**HAOPs Pretreatment to Reduce Membrane Fouling:
Foulant Identification, Removal, and Interactions**

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Abstract

Fouling of an ultrafiltration membrane by raw lake water, the same water after passage through a layer of heated aluminum oxide particles (HAOPs), and the fractionated natural organic matter (NOM) (based on hydrophobicity) of each of those waters was investigated. When each fraction of the raw water was fed to the membrane at the same DOC concentration, the hydrophobic (HPO) fraction was the least well retained by the membrane, but it caused the most fouling, whereas the hydrophilic (HPI) fraction was the most efficiently retained fraction and caused the least fouling. Furthermore, whenever the feed contained mixtures of different fractions, fouling was worse than would be predicted by a simple mixing model, indicating that interactions among the fractions are important factors in the fouling process.

Treatment of the raw water by HAOPs substantially removed fulvics from all five feed solutions (raw water, the HPO, TPI [transphilic], and HPI fractions, and the reconstituted water) and humics from all except the HPI fraction (which contained very little humic material in the first place). In contrast, HAOPs treatment removed aromatic proteins only from the HPI fraction. HAOPs also selectively removed higher-MW NOM. The treatment significantly mitigated membrane fouling by all the fractions to a greater extent than would be expected based on DOC removal.

The fouling of membranes fed either raw water or HAOPs-pretreated water was largely reversed by alkaline cleaning. The NOM that was released by the cleaning step was enriched in

20 aromatic proteins and non-fluorescent fractions, but it contained much less humic and fulvic
21 matter and overall fluorescence than raw water. The results suggest that a non-fluorescent HPO
22 fraction of the NOM accumulated on the membrane and is responsible for substantial fouling,
23 and that interactions among different fractions are important contributors to fouling.

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25 **Keywords:** Natural organic matter, Fractionation, Aluminum oxide particles, HAOPs,
26 Membrane fouling, Pretreatment

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1. Introduction

Low-pressure membrane filtration is being used increasingly in water treatment due to its relatively low cost and superior efficacy for producing high-quality water [1-3]. However, the process is not effective for removing natural organic matter (NOM) or the precursors of disinfection byproducts (DBPs) [4-6], and its productivity is limited by membrane fouling [7-9].

When a natural water passes through a low-pressure membrane, colloids and other particulates as well as some dissolved species can accumulate at the membrane surface and decrease the membrane permeability; i.e., they foul the membrane. The dissolved species most responsible for fouling are a diverse group of molecules known collectively as natural organic matter (NOM). Whereas individual colloids and particles can induce fouling by blocking a substantial portion of a pore's cross-section (either at the mouth or deeper into the interior) or by forming a cake layer on the membrane surface, most NOM molecules are far too small to have a similar effect. Rather, they cause fouling primarily by adsorbing on the membrane and coalescing with one another to form a gel that covers and/or constricts the pores [9, 10]. The severity of such fouling depends on the properties of the NOM (e.g., chemical composition, molecular weight, and hydrophobicity), the characteristics of the membrane (e.g., hydrophobicity, roughness, surface charge, and pore size) and the operational parameters (e.g., flux, inorganic composition of the feed, and temperature) [8, 11, 12].

Numerous pretreatment strategies, including coagulation, adsorption, pre-oxidation and

pre-filtration, have been applied to mitigate fouling in full-scale systems [2, 8]. These strategies invariably remove some NOM from the water, and they often reduce the rate of fouling, but frequent backwashing and intermittent chemical cleaning are nevertheless required to sustain long-term operation. In parallel with efforts to mitigate fouling by optimizing operational conditions, a major research effort has been carried out to identify the subgroups (i.e., fractions) of NOM that are primarily responsible for fouling, in the hope that treatment processes that target these fractions can be identified and implemented. In much of this research, NOM has been fractionated based on size or hydrophobicity and then applied to membranes to compare the fouling tendencies of the different fractions, while in other cases, unfractionated NOM has been fed to a membrane and the principal foulants have been inferred based on the fractions that are selectively retained.

The primary tool used to characterize the different fractions is the fractionation procedure itself (e.g., adsorption onto and elution from different resins for hydrophobicity-based fractionation [13] or filtration through membranes with different pore sizes for size fractionation [14]). In addition, analytical tools that can characterize the NOM in small samples but are not appropriate for bulk fractionation are often employed, such as size exclusion chromatography (SEC) [15, 16], UV absorbance (especially at 254 nm) [17, 18], excitation/emission matrix (EEM) fluorescence [19], and FTIR spectroscopy [17]. All of these procedures and analyses can provide insights into the similarities and differences among samples collected from different locations or

66 treated in different ways [11, 20]. Nevertheless, it is important to remember that the NOM
67 molecules are usually highly diverse, with a nearly continuous range of properties [17]; that the
68 fractionation procedures are operational and not definitive (despite the temptation to think of, for
69 example, ‘hydrophobic’ and ‘hydrophilic’ NOM as well-defined, non-overlapping groups); that
70 SEC-based separations can depend strongly on chemical factors in addition to molecular size;
71 and that property assignments inferred from spectral data, whether UV, EEM, or FTIR, are based
72 on an unavoidably imperfect attempt to apply results for pure compounds to the complex
73 mixtures of chromophores in NOM.

