Investigation of NOM size, structure and functionality (SSF): impact on water treatment process with respect to disinfection by-products formation

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ABSTRACT

This study was undertaken to evaluate existing conventional treatment processes, as opposed to specific membrane processes, to minimize haloacetic acid (HAA) formation, by examining in detail the characteristics of natural organic matter (NOM) size, structure and functionality. Through these evaluations, both size exclusion and charge interaction mechanisms, based on NOM size and functionality analyses, were also used to evaluate the performance of each process in conjunction with NOM structural effects. Such integrated evaluations (beyond a simple combination of the characterizations of NOM size, structure and functionality) were shown to be useful for the selection of advanced alternative membrane processes in order to maximize the removal of hydrophilic NOM fractions, which have a relatively high HAA producing potential, as conventional drinking water treatment processes examined in this study are unable to remove the hydrophilic NOM fraction effectively.

Key words | natural organic matter, haloacetic acids, charge interaction, size exclusion, NOM size, structure and functionality

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INTRODUCTION

The disinfection by-products (DBP) regulation demands rigorous evaluation of existing conventional processing plants to improve natural organic matter (NOM) removal, and the adoption of other advanced treatment alternatives, such as membrane processes (USEPA 1998). Our research was undertaken to focus on evaluating procedures (using NOM characterizations in terms of the molecular size, structure and functionality) for the improvement of treatment processes in terms of DBPs (especially haloacetic acids (HAAs), because trihalomethane (THM) formation with the source water tested in this study was very low, less than 30 μg l^{-1}). The main objective of this study was to provide ideas on how to improve treatment processes or how to choose alternatives from the practical point of view. Although the characterization methods applied during this work were not new, we were offered the rare opportunity to examine the three different candidate techniques proposed for

improving conventional treatment plants, and to integrate the various NOM removal mechanisms (for example, size exclusion and charge repulsion). The three different characterization techniques of NOM size, structure and functionality (SSF) are not straightforward in actual treatment plants. However, much research has been performed to develop relatively easy and almost continuous monitoring methods, for example:

1. On-line NOM size distribution measurement was attempted using the high pressure size exclusion chromatography (HPSEC) method (Chin *et al.* 1994) with both UV absorbance and on-line total organic carbon (TOC) detectors (Huber *et al.* 1994; Her *et al.* 1999).
2. NOM aromaticity (and resulting hydrophobicity) is closely related to the UV absorbance of NOM (on-line measurement is possible), which is ascribed

primarily to aromatic chromophores, thus relative hydrophobic or hydrophilic content can be easily determined by simply determining the specific UV absorbance (SUVA = UV absorbance at 254 nm (UVA_{254}/TOC) (of course, more studies should be undertaken to determine rigorously the relationships between SUVA and the hydrophobic and hydrophilic contents of various waters)).

3. Ionizable functionality is related to humic content (mainly hydrophobic acids) and is also related to SUVA.

4. HAAs are not easily measured, but Li *et al.* (1998, 2000) reported good relationships between DBP concentrations and changes in UV absorbance during chlorination.

Based on these and ongoing studies, it does not seem difficult to evaluate existing treatment processes by collectively applying almost on-line SSF evaluating procedures (even though they provide approximate measurements for evaluation, they are nevertheless informative) in terms of NOM and DBPs determination, as well as facilitating the selection for more advanced processes such as membrane filtration, as opposed to conventional processes. Through this evaluation procedure, it is anticipated that NOM removal by a particular process (either a conventional or an advanced one) can be explained using the three different rejection mechanisms (size exclusion, hydrophobic and electrostatic interactions) either separately or when integrated.

NOM removal mechanisms (charge interaction, size exclusion) and the NOM structure effect

Chemical coagulation (as a conventional treatment process) has been evaluated from the perspective of TOC and UVA removal as well as DBP precursor removal, and optimal pH and coagulant doses have been thoroughly investigated, in terms of achieving the best possible NOM removal by coagulation with alum or ferric chloride (Krasner & Amy 1995; Childress *et al.* 1999). Coagulation can reject NOM to some extent. Two possible mechanisms for NOM removal have been suggested, namely, NOM adsorption on to the surface of aluminium or ferric

hydroxide, and the complexation of NOM acids with metals (Krasner & Amy 1995). Both mechanisms can be explained on the basis of charge interactions derived from the opposite charges of NOM acids and the coagulant metal. NOM acidity and coagulant charge can be identified by titration and zeta potential measurement methods, respectively. Functionality (charge density) analysis based on carboxylic acidity, as determined by a potentiometric titration, has been used to demonstrate charge interactions and charge neutralization for NOM removal for a particular process (Collins *et al.* 1986). In this article, both the carboxylic and phenolic acidities of hydrophobic and hydrophilic acids (isolated using XAD-8/4 resins) were characterized for water samples before and after the treatment processes, which included chemical coagulation, sand filtration and membrane filtration, and the results were used to determine which processes utilized charge interaction mechanisms (in conjunction with the NOM structure effect) most efficiently for the removal of NOM acids.

