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Size Exclusion Chromatography To Characterize DOC Removal in Drinking Water Treatment

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A full-scale (110 ML/d) potable water treatment plant (WTP) based on the MIEX process, an innovative new process based on a strong base anion-exchange resin with magnetic properties, has been operating in Perth Western Australia since 2001. This plant has been configured so that a combined MIEX-coagulation (MIEX-C) process can be operated in parallel with a conventional enhanced coagulation (EC) process, allowing comparison of the performance of the two processes. Here, we report the use of size exclusion chromatography (SEC) to compare the removal of different apparent molecular weight (AMW) fractions of DOC by the two processes. Water was sampled from five key locations within the WTP, and SEC was carried out using three different on-line detector systems, DOC-specific detection, UV absorbance detection at $\lambda = 254$ nm, and fluorescence detection ($\lambda_{\text{ex}} = 282$ nm; $\lambda_{\text{em}} = 353$ nm). This approach provided information on the chemical nature of the DOC comprising the various AMW fractions. The study showed that the MIEX-C process outperformed the EC process with greater removal of DOC in each of the eight separate AMW fractions identified. While EC preferentially removed the fractions of highest AMW, and those exhibiting the greatest aromatic (humic) character, MIEX-C removed DOC across all AMW fractions and did not appear to discriminate as strongly on the basis of differences in aromatic character or AMW. The results demonstrate the benefits of combining these complementary treatment processes. The study also demonstrates the utility of SEC coupled with multiple

detection systems in determining the characteristics of various AMW components of DOC.

Introduction

Knowledge of the molecular weight (MW) of natural organic matter (NOM) is of importance in drinking water treatment process operations for several reasons. Previous research has demonstrated that low MW NOM components decrease the efficiency of treatment with activated carbon because they compete for adsorption sites with target compounds (1). These low MW compounds are thought to comprise the fraction that is the most difficult to remove using conventional coagulation treatment (2, 3). The MW distribution of NOM has also been shown to be a significant factor in the fouling of membranes used in drinking water treatment (4). Some studies have shown that the low MW fractions contribute disproportionately to bioavailable organic matter (BOM), and thereby promote biofilm formation in drinking water distribution systems (5, 6). Therefore, considerable efforts have been made to develop techniques to distinguish between various MW fractions of NOM. These include analytical ultrafiltration (7), field flow fractionation (8), vapor pressure osmometry (9), and size exclusion chromatography (SEC) (10–15).

SEC is an attractive option for determining the MW distribution of NOM, due to its ease of operation, and because of the simplicity of sample preparation and requirement for minimal sample volumes. However, the technique has several important limitations that need to be considered during data interpretation. First, a series of nonideal interactions between the column stationary phase and solute result in separation that is not based entirely on molecular size or on MW. With this in mind, the term “apparent molecular weight” (AMW) will be used in this discussion, rather than the terms “MW” or “molecular size”. Another limitation of many of the existing methods of SEC is that UV absorbance (UVA) detection is used to determine the concentration of dissolved organic carbon (DOC), and these detectors are sensitive only to UV-absorbing species. Although many organic compounds absorb in the UV spectrum, this method is not quantitative for organic carbon because absorbance is dependent on molecular structure, rather than on the mass of organic carbon. For this reason, DOC-specific detection methods have been developed. The advantages of these methods are that the detector signal is directly proportional to the concentration of organic carbon and that, irrespective of functionality, any type of organic carbon bonded species can be detected. These DOC detection methods can be used in tandem with other (nondestructive) methods of detection, such as UVA and fluorescence. The use of such a multi-detector system coupled with SEC affords a powerful and sensitive analytical tool for characterization of the MW fractions of NOM in both natural and altered environments. In the present study, the techniques of SEC-UV₂₅₄, SEC-DOC, and SEC-fluorescence were used to evaluate and compare two drinking water treatment processes, specifically the MIEX process and an alum coagulation process, for their capacity to remove different AMW fractions of DOC.

The MIEX process is an innovative, new water treatment process jointly developed by SA Water, Orica Australia Pty Ltd. and CSIRO Australia (16, 17). The process is based on a micro-sized, macroporous, strong base anion-exchange resin with magnetic properties, which is used in a continuous process that incorporates a resin regeneration side-process.

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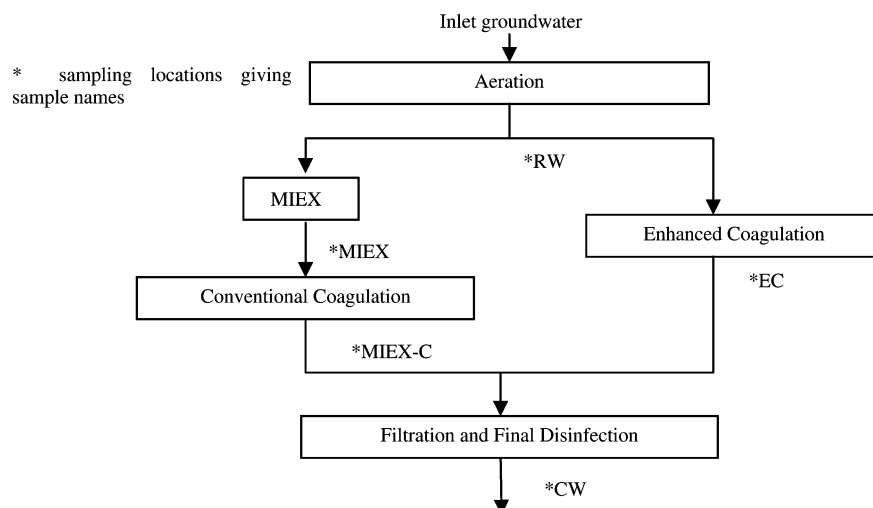


FIGURE 1. Schematic of Wanneroo groundwater treatment plant (WTP), showing sampling locations.

The world's first full-scale MIEX water treatment plant was commissioned at the Wanneroo water treatment plant (WTP) in Perth, Western Australia, in December 2001 (17). This plant is the largest groundwater treatment facility supplying the city of Perth (pop. 1.4 million) and is capable of processing 225 ML/day at full capacity. At the Wanneroo WTP, the MIEX process is operated in combination with a conventional alum clarifier for maximum removal of DOC (this combined process will be referred to as MIEX-C). The plant was configured such that the MIEX-C process can be operated in parallel with the preexisting conventional (enhanced coagulation) process (EC), as shown in the schematic in Figure 1. In this way, the raw water supplying the two process streams is identical, and water can be sampled from comparable locations in the parallel streams, facilitating accurate comparison of the two processes. In the MIEX process, the aerated raw water and the MIEX resin are intimately mixed within two 400 m³ contactors in series, where the process of DOC adsorption takes place. After the prescribed contact time, the water/resin mixture enters the settlers, where the magnetic properties of the resin particles effect agglomeration and settling of the resin. The resin slurry is separated from the supernatant water, which then enters a conventional clarifier (i.e., a conventional alum coagulation process) (17). After coagulation and clarification, the water from both the MIEX-C and the EC process streams is combined and filtered through conventional sand and anthracite filter media. The filtered water is then chlorinated, before being distributed to consumers. At the Wanneroo WTP, the EC process is similar to the coagulation process that occurs after the MIEX settlers and differs only in that a higher alum dose and a lower process pH are used. In EC, the process chemistry (e.g., coagulant dose and pH) is optimized for maximum DOC removal, while, traditionally, coagulation has been directed at turbidity and particle removal, which generally requires lower alum doses (6).