74 Perhaps because of these complexities, the identities of the membrane foulants in NOM
75 have long been in dispute, with different researchers attributing fouling primarily to colloids [2,
76 21], the large-MW fraction [9, 22], the hydrophobic fraction [22], or the neutral hydrophilic
77 fraction [20, 23, 24]. For example, Howe and Clark [14] fractionated NOM by passage through
78 membranes with different pore sizes and concluded that very small colloids (3-20 nm in diameter)
79 were the major contributors to fouling. On the other hand, many early studies seemed to indicate
80 that hydrophobic NOM, composed primarily of humic and fulvic substances, was the critical
81 foulant [9, 25], and, more recently, fouling caused by hydrophilic organic matter (more aliphatic,
82 and containing more proteins, polysaccharides and hydroxyl groups than the hydrophobic
83 fraction) has received greater attention [20, 26, 27].

84 In addition to the identities of the individual foulants, interactions among the foulants might

play a critical role [23, 28, 29]. For example, Jermann et al. [28] found that the fouling induced by humic acid and alginate was exacerbated by the presence of kaolinite particles, and Zheng et al. [11] reported that the increase in fouling of a membrane by biopolymers was greater when the membrane was pre-loaded with various fractions of effluent organic matter than when the biopolymers were applied to a virgin membrane.

Prior work by our group has demonstrated that passing natural water through a thin (~200- μ m) layer of micron-sized heated aluminum oxide particles (HAOPs) ('microgranular adsorptive filtration' [μ GAF]) promotes NOM removal and dramatically mitigates fouling [30-35]. In one of these studies [30], water samples that had been pretreated by μ GAF or by exposure to an ion exchange resin had virtually identical HPSEC-UV₂₅₄ spectra, but dramatically different tendencies to foul a membrane, demonstrating that fouling could not be attributed to an identifiable group of UV-absorbing molecules. Other results suggested that fouling might be associated with non-fluorescent NOM [12, 30], based on comparisons of spectra obtained before and after membrane filtration.

To date, no studies have been reported addressing the fouling tendencies of individual NOM fractions in μ GAF systems or the interactions among the fractions and the effects of those interactions on fouling. In this paper, we report on studies of HAOPs-based μ GAF systems fed NOM fractions separated based on hydrophobicity. The removal of each fraction by the HAOPs layer was characterized by UV, SEC and EEM/PARAFAC analysis, and the effectiveness of

HAOPs pretreatment at mitigating fouling by the individual fractions and by mixtures of the fractions was assessed. Finally, the chemical properties of NOM accumulated on a membrane were investigated with and without HAOPs pre-treatment of the feed.

2. Materials and Methods

2.1 Source Water, HAOPs and Membrane

Water from Lake Pleasant in Seattle, WA (47°46'44.59" N, 122°13'3.51" W) was collected and filtered through a 5- μ m filter on several occasions between October 2015 and April 2016. The pH and DOC concentrations in the raw water were in the ranges 7.2-7.6 and 19.8 ± 3.5 mg-C/L, respectively, and the turbidity of the pre-filtered water was 3.2 NTU. Concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} and NO_3^- were analyzed in one sample and were 19.8, 8.2, 7.0, 2.7, 5.1, 6.1 and 1.8 mg/L, respectively.

HAOPs containing ~28% Al by mass were synthesized by heating precipitated $\text{Al}(\text{OH})_3$, following a previously described procedure [31]. Membranes used in the tests were 47-mm-diameter polyethersulfone (PES) disks with a nominal pore size of 0.05 μ m (Microdyn-Nadir MP005). The manufacturer reports that these membranes are hydrophilic, with a contact angle of 48.5°. All membranes were conditioned by soaking in deionized (DI) water (Millipore Milli-Q) for at least two hours prior to use.

