*Desalination and Water Treatment*
www.deswater.com

doi: 10.1080/19443994.2012.751149

51 (2013) 3639–3649
April

Taylor & Francis
Taylor & Francis Group

# Chemometric approaches to data assessment for a long-term case study of MIEX pretreatment performance

Zeeshan Aslam[a], Mike Dixon[a,c], Christopher W.K. Chow[a,c,*], Jim Morran[c], Mary Drikas[a,c], John A. van Leeuwen[a,b]

[a]*SA Water Centre for Water Management and Reuse, University of South Australia, South Australia, Australia*
*Tel. +61 8 7424 2109; Fax: +61 8 70032109; email: chris.chow@sawater.com.au*
[b]*Barbara Hardy Institute, University of South Australia, South Australia, Australia*
[c]*Australian Water Quality Centre, SA Water, South Australia, Australia*

Received 12 July 2012; Accepted 29 October 2012

ABSTRACT

A specifically designed pilot plant facility located at the Mount Pleasant Water Treatment Plant in South Australia was used to investigate the efficiencies of several drinking water treatment processes, including (1) magnetic ion exchange (MIEX) as a pretreatment followed by conventional coagulation treatment, (2) conventional coagulation at pilot the plant alone, (3) MIEX followed by microfiltration (MF), and (4) MF alone. Dissolved organic matter (DOM) removal efficiency of the treatment processes and more importantly the treated water quality was assessed using dissolved organic carbon (DOC) measurement and together with the changes in the chromophoric organics character based on their molecular weight profiles determined by high-performance size exclusion chromatography (HPSEC) were also reported. Cluster analyses (CAs) were performed using the HPSEC peak area (after separated by peak fitting), and supported by DOC, UV absorbance at 254 nm, and SUVA in order to compare treatment efficiencies of these technologies. It was a novel way of applying CA as a data mining tool to interpret and assess DOM removal results. From the results of these CA, it was found that the MIEX process provided consistent treatment performance and highest removal of DOM, as well as removal of a broad range of molecular weight organics. In comparison coagulation with alum tended to remove the high molecular weight (>1000 Da) compounds. This statistical approach provided improved understanding of the performances of the treatment processes, investigated at a molecular level, for the removal of DOM.

*Keywords:* Natural organic matter; Dissolved organic matter; Magnetic ion exchange resin; High-performance size exclusion chromatography; Cluster analyses

## 1. Introduction

Surface waters used for drinking purposes can vary seasonally throughout the year and treatment engineers need to respond to these changes to ensure selection of the optimum treatment option for safe drinking water supply. Water quality is impacted by a wide range of factors including suspended solids measured as turbidity, the presence of any synthetic organic compounds, and natural organic matter (NOM). NOM consists of a complex mixture of organic

---

*Corresponding author.

compounds resulting from decaying flora, microbes, and aquatic organisms. Change in source water quality for drinking water supply is an important issue and the potential effects of climate cycling and change have been increasingly reported [1]. Several methods have been proposed to assess potential changes in water quality due to climate effects [2,3]. In recent years, there has been a focus on improving treatment processes for removal of NOM and for development of advanced analytical techniques to better assess NOM removal with treatment [4–6].

Conventional treatment comprising coagulation/flocculation/sedimentation and filtration is one of the most widely used methods to remove NOM. Broad research has been undertaken to increase the extent of NOM removal by conventional coagulation, including the use of increased coagulant doses and selecting the pH, which is referred to as enhanced coagulation [7–11]. A more recent technology developed specially for NOM removal is the magnetic ion exchange resin–dissolved organic carbon (MIEX–DOC) treatment process [12,13]. This resin incorporates magnetic iron oxide particles within its core. Its small resin beads facilitate the fast reaction while the magnetic portion allows separation and recycling of the resin during continuous processing. A number of studies have been reported on the efficiency of MIEX process for NOM removal in source water [14,15] and also some more detailed laboratory-scale evaluations to compare the effectiveness of the MIEX process with conventional or enhanced coagulation for rapid removal of NOM in drinking water [16,17]. There were also few case studies to compare pilot plant or full-scale MIEX treatment with coagulation against water quality variations [18–22]. Generally, MIEX has found to remove a broader range of molecular weight organic components and conventional coagulation with alum can only remove the high molecular weight portion [15,18].

Ultraviolet and fluorescence spectroscopy, solid state $^{13}$C nuclear magnetic resonance spectroscopy, elemental analysis (e.g. DOC), and pyrolysis gas chromatography mass spectrometry are examples of techniques that have been used to characterize the NOM in a wide range of surface waters, before and after treatment for drinking purposes [10,23,24]. Each technique has its own benefits including simplicity or molecular-level characterization and disadvantages such as sample preparation and complex interpretation of results. High-performance size exclusion chromatography (HPSEC) is an informative technique that can be readily used for characterization of the NOM [25,26] based on its molecular size distribution profile. Reported benefits of using HPSEC including minimal sample preparation, small sample size and provides reliable information on the molecular weight distribution of organics. There were also specific applications of the technique to characterize NOM by determining and comparing their HPSEC molecular profiles before and after MIEX or conventional coagulation treatment [27–29]. In this method, higher molecular weight organic compounds elute faster than smaller molecular weight compounds because of their overall lower transport into the stationary phase. Hence, the larger-sized compounds preferentially move through macropores of the stationary phase material. Recently, a peak fitting procedure to resolve overlapping peaks of HPSEC chromatographs has been reported [5,30]. This peak fitting procedure was developed in order to predict NOM removal by conventional coagulation.

Most previous studies reported were short term and lacking long-term information about molecular weight profiles of organics caused by seasonal water quality and treatment changes, and also the use of statistical approaches for NOM removal with special type of clustering to assess different treatment performances have not been fully explored. The objective of this case study was to use cluster analyses (CAs) as a data mining approach to assess UV absorbing, chromophoric NOM removal, and to evaluate removal in terms of treatment performance including (1) MIEX alone, (2) coagulation alone, (3) MIEX combines with conventional coagulation, (4) MIEX with microfiltration (MIEX–MF at plant scale), (5) MF alone, and (6) MIEX MF at pilot scale. HPSEC analyses of raw water organics and those remaining after treatment were conducted in order to assess the performances of several treatment options for drinking water supply. A peak fitting technique was used to resolve peaks of HPSEC chromatograms of dissolved organic matter (DOM) in raw and treated waters for each of the above treatment options to facilitate assessment of their relative efficiencies for DOM removal. Data of resolved peaks, DOC, UV absorbance at 254 nm, and SUVA were evaluated using CAs in order to further assess treatment performances.