The primary aims of this study were to measure and characterize the AMW fractions of DOC that were removed in the various steps of the combined MIEX-C process, and to compare the performance of the MIEX-C process with that of the EC process, in terms of DOC removal. Previous studies had shown that the MIEX-C process preferentially removed the lower AMW DOC fractions, while EC treatment preferentially removed those of higher AMW (3, 16, and references therein). However, these previous investigations had been conducted using SEC with UV₂₅₄ detection only and were hampered by the lack of availability of a DOC-specific detector. Furthermore, they had been conducted either in pilot scale or in laboratory simulation experiments,

which cannot fully represent on-plant conditions. In the present paper, these investigations were extended, first by studying real-world samples from a full-scale MIEX treatment plant, and second by conducting the analyses using SEC coupled with DOC-specific, UV₂₅₄, and fluorescence detectors. These additional methods of characterization provided information on the effects of the treatment processes on the AMW and molecular (spectroscopic) characteristics of the DOC that was not previously available. Further aims of the study were to demonstrate the usefulness of SEC coupled with multiple detection systems in the characterization of DOC, and to confirm the results of SEC using three differently configured systems developed in three different laboratories.

Materials and Methods

Samples. Samples were collected from five points at the Wanneroo WTP (Figure 1). These were (a) the aerated raw water (RW); (b) water after treatment with MIEX only (MIEX); (c) water after treatment with MIEX followed by conventional coagulation (MIEX-C); (d) water after treatment with EC only (EC), and (e) "clear water", after pH adjustment and chlorination for disinfection (CW). Data on chemical doses, plant operating parameters, and raw water chemistry are provided in Table 1.

SEC. The SEC systems that were used in this study included (a) a system utilizing a preparative-scale column coupled with a UV₂₅₄ detector in series with a DOC-specific detector (13) (method A); (b) a system utilizing an analytical column, to provide optimum separation, coupled with a UV₂₅₄ detector (method B); and (c) a system using a preparative-scale column interfaced with UV₂₅₄, fluorescence, and DOC-specific detectors in series (18) (method C).

Method A: SEC of filtered samples was performed according to a previously described method using a TSK HW-50S gel column (length 25 cm, inner diameter 2 cm, particle size 30 μm), a 26.8 mM phosphate eluent ($\rho(\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}) = 1.5 \text{ g/L}$, $\rho(\text{KH}_2\text{PO}_4) = 2.5 \text{ g/L}$, pH 6.6, ionic strength 39.0 mM), and on-line UV_{254nm} and DOC-detection (19, 20). The flow rate was 1 mL/min, and the injection volume was 2 mL. A cylindrical thin film reactor with a rotating inner cylinder and a low-pressure mercury lamp in the middle served to oxidize DOC to CO₂, which in turn was quantified by a nondispersive IR spectrometer (10). The void volume $V_0 = 21 \text{ mL}$ was determined using dextran blue, and the permeation volume $V_p = 47 \text{ mL}$ was determined by injecting deionized water and using an electrical conductivity detector. Standards for MW calibration were polystyrene sulfonates (PSS), 35.7, 15.8, 4.48 kDa.

TABLE 1. Water Quality and Chemical Dose Parameters at Sample Locations at the Wanneroo WTP

water quality parameter/ chemical dose	raw water (RW)	MIEX treated (MIEX)	MIEX- coagulation (MIEX-C)	enhanced coagulation (EC)	clear water (CW)
alum dose (mg/L)			55	70	
polyelectrolyte dose (mg/L)			0.75	0.62	
DOC (mg/L)	5.70	2.46	1.59	2.14	1.74
color (at 400 nm)	45	29	2	3	2
UV ₂₅₄ (cm ⁻¹)	0.326	0.175	0.025	0.047	0.035
SUVA (L/(mg·m))	5.7	7.1	1.6	2.2	2.0
pH	7.14	7.46	6.61	6.45	6.74

The recovery of DOC from each sample was determined as follows: DOC concentrations were determined both before and after the sample had passed through the SEC column. This was done because irreversible adsorption of some sample components onto the stationary phase meant that not all of the sample eluted from the column. The concentration of the “lost” fraction of DOC was determined by comparing the peak area of a sample that eluted from the column with the peak area of the same sample that had bypassed the column. Potassium hydrogen phthalate standards served to calibrate the instrument. Recoveries ranged from 78% to 91%, which is reasonably consistent with previous observations of SEC analysis of NOM, and model compounds used to represent NOM (21).

Method B: SEC was performed using a TSK G3000SW_{xl} (TOSOH Biosep, 5 μ m resin) column and a Hewlett-Packard 1090 Series II HPLC instrument with filter photometric detection (FPD) at $\lambda = 254$ nm. The column had an internal diameter of 7.8 mm and a length of 30 cm, with a void volume of 5.5 mL, as determined with dextran blue. The eluent was 20 mM phosphate buffer (1.36 g/L KH₂PO₄ and 3.58 g/L Na₂HPO₄) at a pH of 6.85. Samples were injected manually with a Rheodyne 7125 6-port injection valve equipped with a 100 μ L sample loop. The flow rate was 1 mL/min. Samples were first filtered through a 0.45 μ m nylon filter, and then the ionic strength was adjusted to that of the eluent (20 mM) using a concentrated phosphate buffer. Data analysis was performed using HP Chemstation software. The system was calibrated using a combination of standards, as follows: poly(ethylene glycol)s (PEGs), kDa: 0.106, 0.194, 0.400, 0.580, 0.940, 1.47, 3.06, 6.00, 11.6, 22.5, trypan blue, cyanocobalamin, tannic acid, ribonuclease A, and albumin (0.96, 1.36, 1.70, 13.7, and 66 kDa, respectively). The calibration curve was linear ($R^2 = 0.991$) over the AMW range tested.