2.2 Fractionation of NOM

NOM in the raw water was fractionated using Amberlite DAX-8 and Amberlite XAD-4 resins, following the method of Aiken et al. [36] as modified by Yamamura et al. [20]; detailed procedures are provided in the Supplementary Information (SI). The NOM retained on the DAX-8 and XAD-4 resins was designated as the hydrophobic (HPO) and transphilic (TPI) fractions, respectively, and the portion that passed through both resins was designated as the hydrophilic (HPI) fraction. The raw water and the fractionated solutions were all diluted to ~4 mg-DOC/L with DI water. A reconstituted raw water (RRW) was prepared by mixing the HPI, HPO and TPI solutions in ratios corresponding to their DOC concentrations in the raw water, as detailed in Table SI-1. The samples were adjusted to pH 7.0 with 0.1 M HCl or NaOH solution and were stored at 4°C for subsequent use. A portion of each solution was lyophilized for FTIR spectroscopy.

2.3 HAOPs Pretreatment and Membrane Filtration

To pretreat water using HAOPs-based μ GAF, a slurry of the particles was filtered through a nylon mesh with 5- μ m openings (Product 03-5/1, Sefar, Inc., Buffalo NY). This step deposited a layer of the particles on the mesh at a surface loading of 10 g Al/m². The desired feed solution was then filtered through the HAOPs at a flux of 100 L/m²-h (LMH), and samples of the filtrate were collected intermittently for analysis. In other tests, 1.5 L of water was passed through a HAOPs layer (total HAOPs mass 10 mg as Al, for an effective dose of 6.67 mg Al/L), and the treated water was collected for use in membrane filtration tests.

All membrane tests used dead-end filtration through new PES membranes in polycarbonate in-line filter holders. To initiate a test, DI water was filtered for 30 min at a constant flux of 100 LMH, after which the feed was switched to the desired solution at the same flux. A summary of all the feed solutions investigated is provided in Table SI-1. The transmembrane pressure (TMP) was measured online with a pressure transducer and recorded via a data acquisition system. All filtration tests were conducted in duplicate and yielded consistent results.

For some tests, a new membrane was soaked in an alkaline solution prepared by addition NaOH to deionized (DI) water to adjust the pH to 12. The membrane was then thoroughly rinsed and was used to filter first the lake water and then DI water at a flux of 100 LMH. The membrane was then removed from the cartridge, soaked for two hours in a fresh batch of pH 12 water to extract the base-soluble NOM, and placed back in the cartridge for another filtration test with DI water as the feed. The extracted solution was titrated to pH 6.8 using dilute HCl, and the NOM was quantified and characterized. These experiments were conducted in duplicate, and the results were averaged. Additional details of the extraction procedure are provided in the SI.

2.4 Chemical Analyses

UV₂₅₄ was determined using a dual-beam spectrophotometer (Perkin-Elmer Lambda-18), and DOC was measured with a TOC analyzer (Shimadzu TOC-VCSH). The apparent molecular weight (AMW) distribution of the NOM in the raw water and in the fractionated and diluted solutions was determined with a DIONEX Ultimate 3000 HPLC system coupled to a Sievers

(Boulder, Colorado) turbo total organic carbon analyzer, using isocratic flow of 0.01 M NH_4HCO_3 at 0.5 mL/min. The calibration curve for AMW was generated using polyethylene glycol (PEG) standards (Agilent EasiVial PEG).

EEM fluorescence spectra were obtained at room temperature ($20 \pm 0.5^\circ\text{C}$) using a luminescence spectrophotometer (LS-55, Perkin-Elmer Co., USA). The scanning wavelength ranges for excitation (Ex) and emission (Em) were 200 to 450 nm and 300 to 600 nm, respectively. The spectrum of DI water was subtracted from the spectra of samples, and interference from Rayleigh scattering was eliminated by setting signals close to the Rayleigh scattering line to zero [37, 38]. PARAFAC analysis was applied to identify the major contributors to the fluorescence spectra, using the N-way Toolbox for MATLAB (Matlab 6.5, MathWorks Inc., USA; available at <http://www.models.kvl.dk>).

A Vector 33 Fourier transform infrared spectrophotometer (Bruker Co., Germany) was used to collect FTIR spectra of NOM (several mg of NOM in KBr powder). The instrument scanned the range $4000\text{--}800\text{ cm}^{-1}$ at intervals of 2 cm^{-1} . The polysaccharide content of samples was analyzed with the anthrone method using glucose as the standard [39].

3. Results and Discussion

3.1 Chemical and photometric characterization of NOM

The HPO, HPI and TPI fractions consistently accounted for approximately 64%, 20% and

16%, respectively, of the DOC in the raw water (Table 1). The HPO fraction had the highest $SUVA_{254}$, and the HPI fraction had the lowest. A high $SUVA_{254}$ is generally attributed to high hydrophobicity and aromaticity, so the results suggest that HPO is more aromatic and more enriched in phenolic groups than the other fractions, as is commonly reported [17, 18, 28]. By contrast, the HPI fraction was richer in polysaccharides than the HPO and TPI fractions, consistent with its lower $SUVA_{254}$ and aromatic content.