Humic and fulvic substances (i.e. hydrophobic NOM) were reported to be preferentially removed by coagulation, in comparison with the other NOM fractions (transphilic and hydrophilic NOM) (Krasner & Amy 1995; Childress *et al.* 1999), which is believed to be because of charge interactions. NOM acids were also preferentially removed by a negatively charged membrane as opposed to the non-charged NOM fractions (Cho *et al.* 2000). Thus, charge interactions have a major influence on NOM removal in both the chemical coagulation and membrane processes. Because different NOMs show different charge densities as a result of the different ionizable functional groups, it may be suggested that charge interactions should always be combined with NOM structure analysis. In conjunction with the effects of both charge interaction and NOM structure, size exclusion may be crucial to NOM removal, not only for membrane filtration but also for chemical coagulation; the greater molecular weight the NOM contains, the higher NOM removal the process achieves. For membrane applications, much higher NOM rejection was obtained than anticipated on the basis of the membrane molecular weight cut-off (MWCO) (Cho *et al.* 2000). The effective MWCO, which combined charge repulsion and size exclusion mechanisms, was then used

to explain this extraordinarily high NOM rejection behaviour (Braghetta *et al.* 1997; Cho *et al.* 2000). Thus, we can speculate that in order to evaluate existing water treatment processes efficiently, both charge interaction and size exclusion mechanisms should be considered collectively by SSF analysis.

Haloacetic acids reactivity

It has also been reported that humic NOM exhibits a greater potential for trihalomethane (THM) formation than non-humic NOM (Collins *et al.* 1986; Owen *et al.* 1993; Krasner & Amy 1995; Childress *et al.* 1999), and these workers suggested that non-humic NOM could have a similar or higher reactivity for chlorinated DBPs than humic NOM. Previous research (Cowman & Singer 1996; Pomes *et al.* 2000) investigated HAA formation mainly from humic substances; however, hydrophilic NOM has not been well analysed in terms of HAA formation and reactivity (HAA concentration (μg l^{-1})/DOC (mg l^{-1})) on chlorination, as compared with humic substances.

Thus, this study included relative HAAs formation potential from hydrophilic NOM as opposed to that of the hydrophobic and transphilic NOM fractions, along with measurements of their rejections by various processes. These analyses may provide an insight into a way of determining which processes are more efficient for the minimization of HAAs formation.

MATERIALS AND METHODS

NOM characterization

NOM size analysis

The NOM size distributions were measured using high performance size exclusion chromatography (HPSEC) with a preteinacious silica column (Protein Pak 125, Waters, Milford, Massachusetts) and a HPLC (Waters 510, Milford, Massachusetts)/autosampler (Waters 717 plus, Milford, Massachusetts). Polystyrene sulfonates (1,800, 4,600, 8,000 and 18,000 mass units) were used to calibrate the standard equation involving molecular weight (MW) and retention time, and a lower range of

MW for this calibration curve was identified with salicylic acid with a molecular weight of 138.12 g mol^{-1}. A 4 mM phosphate buffer solution (at pH 6.8) with added NaCl (to an ionic strength of 0.1 M) was used as an eluent (Chin *et al.* 1994). Argon gas was bubbled through the eluent for 15 min prior to use, to remove dissolved air, and then pumped into the size exclusion chromatography (SEC) column set up inside a constant-temperature chamber at 40°C. The SEC results were obtained every second from a UV detector (Photo diode Array Detector 996, Waters, Milford, Massachusetts) and saved in a personal computer using an automatic data acquisition system (Software Millennium). The data was transferred later into an Excel file. The fractional NOM removal was calculated using the following equation (Mulder 1996):

$$R_{M_i} = \frac{W_{M_i}\,(feed) - W_{M_i}\,(treated)\,(1 - R_{overall})}{W_{M_i}\,(feed)} \qquad (1)$$

where R_{Mi} is the fractional removal of the specific MW 'i'. W_{Mi} is the fraction of that MW in the sample based on UV absorbance detection, and $R_{overall}$ is the overall solute rejection by the process based on DOC measurements.