Method C: SEC was performed using a TSK-50S (Toyo-pearl HW 50S, 30 μ m resin, diameter 20 mm, length 200 mm) coupled with a UVA detector (SPD-6A Shimadzu), a fluorescence detector (Waters 470 scanning fluorescence detector), and a DOC-specific detector (Modified Sievers TOC 800 Turbo). The eluent system consisted of phosphate buffer (2.4 mM NaH₂PO₄ + 1.6 mM Na₂HPO₄; pH 6.8), containing sodium sulfate (25 mM), to achieve an ionic strength of 100 mM. The eluent flow rate was 1 mL/min, and the sample volume was 2 mL. PEG standards were used for determination of AMW. This method is described in detail elsewhere (18).

SEC Data Treatment. Calculation of number average molecular weight (M_n) and weight average molecular weight (M_w) was based on the method of Zhou et al. (22), who recommended a value of 1% of the maximum chromatogram height as the high molecular weight (HMW) cutoff, and 2% of the maximum chromatogram height as the low molecular weight (LMW) cutoff. Peak tailing has a marked effect on M_n , and, consequently, careful selection of the LMW cutoff is especially important. For Wanneroo raw water, fraction 1 eluted outside the calibration range in all of the methods that were used, so this fraction was not included in the calculation of MW parameters, and the values listed in Table

TABLE 2. Molecular Weight Parameters (M_n , M_w , and ρ for Wanneroo Raw Water (Excluding Fraction 1) Determined Using Two Different SEC Methods with Two Different Detection Methods

detection method	M_n	M_w	ρ
method A DOC	2405	5319	2.21
method A UV ₂₅₄	4273	6371	1.49
method B UV ₂₅₄	3407	5294	1.55

2 relate to fractions 2–8 only. However, omission of fraction 1 led to complications in selection of the HMW cutoff for chromatograms obtained using method A. Incomplete resolution of fractions 1 and 2 meant that the detector response did not decrease to 1% of the maximum response prior to the commencement of elution of fraction 2, and the HMW cutoff could not be determined using the specified method. In the case of method A, the HMW cutoff was therefore taken as the minimum detector response between fractions 1 and 2.

Results and Discussion

Comparison of SEC Methods. To gauge the validity of SEC MW determinations and to gain spectroscopic as well as DOC-specific information, the samples in the present study were analyzed using three different methods. In the two methods using DOC-specific detectors (methods A and C), preparative scale columns were used, because these detectors are not sufficiently sensitive to be compatible with analytical columns. The chromatographic results from these methods were compared to those from method B, in which an analytical column was interfaced with a UV detector. Comparison of chromatograms obtained using methods A and B showed that the chromatographic separation obtained using the analytical column (method B; Figure 2) was clearly superior to that which could be obtained with the preparative column (method A; Figure 3). Further, the analysis time required for the latter method was more than 4-fold greater than that required for the method utilizing the analytical column (67 and 15 min, respectively). However, the chromatograms produced by the two methods showed a remarkably similar elution pattern in all samples, and these similarities suggest that direct comparison of results obtained using these two methods is valid. In both cases, the profiles of DOC and UV₂₅₄-active DOC consisted of a peak at V_0 , which was present in both the raw water (Figures 2a and 3a) and the MIEX-treated samples (Figures 2b and 3b), and a smaller, later-eluting group of peaks which was present in all of the samples. The material represented by the peak at V_0 (fraction 1) was completely excluded from the stationary phases of both columns (as shown by dextran blue) and was therefore not subjected to the size exclusion separation process. While the peak represents only a small fraction of the total DOC, the same material represents a major proportion of the total UV₂₅₄-active substances in the sample, illustrating the significant discrepancies that can be obtained between UVA

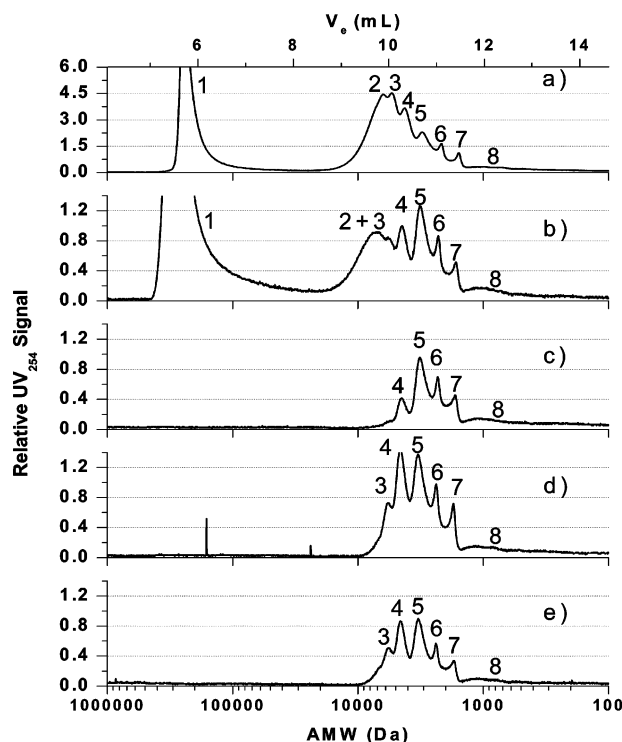


FIGURE 2. SEC chromatograms of UV_{254} -active DOC in water from the Wanneroo WTP (using method B): (a) RW; (b) MIEX; (c) MIEX-C; (d) EC; (e) CW. Fractions in each chromatogram are numbered as referred to in the text. V_e = elution volume.

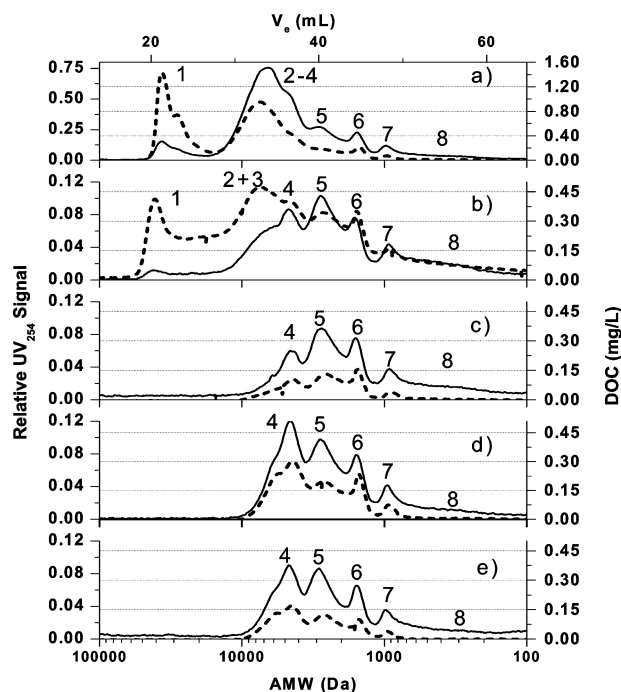


FIGURE 3. SEC- UV_{254} -DOC chromatograms (method A) of water samples from the Wanneroo WTP: (a) RW; (b) MIEX; (c) MIEX-C; (d) EC; (e) CW. Fractions in each chromatogram are numbered as referred to in the text. Black line = DOC response; dashed line = UV_{254} response. V_e = elution volume.

