Assessing Natural Organic Matter Treatability Using High Performance Size Exclusion Chromatography

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This paper reports the use of high performance size exclusion chromatography (HPSEC) as a tool to assess NOM removal by coagulation. Quantitative information such as percentage removal can be determined after “peak-fitting” the HPSEC molecular weight profile of the source water. A peak-fitting approach was developed based on the molecular weight profile of dissolved organic matter from surface water. A sequential jar testing procedure with five treatment steps was used to characterize organics and to confirm that several NOM components were recalcitrant to coagulation with alum. Despite differences found in both the concentration and character of NOM in three surface waters studied, the final concentrations and characteristics (e.g., molecular weight profile) were very similar after five treatment stages. The molecular weight profiles of the recalcitrant organics were subsequently used to build a peak-fitting technique for NOM removal. The approach was validated by further jar test results of several other water sources, such as ground and river waters, including one found to be very difficult to treat in terms of NOM removal by alum treatment. Predictions of removable and nonremovable organic fractions by coagulation using this peak fitting technique were found to be within 10% of actual values.

Introduction

The quality of drinking water in relation to public health is an important issue worldwide, and operators of water utilities have become more aware of the impact of natural organic matter (NOM) on their treatment processes. NOM is a complex matrix of heterogeneous organic material which can be sourced from decaying terrestrial vegetation and aquatic organisms. Its presence in source water can be problematic in the production of drinking water, and it is always considered as a key factor in the determination of both coagulant and disinfectant doses. Furthermore, NOM can react with disinfectants to produce disinfection byproduct (DBPs) and can also act as a carbon food source for bacterial growth in distribution systems (1, 2).

In recent years, considerable research effort has been made on improved understanding of NOM in drinking water. A number of characterization techniques have been developed to provide better understanding of the types of organic compounds present before and after the treatment. Simple techniques such as color, dissolved organic carbon (DOC), and UV absorbance (UVabs or UV₂₅₄) measurements offer limited information on the character of NOM. More advanced methods, such as pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS), solid state C¹³ nuclear magnetic resonance (NMR) spectroscopy, and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, can give greater insight into macromolecular compositions of NOM but are more labor intensive and complex in sample preparation and analyses and require access to suitable analytical instrumentation. Application of these techniques can provide improved understanding of the impact of NOM in treatment processes. However, the results from these types of analyses are not in a form that can be readily applied to assist the operation of a water treatment plant. A suitable analytical tool to assist plant operators should be both practical and sufficiently informative to enable the information to be readily used to optimize or to reach some water quality target(s) in treatment.

High performance size exclusion chromatography (HPSEC) has become a popular technique as an analytical tool for organic characterization studies in the water field (3–6). To date the reported applications have mainly generated qualitative information based on comparisons between raw and treated waters or waters from different stages of the treatment processes. Few studies have attempted to extract quantitative information to correlate with operational performance.

This paper assesses the application of a “peak fitting” technique to resolve the chromatographic peaks of HPSEC to provide quantitative information on DOC removal by alum treatment from the character of NOM in raw surface waters. This is done by identifying the removable and nonremovable components of DOC from the chromatograms. The developed technique was then applied to groundwater and river sources to predict the treatability of NOM from those sources with alum.

Materials and Methods

Water Sources. Water samples from different locations throughout Australia were sourced for this study. Water samples were chosen to represent the wide variation in water quality found in Australia and included both surface and ground waters. Surface water samples from three drinking water supply reservoirs, Myponga (South Australia), Moorabool (Victoria) and Hope Valley (South Australia) were chosen for detailed assessment.

Chemicals. Aluminum sulfate stock solution (20 000 mgL⁻¹ as Al₂(SO₄)₃·18H₂O) was prepared in ultrapure water from liquid aluminum sulfate (approximately 7.5% as Al₂O₃) as used for commercial water treatment. Sodium hydroxide and hydrochloric acid were analytical grade.

