmoghaddas *et al*., 1993; Cowman and Singer, 1996).

The aim of this study is to characterize and compare NOM removal and disinfection by-product formation in the drinking water treatment train that can give valuable information, while optimizing the treatment process.

Materials and methods

Source waters

This study was used the source waters for the Dachung Water Treatment Plant (DWTP) which came from the Daechung reservoir and for the Buyeo Water Treatment Plant (BWTP) which came from the Keum River. The process train included conventional water treatment: coagulation, flocculation, sedimentation, and sand filtration.

Isolation and fractionation of NOM

NOM fractionation was carried out using a modified resin isolation and fraction procedure

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originated by Leenheer (1981). Pre-filtered water samples were processed through XAD-8 followed by XAD-4 resins to isolate hydrophobic (XAD-8 adsorbable), transphilic (XAD-4 adsorbable), and hydrophilic (neither XAD-8 nor XAD-4 adsorbable) NOM fractions. Adsorbed hydrophobic and transphilic acids were eluted using a 0.1N NaOH solution.

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HSPF analysis

Molecular weights (MW) of different treatment steps and source waters were determined by HSPF. The operating system consisted of a Perkin-Elmer LC 200 high-pressure pump, a Perkin-Elmer Diode Array UV/visible detector 235C. 20 µL samples were separated on a Waters Protein-Pak 125 column (Waters Corp., Milford, MA, USA). The carrier solvent consisted of a 4mM phosphate buffer adjusted to an ionic strength of 0.1 M with sodium chloride, with a pH of 6.8. A flow rate of 1.0 mL/min was used, depending on the column. The system was calibrated with PSS standards of the following molecular weights: 1.8 K, 4.6 K, 8 K, 18 K, and 35 K (Polysciences Inc., MA, USA), prepared at 1 g/L concentration. The PSS standard were detected at 224 nm and NOM samples at 260 nm. A linear equation of the form $\log (MW) = a - b(t)$, was obtained, where MW is the molecular weight and t is the peak retention time. A coefficient of determination $R^2 > 0.99$ was consistently obtained.

Analysis of DOC, THMFP and HAAFP

The DOC was measured with the Dohrman TOC analyzer (Phoenix 8000) and analyzed following the Standard Methods 5310C, "Persulfate-Ultraviolet Oxidation Method". Source and treated samples were chlorinated using a concentrated HOCl solution with a chlorine concentration based on $3 \times$ [DOC concentration] $+ 7.5 \times$ [NH_4^+ concentration]. Chlorinated samples were inserted in an incubator at a temperature of 20°C for 72 hours. THMFP was analyzed following the method described the USEPA 502.2 method "Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography" (FID; Flame Ionization Detector, Rtx 502.2 column; ID 0.25 mm × length 30 m, Varian 3600 gas chromatography; 3600GC). HAAFP was determined using the Modified EPA 552 Microextraction method (ECD; Electronic Capture Detector, HP-1 column; ID 0.25 mm × length 60 m).

Results and discussion

In this study, the determination of the hydrophobic (HPO), transphilic (THP) and hydrophilic (HPI) NOM distribution was used in parallel with more related drinking water parameters to compare the selected waters.

The HPO, THP and HPI NOM distribution was determined by dividing the organic matrix into three fractions: two superposed XAD-8 and XAD-4 resin columns at acidic pH, the hydrophobic NOM that adsorbed onto the XAD-8 resin, the transphilic acids that adsorbed onto the XAD-4 resin and the non-adsorbed hydrophilic solutes that are contained into the XAD-4 effluent. Figure 1 showed that the hydrophobic fraction was the largest fraction of the NOM pool with respect to HPO, THP and HPI fractions of each source water. Hydrophobic organic compound consisted of 45–46% of DOC in source waters, whereas the THP and HPI fractions constituted 22–23% and 31–33%, respectively, of the total DOC. The removal of the HPO fraction predominated in conventional water treatment and accounted for 50% of the total amount of HPO NOM in DWTP and 30% in BWTP. However the THP and HPI fractions were not removed. Coagulation was effective in removing HPO fraction but was less effective for THP and HPI fractions.

