The evolution of organic character in a drought- and flood-impacted water source and the relationship with drinking water treatment
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ABSTRACT
A pilot-scale research investigation examining treatment technologies including coagulation, ion-exchange, activated carbon and membrane filtration and their impact on water quality coincided with a period of extensive variability in source water character. Distinct water quality periods as a result of extreme climatic conditions from drought to flood were observed and the natural organic matter (NOM) removal examined using a suite of organic characterisation techniques from simple ultraviolet (UV) absorbance to more advanced spectroscopic and chromatographic methods. The low specific UV absorbance (SUVA) and apparent molecular weight (AMW) distribution of the drought-impacted NOM was recalcitrant to coagulation with significant improvement in NOM removal resulting from the multi-step treatments. Among a number of discernible changes, floodwaters introduced high AMW, UV-absorbing NOM of terrestrial origin, which was shown to be more amenable to coagulation. Nevertheless the application of multi-step treatments resulted in further reduction in both the concentration and diversity of organic components. Filtration through granular activated carbon was observed to be the most variable treatment technology across the investigated period due to diminishing adsorption capacity. Conversely, the dual stage membrane filtration was shown to remove a broad range of organic matter, regardless of source water NOM concentration and character.

Key words | flood waters, GAC, MF, MIEX, NF, NOM characterisation

INTRODUCTION
The variability of supply and quality of a water source impacted by climatic extremes poses considerable challenge to drinking water treatment plant (WTP) operation, especially where treatment options are limited to traditional coagulation-based processes. Regulatory bodies worldwide promote the benefits of health and water quality risk reduction through multiple barrier treatments which have additional capacity to deal with both seasonal and non-seasonal changes (NHMRC & NRMMC 2011; WHO 2011). Difficulties can arise in defining appropriate and practical metrics that measure these benefits. An important aspect with wide reaching implications is natural organic matter (NOM) removal (Owen et al. 1995; Leenheer & Croué 2005). Both concentration and character of NOM are important in many instances, including for the estimation of treatment efficiency. A number of organic characterisation techniques exist that can provide additional information about the functionality and reactivity of NOM, however the challenge lies in making the information operationally relevant. General analytical techniques, such as dissolved organic carbon (DOC) and ultraviolet (UV) absorbance measurements, have been widely accepted by water treatment operators as parameters to assess treatment plant performance. For a better understanding of the types of organic compounds present before and after treatment, several advanced techniques can also be employed that characterise NOM using a range of parameters including humic/non-humic fractions, hydrophobic/hydrophilic character and molecular weights of the constituents.

Resin fractionation is generally used to isolate and characterise organic matter (Croué et al. 1994). A rapid
fractionation technique based on measuring the organic carbon concentrations before and after contact with the resins has been reported (Chow et al. 2004). The concentration of the four NOM fractions, very hydrophobic acids, slightly hydrophobic acids, hydrophilic charged and hydrophilic neutral, in the sample can be determined based on subtraction of the organic carbon concentrations of subsequent resin effluents. In previous work, it was established that the removal efficiency was highly influenced by the character of the fractions (Chow et al. 1999; van Leeuwen et al. 2002). These studies showed that DOC removal was dependent upon treatment conditions and that such conditions can be optimised based on the character of the organic matter present in the source water.

High performance size-exclusion chromatography (HPSEC) has proven to be a useful tool for evaluating various water treatment processes (Vuorio et al. 1998; Nissinen et al. 2001; Reemtsma et al. 2008). The change in NOM molecular weight distribution (MWD) can be determined by comparing NOM profiles before and after treatment. This approach has been utilised to investigate the impact of NOM on processes such as coagulation, disinfection and biodegradation and to assess those NOM fractions most likely to affect treatability (Gjessing et al. 1998; Bolto et al. 1999; Chow et al. 1999; van Leeuwen et al. 2002; Drikas et al. 2005).

Many investigations have examined single sources over an extended time period or a number of sources over a limited sampling duration, but few have investigated a variable source using multiple treatment options over an extended time period. In this work, a research investigation coincided with a period of extensive variability in source water quality due to two extreme climatic events, namely drought followed by flood (Whitworth et al. 2012), providing a unique opportunity to evaluate the response of selected treatment process combinations to variable NOM character and concentration.