Analyses. Turbidity measurement was carried out using a turbidity meter (2100AN, Hach, U.S.). DOC was determined using a total organic carbon analyzer (model 820, Sievers Instruments Inc., U.S.). The absorbance at 254 nm (UV₂₅₄) was measured using a UV/vis spectrophotometer (model 918, GBC Scientific Equipment Ltd., Australia) with a 1 cm quartz cell. Standard methods (7) were used for the measurements mentioned above. Color was measured through a 5 cm cell at 456 nm against a Pt/Co standard (8). Samples

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for color, UV absorbance and DOC were filtered through 0.45 μm membranes.

The apparent molecular weight (AMW) of the NOM constituents was determined by HPSEC using a Waters 2690 separation module and 996 photodiode array detector operating at 260 nm. Separation was performed with a Shodex KW 802.5 column (Shoko Co. Ltd., Japan) and a 0.1 M phosphate buffer solution (pH 6.80, ionic strength adjusted to 1.0 M with sodium chloride). The flow rate was 1 mL/min and the injection volume was 100 μL . The column had an effective resolving range of 50 to 50 000 Daltons (Da) and the retention time was calibrated for AMW using polystyrene sulfonate (PSS) standards (Polysciences Inc., U.S.) of molecular weights 35 000, 18 000, 8000, and 4600 Da. This procedure was adapted from the method described by Chin et al. (9).

Treatment Strategies (Jar Tests). Alum was used as coagulant and jar tests were performed with and without pH control. For experiments with pH control, the amount of acid or alkali required to achieve the target pH was determined by prior pH titration and then added before the addition of coagulant for pH control. A FMS6V (SEM Pty Ltd. Brisbane Australia) variable speed, six paddle gang stirrer with 7.6 cm diameter flat paddle impellers and Gator jars was used. Water samples (2 L) were placed on the gang stirrer with six samples tested at a time and the coagulant added while stirring at 220 rpm ($G = 480 \text{ s}^{-1}$). After 1 min of flash mixing at 220 rpm, the speed was reduced to 25 rpm ($G = 18 \text{ s}^{-1}$) for 14 min. The samples were then allowed to settle for 15 min. The settled water samples were gravity filtered using 11 μm pore-size paper filters (Whatman International Ltd., UK). With the exception of turbidity, the water quality parameters of color, DOC, UV_{254} and AMW were filtered through 0.45 μm before analysis. The optimum dose was determined based on the following treated water quality parameters: residual aluminum less than or equal to 0.2 mg/L, filtered turbidity less than or equal to 0.5 NTU and color 10 HU or less.

For the sequential treatment (treated water collected and retreated) experiment, a similar jar testing procedure was used in five repeated treatments using the determined optimum alum dosage at pH 6 in each treatment. Treated water samples from each treatment step were analyzed for turbidity, color, DOC, UV_{254} , and AMW as previously indicated.

Data Analysis. Chromatograms were analyzed using a peak fitting technique to resolve the overlapped peaks. Peakfit (Version 4, Systat Software Inc.), a commercially available software, was used for this analysis. The peak fitting procedures used in this study were separated into two steps: optimization and analysis. The optimization step determined the optimum peak fitting parameters, such as peak type and fitting method using simulated chromatograms created by mathematical addition of known molecular weight standard peaks (Figure 1). The analytical stage analyzed the chromatograms of different samples (those not used to build the peak-fitting model) using the determined optimum parameters. The peak area under each peak was subsequently determined.

Results and Discussion

Organic Characterization using High Performance Size Exclusion Chromatography. HPSEC has been shown to be a useful technique for evaluating various water treatment processes (10–13). It separates NOM constituents based on a differential permeation process, according to molecular weight (size). NOM is eluted through a porous solid phase; large molecules are unable to penetrate the pores so elute more quickly than small molecules, which are adsorbed and therefore elute more slowly. The AMW of the eluting fractions can be determined by calibration of retention time using

FIGURE 1. Peak fitting optimization and validation. (a) Chromatograms of individual molecular weight standards, (b) individual peaks in (a) mathematically added and (c) peaks resolved by peak fitting.

known molecular weight standards, such as polystyrene sulfonate (PSS) or polyethylene glycol (PEG). While these compounds may not necessarily be representative of the true hydrodynamic size of NOM molecules during analysis, the calibration process can provide a measure of “apparent” molecular weight (AMW) that is reproducible across the life of the column and can provide good consistency for comparison of chromatograms determined at different times (different batches).