Fluorescence spectra of the raw and fractionated water are shown in Figure 1. The HPO and TPI fractions, reconstituted water and raw water (Figures 1a, 1b, 1d, and 1e) all had similar fluorophores at similar relative concentrations. The two main peaks in all these spectra were at Ex/Em wavelengths near 220/415 nm and 335/420 nm, which are typically assigned to fulvic-like and humic-like substances, respectively [19, 40, 41]. The HPI fraction had much lower fluorescence intensity in both of those regions, while exhibiting far stronger intensities around Ex=200-250 nm and Em=300-380 nm (Figure 1c), which are associated with aromatic proteins such as tyrosine and tryptophan [42]. These observations, along with the $SUVA_{254}$ values, suggest that the HPI fraction contained less total aromatic NOM, but more aromatic proteins, than the HPO fraction, the raw water, or the RRW [19].

FTIR spectra for these samples are shown in Figure 2a. The TPI and HPO fractions both had peaks at 1643-1636, 2200 and 3300-3600 cm^{-1} , which are attributed, respectively, to C=C-C=C, COOH and O-H groups in humic substances [17, 18]. The higher intensities at

1000-1100 cm^{-1} in the HPI spectrum indicate the presence of more carbohydrate-like substances. The region from 1700 to 1500 cm^{-1} is correlated with amides and amines, which are indicative of the presence of proteins and amino sugars. Higher intensities were also found in the HPI fractions at 1380, 1555 and 1650 cm^{-1} , representing amino sugars, N=C–O in the amide II fraction, and C=O in the amide I fraction, respectively. The peaks at 2850 and 2960 cm^{-1} can be attributed to CH_2 and CH_3 groups in lipids and hydrocarbon segments in the NOM. These results provide additional support that the HPI fraction of Lake Pleasant water contains more aromatic proteins and carbohydrate than the other fractions.

Figure 2b compares the SEC curves for the samples for AMWs from ~200 to ~200,000. Two main size fractions, with AMWs around 20000 and 1500, can be identified in the raw water. As noted in the introduction, SEC fractionation of NOM responds to differences in chemical properties of the molecules as well as their size, so the main peaks probably include contributions from more than one size component [26]. While acknowledging that caveat, we attribute the higher-AMW fractions to biopolymers, building blocks and humic substances, and the peak at AMW~1500 to low-MW organics and neutrals [26, 43, 44]. The AMW distributions varied among the individual NOM fractions, but when the fractions were recombined to generate the reconstituted water, the AMW distribution was similar to that of the raw water.

3.2 Membrane Fouling by Individual NOM Fractions

The NOM removal and TMP buildup in tests where the individual fractions were fed to a

PES membrane at a fixed DOC concentration of 4.0 ± 0.2 mg/L are shown as a function of the specific volume filtered (V_{sp} , the cumulative volume of water filtered per unit membrane area) in Figure 3. The membrane removed little (~5-20%) of the UV_{254} or DOC from the raw water, RRW, or the HPO or TPI fraction (Figure 3a). UV_{254} removal remained approximately constant throughout these runs, while the removal of DOC increased slightly as the run progressed. The removal of both UV_{254} and DOC from the HPI fraction was substantially greater than from the other samples (40-55% for UV_{254} and 15-40% for DOC) and increased during the run. Visually, the HPI foulant layer was darker than the others, even though that fraction had the lowest UV_{254} (Figure SI-1).

Because the samples were all adjusted to the same DOC concentration, the fractional removal of DOC is a direct indicator of the mass of DOC retained by the membrane. Surprisingly, this mass bore no correlation to the fouling induced by the samples. For instance, the HPO fraction was retained less efficiently by the membrane than either the TPI or HPI fraction was (especially with respect to UV_{254} retention), but it caused far more fouling than those fractions did (Figure 3b). Conversely, the HPI fraction was retained more efficiently than either of the other two fractions, but it induced almost no fouling at all. At a macroscopic scale, the layer of rejected NOM formed by the HPI fraction was looser, less continuous, and more easily broken than those formed by the other fractions (Figure SI-1).