detection and DOC-specific detection. The material represented by the later-eluting group of peaks (fractions 2–8) did permeate the pores of the stationary phases and provides a valid comparison of the separation efficiency of each column. For example, in the case of the raw water sample (Figures 2a and 3a), this material was separated into six

resolvable fractions when using the analytical column, but into only three fractions with some shoulders when using the preparative column. In the experiment using the preparative column, even the material eluting at V_0 was not completely resolved from the later-eluting material, but these two fractions were clearly well separated, to the baseline, by the analytical column. In the case of treated water samples, EC-treated (Figures 2d and 3d) and CW (Figures 2e and 3e), fractions 3 and 4 could not be resolved using the preparative column, while these were well separated using the analytical column. The improved resolution provided by the analytical column has the potential to provide more information on the character of DOC, and on the fractions of DOC that were removed by the water treatment processes, than is available when using the preparative column. These observations illustrate the need for DOC-specific detectors that have signal-to-noise characteristics that are compatible with analytical-scale columns.

Results using method C were broadly comparable to those obtained using the other two methods (AMW profiles for method C are shown in the Supporting Information). Chromatograms obtained using each of the three methods all showed similar AMW profiles for the raw water sample, that is, two major, well-resolved, peaks (fraction 1 and fractions 2–8). When using methods A and B, fractions 2–8 were partly resolved, but these eluted as one peak with a shoulder and a tailing baseline using method C. The comparatively poor separation afforded by the latter method was probably primarily due to the use of an eluent of higher ionic strength than those used in methods A and B. Increasing the eluent ionic strength increases the elution volume of sample components by allowing greater permeation into the pores of the stationary phase (12). However, use of a lower ionic strength buffer appeared to resolve the DOC into a greater number of fractions, as observed in results from methods A and B. The improved resolution of these fractions allowed more precise comparison of the different water treatment processes in this study.

Raw Water Characteristics. To compare the MW characteristics of DOC in the Wanneroo raw water with those of DOC from other sources, number average molecular weight (M_n) and weight average molecular weight (M_w) were calculated. Values of M_n and M_w obtained for Wanneroo raw water (Table 2) agreed reasonably well, even though different methods of detection and calibration were used. Values of M_w were remarkably consistent for method A (with DOC detection) and method B, but M_w was excessively high for method A when using UV detection. This high value was probably caused by the incomplete resolution of fractions 1 and 2 in this chromatogram and was exacerbated by the high UV response of fraction 1. Values of M_n were highly dependent on the LMW cutoff, especially in the case of method A (DOC), where significant peak tailing occurred. Peak tailing was much less evident in the case of both of the chromatograms obtained using UV detection, and this may explain the relatively high values of M_n obtained by these methods.

Molecular weight parameters determined using both methods A and B showed that M_n and M_w for DOC in Wanneroo raw water were relatively high when compared to published values for NOM from other sources. For example, previously established values of M_n for the IHSS reference material Suwannee River Fulvic Acid (SRFA) ranged from 1160 to 1385 Da, while those for M_w ranged from 2114 to 3120 Da (15). Although comparison with published values is complicated by differences in methodologies (e.g., use of different calibration standards, eluent systems, and SEC columns), even when these differences are taken into consideration, our values for Wanneroo raw water appear to be similar to those of northern European swamp water fulvic

acids (15) and lake waters (12). For example, the values for M_n and M_w for Nordic Reference Fulvic Acid were reported as being 3870 and 6100 Da, respectively, and these appeared to be typical of waters from some Finnish lakes (12).

The AMW distribution of both UV₂₅₄-active DOC and total DOC in Wanneroo raw water is broadly bimodal in nature, as shown by chromatograms derived using both UV₂₅₄-specific and DOC-specific detectors (Figures 2a and 3a). The peak denoted as fraction 1 in these chromatograms represents material eluting at V_0 and is the principal cause of the high SUVA in this sample. Although the high AMW and very high SUVA of this peak are suggestive of humic substances that are highly aromatic in character, it is more likely that this material is colloidal in nature and may also comprise some inorganic substances. Although samples were filtered (0.45 μ m nylon membrane) prior to injection onto the SEC column, colloidal material is well known to permeate membranes of much smaller pore size (23). Previous workers (19, 24) observed similar characteristics in a German lake water sample and attributed a similar early eluting fraction with high SUVA to inorganic colloidal material (which would produce a UVA signal due to light-scattering effects), speculating that it may contain silicates, iron oxyhydroxides, and aluminum. The presence of colloidal material in our raw water sample is entirely consistent with the composition of the source water and the sample history: prior to aeration, the raw groundwater from this aquifer contains appreciable levels of sulfide, iron, and DOC and is depleted in oxygen (<1 mg/L). Thus, one potential source of colloidal material is from the formation of iron-oxyhydroxides from oxidation of ferrous iron upon aeration of the water. Iron from this water source is strongly complexed with organic matter, and precipitated iron would be associated with organic matter, which could explain why some DOC was observed in this fraction (Figure 3a). Alternatively, the material in fraction 1 may consist of sulfur species associated with organic matter, either in colloidal form as elemental sulfur or in solution (partially oxidized sulfur compounds such as polythionates and polysulfides absorb at $\lambda = 254$ nm). Elemental sulfur is a product of the oxidation of sulfide, but in the presence of organic matter, as occurs in the groundwaters in our study, the formation of crystalline sulfur is inhibited, and "dirty" sulfur is formed instead (25). Dirty sulfur consists of liquidlike clusters of cyclic sulfur (S_6 – S_8), incorporating hydrophobic organic molecules, and does not crystallize and separate from solutions in the same way that pure elemental sulfur does (26). Either colloidal or dirty sulfur, both associated with organic matter, or colloidal iron associated with organic matter could therefore produce the DOC and UV₂₅₄ responses observed for fraction 1.