High-performance size-exclusion chromatography (HPSEC) was applied to evaluate the relative changes of molecular size distribution of NOM in different treatment steps and source waters. As seen from Figure 2, the MW distribution in two source waters was mainly
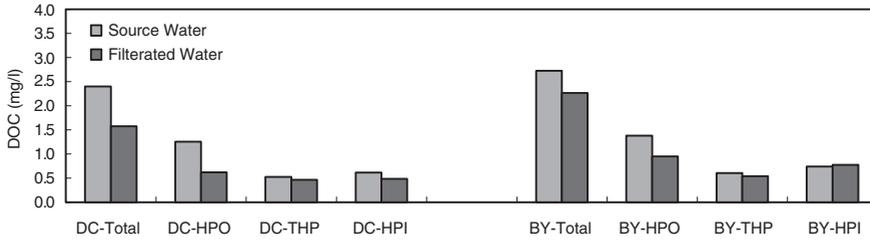
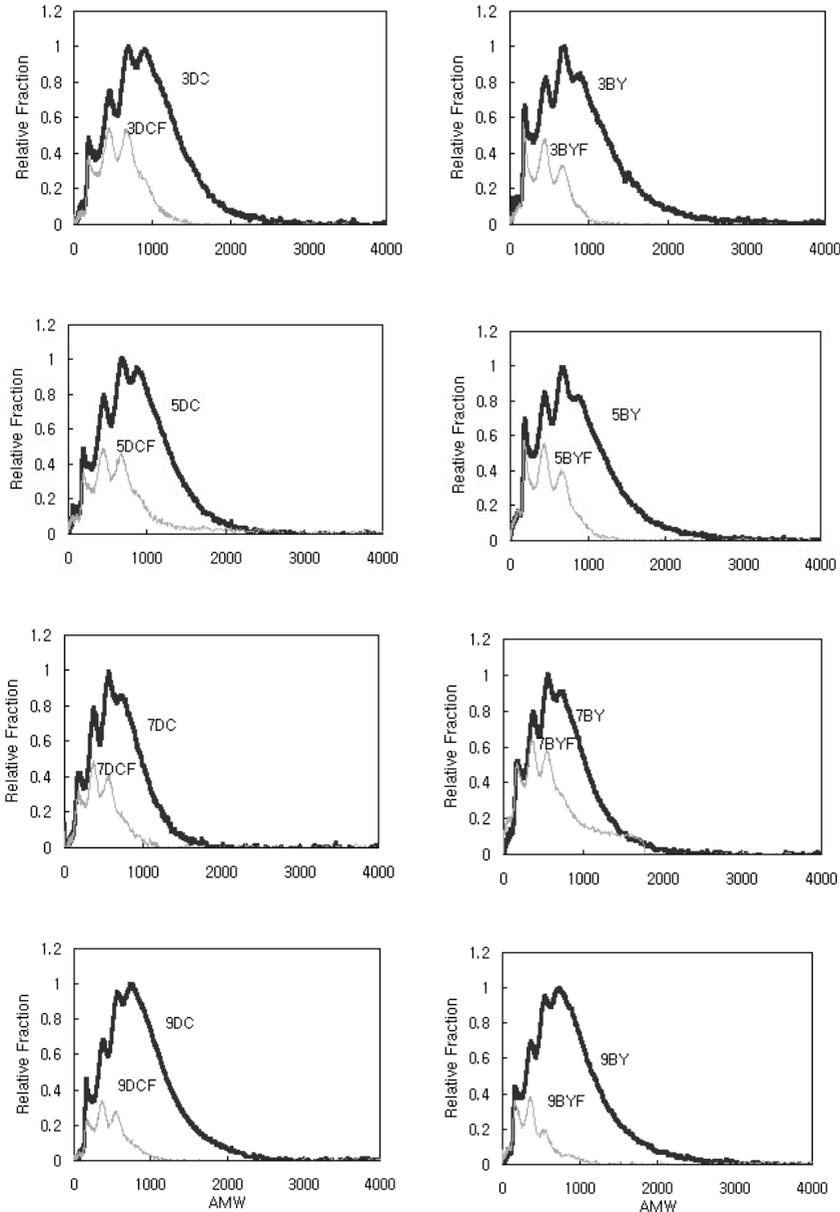**Figure 1** NOM structure variation for source and treated waters (DC: DWTP; BY: BWTP)

Figure 2 NOM MW distribution comparison of source and treated waters (DC: DWTP source water; DCF: DWTP filterated water; BY: BWTP source water; BYF: BWTP filterated water)

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related to the fraction of NOM with MW <2,000 daltons. According to the HPSEC results, the four MW fractions <500, 500–1,000, 1,000–1,500 and >1,500 of the source waters were 14.4%, 43%, 33% and 8.6% respectively. Coagulation process with subsequent sand filtration decreased 66% of the total sum of peak heights and concentrated the molecular weight distribution towards the smaller molecules of less than 1,000 daltons. This shows that conventional water treatment process including coagulation was efficient for the removal of large molecular weight molecules of more than 1,000 daltons. This indicated that the HPSEC results could provide a process evaluation indicator for removal of NOM in drinking water treatment.

This study was devoted to comparing the reactivity of hydrophobic and hydrophilic NOM isolated from reservoir and river waters, as shown in Figure 3. The isolation of DBP precursors with XAD resins is used to study the reactivity of NOM with chlorine. 85% of the DOC and more than 90% of the DBP precursors of the reservoir and river waters were adsorbed onto the XAD-8 and XAD-4 resins when used in series.

The hydrophobic and transphilic NOM exhibited the largest THMFP and HAAFP reactivity. As seen from Figure 4, the THMFP formed from hydrophobic and transphilic NOM was preferentially removed by the GAC adsorption process compared to THMFP formed from hydrophilic NOM, and HAAFP formed from hydrophilic NOM was preferentially removed by GAC adsorption process compared to transphilic and hydrophobic NOM. This showed that the quantity, speciation and activated carbon adsorption of DBPs could vary not only by water quality, but also by the distribution and properties of the organic molecules that comprise NOM.