EEM spectra were collected for the permeates from filtration of the raw water, the RRW,

and the three solutions containing fractionated NOM at a few times during the filter run; the spectra at V_{sp} 's of 100 and 700 L/m² are shown in Figure SI-2. When all of these spectra, along with those of the unfiltered solutions (shown in Figure 1) and of several samples of HAOPs-treated water (discussed subsequently) were processed using PARAFAC analysis, three model components were identified that could be combined in various ratios to reproduce the experimental spectra with good precision. The spectra of these model compounds are shown in Figure 4 and are dominated by peaks at Ex/Em of: 220-240/330-350 nm (Peak A), attributable to aromatic proteins; 330-340/425-430 nm (Peak B), attributable to fulvic-like substances; and 380-390/450-470 nm (Peak C), attributable to the visible fluorescence of humic-like substances [19, 41, 42, 45]. The changes in the fluorescence intensity scores of the three model components between the feed and the permeate were then used to quantify changes in the NOM when each solution was filtered. Furthermore, in most cases, the attenuation of this peak increased as the run proceeded.

As shown in Figure 5, membrane filtration had almost no effect on the intensity of the peaks attributed to fulvic- and humic-like substances in any of the samples. On the other hand, the peak attributed to aromatic proteins was attenuated in several of the solutions, and especially in the HPI fraction, which had by far the highest intensity for this peak among the feed solutions.

The fact that humic- and fulvic-like molecules were minimally removed by the membrane suggests that they were not broadly responsible for the observed fouling. Aromatic proteins were

removed much more substantially, but their removal was not correlated with the severity of fouling; for example, the removal of these proteins was greatest from the HPI fraction, which caused almost no membrane fouling. Furthermore, neither the retention efficiency nor the fouling tendency was correlated in any obvious way with the AMW of the fractions.

As noted earlier, unfractionated NOM and even individual NOM fractions comprise a complex, heterogeneous continuum of species [17]. The results indicate that the small amount of HPO NOM retained on the membrane included strong foulants, while the larger amounts of TPI and HPI NOM did not, but that in none of these cases was the fouling behavior closely linked to the bulk fluorescence or AMW properties of the fractions. The results thus reinforce the idea that membrane foulants comprise a very small portion of the total NOM, or even of the NOM in the most strongly fouling fraction, and that although the strongest foulants might be found primarily in certain NOM fractions, they cannot be assumed to possess the average characteristics of those fractions.

3.3 Membrane Fouling by Combined NOM Fractions

Interestingly, both the raw and reconstituted waters fouled the membrane more severely than any individual component of the NOM did, with the raw water causing more fouling than the reconstituted solution. That is, when the HPO fraction, which caused a significant amount of fouling by itself, was “diluted” by mixing with two other fractions that caused little to no fouling, the mixture fouled the membrane more severely than any of the three individual fractions.

Furthermore, fouling was even more severe in the original “mixture” of these three fractions (i.e., the raw water) than in the reconstituted water. These results offer compelling evidence that intermolecular interactions among molecules in different fractions can play an important role in fouling.

To explore these interactions, the different fractions were mixed in various combinations and fed to the membranes. Each solution used in each mixture contained 4 mg/L DOC, so all the mixtures had the same DOC concentration. Two-component mixtures containing the HPO+HPI, HPO+TPI or TPI+HPI fractions caused more fouling than either of the individual components, but not as much as a three-component mixture containing all three fractions (Figure 6). Among the two-component mixtures, the HPO+TPI combination fouled the membrane more than either the HPO+HPI or the HPI+TPI combination did. The implications are that at least some components of all the NOM fractions contribute to membrane fouling and that these contributions are not simply additive. Rather, interactions among the different NOM fractions exacerbate the potential for the NOM to foul the membranes.

Although these experiments were designed to elucidate the effects of interactions among NOM molecules on fouling, the results might also have been influenced by the different salt concentrations in the solutions being mixed. The raw water was acidified with HCl before fractionation and, since DAX-8 and XAD-4 resins possess negligible ion exchange capacity [46], the majority of the salt ions in that solution likely passed through both resin columns. These ions

were therefore excluded from the HPO and TPI fractions and collected in the HPI fraction. However, the NOM adsorbed on the resins was then eluted with NaOH and neutralized with HCl, adding salts to the HPO and TPI fractions but not the HPI fraction. As a result, all three fractions and the RRW had higher salt concentrations than the raw water; this situation was reflected in the conductivities of the different solutions (Table SI-1).

While the salt ions could conceivably have altered the fouling tendencies of the solutions, the likelihood of this factor playing a dominant role is small for several reasons. First, the concentrations of all salt ions in the raw water were low (see Section 2.1), and based on the conductivities of the samples, the concentrations were also low in the fractions. Second, the only ions added were monovalent (Na^+ and Cl^-), and such ions are expected to have a minimal effect on fouling except at very large concentrations [10, 47]. Third, the TPI and HPO fractions were expected to contain similar concentrations of monovalent ions and almost no divalent ions, so any effect of salts would have been negligible when those fractions were mixed. Yet the HPO+TPI mixture caused more fouling than expected based on a simple mixing model, just as occurred in the mixtures where larger effects of the salts might have occurred. And, finally, in separate tests where NaCl was added to the raw water at concentrations of 10 to 700 mmol/L, the saltier water caused more membrane fouling [48], whereas in the current tests, the RRW (with increased NaCl) fouled the membrane less than the raw water. Based on all these considerations, we conclude that the fouling patterns observed in the mixing tests can be attributed to inherent

differences and interactions among the fractions, rather than differences in the inorganic composition of the test solutions.