The later-eluting UV₂₅₄-active and DOC fractions (fractions 2–8 in Figures 2 and 3) are more alike than the earlier-eluting fraction discussed above, but there are nevertheless some notable differences. Fractions 2–4, which elute as one unresolved peak in Figure 3a and three partly resolved fractions in Figure 2a, are likely to be enriched in humic substances of relatively high MWs (up to around 10 000 Da). Humic substances are considered to be rich in aromatic functional groups, and these are easily detected by both DOC-specific and UVA detectors. In our sample, fractions 5–7 have moderate UV absorbance when compared to DOC and may thus comprise fulvic acids, conjugated unsaturated acids, or keto-acids, as have been observed in previous studies (19, 21). Fraction 8 comprised DOC of lowest AMW, which eluted as a broad band of poorly resolved material that merged gradually into the baseline. The lowest MW DOC fractions are thought to be important in drinking water treatment as these are poorly removed by conventional processes and are considered to be bioavailable (6). Significantly, in our study,

the UV₂₅₄ detection method underestimated the relative proportion of this fraction.

Evaluation of Water Treatment Processes. Analysis using both the SEC-UV₂₅₄ (Figure 2a–e) and the SEC-UV-DOC (Figure 3a–e) methods showed that a significant proportion of the DOC in the aerated raw water was removed by the combined MIEX-C process and by the EC process. To quantitatively demonstrate the effects of these treatment processes on each of the DOC AMW fractions shown in Figures 2 and 3, the concentration of DOC represented by each fraction was calculated, with results shown in Figure 4. In general, the coagulation processes preferentially removed the higher AMW material, while MIEX appeared to remove organic matter over a wide range of AMWs, favoring the medium AMW range. The highest AMW fractions (fractions 1 and 2) were very effectively removed by coagulation processes: there was no trace of these fractions in water that was treated by either of the two coagulation processes (Figures 2 and 3, c and d); however, fraction 1 was poorly removed by the MIEX-only step (Figure 2b), and material in fractions 2 and 3 was also more resistant to removal by MIEX than by coagulation. The poor removal of fraction 1 by MIEX is consistent with suggestions that this fraction may comprise colloidal organic and inorganic material, because colloids would not be removed by an anion-exchange process, but are known to be very effectively removed by alum coagulation processes (27). The increase in SUVA observed after treatment of raw water by MIEX (Table 1) was clearly due to the poor removal of fraction 1, and any effect from the other fractions was negligible in comparison. The present example illustrates the application of SEC-UV-DOC to improved understanding of water treatment operations. For example, because fraction 1 is probably colloidal material, it could be removed by alternative processes, such as nanofiltration, which, when combined with MIEX, could give low SUVA values, comparable to MIEX-C. However, aggregate parameters, such as total SUVA, do not provide sufficiently detailed information to offer such insights.

The observation that fractions 2 and 3 were effectively removed by both coagulation processes, but poorly removed by MIEX-only, is also in agreement with the probable nature of the material within these fractions, that is, of intermediate AMW (~5000–7000 Da), enriched in humic and fulvic hydrophobic material. Much of the NOM in groundwaters from this region is thought to consist largely of tannin-derived substances, probably from condensed tannins (25), which are composed predominantly of phenolic moieties, with relatively minor carboxylic acid content. Phenolic moieties would not be amenable to removal via the MIEX ion-exchange mechanism because they are likely to be present in their protonated (uncharged) form at the pH of treatment (7.0–7.5; pK_a phenol = 9.82 (28)), whereas the hydrophobic, high SUVA, high MW material that probably comprises most of fractions 2 and 3 is known to be well-suited to removal by alum coagulation. These observations were confirmed by the SUVA profiles (Figure 5a), which showed that coagulation treatment preferentially removed aromatic components, but, while MIEX treatment removed DOC, it did not remove aromatic compounds in preference to nonaromatic moieties. The SUVA profile of the MIEX-treated water was lower than that of the raw water over the entire MW range, but the shapes of the two profiles were not markedly different. Indeed, in the MIEX treatment process, the removal of UV-absorbing moieties appeared to be lowest at high AMW, in agreement with suggestions above that these high AMW fractions (fractions 2 and 3) are enriched in uncharged phenolic moieties, which would not be readily removed by the ion-exchange process. However, as expected, both of the coagulation processes removed the UV-absorbing species in these medium to high AMW fractions much more effectively