## 2. Materials and methods

### 2.1. Water treatment methods

Raw and treated water quality data was acquired from pilot plant studies performed at an established MIEX treatment plant (Mt Pleasant WTP, South Australia) that incorporates coagulation, flocculation, sedimentation, and rapid filtration [6]. The treatment processes included (1) MIEX alone, (2) conventional treatment (alum coagulation, flocculation, settling, and

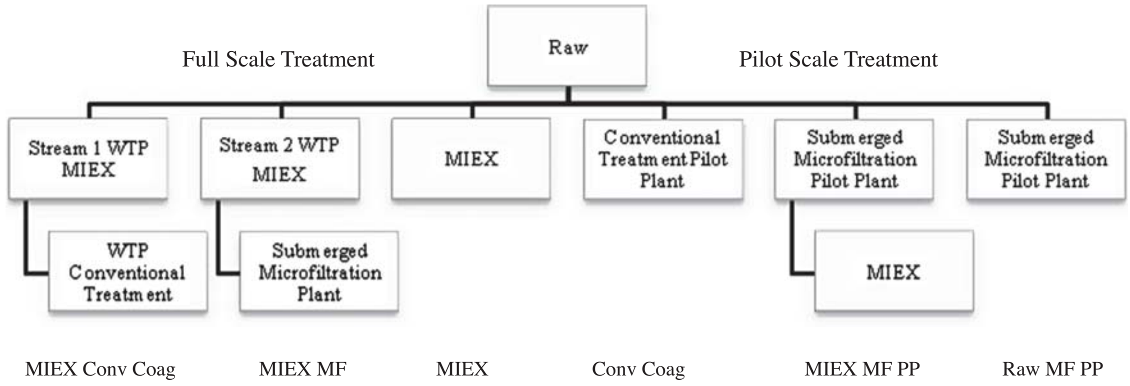

Fig. 1. Schematic of treatment trains. MIEX Coag-S1 at Mt Pleasant water treatment plant (WTP) consisting of MIEX followed by conventional treatment utilizing coagulation, flocculation, sedimentation, and rapid filtration; conventional treatment pilot plant consisting of coagulation, flocculation, sedimentation, and rapid filtration; MIEX–MF-treated water sourced from S1 at Mt pleasant WTP or microfiltration pilot plant followed by passage through submerged microfiltration membrane plant referred to as S2 and pilot plant, respectively; raw MF–raw water followed by passage through submerged microfiltration membrane in pilot plant [6].

filtration) alone (pilot scale), (3) MIEX with conventional treatment, S1 (stream 1 full-scale plant operation), (4) MIEX with MF, S2 (stream 2 full-scale plant operation), (5) MF (pilot scale), and (6) MIEX with MF (pilot scale) (see Fig. 1).

For conventional treatment, alum dose of 40 mg/L was used at pH 6.4–6.8. MIEX was applied with the aim of maintaining a resin dose at or above 10 mL/L for 10 min contact time. The actual resin doses varied between 8 and 16 mL/L over this study period. The resin was recirculated in a continuous process with 10% removed for regeneration using sodium chloride. Fresh-regenerated resin was reverted constantly to the resin contact tank to keep a constant resin dose while regeneration was undertaken separately on a batch process as essential. Virgin makeup resin was added on an infrequent basis to compensate for resin lost due to attrition. Another treatment train incorporates MIEX followed by submerged microfiltration (CMF-S) with polyvinylidenefluoride (PVDF) membranes (MIEX MF) that have a nominal pore size of 0.04 μm. MIEX MF was used to enable comparison of MF with coagulation treatment that is established at the full-scale plant.

However, the MF pilot plant was also used to provide the evaluation of MF with and without MIEX pretreatment to ensure operational conditions were the same for both operating systems but in this paper, it can be viewed as creating another treated water quality for the CA study. The MF pilot plant comprised of a single module CMF-S membrane, the same type as used in the Mt. Pleasant full-scale WTP.

## 2.2. Quantification and characterization of DOM

### 2.2.1. High-performance size exclusion chromatography (HPSEC)

Apparent molecular weight (AMW) distribution profiles of organics in water samples were determined on a monthly basis using HPSEC with UV detection at 260 nm. This was done after filtration of water samples through 0.22 μm, mixed cellulose esters (nonsterile) prerinsed membranes supplied by MicroAnalytix Pty Ltd. Membranes were rinsed two times with 5 mL of Milli Q water and prerinsed with samples (5 mL) before filtration. Separation of organics was performed with a Shodex KW 802.5 column (Shoko Co. Ltd., Japan) with a 0.02 M phosphate buffer solution (pH 6.8, ionic strength adjusted to 0.1 M with sodium chloride) as the mobile phase. Flow rate and injection volume were maintained at 1 mL/min and absorbance was measured in terms of absorbance units and calibration was performed using polystyrene sulfonate (PSS) standards of 35, 18, 8, and 4.6 kDa.

### 2.2.2. Dissolved organic carbon and UV absorbance

Samples for DOC and $UV_{254}$ analyses were filtered through 0.45 μm, mixed cellulose esters (nonsterile) prerinsed membranes supplied by MicroAnalytix Pty Ltd. (same pretreatment procedures as stated previously). The UV absorbance at 254 nm was measured using a UV/Vis spectrophotometer (Model 918, GBC Scientific Equipment Ltd., Australia), with 1 cm quartz cell and DOC was measured using a Total Organic

Carbon Analyzer (Sievers 820, GE Analytical Instruments, USA). SUVA values were determined by the following formula:

$$\mathrm{SUVA} = 100 * \frac{\mathrm{UV}_{254}\ (\mathrm{cm}^{-1})}{\mathrm{DOC}\ (\mathrm{mg/L})}$$

Raw water DOC ranged (3.0–5.5 mg/L), $UV_{254}$ (0.061–0.281 $cm^{-1}$), SUVA (1.8–5.1 $m^{-1}\,mg^{-1}\,L^{-1}$), and turbidity (20–29 NTU) measured by Hach ratio turbidimeter throughout this study period. This sample set provided a good case study to observe the variations and assessment between different treatment processes for NOM removal.