3.4 Effects of HAOPs Pretreatment on Membrane Fouling

The NOM removal achieved by passing the various samples through a thin layer of HAOPs is shown in Figure 7a. Since the TPI fraction caused almost no membrane fouling (Figure 3b), the NOM removal from this fraction by HAOPs was not analyzed. Pretreatment with HAOPs was very efficient at removing UV_{254} , achieving removals of ~85% for all of the feed solutions. The removal of DOC was lower than that of UV_{254} in all cases and also varied more among the different feeds. The discoloration of the HAOPs by the adsorbed NOM was correlated closely with the UV_{254} of the feed (Figure SI-3).

The pretreated solutions caused far less membrane fouling than the untreated solutions had (Figure 7b). (Note that, although the feed solutions applied to the HAOPs layer all contained 4.0 ± 0.2 mg/L DOC, the DOC concentrations reaching the membranes were different in each system.) As was the case for untreated solutions, fouling caused by the raw water and RRW was much more severe than by any of the individual fractions, and the HAOPs-treated raw water fouled the membrane more than the HAOPs-treated reconstituted water. Furthermore, the fouling reduction accomplished by HAOPs treatment was greater than the DOC removal efficiency, though not dramatically so. For example, one might anticipate that removal of 50% of the DOC would allow the system to treat twice as much water before an equivalent amount of fouling

occurred. However, when approximately 50% of the DOC was removed by HAOPs treatment, the membrane was able to treat approximately 2.5 times as much HAOPs-treated water as raw water before the TMP increased by 25 kPa. Thus, the HAOPs selectively removed NOM with higher-than-average fouling potential.

3.5 Removal of Fluorophores and AMW Fractions by HAOPs

As noted earlier, the EEM spectra of the raw water, the RRW, and HPO and TPI fractions bore many similarities to one another and differed significantly from the spectrum of the HPI fraction (all shown in Figure 1). In particular, the HPI fraction had much higher fluorescence attributable to proteins and much lower fluorescence attributable to humic material than any of the other solutions.

EEM spectra of HAOPs-treated raw water samples at V_{sp} 's of 100, 400 and 700 L m⁻² are shown in Figure SI-4. Passage through the HAOPs reduced the total fluorescence of the raw water far more than filtration through the bare membrane did. The fluorescence intensity of the filtrate increased, but only slightly, as the run proceeded.

Fluorescence intensity scores for the model components in the HAOPs-treated samples are shown in Figure 8. The scores for the fulvic-like molecules in all five feed solutions declined dramatically when the solutions passed through the HAOPs, as did the scores for the humic-like material in all the solutions except the HPI fraction. By contrast, HAOPs treatment was effective in removing aromatic proteins only from the HPI fraction.

Although the HPO and TPI fractions and the raw and reconstituted water all had similar trends with respect to fluorophore removal by HAOPs, the corresponding treated solutions had significantly different effects on membrane fouling (Figure 7b). Thus, it appears that at least some key foulants are part of the non-fluorescent NOM, similar to the inference drawn previously that the key foulants are non-UV₂₅₄-absorbing [30].

Figure 9a compares the SEC profile of untreated raw water with profiles of the HAOPs-filtered water at various V_{sp} 's. Three main peaks can be identified in the chromatograms for the raw water, with some overlap between Peaks 1 and 2 (at AMW's around 15000 and 8000, respectively). HAOPs removed the high-AMW material (Peaks 1 and 2), but collected little of the lower AMW material (Peak 3 at AMW ~2000), consistent with the inference from Figure 8 that HAOPs preferentially remove humic- and fulvic-like (i.e., higher-MW) molecules. During the run, the NOM responsible for Peaks 1 and 2 gradually broke through the HAOPs and appeared in the treated water.

The general trends in the SEC profiles for filtration of reconstituted water were similar to those for raw water, except that Peak 2 was virtually undetectable in these samples (even without passage through the HAOPs layer) (Figure 9b). This disappearance of Peak 2 suggests that the fractionation procedure led to either loss of a portion of or alteration of the NOM in a way that destroyed some intermolecular interactions. Reconstitution of the raw water apparently did not fully restore these interactions.