For membrane samples, W_{Mi}(treated) corresponds to the mass fraction of the membrane permeate sample.

NOM structure (hydrophobic, transphilic and hydrophilic) analysis

Water samples containing NOM were filtered through a 0.45 μm filter, and acidified to lower the pH to 2. Samples (volume ranging from 700 to 900 ml) were then processed through XAD-8 and XAD-4 resins (volume of 8 ml) sequentially to isolate the hydrophobic (XAD-8 adsorbable), transphilic (XAD-4 adsorbable) and hydrophilic (neither XAD-8 nor XAD-4 adsorbable) NOM fractions (Thurman & Malcolm 1981; Leenheer & Noyes 1984; Aiken *et al.* 1992). The adsorbed hydrophobic and hydrophilic acids were eluted using a 0.1 N NaOH solution; the volume of the NaOH solution was determined by the adsorbed mass onto XAD resins, which generally ranged between 50 and 80 ml. The separated NOM fractions were used to determine the relative mass fractions

Table 1 | Water qualities of the raw and treated samples used

Samples	DOC (mg l^{-1})	UVA$_{254}$ (cm^{-1})	SUVA (l mg^{-1} m^{-1})	pH	Br$^-$ (µg l^{-1})	Conductivity (µS cm^{-1})	Br$^-$/DOC (µg mg^{-1})	Molecular weight (g mol^{-1}) Number, avg.	Weight, avg.
Nakdong River water	3.06	0.073	2.40	7.7	58.1	373	19.0	1,121	1,423
Coagulation	2.75	0.047	1.71	7.0	44.3	398	16.1	945	1,278
Sand filtration	2.39	0.044	1.65	6.9	52.7	394	22.0	882	1,129
GM	1.60	0.042	2.62	7.5	30.1	322	18.8	792	1,004
ESNA	0.42	0.008	1.90	7.3	20.5	62	48.8	139	205

(hydrophobic vs. transphilic vs. hydrophilic), and also for MW distribution and acidity measurements.

NOM functionality (charge density) analysis

Carboxylic and phenolic acidities were measured for XAD-isolated hydrophobic and hydrophilic acids using a micro titrator (Metrohm 702 SM Titrino, Switzerland) with a stirrer (Metrohm 728, Switzerland). The sample pH was initially lowered to below 3.0 and the carbonate in the sample was removed by nitrogen purging for period of at least 10 min prior to actual titration. A 0.05 N NaOH solution was used to increase the pH of the sample, and the amount of NaOH consumed to increase the pH from 3 to 8 and from 8 to 12, which corresponds to the carboxylic and phenolic acidities, respectively, was recorded. Acidity was calculated using the following equation:

$$Acidity = \frac{50,000 \, x}{DOC \cdot y} \, (meq/gC) \qquad (2)$$

where x is the added volume (ml) of 0.05 N NaOH, DOC is the NOM concentration (mg l^{-1}), and y is the sample volume (ml).

Raw water and treated samples

Water samples were obtained from the Bansong water treatment plant and treated waters were obtained from each stage of the conventional process (coagulation and sand filtration). The Bansong plant takes its source water from the Nakdong River, and treats incoming water by chemical coagulation with an alum dose of 45 mg l^{-1}, sedimentation and sand filtration. All of the raw and treated samples were pre-filtered with a 0.45 µm filter and stored in a refrigerator at a temperature of 5°C prior to NOM characterization. To prevent any leaching from the micro filter, it was rinsed with 1.0 litre of de-ionized (DI) water before sample filtration. The water qualities of the source and treated samples are shown in Table 1. The Nakdong river water appears to contain relatively high fractions of hydrophilic NOM (i.e. hydrophilic NOM + transphilic NOM > 60%), which was identified with XAD fractionation results (shown later in this paper; Figure 3). The conductivity of the raw water is relatively low, thus ionic strength effects on NOM removal by membrane process is anticipated to be insignificant. The ratio of bromide ion concentration to total dissolved organic carbon concentration was measured to investigate a formation potential of brominated HAAs relative to non-brominated HAAs. TOC and bromide ions were measured by a TOC analyser (Sievers) and an IC (Dionex), respectively; the detection limits for TOC and Br$^-$ are 100 µg l^{-1} and 10 µg l^{-1}, respectively. For better detection of bromide ion, a high capacity column for anions of low concentration (AS-9H, Dionex) was used with carbonate eluent.