### 2.3. Analyses of HPSEC data

#### 2.3.1. Peak fitting approach

A commercially available software, Peak fit (Version 4, Systat Software Inc.), was used to resolve overlapped peaks of HPSEC chromatograms. The first step was determination of optimum peak fitting parameters, such as peak type and fitting method [5,28]. The second step involved analyses of the chromatograms of raw and treated water samples in each month. The peak areas under each chromatogram were subsequently determined by the above peak fitting software.

#### 2.3.2. Cluster analyses

To investigate comparisons between these treatment trains, hierarchical agglomerative tree joining (dendrogram), and *k*-mean cluster (CA) analyses were performed using Euclidean distances as a measure of similarity. Statistical software STASTICA 10 for Windows was used for these analyses. CA was used to search for groupings among different treatment processes based upon their performances to remove DOM. Analyzed parameters were sorted into groups, or cluster (tree joining), so that the degree of association between members of the same clusters (*k*-mean) could be investigated. The Euclidean distance between two or more groups gives a measure of similarity or difference between the groups. The general formula (Euclidean distance, *d*) is detailed below:

$$d = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} \tag{1}$$

$x_1$ and $y_1$ are the $x$, $y$ coordinates of the first point, $x_2$ and $y_2$ are the $x$, $y$ coordinates of the second point, and $d$ is the distance between two points.

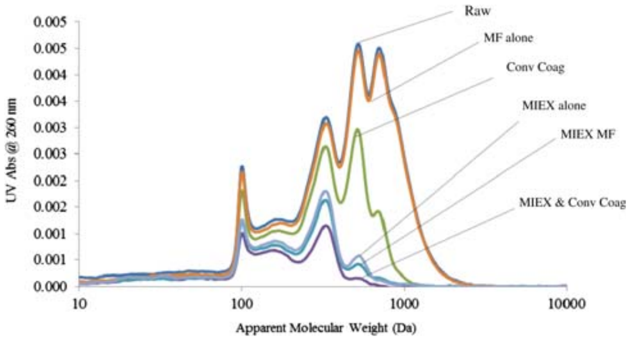

Fig. 2. Apparent molecular weight distributions of UV absorbing (260 nm) organics present in raw and treated waters (MF: microfiltration, Conv Coag: conventional coagulation, MIEX: magnetic ion-exchange resin) for August 2005.

This can be extended to any number of potential data populations with any number of variables describing each population and multidimensional space.

## 3. Results and discussion

### 3.1. Molecular weight profiles

An example of HPSEC chromatograms of organics present in raw water and following treatment methods previously detailed is shown in Fig. 2.

MF removed a very minimum DOC from raw water and consequently the resulting molecular profile distribution was similar to that of the raw water. Maximum removals of UV absorbing DOM measured occurred with combined treatment by MIEX and conventional coagulation. From visual inspection of the chromatographs (Fig. 2), it is apparent that high molecular weight organics (>1000 Da) were readily removed by conventional coagulation treatment while MIEX alone removed a broad range of DOM including molecular weight compounds below 700 Da. These results were also in agreement with the findings from a study by Humbert et al. [15] and Kaewsuk and Seo [31], where it was found that MIEX removed NOM over a molecular weight range of 400–2000 Da. It is also cleared from Fig. 2 that MIEX alone removed NOM having molecular weight ranged from 500 to 700 Da. Improved removal is observed when MIEX combined with MF and removed those organics having molecular size larger than 0.04 μm. Coagulant dose for conventional treatment and virgin resin dose was kept constant throughout this study period.

The performances of the five treatment methods can be evaluated from HPSEC chromatographs as shown in Fig. 2, including by quantification and comparison of total peak areas, i.e. through integration of the curves. However, the assessment of specific peak