MATERIALS AND METHODS

The source water for the investigation was from the inlet to the Mt Pleasant WTP in South Australia. This water is sourced from the River Murray via a 60 km pipeline pumping water from the river at Mannum to Adelaide. Owing to variable residence time in transit, inlet water quality at Mt Pleasant WTP may often be different from the water entering at Mannum, providing a variety of seasonal challenges to drinking water treatment. The source water was the same for all the treatment processes used. Details of the process streams are described herein.

Stream 1: conventional treatment

The pilot conventional treatment comprised of coagulation/flocculation/dual media (sand/anthracite) filtration utilising an upward flowing clarifier and gravity fed filter column. The primary coagulant was aluminium sulphate octodecahydrate (Al₂(SO₄)₃·18H₂O). In addition, a coagulant aid, either anionic polyacrylamide (LT20, BASF Performance Chemicals, Melbourne, Australia) or high molecular weight poly-DADMAC (LT425, BASF Performance Chemicals, Australia) was dosed downstream of the coagulant inline mixer as required to improve floc growth and clarified water turbidity, thus improving filter run times. Coagulation pH of 6.0–6.5 was maintained through pH adjustment (sodium hydroxide) or sodium bicarbonate buffering, depending on source water alkalinity. Optimised DOC removal was targeted through enhanced coagulation conditions throughout the investigation but due to manual control, coagulant dose changes were reactive to inlet water quality variation.

Stream 2: MIEX/coagulation

The second stream utilised product water from the full-scale Mt Pleasant WTP comprising the dual-stage process of magnetic ion-exchange contact (MIEX DOC® process, Orica, Australia) for DOC removal followed by coagulation/flocculation/dual media (sand/anthracite) filtration. The coagulant used was aluminium sulphate octodecahydrate (Al₂(SO₄)₃·18H₂O), however additional coagulant aids, LT22 and LT425 (BASF Performance Chemicals, Australia) were also dosed as required to achieve filtered water quality targets (turbidity <0.1 NTU; colour <5 HU).

Stream 3: MIEX/coagulation/GAC

The third treatment stream comprised Stream 2 water (described above) with the addition of two parallel granular
activated carbon (GAC) pilot filters (0.2 m external diameter) with gravity fed empty bed contact time of approximately 14 min at 125 L/h. The filtrate from both columns was blended in a single storage tank prior to analysis. Filtrasorb 400 GAC (Calgon Carbon Corporation, Pittsburgh, PA, USA), a bituminous coal-based GAC with effective granule size 0.55–0.75 mm was used. F400 represents the most commonly applied activated carbon in South Australian drinking water treatment.

**Stream 4: microfiltration/nanofiltration**

The dual membrane pilot plant consisted of microfiltration (MF) pre-treatment for bulk particulate removal using a single submerged hollow fibre module (Memcor CMF-S system, South Windsor, NSW, Australia) followed by a single FILMTEC NF 270-4040 spiral wound nanofiltration (NF) membrane (DOW Chemical Company, Altona, Australia). The MF system was fed with raw source water at 1,000 L/h and operated at 75% permeate recovery, producing a constant flux of 750 L/h fed to the inlet of the NF membrane. The MF membrane was automatically backwashed with permeate every 60 min and a chemical ‘clean in place’ (CIP) performed with ethylene-diamine-tetraacetic acid (EDTA)/H₂SO₄ and sodium hypochlorite at six-monthly intervals. The NF system operated in dead-end configuration at 43% permeate recovery, targeting a flux of 325 L/h. Owing to system design constraints, the NF membrane could receive neither backwashing, nor CIP and was replaced when flux declined to 280 L/h. Nominal pore size for the MF is reported as 0.2 μm with the molecular weight cut-off for the NF being 270 Da.