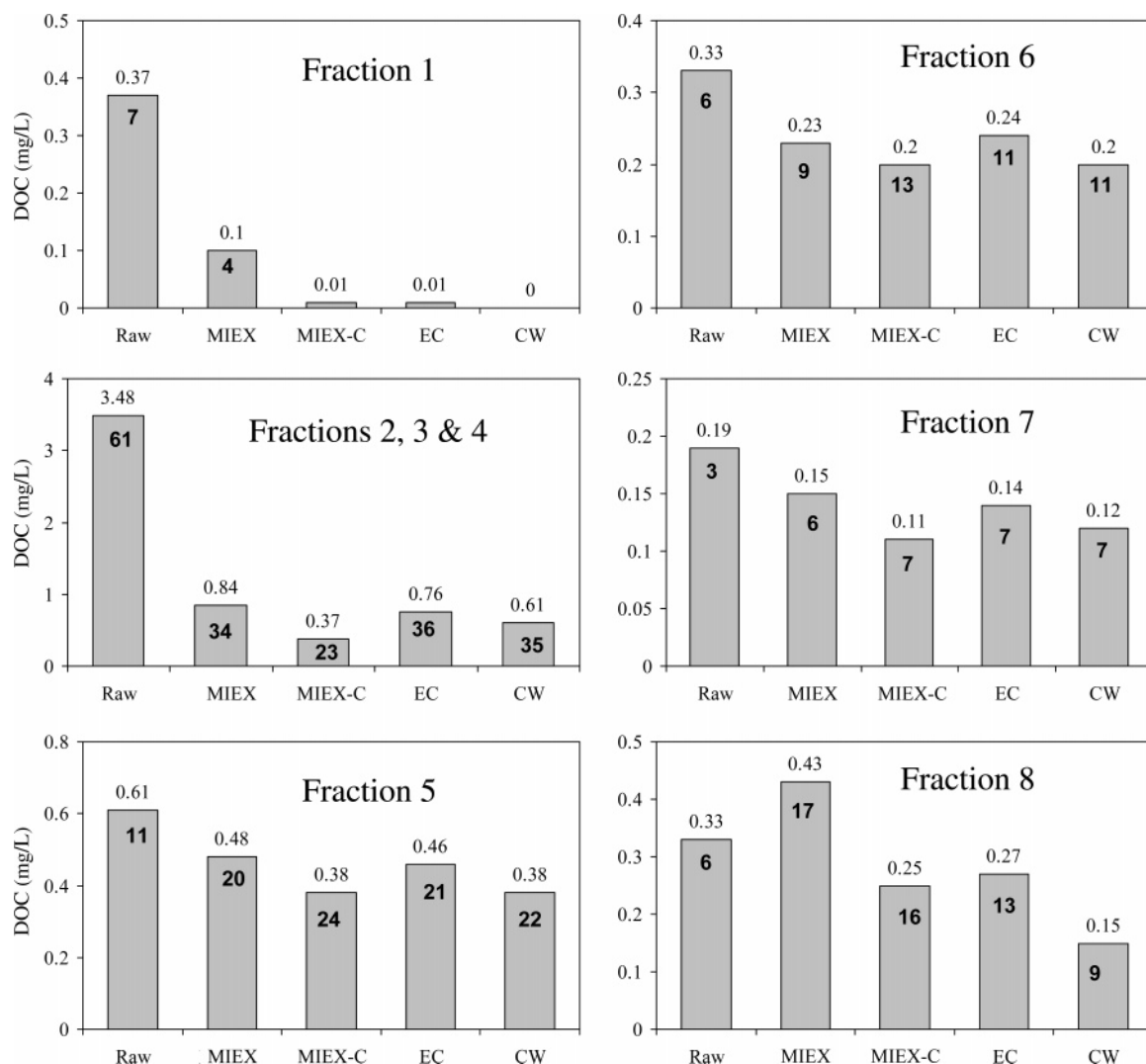


FIGURE 4. DOC concentrations (mg/L) in different AMW fractions of samples from Wanneroo WTP. Values above bars represent DOC concentrations in each fraction. Values in bold represent the percentage of total DOC in each fraction (total DOC values are listed in Table 1).

than the MIEX-only process. The SUVA profiles of both coagulation processes paralleled each other, clearly demonstrating how these similar processes removed similar DOC species. Fraction 4 appeared to be much more effectively removed by the MIEX process than by EC, but because it was difficult to resolve this peak from fraction 3 using SEC-DOC (method A), this fraction was not represented separately in Figure 4. Preferential removal by MIEX suggests that the material in this fraction contains anionic species. Material represented by peaks 5–7 was removed to a similar extent by both MIEX and EC (Figure 4). This suggests that these fractions are probably enriched in negatively charged species such as carboxylic acids, and, accordingly, these anionic species of relatively low MW (AMW = 1000–4000 Da) should be readily removed by ion-exchange. Fraction 8 was the only fraction that appeared to be poorly removed by both processes, and, in fact, the concentration of this fraction appeared to increase after MIEX treatment. However, quantification of this fraction was not as reliable as for the other fractions, because the chromatographic resolution for this peak was very poor due to strong interactions of the analytes with the SEC stationary phase. If fraction 8 is indeed bioavailable, it would be significant in the water treatment context, and it would be beneficial to further develop the SEC analytical technique so that this material can be better

resolved and detected. These techniques would need to utilize DOC detection, because the material has very low SUVA.

The MIEX-only process outperformed EC in the removal of only one fraction (i.e., fraction 4), but when MIEX was combined with alum coagulation, significantly lower DOC concentrations were obtained across all AMW fractions compared with EC. The improved performance of MIEX when combined with other processes is consistent with previous observations (3, 17). The application of alum coagulation after MIEX treatment appeared to render the coagulation process more effective than when the latter process (as EC) was used in isolation. For example, even the fractions that were preferentially removed by EC (e.g., fractions 2 and 3) were removed more effectively when MIEX treatment preceded the coagulation step (see Figure 4). Chromatograms obtained using the analytical SEC column, in which fraction 3 is clearly separated from fraction 4 (Figure 2), show that the UV₂₅₄-active component of fraction 3 could not be removed by either process in isolation: this fraction was poorly removed by MIEX-only and only marginally better removed by EC. However, fraction 3 was almost totally removed by the combined MIEX-C process. Even though EC had been optimized for maximum removal of DOC, the combined MIEX-C process was still more effective at removing all fractions of DOC (including those that were prefer-