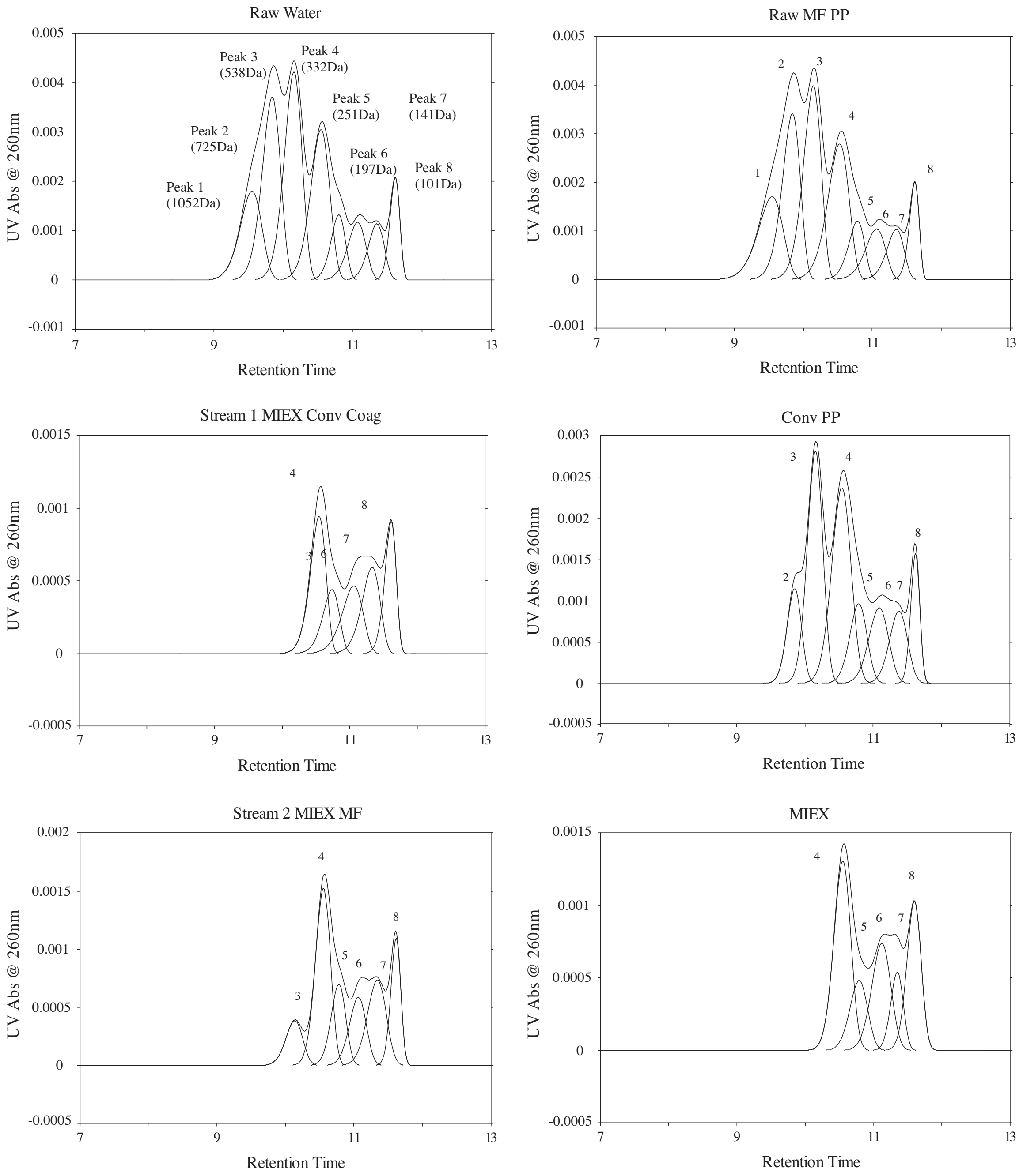

Fig. 3. Resolution of chromatograph data to distinct peaks using Peak fit Software for raw water and water treated by the four processes (August 2005).

removals is semi-quantitative where these are unresolved and may be estimated from peak heights where peaks are distinct. The aim of this study was to improve the understanding of removal of organic components based upon molecular weights by fitting of peaks to the HPSEC chromatographs. To then further investigate the relative treatment performances CA was conducted to establish similarities and differences between the treatment methods. In broad-scale comparison, clear differences would be expected between treatment by MIEX alone and MIEX combined with MF and conventional coagulation, as evidenced from Fig. 2. However, when comparing combined methods such as MIEX with coagulation and MIEX with MF, differences between these and with MIEX alone may be less apparent. In this study, monthly data from August 2005 to December 2006 was tested by CA to compare the various treatment methods.

### 3.2. Peak fitting of HPSEC data

For resolution of the HPSEC peaks, optimization options (referred to as Log Normal-4 Area and Refine Shape) available in the Peak fit software were applied which provide fits with $R^2$ values of $0.96 \pm 0.03$. Numbers of peaks selected were based on the presence of peak shoulder and peak apex. Using this peak fitting procedure, it is clear that HPSEC chromatographic data can be resolved into a number of peaks and optimized to minimize deviation of data from actual data, where $R^2$ is maximum. Fig. 3 shows examples of resolved peaks of the HPSEC chromatogram for each treatment process. Eight peaks were resolved for the raw water and these can be associated with the chemical groups of organometallic colloids, biological residues, high molecular weight humic substances, low molecular weight humics, building blocks, low molecular weight acids, and nitrogen containing aromatics [5]. However, in this paper, the emphasis is the peak area of these peaks can be used to assess NOM removal rather than identifying individual compounds. These raw water and following treatment peaks 1–4, representing the high molecular weight components were able to be removed some or all of the various treatment methods investigated. With advanced treatment, MIEX with coagulation, all four peaks (1–4) were able to be removed.

### 3.3. Peak areas

Peak fitting was undertaken for all HPSEC chromatograms acquired of samples collected monthly for each treatment method over the period of 17 months. Total areas (integration of UV absorbance data for each peak) in arbitrary units (AUs) were calculated and are shown in Table 1. By peak fitting and integration of the various peaks, there is capacity to differentiate between various similar removal efficiencies e.g. between raw and treated waters, based on total and individual peak areas. The variation in treatment performances indicated the presence of different components of DOM in raw and treated water due to changes in water quality with time.

### 3.4. Cluster analyses

CA is the generic term applied for a wide variety of statistical procedures that can be used to identify homogeneous groups within heterogeneous data. An objective of this study was to identify similarities and differences between the treatments methods investigated based on treated water quality and treatment efficiency. Data was analyzed using tree joining (dendrogram) and *k*-mean CAs. Total areas of the peaks of raw and treated waters after peak fitting were calculated and hierarchical agglomerative (tree joining) CA was performed for each data set.

When CA was applied, the dendrogram showed three major clusters identified as C (combination of A and B merged into this cluster), D, and E (Fig. 4). As expected, there were clear differences between MF, coagulation, and MIEX. Nonetheless, this technique enabled assessment of differences between apparently similar treatment options, i.e. those incorporating MIEX.

The two closest cluster populations (MIEX alone and MIEX–MF PP) were joined together to form a single new cluster population A in Fig. 4. This means MIEX alone and combined with MF preferentially