**Data collection**

Grab samples for DOC, colour and UV absorbance at 254 nm (UV₂₅₄) analyses were filtered through 0.45 μm pre-rinsed membranes. UV₂₅₄ and colour were measured using an Evolution 60 Spectrophotometer (Thermo Scientific, Scoresby, Australia). DOC was measured using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, Boulder, CO, USA). Low specific UV absorbance (SUVA) was calculated as UV absorbance (per metre) divided by DOC. HPSEC was analysed using a Waters Acquity H-Class system with a photodiode array detector (Waters Corporation, Rydalmere, NSW, Australia) acquiring between 200 and 460 nm and extracted at 260 nm. Phosphate buffer (0.02 M) with 0.1 M NaCl was flowed through a Shodex KW802.5 packed silica column (Showa Denko, Minato-ku, Tokyo, Japan) at 1.0 mL/min. This column provides a claimed separation range from approximately 50 to an exclusion limit of 50,000 Da. Apparent molecular weight (AMW) was derived by calibration with polystyrene sulphonate molecular weight standards of 35, 18, 8 and 4.6 kDa (Polysciences Inc., Warrington, PA, USA).

A resin fractionation technique was used to separate NOM into two fractions based on hydrophobicity. Fractions produced are defined as hydrophobics (HPO) and hydrophilics (HPI). Samples were acidified to pH 2 and passed through Supelite DAX-8 and Amberlite XAD-4 resins (Sigma-Aldrich, Castle Hill, NSW, Australia) with the effluent DOC measured and fraction concentrations determined by subtractive mass balance from the influent DOC, adapted from the method of Chow et al. (2004). Fluorescence excitation–emission matrices (EEMs) were generated on an LS55 Fluorescence Spectrophotometer (Perkin Elmer, Waltham, MA, USA). Samples were measured in a 1 cm quartz cuvette with an excitation range of 200–400 nm in 5 nm increments and emission scanned from 280 to 540 nm at 300 nm/min. Mathematical background correction using ultrapure water blanks (Milli-Q, Merck Millipore, Bayswater, Australia) was conducted to minimise matrix artefacts including Raman and Raleigh scatter lines.

**RESULTS AND DISCUSSION**

**Source water character changes**

The Murray–Darling basin is one of the world’s largest river systems with a catchment area covering 1.06 million square kilometres, or approximately 14% of Australia’s land area. Owing to the high degree of complexity and abundance of off-stream storages, the relationship of rainfall to water supplied to South Australia is indirect and inadequate for describing water supply changes to the Mt Pleasant WTP. A more applicable measure, namely the average recorded water flow in the River Murray as it entered South Australia,
was collated using information from the SA Waterconnect website (http://www.waterconnect.sa.gov.au) and is presented in Figure 1(a) for the period July 2009 to January 2012. During the course of this investigation, the source water was characterised by a number of major events (Whitworth et al. 2014) resulting in four definable water quality periods (Braun et al. 2014). In the first period (designated as the drought period), water quality was characterised by having had long exposure to environmental processes, including sedimentation, biodegradation, solar photolysis and oxidative decomposition due to long travel time from source to the abstraction point. As a result, the dissolved organics were low in UV absorbance (Figure 1(b)) which presented challenges for removal by a range of treatment processes. This is discussed more extensively in subsequent sections. From November 2009 to March 2010 (within the drought period) all treatment systems were offline for maintenance. During this time, source and treatment monitoring data was not collected. The second water quality period (pipe flush) occurred when the feed pipeline to the plant experienced significantly increased flow after a long period of low demand. This resulted in re-suspension of deposited material and reduced the water age. The third period (flood inflows) marked the arrival of flood waters from the upstream catchment, resulting in an initial large increase in DOC having high UV absorbance. The fourth period (stable) was defined by diminished UV absorbance as flows decreased and secondary catchment waters with lower DOC concentration arrived.

Despite DOC and UV<sub>254</sub> increases recorded within the pipe flush period, the AMW distribution of the UV-absorbing NOM did not change until the arrival of the flood inflows (Figure 2) when additional high AMW humic materials and organo-metallic colloids (>50,000 Da) were detected in the raw water. The presence of the organo-metallic colloids (Allpike et al. 2005) in surface water is evidence of freshly introduced allochthonous organic matter of short residence in the catchment. Owing to their...
high susceptibility to degradative processes, these organo-metallic colloids are key factors in assessing the residence time and evolution of NOM character in a source catchment with seasonal variations. This same NOM character persisted throughout the flood inflows until the DOC diminished through April and June 2011, when the colloids were no longer detectable and the AMW profile shifted away from the higher AMW humic materials. This was potentially caused both by dilution of existing DOC as the loading of soluble organic matter in the catchment area was diminished after the ‘first flush’, as well as the natural impact of biological and photo-degradation from greater residence time and better sunlight penetration within the source as high floodwater turbidity settled.