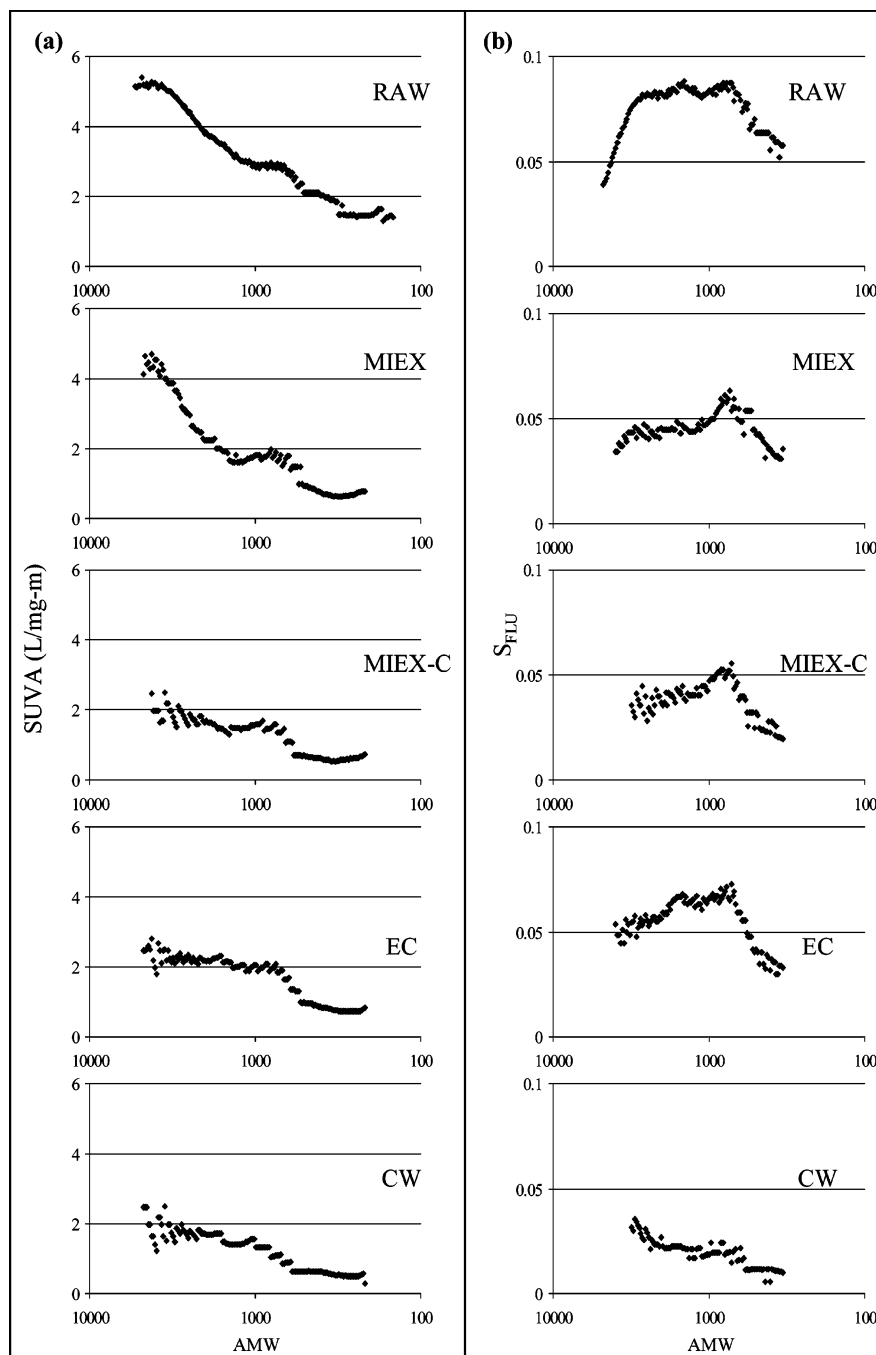


FIGURE 5. (a) SUVA and (b) S_{FLU} ($\lambda_{\text{ex}} = 282 \text{ nm}$; $\lambda_{\text{em}} = 353 \text{ nm}$) profiles of water sampled from Wanneroo WTP obtained using method C. Note that fraction 1 is not shown.

entially removed by EC) than either the MIEX-only or the EC process. MIEX, when combined with alum coagulation, proved to be by far the most effective treatment, removing the greatest amount of DOC over the greatest AMW range, demonstrating the eminently complementary functions of these two processes.

The present study confirmed previous results that showed that DOC removal using MIEX-C surpassed that achieved using EC by about 25% (17), but it also showed that most of the additional DOC removed by MIEX-C comprised DOC of a surprisingly narrow range of AMWs. DOC concentrations achieved after MIEX-C and EC treatments were 1.59 and 2.14 mg/L, respectively, a difference of 0.55 mg/L. According to results shown in Figure 4, almost 70% of this differential portion of DOC can be attributed to fractions 2–4 (i.e., the amount of DOC in fractions 2–4 that was removed by MIEX-C

was 0.39 mg/L more than the amount of DOC in these fractions removed by EC). Examination of chromatograms in Figures 2 and 3 shows that fraction 2 was equally well removed by both processes, so the most important fractions in the context of the present discussion are fractions 3 and 4, which fit within a relatively narrow AMW range (4000–7000 Da).

SEC-Fluorescence Spectroscopy. Measurement of the fluorescence of AMW fractions (SEC-FLU) of raw and treated water samples was carried out using a multidetection system, as described by Her et al. (18) (method C). This method was used to calculate the specific fluorescence (S_{FLU}) in each sample. S_{FLU} is the DOC-normalized fluorescence, obtained by dividing the fluorescent response (peak height) at a particular MW by the DOC response (peak height) at that MW. Whereas SUVA tended to decrease with decreasing

AMW, especially in the raw and MIEX-treated samples, the MW profiles of S_{FLU} were quite different from the SUVA profiles, demonstrating the distinction between the types of chemical substructures and functionalities that were detected by these two methods (cf., Figure 5a and b). In all samples, with the exception of the clear water, the S_{FLU} increased with decreasing AMW, to a maximum around 750 Da, and then decreased. The S_{FLU} in the raw water sample was relatively low at high AMW (~5000 Da), increasing rapidly to a broad maximum at 1000–5000 Da, and then decreasing steadily with decreasing AMW from 750 Da (Figure 5b). The combination of low S_{FLU} and high SUVA at relatively high AMW (5000 Da) observed in this sample is consistent with similar observations in previous studies (15). Low S_{FLU} combined with high SUVA suggests the presence of aromatic substances with low structural rigidity, that is, high MW (15). The decrease in S_{FLU} at low AMW (<750 Da) agrees with other findings in this study that these fractions consist of compounds that contain lower relative amounts of aromatic or conjugated moieties than the higher AMW fractions.

While the AMW profiles of DOC and UV₂₅₄-active substances in the CW sample were an approximate average of those from the EC and MIEX-C process, surprisingly, the S_{FLU} profile of the CW sample was much lower than the corresponding profiles from the coagulation processes. The CW sample essentially comprised equal proportions of water exiting the MIEX-C and the EC processes, and it was therefore expected that the quality of this water would be approximately representative of the average of these two samples. Water exiting the coagulation processes (i.e., clarifiers) is filtered through conventional sand/anthracite filters and is then disinfected by chlorination prior to distribution (chlorine dose = 4.4 mg/L). Values of DOC and UV₂₅₄ for CW were close to the average of those in the samples from treatment by MIEX-C and EC, showing that the processes of filtration and chlorination did not significantly affect these aggregate water quality characteristics (Table 1). However, chlorination can affect the fluorescent characteristics of DOC by altering the molecular structure of aromatic and/or other moieties, changes which would not necessarily be detectable by alternative methods such as SUVA or total DOC (29). The substantial decrease in fluorescence observed in the CW sample probably occurred as a result of substitution of bromine or chlorine atoms onto aromatic or heterocyclic rings within the DOC. The SUVA profile for this sample was only marginally lower than that expected from equal mixing of water from MIEX-C and EC, suggesting that only a minor loss of aromaticity occurred (i.e., substitution of halogens predominated over ring cleavage).

The present study illustrated the differences in the character of DOC that was removed by two water treatment processes and demonstrated the beneficial effects of integrating these two treatment processes. It was shown that when the two processes operated in combination (MIEX-C), more fractions of DOC were removed than the sum of the fractions that could be removed by each process in isolation. MIEX pretreatment improved the efficiency of the subsequent alum coagulation step, not just in terms of the total DOC removed, but also in terms of the type of DOC removed. This is the first study to apply SEC with multiple detection systems (including DOC-specific detection) to real-world samples from a full-scale MIEX water treatment plant, and thus the only detailed characterization study of DOC from these processes. Two different methods, one using an analytical column and the other a preparative column, with different eluent systems gave similar results, confirming the authenticity of the individual fractions. The study showed that both DOC and UV₂₅₄ detectors detected the same peaks in these samples but with different peak intensities, illustrating the utility of using these detectors in combination. While the

study re-affirmed previous studies showing that all major DOC components are detected by the simpler UV₂₅₄ detector, the use of UV₂₅₄ and DOC-specific detectors in series clearly provided the most valuable information for water treatment process optimization.