Table 1
Total resolved peak areas after peak fitting for entire study period (raw compared with treated water after each treatment process)

| Study period | Raw water | MIEX | Conv coag PP | S1 MIEX conv coag | S2 MIEX MF | Raw MF PP | MIEX MF PP |
|---|---|---|---|---|---|---|---|
| August-05 | 0.575 | 0.153 | 0.311 | 0.098 | 0.135 | 0.567 | 0.153 |
| September-05 | 0.506 | 0.095 | 0.270 | 0.078 | 0.113 | 0.633 | 0.108 |
| October-05 | 0.453 | 0.086 | 0.184 | 0.077 | 0.051 | 0.405 | 0.092 |
| November-05 | 0.579 | 0.103 | 0.282 | 0.095 | 0.115 | 0.569 | 0.161 |
| December-05 | 0.890 | 0.080 | 0.521 | 0.083 | 0.208 | 0.374 | 0.097 |
| January-06 | 0.811 | 0.097 | 0.376 | 0.100 | 0.165 | 0.837 | 0.099 |
| February-06 | 0.659 | 0.101 | 0.371 | 0.100 | 0.145 | 0.835 | 0.101 |
| April-06 | 0.696 | 0.117 | 0.473 | 0.081 | 0.122 | 0.703 | 0.118 |
| June-06 | 0.378 | 0.097 | 0.251 | 0.073 | 0.133 | 0.575 | 0.072 |
| August-06 | 0.468 | 0.055 | 0.259 | 0.061 | 0.127 | 0.325 | 0.082 |
| October-06 | 0.443 | 0.084 | 0.196 | 0.139 | 0.116 | 0.453 | 0.090 |
| December-06 | 0.452 | 0.080 | 0.316 | 0.078 | 0.134 | 0.452 | 0.090 |

Note: Peak area in arbitrary unit (A.U.).

Table 2
Euclidean distance matrix and formation of clusters for the various water qualities (before and after treatment) based on HPSEC peak areas in which two closest cluster populations are indicated by bold values

*Euclidean distance matrix*

| | Raw water | MIEX | Conv coag PP | S1 MIEX conv coag | S2 MIEX MF | Raw MF PP | MIEX MF PP |
|---|---|---|---|---|---|---|---|
| Raw water | 0.000 | 0.017418 | 0.009371 | 0.01767756 | 0.016076 | 0.00612 | 0.01708 |
| MIEX | | 0.000 | 0.008404 | 0.00091354 | 0.001877 | 0.01693 | **{0.0007}** |
| Conv coag PP | | | 0.000 | 0.00871885 | 0.007021 | 0.01 | 0.00812 |
| S1 MIEX conv coag | | | | 0.000 | 0.001972 | 0.0172 | 0.00114 |
| S2 MIEX MF | | | | | 0.000 | 0.0159 | 0.00176 |
| Raw MF PP | | | | | | 0.000 | 0.00169 |
| MIEX MF | | | | | | | 0.000 |

*Formation of clusters*

Cluster A

| | Raw water | Conv coag PP | S1 MIEX conv coag | S2 MIEX MF | Raw MF PP | A |
|---|---|---|---|---|---|---|
| Raw water | 0.00 | 0.009371 | 0.017678 | 0.01607628 | 0.00612 | 0.017249237 |
| Conv coag PP | | 0.00 | 0.008719 | 0.0070212 | 0.01 | 0.008262057 |
| S1 MIEX conv coag | | | 0.00 | 0.00197217 | 0.0172 | **{0.001026771**} |
| S2 MIEX MF | | | | 0.00 | 0.0159 | 0.001818327 |
| Raw MF PP | | | | | 0.00 | 0.016915 |
| A | | | | | | 0.00 |

Cluster B

| | Raw water | Conv coag PP | S2 MIEX MF | Raw MF PP | B |
|---|---|---|---|---|---|
| Raw water | 0.00 | 0.009371 | 0.016076 | 0.00612 | 0.017463 |
| Conv coag PP | | 0.00 | 0.007021 | 0.01 | 0.00849 |
| S2 MIEX MF | | | 0.00 | 0.0159 | **{0.001895}** |
| Raw MF PP | | | | 0.00 | 0.017058 |
| B | | | | | 0.00 |

Cluster C

| | Raw water | Conv coag PP | Raw MF PP | C |
|---|---|---|---|---|
| Raw water | 0.00 | 0.009371 | **{0.00612}** | 0.01676984 |
| Conv coag PP | | 0.00 | 0.01 | **{0.00775582}** |
| Raw MF PP | | | 0.00 | 0.01647875 |
| C | | | | 0.00 |

Cluster D

| | Conv coag PP | C | D |
|---|---|---|---|
| Conv coag PP | 0.00 | **{0.007756}** | **{0.009686}** |
| C | | 0.00 | 0.016624 |
| D | | | 0.00 |

Cluster E

| | D | E |
|---|---|---|
| D | 0.00 | 0.013155 |
| E | | 0.00 |

remove DOM larger than 40 nm (membrane pore size 0.04 µm) in diameter. This statement also confirmed from Fig. 2 where MIEX combined with MF and MIEX alone removed broad range of organics. The distances to each of the remaining clusters were then calculated as the average from the new cluster to each of the remaining ones, as shown in Table 2. This process was continued until there are only two final cluster populations. Each of the columns in Table 2 represents a distinct cluster population and rows show the treatment variable which characterized each population. The distances between the populations were calculated using Eq. (2) shown below:

$$d = \sqrt{\sum_{i=1}^{k} (x_i - y_i)^2} \qquad (2)$$

where $k=7$ for the seven variables from raw water to MIEX MF PP. The distance $d$, is the distance between any two populations, e.g. raw water and MIEX.

It is clear that the closest distance is between MIEX alone and MIEX MF, with a Euclidian distance of 0.0007 and these two cluster populations were combined, referred to as Cluster A.

The distance between Clusters A and S1 MIEX Conv Coag (0.0010) was then used to produce Cluster B (Table 2). Cluster C was formed by the combination of Cluster B and S2 MIEX MF (0.0019). The Euclidean distance between Cluster C and Conv Coag PP was 0.0077, producing Cluster D, and the distance between Clusters D and E was 0.0132. Cluster E was produced from the raw water and MF (0.0061).

### 3.4.1. *k*-Means cluster

Fig. 5 shows clustering of means of peak areas for organics of treated waters by MIEX, conventional coagulation, and MF over time (from August 2005 to December 2006). It was determined that processes with MIEX showed similar treatment efficiencies throughout the study, based on removal of NOM and were therefore combined. The means of overall peak areas generated by MIEX treatment processes were very similar to each other so they were combined to formed a cluster (Cluster 2). Similarly, the efficiency of conventional treatment based on peak area reductions was entirely different to other treatment methods and therefore, formed a separate cluster (Cluster 3). Microfiltration performance for removal of NOM was of minimum effect and therefore similar to raw water throughout this study. This resulted in generation of similar peak area means and accordingly these two clustered together (Cluster 1).

