Changes in the quality of river water before, during and after a major flood event associated with a La Niña cycle and treatment for drinking purposes

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ABSTRACT

The treatment of organics present in the lower reaches of a major river system (the Murray–Darling Basin, Australia) before (March–July 2010), during (December 2010–May 2011) and after (April–December 2012) a major flood period was investigated. The flood period (over 6 months) occurred during an intense La Niña cycle, leading to rapid and high increases in river flows and organic loads in the river water. Dissolved organic carbon (DOC) increased (2–3 times) to high concentrations (up to 16 mg/L) and was found to correlate with river flow rates. The treatability of organics was studied using conventional jar tests with alum and an enhanced coagulation model (mEnCo©). Predicted mean alum dose rates (per mg DOC) were higher before (9.1 mg alum/mg DOC) and after (8.5 mg alum/mg DOC) than during the flood event (8.0 mg alum/mg DOC), indicating differences in the character of the organics in raw waters. To assess the character of natural organic matter present in raw and treated waters, high performance size exclusion chromatography with UV and fluorescence detectors were used. During the flood period, high molecular weight UV absorbing compounds (>2 kDa) were mostly detected in waters collected, but were not evident in waters collected before and afterwards. The relative abundances of humic-like and protein-like compounds during and following the flood period were also investigated and found to be of a higher molecular weight during the flood period. The treatability of the organics was found to vary over the three climate conditions investigated.

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INTRODUCTION

Water resources used for drinking purposes can be impacted by a wide range of organic and inorganic contaminants that may be derived from natural processes or from anthropogenic activities. Impacts on water quality may be from contaminants transported from catchments through surface and subsurface water flows and/or from processes within the water resource. Natural organic matter (NOM) present in waters can comprise a complex mixture of organic compounds including humic substances and non-humic compounds that reflect source biopolymers such as aliphatic acids, proteins and carbohydrates (Leenheer and Croué, 2003). In river ecosystems, NOM concentration may vary spatially and temporally and when such waters are used for potable supply, high organic load can challenge water treatment utilities (Wang et al., 2010). Where chlorination is used to disinfect potable water supplies,
residual NOM in treated waters becomes a potential health issue as it is a precursor in the formation of disinfection by-products such as trihalomethanes and haloacetic acids. In many countries, state and/or federal government authorities either regulate for the maximum permissible limits of specific disinfection byproducts (DBPs) in potable waters or issue guidelines to the water industry. Hence, in meeting regulated and guideline DBP limits, the water industry generally aims to treat waters for targeted removal of NOM, often to maximum levels that can be attained under practical conditions. Flood and drought events are the effects of climate cycling and change, impacting on water availability for human needs and ecosystems (Matilainen et al., 2010; Whitworth et al., 2012). During flood events such as in La Niña and El Niño cycling, organic compounds are leached from plant detritus that has accumulated on floodplains and in dry channels. These can then be transported into waterways (Whitworth et al., 2012). It has been reported in the literature that climate change may be the reason for increase in dissolved organic carbon (DOC) in source waters used for drinking water supply in some areas around the world (Matilainen et al., 2010; Kerr et al., 2013) and this DOC is more hydrophobic in character, requiring increased dosing of coagulant (Sharp et al., 2006).

The Australian continent is highly influenced by the cycling of climate conditions leading to extended periods of drought and shorter, wet periods, influenced by the Walker Cycle. The Walker Cycle refers to a pattern of air movement that rises in the west of the tropical Pacific Ocean and falls in the east with westward moving air (trade winds) at the surface. In an El Niño event, trade winds weaken and warmer waters occur in the central regions of the pacific where convection occurs resulting in increased rainfalls in the west of South America but less in Australia. Conversely when the Walker Cycle intensifies, stronger trade winds occur with greater convection over the western pacific, waters are then cooler in the central pacific region and warmer in the west. Under this condition the La Niña event occurs with heavy rainfalls on the eastern side of Australia (BOM, 2012).

The Murray–Darling Basin comprises about one seventh of the Australian continent. Rivers flow from the upper reaches of the catchment (Darling River and tributaries from the north; the Lachlan and Murray–Bidgee from the east in New South Wales and the Murray River on the New South Wales and Victorian border) through the Murray River in South Australia. In drought and flood periods the water quality is subject to significant change in these rivers. In late 2010 and early 2011, a La Niña event occurred that was one of the strongest on record, bringing with it very heavy rainfall in the Murray Darling Basin with extensive flooding. This followed a period of extensive drought. From the conditions of drought to flood and afterwards, there was significant change in the water quality of the Murray River, including from low to high organic loading and with variable high turbidity. This led to significant challenges at water treatment plants along the river that supply potable waters to the local communities, and remote plants to the river where extracted water was transported and then directly treated.