Based on the work reported herein, NOM characterization of source water can provide designers and operators with additional insight into treatment processes selection and operation, and treated water characterization can confirm process performance.

Conclusion

HPO fraction was the largest fraction of the NOM pool with respect to HPO, THP and HPI fractions of source water. Coagulation was effective in removing HPO fraction but was less effective for THP and HPI fractions.

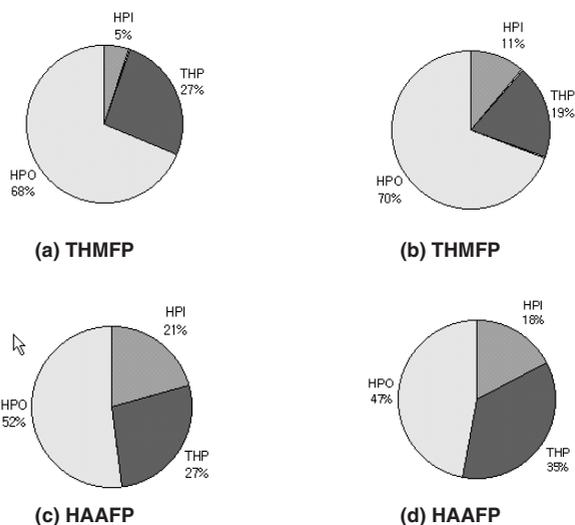The MW distribution in two source waters was mainly related to the fraction of NOM

Figure 3 Percentages of THMFP and HAAFP formed from NOM fractions at: (a) and (c) DWTP and (b) and (d) BWTP
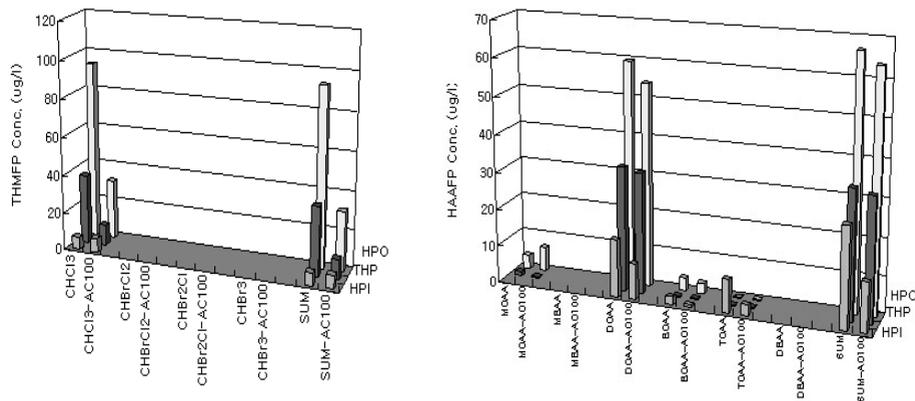
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Figure 4 Activated carbon adsorption of THMFP and HAAFP formed from NOM fractions at DWTP
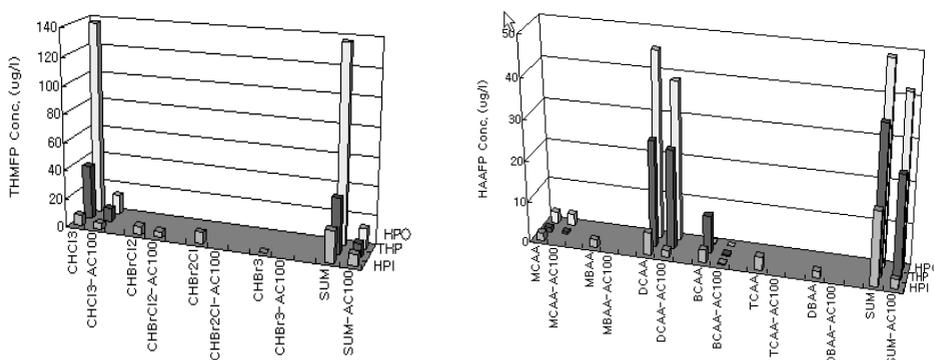

Figure 5 Activated carbon adsorption of THMFP and HAAFP formed from NOM fractions at BWTP

with MW <2,000 daltons. Conventional water treatment process including coagulation was efficient for the removal of large molecular weight molecules of more than 1,000 daltons. This indicated that the HPSEC results could provide a process evaluation indicator for removal of NOM in drinking water treatment.

The hydrophobic and transphilic NOM exhibited the largest THMFP and HAAFP reactivity. The THMFP formed from hydrophobic and transphilic NOM was preferentially removed by the GAC adsorption process compared to THMFP formed from hydrophilic NOM, and HAAFP formed from hydrophilic NOM was preferentially removed by GAC adsorption process compared to transphilic and hydrophobic NOM. This showed that the quantity, speciation and activated carbon adsorption of DBPs could vary not only by water quality, but also by the distribution and properties of the organic molecules that comprise NOM.

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