Bench-scale membrane filtrations were conducted using 0.45 μm-filtered coagulated water samples with an ultrafiltration membrane (UF: GM from Desal.) and a nanofiltration (NF: ESNA from Hydranautics) membrane to evaluate the potential of membrane filtration with respect to the removal of both bulk NOM and chlorinated DBP formation potential. The MWCO of the GM and ESNA membranes, as provided by the manufacturers, were 8,000 and 250 mass units, respectively. More details of these membranes are provided in a previous report (Cho *et al.* 2000). The membrane filtration unit accommodated an active polymeric membrane filtration area of 60.0 cm^2 and a membrane holder, gear pump, needle valves (for the feed, retentate and permeate streams), and pressure and flow-rate gauges. A feed-water volume of 4 l was used, and the retentate and permeate waters were recycled into the feed reservoir. Permeate samples were taken after a filtration duration of approximate 1 h. Feed flow-rate and the resulting cross-flow velocity were adjusted by varying the pump head rpm. Trans-membrane pressure was controlled using a needle valve located at the retentate stream. The water temperature was maintained in the range (21–23°C) because the gear pump used did not produce sufficient heat to increase the water temperature, even in this recycling batch type filtration unit.

HAA measurement

Raw and treated samples were chlorinated using a concentrated HOCl solution (Fisher, US) at a chlorine dosage level based on 3 times the dissolved organic carbon (DOC) concentration and 7.5 times the NH_4^+ concentration. Chlorinated samples were incubated at a temperature of 20°C for 72 h (the residual chlorine concentration was between 0.8 and 1.0 mg l^{-1} for all samples), and the HAA formation potential (HAAFP) was measured using the Modified EPA 552 micro-extraction method with diazo methane addition. HAAs were measured by GC (HP 5890 Series II Plus) with an autosampler (HP 6890 Series).

The HAA reactivity is defined as the HAA formation potential per unit NOM mass (= HAAFP (μg l^{-1})/DOC (mg l^{-1})). Chlorination of the three different NOM fractions isolated from the raw and treated waters enabled us to determine which NOM fraction has the greatest potential to form HAA and which process was the most effective at removing the particular NOM fractions.

RESULTS AND DISCUSSION

Process evaluations

Size exclusion combined with charge interaction

A comparison of the MW distributions of NOM included in the raw and treated water samples is shown in Figure 1(a), with the respective NOM fractional removals (FR) (Cho *et al.* 1999) calculated from the MW distributions for each process, which are shown in Figure 1(b). The processes caused MW distribution shift towards lower MWs to different extents, exhibiting a size exclusion mechanism for NOM removal (see Figure 1(a)). As expected, the NF membrane (ESNA) with a MWCO of 250 exhibited significant size exclusions for NOM removal compared with the UF membrane (GM) with a nominal MWCO of 8,000 or chemical coagulation with alum. The MW distributions of the two NOM samples treated either by coagulation or with the UF membrane showed similar trends, and both exhibited higher relative fractions in the lower MW range than the raw water NOM. To evaluate the NOM removal efficiencies of coagulation and the UF membrane rigorously in terms of NOM size, the NOM fractional rejections of the two processes were compared, as shown in Figure 1(b). The FR of the UF membrane increased from a MW of approximately 400 to a MW of 2,200. Meanwhile, chemical coagulation could not remove NOM with a MW of less than 1,000. However, the NOM FR of the coagulation process increased with a steeper slope from a MW of 1,000 compared with that of the UF membrane and exhibited even higher FR values in the MW range above 1,520. From these results, it is envisioned that the UF membrane can reject a wide range of NOM (MW range: 0–2,200), while coagulation can only remove a relatively narrow range of NOM (MW range: 1,000–2,000). Moreover, coagulation proved more effective at removing NOM with MWs greater than 1,520 than the UF membrane, as based on the NOM MW distribution results.
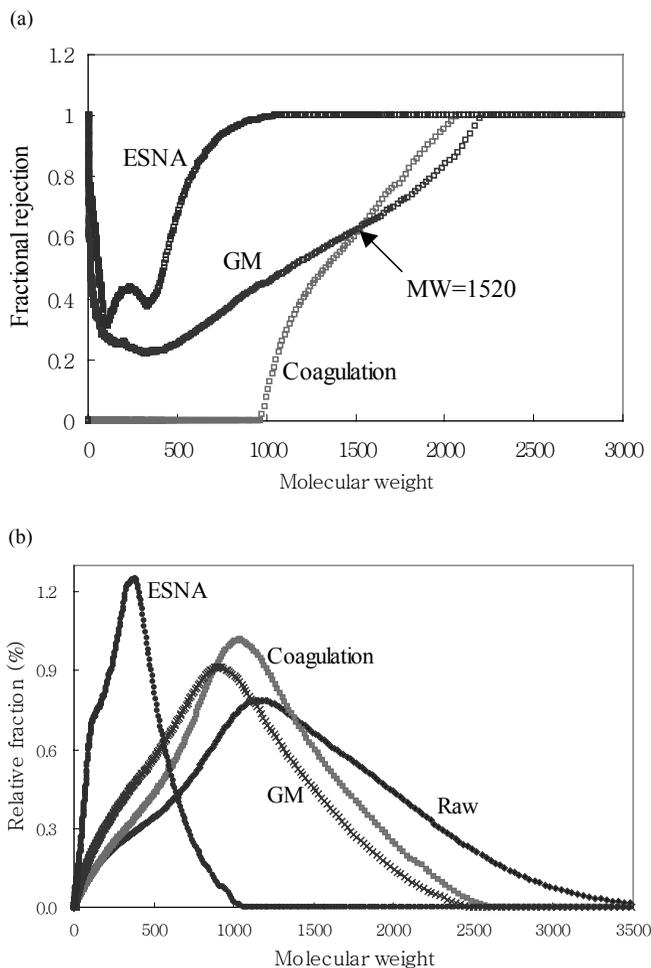
(a)