In this article we report the changes in water quality in the preceding drought period, during the flood and afterwards. The characters of organics present in waters are described in context of their treatability under simulated conventional treatment using alum as coagulant.

1. Materials and methods

1.1. Water sources

Water samples were collected from the lower River Murray system at Palmer (−34.851, 139.159), Mannum (−34.914, 139.312) and mostly at Morgan (−34.021, 139.689), in South Australia. Water samples were collected from the Murray River between July 2010 and December 2012. Colour, UV absorbance at 254 nm, pH, turbidity and alkalinity of raw water samples were determined within 2 days upon arrival at the laboratory, and subsequent jar testing and associated analyses within 7 days. Samples were stored at 4 °C prior to analyses. Sample bottles were rinsed with high purity Milli-Q water (Millipore) and then with the source water, prior to sample collection.

1.2. Water quality analyses

The pH of water samples was measured using a TPS pH meter (Model WP-80). Turbidity (NTU) was measured using a Hach 2100AN turbidimeter (Hach, USA). Alkalinity (as CaCO3 mg/L) was determined by titration using 0.2 mol/L HCl to pH 4.5. Measurements were conducted according to standard methods (APHA, 1998).

Ultraviolet light absorbance (UV254 nm) and visible light absorbance at 456 nm (Colour at 456 nm) were measured with 1 cm quartz and 5 cm glass cells, respectively, using a UV/Vis spectrophotometer (Evolution 30, Thermo Scientific, USA). Colour was determined by comparison with a platinum/cobalt standard of 50 Hazen units. DOC was measured using a total organic carbon (TOC) analyser (Sievers 900, GE Analytical Instruments, USA). Each water sample was filtered through a 0.45 μm membrane filter for DOC, UV254 nm and colour at 456 nm measurements. SUVA was determined as UV254 nm × 100/DOC and specific colour as colour (HU) of 456 nm/DOC.

Apparent molecular weight (AMW) distribution profiles of organics were determined by high performance size exclusion chromatography (HPSEC) using a Waters Alliance 2690 separation module attached with 996 photodiode array detector at 260 nm (Waters Corporation, USA) according to Chow et al. (2008). Phosphate buffer (0.02 mol/L) with 0.1 mol/L NaCl was used as a mobile phase for separation of organics, based on molecular size using a Shodex KW802.5 packed silica column (Showa Denko, Japan). The flow rate of solvent was 1.0 ml/min. This column provides a separation range from 50 to 50,000 Da. AMW was calibrated with poly-styrene sulphonate molecular weight standards of 35, 18, 8 and 4.6 kDa. Detection was by UV absorbance (at 260 nm, HPSEC-UV) and fluorescence. For the HPSEC-UV method applied, emitted light at 330 nm was measured after excitation at 280 nm (λex280 and λem 330 nm) to identify and quantify protein-like (including tryptophan-like and phenol-like) materials (Peak T) (Leenheer and Croué, 2003; Lanciné et al., 2011). For humic-like materials, λex320 and λem430 nm (Peak C1) were used, as detailed by Bridgeman et al. (2013). HPSEC-UV fluorescence data was acquired only for samples collected during and after the La Niña event due to instrument availability. For HPSEC-UV, both the weight-average (Mw) and number-average (Mn) molecular weights were determined as detailed by Chin et al. (1994).

1.3. Prediction and determination of alum doses

1.3.1. mEnCo® modelling software

mEnCo® is a modelling software package that was designed to assist WTP operators in managing chemical dosing for DOC removal (van Leeuwen et al., 2003, 2005; Kastl et al., 2004). Model inputs are four raw water quality parameters, UV measured at 254 nm, colour measured at 456 nm, turbidity
and alkalinity which are routinely measured at the WTP laboratory (van Leeuwen et al., 2009).

1.3.2. Jar tests
Alum stock solution (20,000 mg/L as Al₂(SO₄)₃·18H₂O) was prepared from liquid aluminium sulphate (7.5% as Al₂O₃), sourced from a commercial water treatment plant, diluted in high purity water (Milli-Q water). The concentration of aluminium in the stock solution was verified by an ICP-OES instrument (Varian Vista Pro). Analytical grade NaOH and HCl solutions were used for pH control during coagulation.