3.6 Variations among Feed Water, Permeate and Membrane-Accumulated NOM

Next, either unaltered or HAOPs-treated raw water was fed to a membrane until 9.9 mg of DOC had been applied, and the membrane was soaked in an alkaline solution to extract the accumulated NOM. The cumulative masses of DOC in the feed, permeate, and alkaline extract, and the TMPs required to filter DI water through the membrane prior to the test, after it had become fouled, and after it was cleaned were then compared.

The mass balances indicated that, when the feed was raw water, the membrane retained 8.5% of the organic matter, and alkaline cleaning extracted 78% of that NOM from the fouled membrane; the corresponding values when the feed was pretreated water are 10.6% retained on the membrane and only 42% recovered by alkaline extraction (Table 2). Both membranes suffered significant fouling during the test, with the untreated water causing more fouling than the pretreated water (Figure 10). In both cases, the fouling was largely reversed by alkaline cleaning – by 80% and 77% in the tests using raw and HAOPs-treated water as feed, respectively. Thus, despite the fact that only a portion of the NOM that accumulated on the membranes was released by the cleaning step, that NOM appears to have been responsible for a large fraction of the fouling.

In the tests with raw water as feed, the fluorescence intensity of the permeate was slightly less than that of the feed (Figures 11a and 11b), but the two spectra were qualitatively similar and were dramatically different from the spectrum of the NOM extracted from the fouled membrane

(Figure 11c). The extract had far less fluorescence at 220/415 nm and 335/420 nm, indicating that it did not contain much fulvic-like or humic-like material [19, 40], as would be expected given the earlier evidence that such materials passed through the membrane almost completely (Figure 5). On the other hand, the fluorescence intensity at Ex/Em of 200-250/300-380, which is mainly associated with aromatic proteins, was considerably higher in the extract than in the feed solutions. Also, the total fluorescence intensity of the extracted NOM was lower than that of the raw water when both solutions were adjusted to the same DOC concentration, implying that the NOM released in the cleaning step was enriched in non-fluorescent material (e.g., polysaccharides). Prior studies have yielded similar results with respect to the enrichment in aromatic proteins and depletion of humics in the NOM released from a fouled membrane relative to the feed NOM [49, 50].

Pretreatment by passage through HAOPs caused the fluorescence intensity of the solution to decline at Ex/Em wavelengths near 220/415 nm and 335/420 nm (Figure 11d), consistent with the earlier finding that HAOPs remove humic-like and fulvic-like molecules selectively relative to other fluorophores. The fluorescence intensity of this solution underwent no detectable change when it passed through the membrane (Figure 11e). The key fluorescence properties of the extracted NOM (Figure 11f) were similar to those for the sample extracted from the foulant layer after filtration of raw water; i.e., it was relatively enriched in aromatic proteins. Once again, the fluorescence intensity of the extracted NOM was lower than that of the feed when both solutions

were adjusted to the same DOC concentration.

Given the earlier result that a small portion of the HPO fraction is particularly problematic with respect to fouling, and the additional finding that a cleaning step that selectively releases non-fluorescent NOM from the membrane surface substantially reduces the extent of fouling, we infer that small amounts of hydrophobic but non-fluorescent (i.e., non-humic) NOM have disproportionately high fouling potentials and can be responsible for a substantial portion of membrane fouling.

4. Conclusions

Fractionated NOM components differ in chemical properties and in the potential to foul a PES membrane. Compared to the raw water, the HPO and TPI fractions are enriched in aromatic humics and fulvics and have higher $SUVA_{254}$, whereas the HPI fraction is enriched in polysaccharides and aromatic proteins. The membrane is less effective at rejecting DOC and UV absorbance from the HPO than from the HPI fraction, but the HPO fraction causes more membrane fouling.

When the feed contains mixtures of various NOM fractions, it fouls the membrane more than any of the individual components do at the same DOC concentration. In addition, unaltered raw water fouls the membrane more severely than a reconstituted raw water generated by fractionating the source water and then recombining the fractions. These findings indicate that

the fouling contributions of different fractions are not simply additive, but rather that interactions among the fractions exacerbate the fouling.

Pretreatment of the raw water by passage through a layer of HAOPs is effective at removing DOC, UV absorbance, and high-AMW molecules from the raw water, the reconstituted water, and all the fractions. It is also effective at removing humics and fulvics from all these solutions, with the exception of humic removal from the HPI fraction. However, the same process removes aromatic proteins only from the HPI fraction.