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Supporting Information Available

AMW profiles obtained using method C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Newcombe, G.; Drikas, M.; Assemi, S.; Beckett, R. Influence of Characterised Natural Organic Material on Activated Carbon Adsorption: I. Characterisation of Concentrated Reservoir Water. *Water Res.* **1997**, *31*, 965–972.
- (2) Chow, C. W. K.; van Leeuwen, J. A.; Drikas, M.; Fabris, R.; Spark, K. M.; Page, D. W. The Impact of the Character of Natural Organic Matter in Conventional Treatment with Alum. *Water Sci. Technol.* **1999**, *40*, 97–104.
- (3) Drikas, M.; Chow, C. W. K.; Cook, D. The Impact of Recalcitrant Organic Character on Disinfection Stability, Trihalomethane Formation and Bacterial Regrowth: An Evaluation of Magnetic Ion Exchange (MIEX) and Alum Coagulation. *J. Water Supply: Res. Technol. AQUA* **2003**, *52*, 475–487.
- (4) Aoustin, E.; Schäfer, A. I.; Fane, A. G.; Waite, T. D. Ultrafiltration of natural organic matter. *Sep. Purif. Technol.* **2001**, *22*–23, 63–78.
- (5) Hem, L.; Efraïmsen, H. Assimilable Carbon in Molecular Weight Fractions of Natural Organic Matter. *Water Res.* **2001**, *35*, 1106–1110.
- (6) Volk, C.; Bell, K.; Ibrahim, E.; Verges, D.; Amy, G.; LeChevalier, M. Impact of Enhanced and Optimized Coagulation on Removal of Organic Matter and its Biodegradable Fraction in Drinking Water. *Water Res.* **2000**, *34*, 3247–3527.
- (7) Buffle, J.; Deladsey, J. P.; Haerdi, W. The Use of Ultrafiltration for the Separation and Fractionation of Organic Ligands in Freshwaters. *Anal. Chim. Acta* **1978**, *101*, 339–357.
- (8) Giddings, J. C.; Williams, P. S.; Beckett, R. Fractionating Power in Programmed Field-Flow Fractionation: Exponential Sedimentation Field Decay. *Anal. Chem.* **1987**, *59*, 28–37.
- (9) Figini, R. V.; Marx-Figini, M. On the molecular weight determination by vapour pressure osmometry. 3a, relationship between diffusion coefficient of the solute and noncolligative behaviour. *Macromol. Chem. Phys.* **1981**, *182*, 437–441.
- (10) Huber, S. A.; Frimmel, F. H. Flow Injection Analysis of Organic and Inorganic Carbon in the Low-ppb Range. *Anal. Chem.* **1991**, *63*, 2122–2130.
- (11) Specht, C. H.; Kumke, M. U.; Frimmel, F. H. Characterisation of NOM Adsorption to Clay Minerals by Size Exclusion Chromatography. *Water Res.* **2000**, *34*, 4063–4069.
- (12) Peuravuori, J.; Pihlaja, K. Molecular Size Distribution and Spectroscopic Properties of Aquatic Humic Substances. *Anal. Chim. Acta* **1997**, *337*, 133–149.
- (13) Nissinen, T. K.; Miettinen, I. T.; Martikainen, P. J.; Vartiainen, T. Molecular Size Distribution of Natural Organic Matter in Raw and Drinking Waters. *Chemosphere* **2001**, *45*, 865–873.
- (14) Conte, P.; Piccolo, A. High-Pressure Size Exclusion Chromatography (HPSEC) of Humic Substances: Molecular Sizes, Analytical Parameters, and Column Performance. *Chemosphere* **1999**, *38*, 517–528.
- (15) Perminova, I. V.; Frimmel, F. H.; Kudryavtsev, A. V.; Kulikova, N.; Abbt-Braun, G.; Hesse, S.; Petrosyan, V. S. Development of a Predictive Model for Calculation of Molecular Weight of Humic Substances. *Environ. Sci. Technol.* **2003**, *37*, 2477–2485.
- (16) Slunjski, M.; Cadee, K.; Tattersall, J. MIEX Resin Water Treatment Process, Aquatech Amsterdam, Amsterdam, Netherlands, 2000.

- (17) Smith, P.; O'Leary, B.; Tattersall, J.; Allpike, B. The MIEX Process – A Year of Operation. *Proceedings Ozwater Convention Perth April 2003* **2003**, on CD.
- (18) Her, N.; Amy, G.; McKnight, D.; Sohn, J.; Yoon, Y. Characterisation of DOM as a Function of MW by Fluorescence EEM and HPLC-SEC using UVA, DOC and Fluorescence detection. *Water Res.* **2003**, *37*, 4295–4303.
- (19) Huber, S. A.; Frimmel, F. H. Gelchromatographie mit Kohlenstoffdetektion (LC-OCD): Ein rasches und aussagekräftiges Verfahren zur Charakterisierung hydrophiler organischer Wasserinhaltsstoffe. *Vom Wasser* **1996**, *86*, 277–290.
- (20) Huber, S. A.; Frimmel, F. H. Direct Gel Chromatographic Characterization and Quantification of Marine Dissolved Organic Carbon Using High-Sensitivity DOC Detection. *Environ. Sci. Technol.* **1994**, *28*, 1194–1197.
- (21) Specht, C. H.; Frimmel, F. H. Specific Interactions of Organic Substances in Size-Exclusion Chromatography. *Environ. Sci. Technol.* **2000**, *34*, 2361–2366.
- (22) Zhou, Q.; Cabaniss, S. E.; Maurice, P. A. Considerations in the Use of High-Pressure Size Exclusion Chromatography (HPSEC) for Determining Molecular Weights of Aquatic Humic Substances. *Water Res.* **2000**, *34*, 3505–3514.
- (23) Buesseler, K. O.; Bauer, J. E.; Chen, R. F.; Eglington, T. I.; Gustafsson, O.; Landing, W.; Mopper, K.; Moran, S.; Santschi, P. H.; VernonClark, R.; Wells, M. An Intercomparison of Cross-Flow Filtration Techniques Used for Sampling Marine Colloids: Overview and Organic Carbon Results. *Mar. Chem.* **1996**, *55*, 1–31.
- (24) Schmitt, D.; Saravia, F.; Frimmel, F. H.; Schuessler, W. NOM-Facilitated Transport of Metal Ions in Aquifers: Importance of Complex-Dissociation Kinetics and Colloid Formation. *Water Res.* **2003**, *37*, 3541–3550.
- (25) Heitz, A. Malodorous dimethylpolysulfides in Perth drinking water. Ph.D. Dissertation, Curtin University of Technology, 2002.
- (26) Steudel, R. Mechanism for the formation of elemental sulfur from aqueous sulfide in chemical and microbiological desulfurisation processes. *Ind. Eng. Chem. Res.* **1996**, *35*, 1417–1423.
- (27) Vrijnenhoek, E. M.; Childress, A. E.; Elimelech, M.; Tanaka, T. S.; Beuhler, M. D. Removing Particles and THM Precursors by Enhanced Coagulation. *J.-Am. Water Works Assoc.* **1998**, *90*, 139–150.
- (28) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley and Sons: New York, 1993.
- (29) Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*, 4th ed.; Saunders College Publishing: Philadelphia, PA, 1982.

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