**Source water treatability**

The percentage DOC removed by the applied treatment technologies over the investigated period was calculated (Figure 3). For the multi-process treatments, the contribution of each treatment towards the total stream DOC removal was able to be partitioned either due to identical feed water (Stream 2 MIEX/coagulation and Stream 3 MIEX/coagulation plus GAC filtration) or intermediate water quality monitoring (Stream 4 MF/NF). The DOC in the drought water was highly recalcitrant to conventional coagulation (average 38% removal). From May 2011 onwards, coagulation efficiency was highly variable, consistent with the reactive nature of the control strategy with lack of automation and dependence on constant manual optimisation by the operator in response to water quality changes. However, average removal improved to 59%, consistent with the improved treatability of the floodwater organic character (Figure 3). For the MIEX/coagulation stream (Stream 2), the improvement in DOC removal (18%) above the conventional stream (Stream 1) at the time of the drought occurred because of two factors. First, the increased capacity of the dual-technology process to remove DOC and also the ability
of MIEX to remove low molecular weight organics that are less effectively removed by coagulation mechanisms alone (Morran et al. 2004; Mergen et al. 2008; Drikas et al. 2011). This difference was less marked once the pipe flush (May 2010) and flood waters arrived (11 and 14%, respectively) as there was a greater proportion of higher AMW DOC amenable to removal by coagulation. As the higher AMW DOC decreased during the stable period, the MIEX/coagulation stream again achieved greater DOC removal than the coagulation stream.

The addition of GAC filtration in Stream 3 initially proved more effective than even the combined membrane treatment with greater than 95% DOC removal by the GAC filter. However, the high removal capacity diminished considerably after the first 3 months of operation, decreasing to approximately 50% DOC removal over the following 21 months. From July 2011 onwards (24 months’ operation), the capacity of the GAC for additional DOC removal became saturated, with evidence of desorption of previously adsorbed DOC, resulting in several sampling events where effluent DOC from the GAC filter (Stream 3) exceeded the influent (Stream 2).

Given that membrane filtration is based mostly on a physical partitioning of solutes, it would generally be expected to be more independent of organic character. Indeed overall DOC removal by the MF/NF (Stream 4) was shown to have poor association with organic characterisation techniques, at least in part due to the high DOC removal efficiency. Since DOC removal was not affected by inlet water quality, DOC removal by the MF/NF stream could be averaged over all periods (94 ± 5% RSD). Decreased removal was only observed due to transient fouling and at the end of the pipe flush period (September 2010) when irreversible fouling ultimately necessitated replacement of the NF membrane module. The increase in trans-membrane pressure (TMP) required to maintain the target flux at the onset of fouling had the effect of increasing the fouling rate but may also have forced additional DOC through the membrane that was rejected at normal TMP conditions. Autopsy of the fouled NF membrane revealed the presence of a highly uniform organic ‘gel-layer’ across the membrane surface, potentially formed by concentration polarisation of DOC at the membrane surface (Thorsen 2004). In addition, interactions with NOM bridging agents such as calcium (Gray et al. 2011) were likely given that 65% of the feed water calcium concentration (average 11 mg/L) was rejected throughout the investigation. The MF pre-filtration unit was shown to remove an average 20% of raw water DOC over the monitored period, despite the fact that MF is generally not expected to be capable of DOC removal without the application of pre-treatment strategies (Kimura et al. 2005; Fabris et al. 2007). Possible explanations included partitioning of the organic colloids (Figure 2(b)); however, these materials were not present in the source water throughout the investigation, suggesting that UV-absorbing DOC of lower AMW was also consistently being rejected by the membrane. Adsorption within deposited
fouling cake layers may offer another possible mechanism for the DOC removal observed (Chen et al. 1997; Lee et al. 2004; Gray et al. 2011).