The pretreatment process mitigates membrane fouling by individual NOM fractions as well as raw water, and the mitigation is greater than expected based on DOC removal. The fouling by either raw or pretreated water can be substantially, but not completely, reversed by alkaline washing. The NOM released in this process is enriched in aromatic proteins but very depleted in humic-like and fulvic-like substances compared to the feed water. The results suggest that the major foulants comprise only a small portion of the NOM, including non-fluorescent hydrophobic material as a major component. HAOPs efficiently collect humic and fulvic material from raw water, which is valuable as a way to reduce DBP formation, but their effectiveness at mitigating membrane fouling is probably more closely related to their ability to collect the non-fluorescent foulants.

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Disclosure

Mark Benjamin is a principal in a company that is attempting to commercialize HAOPs and the HAOPs-based μ GAF process.

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Figure 1 Fluorescence excitation-emission matrices of the HPO, TPI, and HPI fractions, the reconstituted water, and the raw water, each at a concentration of 4 mg/L DOC at pH 7.

Figure 2 (a) FTIR spectra and (b) AMW distribution of HPO, TPI, and HPI fractions of the NOM, RRW, and the raw water, all at a concentration of 4 mg/L DOC at pH 7.

Figure 3 (a) Removal of UV and DOC and (b) TMP increase during ultrafiltration of various

NOM fractions all at 4 mg/L DOC. Initial TMP was 12-18 kPa in all cases. Flux=100

LMH.

Figure 4 Three model fluorescent components of NOM in the samples, derived by PARAFAC decomposition of multiple spectra.

Figure 5 Fluorescence intensity scores of the three model fluorescent components in feed

solutions and membrane permeates. The filled symbols represent scores for the feed solutions.

Figure 6 TMP increase across the bare membrane when fed raw water or 2- or 3-component mixtures of the NOM fractions, all with 4 mg/L DOC at pH 7.

Figure 7 (a) Removal of UV and DOC of various feed solutions (all at 4 mg/L DOC) by HAOPs; (b) TMP development during ultrafiltration of the treated solutions from part (a) at a flux of 100 LMH.

Figure 8 Fluorescence intensity scores of the model components in the filtrate during filtration of various solutions through HAOPs. Solid symbols are for the feed solutions.

Figure 9 SEC profiles of feed water and filtrates for (a) raw water and (b) reconstituted raw water filtered through HAOPs at different V_{sp} 's.

Figure 10 TMP for ultrafiltration of DI water at a flux of 100 LMH by pristine, fouled, and cleaned membranes. Fouling was induced by filtration of raw water (blue bars) or HAOPs-pretreated water (red bars). Data points are for duplicate tests for each condition, and bars show the average of the two values. Experimental details in text.

Figure 11 EEM spectra of NOM in the (a) feed water (b) permeate and (c) alkaline extract from the fouled membrane for ultrafiltration of raw water through a PES membrane. Plots (d, e, f) are corresponding spectra for the corresponding experiment with HAOPs-pretreated water as feed. DOC values were 5.0, 4.5, 5.0, 3.7, 3.3 and 3.7 mg-C/L for (a) through (f), respectively. Experimental details provided in SI.

Table 1. Chemical characteristics of raw water and fractionated NOM

	Unit	Hydrophilic fraction (HPI)	Transphilic fraction (TPI)	Hydrophobic fraction (HPO)	Raw feed water	Reconstituted raw water (RRW)
Contribution to raw water TOC	%	19.9±1.4	16.0±0.7	64.3±1.9	-	-
TOC*	mg/L	3.8±0.4	3.9±0.2	4.0±0.5	4.2±0.4	4.0±0.5
UV ₂₅₄	cm ⁻¹	0.111±0.001	0.137±0.001	0.214±0.030	0.192±0.008	0.166±0.016
SUVA ₂₅₄	m ⁻¹ /(mg/L)	2.92±0.25	3.51±0.05	5.35±0.60	4.57±0.02	4.15±0.03
Polysaccharides	mg-Glu/mg-C	0.55±0.09	0.38±0.03	0.20±0.04	0.41±0.02	0.37±0.02

***After extraction, elution, and dilution**

Table 2. Concentrations and amounts of organic matter in feed water, permeate and fraction extracted from membrane

	Concentration (mg-C/L)	Volume (L)	Total amount of organic matter in each fraction (mg-C)
Raw feed water	4.96 ± 0.13	2	9.92 ± 0.26
Permeate	4.54 ± 0.07	2	9.08 ± 0.14
Extracted fraction from fouled membrane	33.91 ± 1.12	0.019 ± 0.004	0.64 ± 0.17
HAOPs-pretreated water	3.79 ± 0.10	2.6	9.85 ± 0.26
Permeate	3.39 ± 0.20	2.6	8.81 ± 0.15
Extracted fractions from fouled membrane	27.59 ± 5.80	0.016 ± 0.001	0.44 ± 0.06

***All the tests were conducted in duplicate and results were averaged**