NOM removal from drinking water can be determined by comparing molecular weight profiles before and after treatment (10–15). However, this can only provide basic qualitative information, and therefore the focus in this study has shifted to attempts to obtain more quantitative information by applying a peak-fitting technique. The objective was to allow for the prediction of removable or nonremovable NOM fractions from a chromatogram of the source water.

Optimisation of Peak Fitting Parameters. While most peak fitting software is capable of performing autofitting algorithms to obtain statistically ideal fits using unlimited numbers of component peaks with various shapes, it was deemed important for development of the peak fitting technique to ensure that the results closely matched that of the actual molecular weight character of natural water NOM and its fractional components. To setup the peak fitting technique, an appropriate peak type (peak shape) had to be selected to correctly represent the peaks generated from the HPSEC analysis. An initial optimization using chromatograms from low polydispersity standards confirmed that all 12 “chromatography peak types” provided by the Peakfit software achieved r^2 value of 0.985 with five achieving r^2 values of 0.999. From this result, “Log Normal-4 Area” was chosen as the best peak type to represent surface water NOM peaks obtained and thus it was selected for further work.

To validate the accuracy of the peak separation process, a simulated chromatogram was created by mathematical addition of five different molecular weight standards in the range of 1–100 kDa (Figure 1a and b). Following through the chosen peak fitting procedure, it was shown that all five peaks could be resolved again from the simulated chromatogram. By comparing Figure 1a (original peaks) and Figure 1c

(resolved peaks), it is confirmed that the peak fitting parameters were correctly chosen and the determined peak areas were within 10% variation compared with the actual peaks.

The Character of the Recalcitrant Organics. Turbidity and color removal are key operational parameters in drinking water treatment. There are several ways that an optimum coagulant dose can be determined based on different criteria, i.e. the minimum coagulant dose that results in target values for a set number of parameters or the minimum coagulant dose that provides an acceptable treated water quality and where further dosing does not result in any significant improvement. In the present study, the term optimum dose was based on the criteria of residual aluminum ≤ 0.2 mg/L, filtered turbidity ≤ 0.5 NTU and color ≤ 10 HU. In general, the reduction of turbidity and color by alum coagulation can be readily achieved.

Three source waters with different water quality characteristics were selected for this study. Samples from Hope Valley Reservoir had low DOC (3.9 mg/L) and color (9 HU), Moorabool Reservoir had moderate DOC (6.9 mg/L) and color (17 HU) and Myponga Reservoir had high DOC (9.0 mg/L) and color (64 HU). A five-stage sequential treatment procedure, with alum doses of 30 mg/L alum for Hope Valley Reservoir, 80 mg/L alum for Moorabool Reservoir and 100 mg/L alum for Myponga Reservoir for each stage, was applied to determine the DOC reduction possible by alum coagulation and subsequently the character of the recalcitrant (to removal by alum) organics. These doses were selected based on those determined to be "optimum" by prior jar tests performed at pH 6.

In this sequential treatment, the majority of reductions in color and UV_{254} were achieved during the first treatment stage with little or no apparent further improvement of these parameters in the subsequent treatment stages (12). Similarly, the efficiency of DOC removal declined considerably with more sequential treatment stages. This efficiency reduced such that further DOC removal was minor or no longer evident in the treated water after the second stage of coagulation. Despite differences in the DOC concentrations of the source waters, the final DOC concentrations after five treatment stages for all three waters were similar.

Typically, DOC in natural waters includes humic substances (fulvic and humic acids) as well as smaller molecular weight proteins, carbohydrates, and amino acids (16, 17). Certain fractions of NOM, i.e., hydrophobic and higher molecular weight NOM are more effectively removed than other NOM fractions. Some waters with a dominance of lower-molecular weight NOM are difficult to treat by coagulation (18). In some studies it has been found that there is preferential removal of NOM that absorbs ultraviolet light (chromophores), indicating a preferential removal of conjugated or aromatic organic constituents (18).