Figure 4 shows treated water SUVA for the four treatments streams as well as the intermediate MF pre-filtration. Raw water UV absorbance was impacted by light diffraction due to fine colloidal turbidity not removable using the standard 0.45 μm filtration; therefore raw water SUVA is not presented. SUVA gives an indication of the degree of conjugation of the organic material which can relate to reactivity with coagulants and disinfectants employed in the water treatment process (Korshin et al. 1997; White et al. 1997). In general, literature shows that natural waters with high SUVA values (>4 L/mg m) have relatively high contents of hydrophobic, aromatic and high AMW NOM fractions, while waters with SUVA < 2–3 L/mg m contain mostly hydrophilic, non-humic and low AMW fractions (Leenheer & Croué 2003; Weishaar et al. 2003). The data suggest that although the capacity of the chemical addition (coagulation) and adsorption technologies (MIEX and GAC) for SUVA reduction was different, neither appeared to be affected by source water quality change nor were more related to operational factors. Given the difficulties experienced in manual feedback optimisation of the conventional coagulation stream, remarkably stable treated water SUVA was achieved throughout the investigated time period, indicating that the high-SUVA components were easily coagulated, regardless of the degree of optimisation of the treatment. The MIEX/coagulation/GAC stream produced notably lower SUVA product water than the MIEX/coagulation stream for the first 9 months, during which time the virgin GAC filters retained capacity for efficient DOC adsorption. For the remainder of the monitored period, the MIEX/coagulation/GAC stream produced only slightly lower treated water SUVA, suggesting that UV absorbing organic matter was still being preferentially removed, despite the fact that overall DOC removal by the GAC was reduced. For the two membrane filtration treatments, different mechanisms dictated the resultant SUVA. The MF pre-filtration (nominal 0.2 μm) achieved variable SUVA reduction during particular water quality periods. The largest reduction occurred during the floodwater flows when high AMW organic colloids were present, consistent with the understanding that SUVA is generally associated with higher AMW organics (White et al. 1997; Karanfil et al. 2002) (see Figure 2). Notable reduction in SUVA was also seen during the peak of membrane fouling instances when rejection efficiency increased, potentially through irreversible fouling mechanisms. Application of chemical cleaning was observed to diminish this effect, supporting the theory that fouling was at least partly responsible. The NF data appeared highly variable; however, this was due to the near total removal of DOC and UV absorbing matter and hence a loss of UV absorbance resolution at the standard analysis path length (1 cm).
The evolution of organic character removed by the four treatment trains was evaluated using AMW distribution by size-exclusion chromatography. Mathematical subtraction of AMW profiles was employed to calculate delta (Δ) AMW removal by each treatment process for the defined water quality periods. In Figure 5, ΔAMW profiles are overlaid on treated water DOC, with the raw water quality periods identified. Figure 5(c) is unique in that the additional material removed by the GAC (Stream 3) is compared with MIEX/coagulation pre-treatment (Stream 2), rather than comparison of the performance of the treatment of the from the source water (Figure 5(a), 5(b) and 5(d)). In this way it was demonstrable that the initial high capacity of the GAC for adsorption of low to moderate AMW organics was diminished over the drought and pipe flush periods and only increased as a result of the less refractory organic character that arrived with the flood water inflows. This increase was a key observation for the other streams also, with only small amounts of UV absorbing NOM removable from the drought water until the first of the flood inflow samples (9 November 2010) and peaking in March 2011. It was observed that although treated water DOC levels after the subsidence of floodwater flows was very similar to the initial drought conditions; the character of the NOM was different, with retention of the floodwater AMW profile. While the treatments applied were largely ineffective against the recalcitrant NOM within the drought water, DOC reduction achieved during the post-flood ‘stable’ period was dependent on the ability of each treatment technology to remove the character of the organics that persisted from the flood inflows. For the non-membrane technologies, this could be shown by the degree of reduction of the hydrophobic DOC fraction (Figure 6(a)) through treatment.