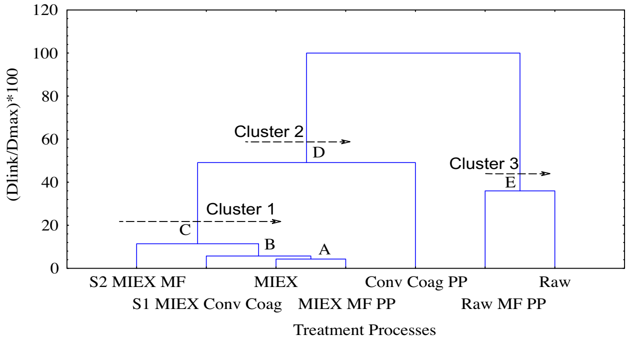

Fig. 4. Dendrogram showing three distinct Clusters C (A and B), D, and E for water qualities before and after treatment based on total peak areas.

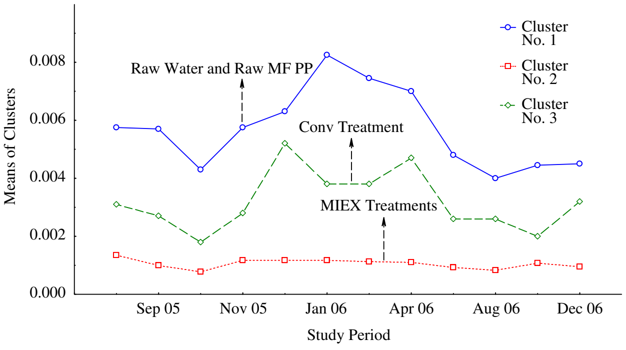

Fig. 5. Clustering of peak areas of organics in waters following treatment by (1) MF, (2) MIEX, and (3) conventional coagulation.

### 3.5. NOM character during the study period

CAs were also applied to data of DOC, $UV_{254}$, and SUVA to further investigate treatment trends over the study period. This was done as, although HPSEC is informative at a molecular level, when used with UV detection (at 260 nm), only a fraction of the organic matter is quantified. Assessment based on DOC provides for broader assessment in that it includes the non-UV absorbing compounds, though this generic measurement provides no information of the character of the organics, unless other information is concurrently acquired, e.g. UV absorbance for SUVA determination. Fig. 6(a–c) shows dendrograms and Fig. 6(d–f) shows *k*-mean clustering over time for DOC, UV, and SUVA, respectively, for the various water qualities before and after treatment.

The results from these analyses were similar to the application of the peak fitted data, in that there was most similarity between MIEX MF and MIEX Conv Coag, and these then being of similarity to Conv Coag and MIEX alone. All these treatments were distinct to

MF as would be expected. Interestingly, MIEX with MF or Conv Coag showed closer similarity to Conv Coag than to MIEX alone.

Specific UV absorbance (SUVA) was used to characterize organics over the period of study with respect to the extent of conjugation and aromaticity of organics in both raw and treated waters. The higher molecular weight humic acids have SUVA values between $3\,m^{-1}\,mg^{-1}\,L^{-1}$ and $5\,m^{-1}\,mg^{-1}\,L^{-1}$, whereas the medium molecular weight compounds such as fulvic acids have a SUVA value around $2\,m^{-1}\,mg^{-1}\,L^{-1}$ [32].

Clustering of data shown in Fig. 6(d–f) is detailed in Table 3. It can be seen that from these data, MIEX with an associated treatment showed consistent clustering (Cluster 3) and with least values for residual DOC and UV and SUVA values after treatment throughout the study period. These results correlate with previous studies of MIEX performance for DOC and UV abs removal [6,14,15]. However, for UV