The specific UV absorbance (SUVA), $UV/DOC \times 100$, can be used to determine the character of the organics with respect to degree of conjugation and aromaticity in both source and treated waters (19). The higher molecular weight humic substances, i.e., humic acids, are characterized as substances having SUVA values between 3 and 5, whereas the medium molecular weight compounds such as fulvic acids have a SUVA value around 2 (20). Raw water from Myponga Reservoir has a high SUVA value ($4.5 \text{ m}^{-1}\text{mg}^{-1}\text{L}$) which indicates a high proportion of humic acids, whereas Hope Valley ($2.5 \text{ m}^{-1}\text{mg}^{-1}\text{L}$) and Moorabool ($2.6 \text{ m}^{-1}\text{mg}^{-1}\text{L}$) reservoirs have lesser humic character. However, after the sequential treatment all waters have a similar value ($1.3\text{--}1.6 \text{ m}^{-1}\text{mg}^{-1}\text{L}$), indicating a similarity in the remaining organic character (Supporting Information Figure S.1).

The chromatograms of the three raw waters show that the AMW distribution is spread from about 500 to several

thousand Daltons. In order to make a comparison of the chromatograms, the weight-averaged molecular weight (MW) was used. The equation for this calculation is as follows:

$$MW = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad (1)$$

The MWs of the raw water samples calculated using this equation show that the sample for Myponga Reservoir (MW = 1500 Da) had the highest MW value, whereas Hope Valley Reservoir (MW = 1100 Da) had the lowest. This is consistent with the generally held contention that the humic acid fraction of the NOM has higher SUVA and higher molecular weight (19). Of the raw waters studied, the NOM in the Myponga Reservoir sample had the highest SUVA and MW value which indicates a higher portion of humic acid materials compared with Hope Valley and Moorabool reservoirs.

The high molecular weight portions of the raw water samples were largely removed after the five treatments (12). The HPSEC results indicate that the humic acid fraction in the NOM of the three waters was predominantly removed by alum treatment. These results correlate well with the overall DOC removal and SUVA reduction that suggests that the humic acid fraction was most effectively removed by coagulation/flocculation.

In all waters studied, the organic fraction remaining after the five stage sequential treatment with alum was of low molecular weight (MW approximately 600 Da) and all three waters had similar SUVA and HPSEC implying that the characteristics of the remaining compounds in all three waters were very similar in molecular size and aromatic content. In other words, compounds that were not removed by alum treatment had similar characteristics (Supporting Information Figure S.2).

Development and Validation of the Peak Fitting Model.

In Figure 2a, the chromatograms of raw Myponga water and treated waters after 1, 3, and 5 successive application of 100 mg/L alum doses are presented. There was a general removal of the higher molecular weight aromatic organic compounds (such as humic substances). As previously explained, the majority of removal occurred during Stage 1 treatment and efficiency reduced in subsequent steps. The removal between Stage 3 and Stage 5 was only marginal (Figure 2a).

In Figure 2b, the HPSEC profile of the raw water was processed using the developed peak fitting procedure. Six peaks were identified in the raw water NOM profile and the MW of the resolved peaks were calculated to be 50 000 Da (Peak 1), 1900 Da (Peak 2), 1200 Da (Peak 3), 800 Da (Peak 4), 500 Da (Peak 5), and 300 Da (Peak 6). These can be associated with the chemical groups of organometallic colloids and biological residues (Peak 1), high molecular weight humic substances (Peak 2), low molecular weight humics (Peaks 3 and 4), building blocks (Peak 5), and low molecular weight acids and nitrogen containing aromatics (Peak 6) (4, 21).

Figure 2c highlights the region between 100–2000 Da after the successive application of alum. After processing using the peak fitting procedure, four peaks were identified and the MWs of the resolved peaks were calculated to be 300, 500, 800, and 1100 Da, respectively. A comparison of the raw water HPSEC profile with the successive treatments indicated that the two peaks of higher molecular weight (MW: 50 000 Da—Peak 1 and 1900 Da—Peak 2) were readily removed by the first alum dose. Although further addition of alum resulted in reduction of the 1200 Da (Peak 3) and some reduction of the 800 Da (Peak 4), a significant proportion of the 1200 Da (Peak 3) was still present, even after five successive alum treatments. Both 500 Da (Peak 5) and 300 Da (Peak 6) remained unchanged.

FIGURE 2. Molecular weight profiles of Myponga water (a) raw and treated (stage 1, 3, and 5), (b) raw with peak fitting, (c) after sequential treatment (successive application of 100 mg/L alum doses).