Resin fractionation was applied throughout 2011 to evaluate if a transition of organic character occurred through the end of the floodwater flows (Figure 6). On the basis of selective adsorption to DAX-8 and XAD-4 resins, organic material was partitioned into HPO and HPI fractions. The amounts of these fractions relate to the treatability of NOM with most of the removal expected from the HPO fraction and the HPI fraction typically being more recalcitrant to treatment, especially coagulation.
Owing to the low (<1 mg/L C) DOC of the MF/NF stream and the limitations of the DOC analysis, fractionation of this stream was not undertaken. Raw water was characterised by a high proportion of HPO (humic-like) organics that steadily diminished through the beginning of 2011 (Figure 6(a)). A clear shift in source water DOC concentration was seen from late May 2011 that persisted through to the end of November 2011 and related to a change in flows between the upstream Murray and Darling River catchments and hence dilution of the predominant source of organic character. After the transition to the stable period, HPO NOM decreased to between 4 and 6 mg/L with a slight trend of increasing HPI (likely autochthonous) NOM, due to greater water age and hence greater exposure to natural degradation processes. In addition to the change in proportions of the fractions, their treatability also varied with the change of water quality period. Reduction of both HPO and HPI fractions through conventional treatment appeared to improve considerably at the onset of the ‘stable’ period in terms of lower DOC residuals (below 2 mg/L HPO versus over 4 mg/L during floodwaters); however, percentage removals were not statistically different. Average HPO removal (54 ± 11.1%) was achievable with enhanced coagulation (conventional) during the floodwater period increasing to an average 59 ± 2.4% during the stable period. Conversely, MIEX/coagulation was significantly more effective for HPO removal within the stable period achieving 83 ± 3.7% compared to 75 ± 0.3% in the floodwater period. Regardless of the change in removal efficiency with different water quality, the MIEX/coagulation treatment remained more effective in removing both types of NOM than the conventional treatment train. Towards the end of the stable period (November 2011), MIEX/coagulation...
treatment offered no better removal of HPI NOM than coagulation alone (Figure 6(b)), suggesting that these fractions were less amenable to ion-exchange mechanisms (Fearing et al. 2004), likely due to longer environmental exposure and further loss of the chemical functionality necessary for ion-exchange interactions. While the GAC filters were beneficial as a polishing step after MIEX and coagulation during the floodwater period, the benefit was marginal. This is likely influenced by the diminished GAC adsorption capacity for low AMW organics (Figure 5(c)).

Analysis of the fluorescence response of the source and treated waters was conducted on a single occasion during the stable period to determine whether the shift in character observed in the organic fraction treatability (Figure 7) was related to raw water organic character. Activity in Regions I, II and IV relates to autochthonous organics that would be expected in a water source after biological degradation had occurred (Chen et al. 2003; Kusakabe et al. 2008). Fluorescence in Regions III and V indicates the presence of allochthonous (terrestrial) organic matter introduced to the catchment through surface and sub-surface runoff (Cronan & Aiken 1985; Page et al. 2001). Analysis of the source water (Figure 7(a)) demonstrated a clear dominance of terrestrially derived organics with minimal evidence of soluble microbially derived products (Maie et al. 2012). Conventional coagulation (Figure 7(b)) showed moderate reduction of fulvic and humic-like fluorophores; however, a residual (50%) was still remaining after treatment, demonstrating the limitations of a single-stage treatment process for the reduction of potentially refractory organic fractions (Bieroza et al. 2009, 2010; Baghoth et al. 2011). When expressed on the same fluorescence response scale, the fluorophores in the advanced treatment streams (MIEX/coagulation; MIEX/coagulation/GAC and MF/NF) were effectively reduced such that visual differentiation by EEMs was not possible. An alternative numerical-based comparison was thus employed (Figure 8).

Conventional coagulation was effective for removal of approximately 50% of fulvic, humic and protein-like materials (T1 and T2) at the end of the flood inflow period (August 2011). The multi-process treatments that included MIEX (Streams 2 and 3) were considerably more effective for removal of all fluorescence character. At the time when the

Figure 7 | Fluorescence matrices of Mt Pleasant (a) source and (b) conventional treated waters from 22 August 2011. Region I = aromatic protein A; Region II = aromatic protein B; Region III = fulvic-like; Region IV = microbial protein; Region V = humic-like.