(b)

Figure 1 | (a) NOM MW distribution comparison of raw and various samples treated by coagulation, sand filtration, and GM and ESNA membranes; (b) fractional NOM removals of coagulation, sand filtration and membrane processes.
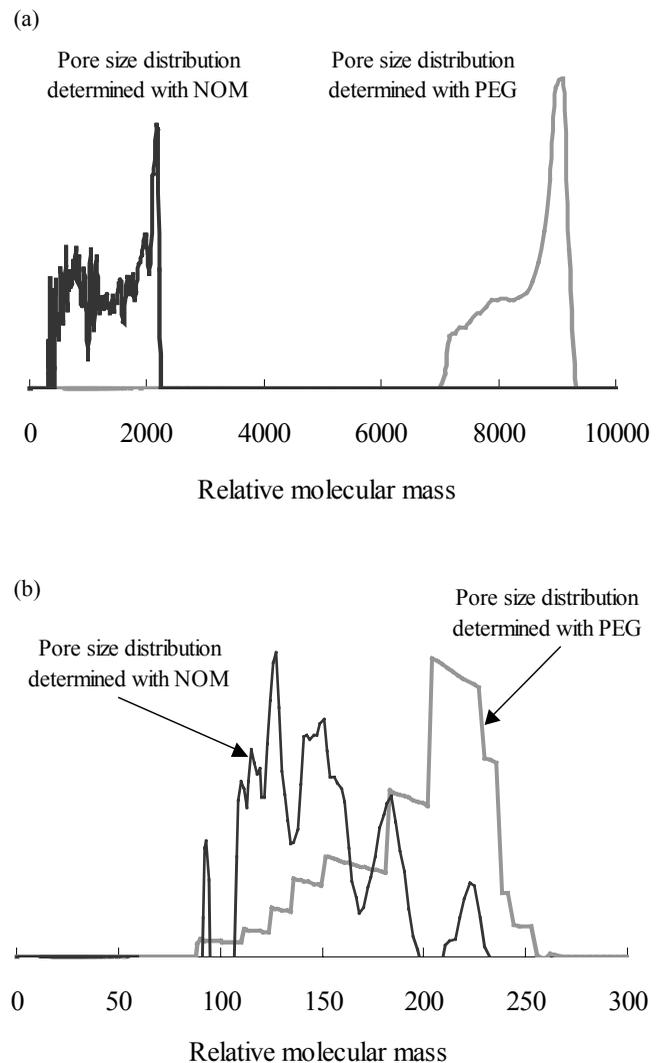
(a)

(b)

Figure 2 | Apparent and absolute pore size distributions of tested membranes in terms of NOM molecular weight with mass units: (a) the UF (GM) membrane and (b) the NF (ESNA) membrane.