TABLE 1. Percentage Distribution of the Resolved Peaks Labelled with Chemical Groups after Peaking Fitting Model Applied and Predicted DOC Removal Compared with Actual DOC Removal from Jar Testing^a

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	DOC removal			
							predicted		actual	
	inorganic colloids and biological residues	humic substances (nonpolar)	low MW humics 2	low MW humics 1	building block	N-containing aromatics	easy removal	maximum removal	1st step	5th step
Myponga	4%	50%	17%	14%	10%	5%	54%	71%	63%	68%
Moorabool	2%	43%	22%	19%	9%	5%	45%	67%	49%	59%
Hope Valley	0%	28%	23%	7%	18%	24%	28%	52%	32%	42%

^a Predicted DOC Removal: Peak 1 + Peak 2, easily removable organics; Peak 1 + Peak 2 + Peak 3, maximum removable organics; Peak 4 + Peak 5 + Peak 6, nonremovable organics.

This suggests that these recalcitrant fractions (Peaks 4, 5, and 6, and a small portion of Peak 3) cannot be removed by conventional water treatment and the character of the recalcitrant organics is captured in these four peaks resolved by the peak fitting procedure. By using the known character of the recalcitrant organics (peak fitting approach), it is therefore possible to predict the removable organic components from the raw water HPSEC profile. The HPSEC

profiles of the three selected waters were analyzed using the peak fitting technique and the peak areas of the resolved peaks are presented in Table 1. It is notable that the low MW humic group was separated into two fractions (Low MW Humics 1 and 2). As evidenced in Figure 2c, the reduction of the Low MW Humics 2 fraction (Peak 3) and Low MW Humics 1 (Peak 4) was different after successive applications of alum treatment.

FIGURE 3. Comparison of NOM molecular weight profiles for different water sources.

TABLE 2. Percentage Distribution of Chemical Groups Determined by Peak Fitting and Predicted DOC Removal for Various Water Sources^a

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Total	easy removable	max removable	nonremovable			
	inorganic colloids and biological residues	humic substances (nonpolar)	low MW humics 2	low MW humics 1	Building Block	N-containing aromatics	DOC (mg/L)	Percent (%)	DOC (mg/L)	percent (%)	DOC (mg/L)	percent (%)	DOC (mg/L)
Ground Water	10%	65%	10%	8%	5%	2%	11.5	75	8.6	85	9.8	15	1.7
Surface Water	2%	57%	11%	14%	8%	9%	12.6	59	7.4	70	8.8	30	3.8
River	0%	25%	20%	32%	11%	13%	6.1	25	1.5	45	2.7	55	3.4
Protected Catchment	0%	35%	26%	21%	9%	9%	3.2	35	1.1	61	2.0	39	1.3
Prolonged Storage	0%	29%	25%	25%	9%	12%	36.0	29	10.5	54	19.4	46	16.6

^a Predicted DOC Removal: Peak 1 + Peak 2, easily removable organics; Peak 1 + Peak 2 + Peak 3, maximum removable organics; Peak 4 + Peak 5 + Peak 6, nonremovable organics.

From the model, Peak 1 and Peak 2 are removed easily by coagulation. Peak 3 can be reduced by “enhanced” coagulation. Peaks 4, 5, and 6 are recalcitrant organics. Based on this hypothesis, the peak fitting model can be used to predict organic removal under conventional coagulation and “enhanced” coagulation. The predicted organic carbon removal for both easy (peak areas of Peak 1 + Peak 2) and maximum (peak area of Peak 1 + Peak 2 + Peak 3) removal from the three raw waters based on peak fitting of the raw water HPSEC profiles was determined and presented in Table 1. The result was compared with the actual DOC removal from jar testing data, Step 1 of the sequential treatment procedure representing easily removable organics and Step 5 maximum removal. The results of the predicted removals matched well with actual data (between 3 and 10% variation).