Figure 8 | Fluorescence response of raw and treated Mt Pleasant water at key character excitation–emission wavelengths. Peak A (λex/em = 235/426 nm); Peak C (λex/em = 325/426 nm); Peak T1 (λex/em = 300/350 nm); Peak T2 (λex/em = 225/350 nm).
fluorescence analysis was performed (25 months), the MIEX/coagulation and MIEX/coagulation/GAC were largely incapable of being differentiated in the defined characteristic fluorescence regions. The MF pre-treatment (Stream 4) decreased a proportion of protein-like material through partitioning of the high molecular weight colloidal biopolymers, most represented by the aromatic protein-like peak \( T_2 \). However the majority of reduction in fulvic, humic and protein-like materials was achieved by the downstream NF unit with a tight molecular weight cut-off of 270 Da. The relative reduction of fluorescence character with each treatment stream shows a similar trend to the SUVA reduction (Figure 4). While this is logical given that the molecular functionality that produces fluorescence response is a subset of the total organic functionality that gives UV absorbance, the additional dimension of organic characterisation that fluorescence EEM offers with minimal extra complexity of analysis demonstrates the value of fluorescence spectroscopy within water treatment optimisation and monitoring.

Summary

Organic characterisation of River Murray water subject to climatic variability yielded important observations for monitoring of four treatment process trains incorporating coagulation, ion-exchange and membrane filtration. Despite recorded DOC and UV\(_{254}\) increases within the pipe flush period, the low SUVA and AMW distribution of the drought-impacted NOM did not change until the arrival of fresh organic material associated with flood waters. Flood water was characterised by a high proportion of allochthonous, high AMW, hydrophobic organic material that steadily diminished through the following months, with fluorescence EEMs demonstrating a clear dominance of terrestrial organic and minimal levels of soluble microbially derived products. As floodwaters diminished, the reduction in DOC was not reflected by a change in character but rather a decrease in concentration via dilution. The high AMW (>50,000 Da) organic colloids seen initially in floodwaters were less prevalent during the stable period, indicating increased water age and hence natural degradation of these complexes.

With respect to treatability, the initial period of drought-impacted water was recalcitrant to coagulation (average 32% DOC removal). The treatment streams incorporating MIEX (Streams 2 and 3) showed improved removal of drought DOC character, with the virgin GAC (Stream 5) effective at polishing the water through adsorption of low AMW organics. In the subsequent floodwater period, average DOC removal by coagulation improved to 59%. The coagulation stream removed approximately 50% of source water fluorescence activity and was limited to removal of high AMW UV-absorbing NOM (high SUVA). The advanced multi-stage treatments removed the majority of detectable humic and fulvic-like character (>92%), considerably greater than what was achievable by coagulation alone (50%). The combination of MIEX treatment followed by coagulation was more effective for removal of a broader AMW range of DOC including the low AMW organic material prevalent in the drought period. As a result, treated water SUVA was stable throughout the investigation and consistently 0.5 L/mg m lower than coagulation alone.

The MIEX/coagulation/GAC stream was the most disparate in performance across the investigated period due to the diminishing adsorption capacity of the GAC. Partial recovery of adsorption efficiency was observed during the floodwater period due to the inherent ease of treatability of the floodwater NOM. Until adsorption capacity was exhausted at the onset of the stable period, the main benefit of the GAC was enhanced removal of low AMW, hydrophobic and hydrophilic NOM that was not conducive to removal through ion-exchange or coagulation mechanisms. DOC removal by the MF/NF stream was shown to be consistently high and was less dependent on source water quality; however, performance was difficult to relate to treated water organic characterisation due to the low concentration of remaining DOC in the product water.

CONCLUSIONS

Understanding the character of NOM can help to explain treatment performance limitations and the benefits of a multi-process treatment for a broader range of organic character removal. In this work, the application of a variety of organic characterisation techniques (UV\(_{254}\), SUVA, resin fractionation, HPSEC and FEEM) has demonstrated that:

- The low SUVA and AMW distribution of the drought-impacted DOC was recalcitrant to coagulation with...
significant improvement in DOC removal resulting from the multi-step treatments, particularly when using virgin GAC where adsorption was effective in removing these low AMW compounds.

- Flood water was characterised by a high proportion of allochthonous, high AMW, hydrophobic organic material that was more easily treated by coagulation than drought-impacted water.
- Nevertheless the application of multi-step treatments utilising different DOC removal mechanisms was still capable of reducing both the concentration and diversity of organic components compared to conventional coagulation and demonstrated a greater capacity to accommodate source water changes as a result of climate variability without compromising treated water quality.
- The effectiveness of DOC removal by all treatments was shown to be related to the character of the organics, with the multi-step treatments more effective at removing DOC across the whole AMW size range and more hydrophobic DOC resulting in significantly lower SUVA in the treated waters.

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