The apparent pore size distribution (PSD) of a membrane with respect to NOM can be determined from the NOM fractional removal curve; as the slope of the FR curve for a certain MW increases, the greater the number of pores with that MW. The method of determining the membrane PSD using nonionic (such as polyethylene glycols (PEG)) and charged (such as NOM) macromolecules was described in detail in a previous report (Lee *et al.* 2002). In this article, only the results of the pore size distribution of the membrane are represented. The apparent PSD of the two membranes with respect to NOM are depicted in Figure 2, as opposed to absolute pore size

distributions determined with PEG. As we found in the fractional rejection analysis, the UF membrane exhibited a fairly wide range of PSD. However, the pore sizes of the UF membrane were much smaller than the nominal MWCO of 8,000, provided by the manufacturer. This was due to charge interactions between the negatively charged membrane surface and NOM acids (Cho *et al.* 2000), which can be better explained by the *effective* MWCO concept (Braghetta *et al.* 1997; Cho *et al.* 2000). The apparent PSD of the NF membrane with respect to NOM
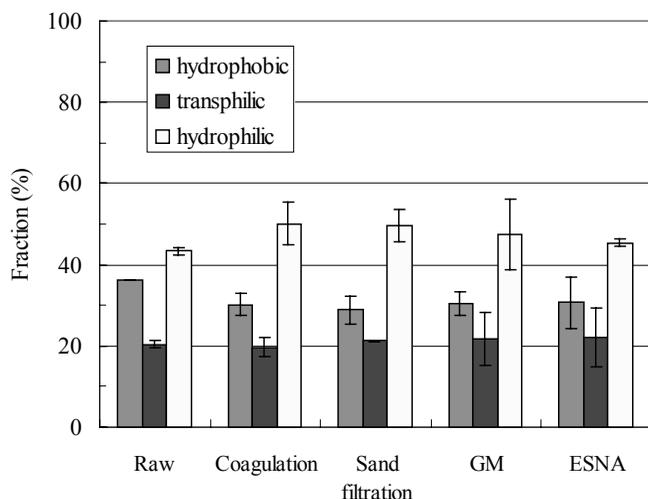
Figure 3 │ Relative percentages (based on DOC) of the three different NOM fractions for raw and various other samples treated by coagulation, sand filtration and membranes.
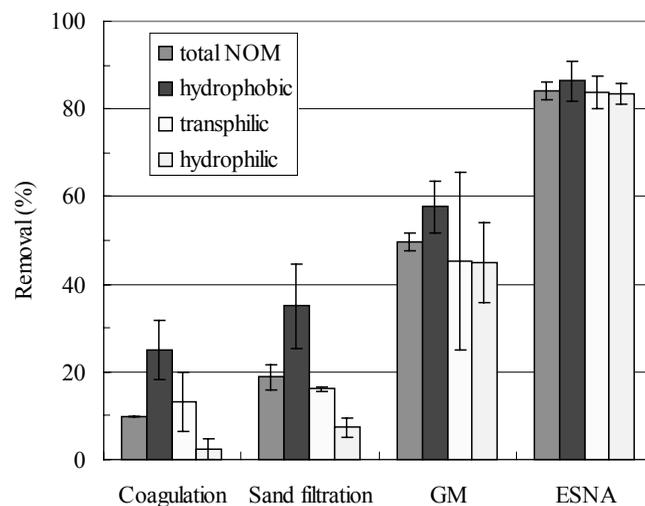

Figure 4 │ Percentage removals (based on DOC) of total (unfractionated) and the three different NOM fractions for raw and various other samples treated by coagulation, sand filtration and membranes.

was relatively narrow compared with that of the UF membrane. Some NOM with MWs between 400 and 900 appeared to pass through the pores of the NF membrane with a MWCO of 250, suggesting that the NF membrane contains both comparatively small (i.e. less than 250 mass unit) and larger pore sizes than that implied by the nominal MWCO, provided by the manufacturer.