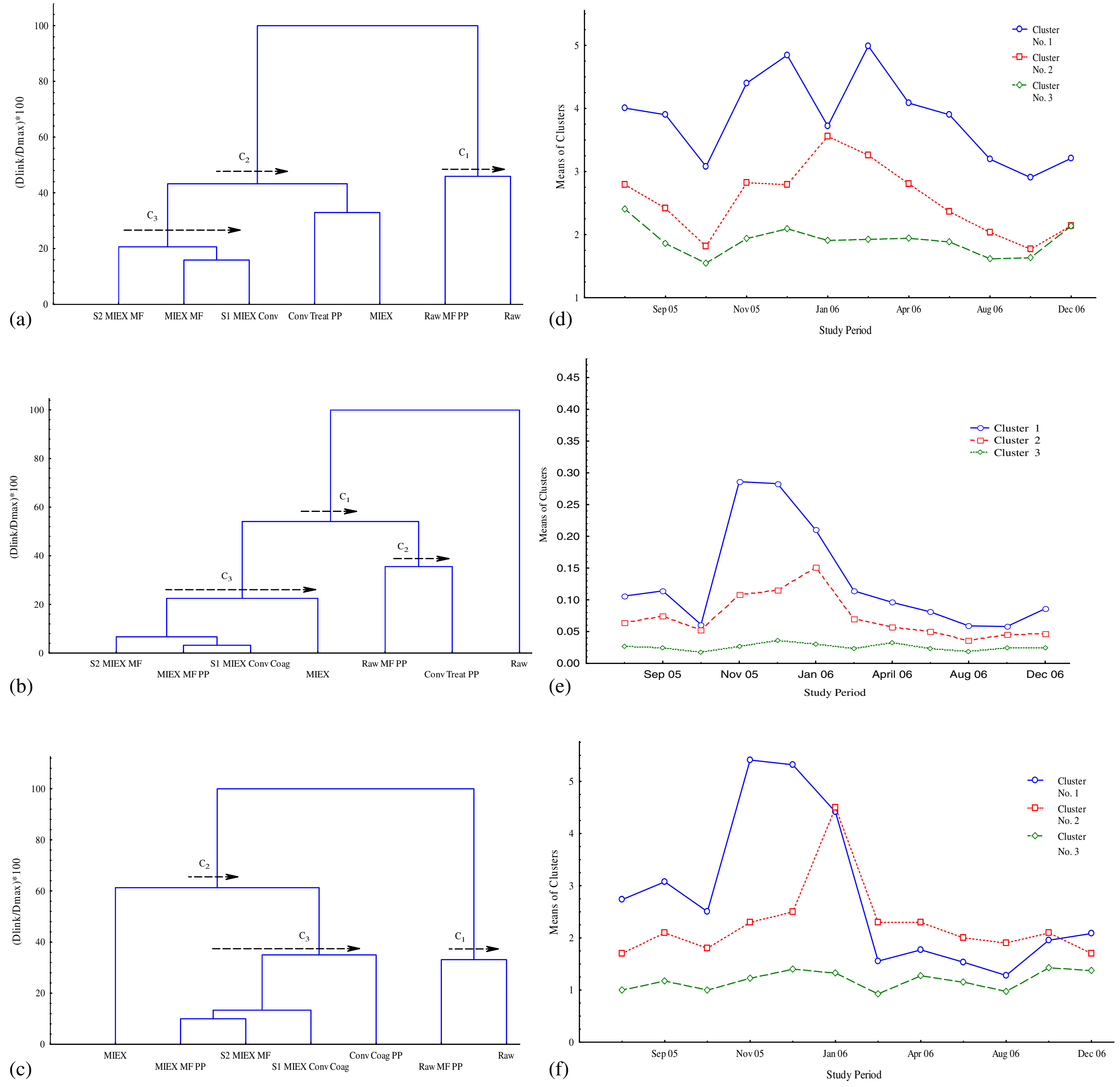

Fig. 6. Dendrograms and *k*-mean clusters for (a) DOC, (b) UV abs, and (c) SUVA.

Table 3
Distribution of treatment processes after CAs

| DOC removal ($mg\,L^{-1}$) | | | UV abs removal at 254 nm | | | SUVA ($m^{-1}\,mg^{-1}\,L^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| $C_1$ | $C_2$ | $C_3$ | $C_1$ | $C_2$ | $C_3$ | $C_1$ | $C_2$ | $C_3$ |
| Raw | Conv treatment PP | S1 MIEX conv coag | Raw | Conv treat PP | S1 MIEX conv coag | Raw | MIEX | S1 MIEX conv coag |
| Raw MF PP | MIEX | Stream 2 MIEX MF | | Raw MF PP | S2 MIEX MF | Raw MF PP | | S2 MIEX MF |
| | | MIEX MF PP | | | MIEX MF PP | | | MIEX MF PP |
| | | | | | MIEX | | | Conv treatment PP |

absorbance (and SUVA) data, the distinct treatment of coagulation, also clustered with MIEX and associated treatments. MIEX alone clustered separately (Cluster 2) indicating distinct effects from this with the two other MIEX treatment methods (with coagulation and MF). The data indicated that temporal effects likely to be from seasonal effects on water quality impacted on the efficiencies of Clusters 1 and 2 treatments but not on those of Cluster 3. This infers that the MIEX treatment with associated MF or coagulation provided for the most consistent and highest level of treated water quality, based on residual chromophoric organics.

It is clear from CAs (tree joining and *k*-mean) of HPSEC–UV peak fitting, DOC, $UV_{254}$ and SUVA data that MIEX alone and its combined treatment processes produced better treated water quality throughout the study period as compared to the conventional treatment and microfiltration. Although, including other more advanced NOM characterization technique can be useful and always there has been an argument regarding HPSEC–UV excluded the fractions of DOM that contain single-carbon bond (non$UV_{260}$ absorbing DOM) but this case study described the additional information and interpretation can be obtained from simple and cost-effective characterization technique such as HPSEC–UV.

## 4. Conclusions

A new way of statistical approach to present the NOM removal provided the better understanding of this long-term study. In this study, we examined changes in the character of most of the chromophoric NOM in both raw and treated waters based on their molecular weight profiles determined by HPSEC. This provided improved information on the removal efficiencies of processes involving MIEX alone and in combination with conventional treatment and microfiltration. Treatment incorporating MIEX alone and combined with conventional or microfiltration resulted in higher percentage removals of organics represented by all fitted HPSEC peak areas. Cluster analysis was applied to HPSEC peak fitted areas of both raw and treated waters as well as for DOC, $UV_{254}$, and SUVA data. From these analyses, it was found that strong associations exist between MIEX alone and MIEX combined with other treatment processes. Moreover MIEX combined with coagulation showing the highest NOM removal (below 700 Da MW). MIEX alone still removed the majority of NOM and by comparison alum coagulation tended to remove the high molecular weight (>1000 Da) compounds only. The NOM characterization techniques and novel statistical approaches reported here used for assessment of water treatment efficiencies should provide further benefit to operations engineers for optimum selection of the treatment process for most of the chromophoric NOM removal, under varying water quality conditions.

## Symbols

| | | |
|---|---|---|
| $(x_1, y_1)$ | — | coordinates of the first point |
| $(x_2, y_2)$ | — | coordinates of the second point |
| $d$ | — | distance between two points |
| $\sum$ | — | summation |

## References

[1] P.S. Murdoch, J.S. Baron, T.L. Miller, Potential effects of climate change on surface-water quality in North America, J. Am. Water Works Assoc. 36 (2000) 347–366.

[2] T. Fukushima, N. Ozamki, H. Kaminishi, H. Harasawa, K. Matsushige, Forecasting the changes in lake water quality in response to climate changes, using past relationships between meteorological conditions and water quality, Hydrol. Process. 14 (2000) 593–604.

[3] B.S. Caruso, Temporal and spatial patterns of extreme low flows and effects on stream ecosystems in Otago, New Zealand, J. Hydrol. 257 (2002) 115–133.

[4] S.R. Sarathy, M. Mohseni, The impact of UV/$H_2O_2$ advanced oxidation on molecular size distribution of chromophoric natural organic matter, Environ. Sci. Technol. 41 (2007) 8315–8320.

[5] C.W.K. Chow, R. Fabris, J. van Leeuwen, D.S. Wang, M. Drikas, Assessing natural organic matter treatability using high performance size exclusion chromatography, Environ. Sci. Technol. 42 (2008) 6683–6689.