Treatability Prediction: Application of Peak Fitting. The HPSEC profile is useful in characterizing water quality and it is also a versatile tool which can be used to assess NOM removal based on the character of the organics (molecular weight profile) of the source water. In addition to the previously evaluated waters, five different drinking water sources from various locations within Australia were analyzed by HPSEC to enable a comparison of molecular weight profiles of different sources, namely protected and unprotected (reservoir) surface catchments, rivers, groundwaters, and an “unusual” source after prolonged open storage. Aside from the obvious difference in NOM concentration, the profiles indicate several notable differences in NOM character, as shown in Figure 3a. It is evident from the water samples presented that the river

and protected catchment sources contained substantially lower DOC concentrations (Protected Catchment 3.2 mg/L and River 6.1 mg/L) than the other water sources (Reservoir 12.6 mg/L and Groundwater 11.5 mg/L) and their profiles were characterized by lower average molecular weights (MW: River 1000 Da and Protected Catchment 900 Da). The reservoir and groundwater sources exhibit similar molecular weight profiles (MW: Surface reservoir water 1300 Da; and Groundwater 1500 Da) and both had higher DOC concentrations and comprised higher molecular weight fractions, relative to the river water sources. These differences were related to both the character and amount of seasonal carbon loading experienced by these water storages and also the influences of residence time and biodegradation. Of the high DOC waters, perhaps the most significant difference between the reservoir and groundwater was the presence of early eluting colloidal fractions, i.e., the peaks above 50 000 Da. The composition of NOM responsible for these high MW fractions is clearly different for each of the water sources. While this multicomponent peak has been reported to compose of some NOM-metal complexes (4) and/or complex amino sugars from bacterial cell walls and other biological sources (22, 23), the proportions and spectral properties of each differ considerably. While the groundwaters typically contain larger amount of high SUVA organometallic complexes, resulting in a sharp pronounced peak, the reservoir sources typically contain more of the low UV adsorbing biological components, resulting in a comparatively smaller, broad colloidal peak.

A detailed analysis of the molecular weight profile of each water was conducted using the peak fitting technique. The resolved peaks for each water source after peak fitting are presented in Figure 3b, c, d, and e. The peak area calculation is presented in Table 2. Using the previously defined terminology of easily removable organic carbon, maximum removable organic carbon and nonremovable organic carbon, the treatability of the four selected water sources can be predicted and compared (Table 2). The waters with lower DOC concentration (River and Protected Catchment), contain larger portions of nonremovable organics. The waters with high DOC concentrations (Ground and Unprotected Surface), contain larger portions of easily removable organics. As a result, improved treatment of these waters is more easily achieved, as coagulation can produce larger DOC reductions. However, high percentage DOC removal from the low DOC waters by coagulation, if required, would be problematic due the recalcitrant nature of the organic composition.

In this study, an unusual water source was included to challenge this peak fitting technique and the accuracy of treatability prediction (Figure 3f). The source water (Prolonged Storage) was chosen as an example of a seasonal extreme and does not necessarily represent typical water quality throughout the year. Due to its long residence time in open storage, the NOM in the water was considered to be highly influenced by algae and concentrated through evaporation. This water exhibited a particularly high DOC (36.0 mg/L) and low SUVA of $1.3 \text{ m}^{-1}\text{mg}^{-1}\text{L}$ at the time of the investigation. From the jar test procedure applied, this water required 200 mg/L alum at pH 6.1 to achieve product water turbidity $<0.5 \text{ NTU}$ and color $<10\text{HU}$. At this dose, DOC removal was only 31%. For maximum DOC removal, 500 mg/L alum at pH 5 was required and DOC removal was 54%. These results match well with the peak fitting data and the prediction of DOC removal of 29% and 54% for easy and maximum DOC removal, respectively (Table 2).

This work has demonstrated that a peak fitting technique, developed using data from surface water coagulation studies, can be successfully applied to describe removable and nonremovable organic fractions by coagulation. Application

of this technique to nonsurface waters, such as river and groundwater sources, showed predicted removal percentages to be within 10% of actual values.

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Supporting Information Available

Figure S.1: The relationship between DOC, UV_{254} and SUVA and each treatment step for Myponga, Moorabool and Hope Valley following sequential coagulation with alum. Figure S.2: High performance size exclusion chromatograms of (a) raw water and (b) treated water after 5 stage sequential treatment for Myponga Reservoir, Moorabool Reservoir and Hope Valley Reservoir. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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