NOM structural and charge interaction effects on the performance of each process

Figures 3 and 4 represent the NOM fractions of the source and treated samples for each process, and the percentage removal of the three different NOM fractions. Chemical coagulation and sand filtration (i.e. conventional processes) preferentially removed the hydrophobic NOM fraction rather than the transphilic and hydrophilic NOM fractions, as shown in Figure 4; i.e. the relative fractions of the hydrophobic and hydrophilic NOM decreased and increased, respectively, after conventional processing (see Figure 3). This is in agreement with previous results, concerning the fact that the humic fraction was preferentially removed by chemical coagulation owing to the charge interaction rather than the non-humic fraction, as reported by Krasner & Amy (1995) and Childress *et al.*

(1999). Hydrophobic and hydrophilic NOM fractions showed comparatively high percentage rejections from the UF membrane, on taking the manufacturer's stated MWCO of the GM membrane into account. The high percentage rejection of the hydrophobic NOM was probably due to charge repulsion, as stated in the previous section. However, the transphilic NOM fraction exhibited variable removal behaviour from the UF membrane (see Figure 4). A significant difference in the NOM removal of the conventional processes and the UF membrane was found in terms of hydrophilic NOM rejection; i.e. 2.3% by coagulation, 7.3% by sand filtration and 45.0% removal by the GM membrane. The NF membrane removed all of the NOM fractions with fairly high efficiencies. Thus, even though some of the NOM with MWs greater than 250 passed through the membrane pores (see Figure 2(b)), the total mass of this NOM appeared to be comparatively small.

Charge interaction mechanism for NOM removal

There was no significant difference between the carboxylic and phenolic acidities of hydrophobic and hydrophilic (i.e. transphilic) acids in the raw water and conventionally treated samples (see Table 2). This result is at odds with the hypothesis by Collins *et al.* (1986), that humic or fulvic
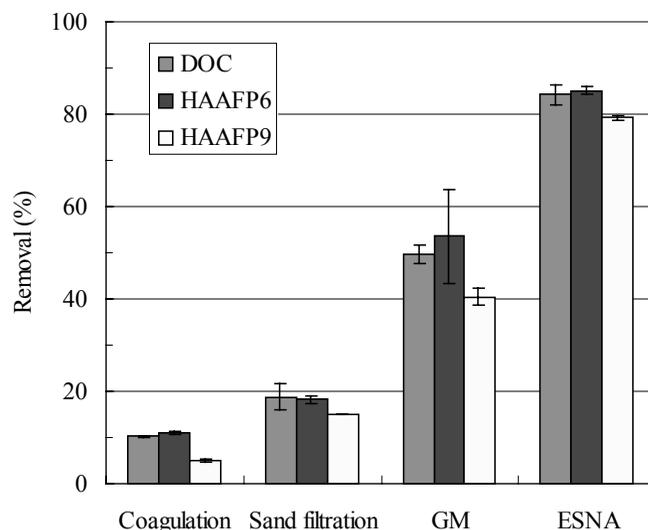
Table 2 │ NOM acidities for raw and treated samples by each process

Sample	Hydrophobic acid (meq g⁻¹ C)		Hydrophilic acid (meq g⁻¹ C)	
	-COOH	-OH	-COOH	-OH
Raw	36.6	17.4	26.3	19.9
Coagulation	34.4	20.6	23.8	21.4
Sand filtration	35.2	19.5	24.9	20.4
GM	19.9	12.1	15.4	9.8
ESNA	3.5	4.9	4.1	5.2

Figure 5 │ Percentage NOM removals in terms of DOC, HAAFP6 and HAAFP9 for raw and various other samples treated by coagulation, sand filtration and membranes.

acids with higher acidities are more difficult to remove by chemical coagulation than those with lower acidities. If this hypothesis was true, the charge density of NOM acids based on carboxylic acidity should increase. Thus, both humic and non-humic acids appear to be removed evenly by conventional processes, regardless of the charge density derived from the ionizable carboxylic groups. However, it should be noted that the above results are not related to the preferential removal of the hydrophobic NOM fraction; these were shown to be preferentially removed by both chemical coagulation and membrane processes. On the other hand, membrane filtration using both UF and NF membranes removed NOM acids with higher acidities more efficiently than those with lower acidities, yielding membrane treated samples with lower acidities. This is in good agreement with the results of previous work (Cho *et al.* 2000), which focused on charge interactions during NOM removal with a charged UF membrane. The much lower apparent PSD (than the nominal MWCO of 8,000 mass units) of the charged UF membrane for NOM (see Figure 2(a)) can also be explained by this charge interaction between the charged membrane surface and NOM acids.