[6] M. Drikas, M. Dixon, J. Morran, Long term case study of MIEX pre-treatment in drinking water; understanding NOM removal, Water Res. 45 (2011) 1539–1548.

[7] G. Crozes, P. White, M. Marshall, Enhanced coagulation: Its effect on NOM removal and chemical costs, J. Am. Water Works Assoc. 87 (1995) 78–89.

[8] M.C. White, J.D. Thompson, G.W. Harrington, P.C. Singer, Evaluating criteria for enhanced coagulation compliance, J. Am. Water Works Assoc. 89 (1997) 64–77.

[9] K. Bell-Ajy, M. Abbaszadegan, E. Ibrahim, D. Verges, M. LeChevallier, Conventional and optimized coagulation for NOM removal, J. Am. Water Works Assoc. 92 (2000) 44–58.

[10] C.W.K. Chow, J.A. van Leeuwen, R. Fabris, M. Drikas, Optimised coagulation using aluminum sulfate for the removal of dissolved organic carbon, Desalination 245 (2009) 120–124.

[11] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, T. Matsuura, Application of coagulation–ultrafiltration hybrid process for drinking water treatment: Optimization of operating conditions using experimental design, Sep. Purif. Technol. 65 (2009) 193–210.

[12] J.Y. Morran, D.B. Bursill, M. Drikas, H. Nguyen, A new technique for the removal of NOM, in: Proceeding of the AWWA Water TECH Conference, Sydney, Australia.

[13] M. Drikas, J.Y. Morran, C. Pelekani, C. Hepplewhite, D.B. Bursill, Removal of natural organic matter—a fresh approach, Water Sci. Technol. Water Supply 2 (2002) 71–79.

[14] C. Chow, M. Drikas, ad.D. Cook, Evaluation of magnetic ion exchange resin (MIEX) and alum treatment for formation of disinfection by-products and bacterial regrowth, Water Sci. Technol. Water Supply 2 (2002) 267–274.

[15] H. Humbert, H. Gallard, V. Jacquemet, J.P. Croue, Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water, Water Res. 41 (2007) 3803–3811.

[16] T. Boyer, H. Singer, Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors, Water Res. 39 (2005) 1265–1276.

[17] D.A. Fearing, J. Banks, S. Guyetand, C.M. Eroles, B. Jefferson, D. Wilson, P. Hillis, A.T. Campbell, S.A. Parsons, Combination of ferric and MIEX (R) for the treatment of a humic rich water, Water Res. 38 (2004) 2551–2558.

[18] B.P. Allpike, A. Heitz, C.A. Joll, R. Kagi, G. Abbt-Braun, F. Frimmel, T. Brinkmann, N. Her, G. Amy, Size exclusion chromatography to characterize DOC removal in drinking water treatment, Environ. Sci. Technol. 39 (2005) 2334–2342.

[19] P. Jarvis, M. Mergen, J. Banks, B. McIntosh, S.A. Parson, B. Jefferson, Pilot scale comparison of enhanced coagulation with magnetic resin plus coagulation systems, Environ. Sci. Technol. 42 (2008) 1276–1282.

[20] P.C. Singer, M. Schneider, J. Edwards-Brandt, G.C. Budd, Magnetic ion exchange for the removal of disinfection byproduct precursors: Pilot plant findings, J. Am. Water Works Assoc. 99 (2007) 128–139.

[21] M. Drikas, M. Dixon, J. Morran, Removal of MIB and geosmin using granular activated carbon with and without MIEX pre-treatment, Water Res. 43 (2009) 5151–5159.

[22] M.B. Dixon, J. Morran, M. Drikas, Extending membrane longevity by using MIEX as a pre-treatment, J. Water Supply Res. Technol. AQUA 59 (2010) 92–99.

[23] D.S. Wang, H.X. Tang, J. Gregory, Relative importance of charge neutralization and precipitation on coagulation of kaolin with PACI: Effect of sulfate ion, Environ. Sci. Technol. 36 (2002) 1815–1820.

[24] G. Abbt-Braun, U. Lankes, F. Frimmel, Structural characterization of aquatic humic substances—the need for a multiple method approach, Aquat. Sci. 66 (2004) 151–170.

[25] B.P. Allpike, A. Heitz, C.A. Joll, R.I. Kagi, Size exclusion chromatography to characterize DOC removal in drinking water treatment, Environ. Sci. Technol. 39 (2005) 2334–2342.

[26] Q. Zhou, S.E. Cabaniss, P.A. Maurice, Considerations in the use of high pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances, Water Res. 34 (2000) 3505–3514.

[27] M. Drikas, C.W.K. Chow, D. Cook, The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth—an evaluation of magnetic ion exchange resin (MIEX®) and alum coagulation, J. Water Supply Res. Technol. AQUA 25 (2003) 475–487.

[28] B. Bolto, D. Dixon, R. Eldridge, S. King, Cationic Polymer and clay or metal oxide combinations for natural organic matter removal, Water Res. 35 (2001) 2669–2676.

[29] E.T. Gjessing, J.J. Alberts, A. Bruchet, P.K. Egeberg, E. Lydersen, L.B. Mcgrown, J.J. Mobed, U. Munster, J. Pempkowiak, M. Perdue, H. Ratnawerra, D. Rybacki, M. Takacs, G. Abbt-Braun, Multi-method characterization of natural organic matter isolated from water: Characterization of reverse osmosis-isolates from water of two semi-identical dystrophic lakes basins in Norway, Water Res. 32 (1998) 3108–3124.

[30] D. Wang, L. Xing, J. Xie, C.W.K. Chow, X. Zhizhen, Y. Zhao, M. Drikas, Application of advanced characterization techniques to assess DOM treatability of micro-polluted and unpolluted drinking source waters in China, Chemosphere 81 (2010) 39–45.

[31] J. Kaewsuk, G.T. Seo, Verification of NOM removal in MIEX-NF system for advances water treatment, Sep. Purif. Technol. 80 (2011) 11–19.

[32] N. Tambo, T. Kamei, Coagulation and flocculation on water quality matrix, Water Sci. Technol. 37 (1998) 31–41.