HAA formation potential (HAAFP) and reactivity

Conventional treatments (alum coagulation/ sedimentation/sand filtration) exhibited no significant differences in terms of percentage NOM removal based on DOC, HAAFP6 (six HAAs: monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid and bromochloroacetic acid) and HAAFP9 (HAAFP6 plus other three HAAs: dichlorobromoacetic acid, dibromochloroacetic acid and tribromoacetic acid) (see Figure 5). In the previous section on NOM structure, conventional processes were said to reject hydrophobic NOM fractions preferentially (see Figure 4), providing indirect evidence that hydrophobic NOM (mostly humic acids) contains relatively low HAA reactivity. This inference can be proved by HAA reactivity measurements for the three different NOM fractions (see Figure 6). Both the NF and UF membranes removed fairly high percentages of total NOM, HAAFP6 and HAAFP9, and the results were from similar removals of the three different NOM fractions by both membranes. Even though the GM membrane showed large fluctuations in terms of transphilic NOM rejection, the transphilic NOM fraction in raw water was relatively small. Thus, transphilic NOM contributed only marginally to total NOM and HAAFP removal.

HAA reactivities of non-fractionated and fractionated (by XAD-8/4 resins) NOM for raw and treated water samples are depicted in Figure 6. Overall, there was no
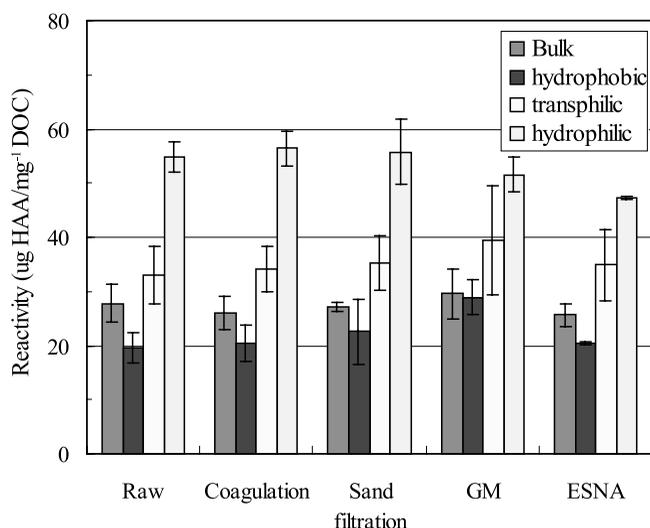
Figure 6 | HAAFP6 reactivity of bulk NOM and three isolated NOM fractions for raw and various other samples treated by coagulation, sand filtration and membranes.

significant difference in the HAA reactivities of non-fractionated NOM for raw water and the various other samples treated by either conventional or membrane processes. Hydrophilic and hydrophobic NOM exhibited the highest and lowest HAA6 reactivities, respectively. These results are in good accordance with the results of Pomes *et al.* (2000), which showed that the humic substances have very low HAA5 reactivities ranging from 2.90 to 4.20 (μg mg^{-1}). As shown previously, the hydrophilic NOM fraction represented the highest portion for the raw water tested (see Figure 3) and was difficult to remove efficiently by conventional processes (see Figure 4). Thus, it can be suggested (at least for the source water examined in this study) that either an advanced treatment alternative or process optimization may be adopted to minimize HAA formation potential; for the case of advanced treatment, existing conventional processes can be used as pretreatments. Once the optimized process solution for the minimization of HAAs is determined, then an optimum pH condition can be selected depending on HAA speciation (i.e. mono- vs. di- vs. tri-halogenated species containing either (both) chlorine or (and) bromine) to further reduce the level of HAAs, as suggested in a previous study (Cowman & Singer 1996). In order to elucidate the HAA formation potential of different NOM fractions,

it would seem that there is a real need to characterize the appropriate mechanisms involved and in particular the reaction sites in hydrophilic NOM molecules.

CONCLUSIONS

Adopting the process evaluating procedures (by using the SSF collectively) helps treatment plants with conventional treatment processes not only to determine how their processes should be improved to minimize HAA formation, by using various conditions (including coagulant dose, pH, etc.), but also to facilitate the selection of a better alternative process to maximize process performance.

- As hypothesized, the nanofiltration membrane process could give much better NOM performance in the aspects of MW distribution and DOC/DBPs, as compared with the UF membrane and conventional treatment processes.
- The NOM molecular size distribution, NOM structure and NOM charge density of each treated sample (from different processes) were revealed to be informative for the evaluation of the processes by providing quantitative comparison results.

The hydrophilic NOM exhibited relatively high HAA reactivity (HAAFP/DOC; μg mg^{-1} C) compared with the hydrophobic and transphilic NOM fractions for the raw water and all treated samples examined in this study. From this result, it is suggested that an appropriate process (the NF membrane in this study) should be determined to remove the hydrophilic NOM fraction for the minimization of HAAs formation.

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