Jar tests were performed using 6 jars (Model FMS6V, SEM, Brisbane, Australia) with the waters at ambient temperature and with the coagulation pH at 6.0 ± 0.1. A six paddle gang stirrer with 7.6 cm diameter flat paddle impellers and Gator jars was used. The operation procedure was as follows: 2 L water samples were placed on the gang stirrer and the jar tester was started with a rapid mixing speed of 230 t/min for 1 min. Subsequently, the speed was reduced to 20 t/min for 14 min and then the floccs quiescently settled for 15 min. Water samples were filtered using Whatman No. 1 filter papers to simulate the plant filtration process. The amounts (mL) of 0.2 mol/L NaOH and 0.1 mol/L H₂SO₄ added for pH adjustment were estimated using a separate process. The amounts (mL) of 0.2 mol/L NaOH and 0.1 mol/L Whatman No. 1 filter papers to simulate the plant filtration process. The amounts (mL) of 0.2 mol/L NaOH and 0.1 mol/L H₂SO₄ added for pH adjustment were estimated using a separate process.

An initial dose for enhanced coagulation (EnCD) was predicted using mEnCo as described by van Leeuwen et al. (2009). Alum doses used in jar tests included 0.25 EnCD, 0.5 EnCD, 0.75 EnCD, 1.0 EnCD, 1.5 EnCD and 4 EnCD. For comparison of the characters of organics in these waters before and after alum treatment, three alum doses were selected: (1) the mEnCo predicted dose (EnCD), (2) at 0.75 of the EnCD, and (3) at a very high coagulant dose which more than double the EnCD. The 0.75 EnCD was used to compare removals of organics at a nominal dose rate lower than that considered needed for enhanced coagulation, while the very high coagulant dose was used to ensure differentiation between the coagulable and non-coagulable organics (Kastl et al., 2004) at pH 6.

1.4. Data and analysis
Data of River Murray flows into South Australia were acquired from the website of the Murray–Darling Basin Commission and Southern Oscillation Index data were acquired from the Bureau of Meteorology, Australia. Monthly inflow data presented in this article are averages of weekly inflow data for each month reported by Bureau of Meteorology.

To resolve the overlapping HPSEC peaks and to determine individual peak areas of organics, peak fitting software (Version 4, copyright 1991–1995, AISN Software Inc.) was employed according to the method described by Chow et al. (2008). For HPSEC data analyses, chromatograph areas were determined for various molecular weight ranges including <0.5, 0.5–1, 1–2 and >2 kDa.

2. Results and discussion

2.1. Raw water characteristics of River Murray
Water quality data, river flow rates and Southern Oscillation indices before (March–July 2010), during (December 2010–May 2011) and after (April–December 2012) the major flood period associated with the La Niña cycle are shown in Table 1. River Murray flow rates (into South Australia) generally correlated with rolling monthly (previous 12 months) average Southern Oscillation Index values as might be expected, with flooding a result of high rainfalls in the Murray–Darling Basin associated with the strong La Niña event.

Water quality data acquired prior to the flood event for three locations (Morgan, Palmer and Mannum) showed consistency. Turbidity was highest in this period, in contrast to DOC which was then lowest in concentration. Trends were found between river flow rate and colour, DOC, specific colour, SUVA and the molecular weights of organics (by HPSEC-UV). Correlations between organics (DOC, UV₂₅₄ nm) with river flow are shown in Fig. 1 and this indicates significant increase in the transport of organics from catchments into waterways of the Murray–Darling Basin. For instance, if the mean DOC values of the three periods (Table 1) were assumed to be of the inflow waters, then this would equate to mass transport of 17.5, 755 and 261 t/day, respectively. Based on this data, differences in DOC flux between the three periods and especially between the preceding dry and very wet La Niña event were very high, with a ratio of 14:3:15 for the three periods. By comparison, Burns et al. (2008) reported about 25% lower levels of several water constituents including organic carbon in El Niño (1997) affected waters of the Sepik River, New Guinea, than waters collected in La Niña (1996, 1999, 2000) events.

Whitworth et al. (2012) attributed the high flux of DOC into waters of the southern Murray–Darling Basin in the spring and summer floods of 2010–2011, to inundation of forested and agricultural floodplains, flushing of post-drought upper catchments and hypolimnetic discharge from weirs. Our findings of water quality during the flood period, with comparatively highest concentrations of DOC found, are consistent with that reported by Whitworth et al. (2012).

During the flood period, both SUVA and specific colour levels of waters were highest, inferring shift from autochthonous organics in the dry period (mean values of 2.85 and 3.23, respectively) to allochthonous organic matter in the La Niña event (3.87 and 6.65, respectively). Percentages of very hydrophobic acid fractions were lowest (<60%) in the samples collected prior to the La Niña event, after which they were mostly at higher percentages (>70%), including after the event. Apparent molecular weight distributions of UV absorbing compounds were also highest in the flood period assessed, compared with the before and after periods (Table 1). Alkalinity was found to broadly correlate with the flow rates of river water, where alkalinity = 0.87 × flow rates + 44.4 (R² = 0.51). In contrast to the concentration and character of organics and alkalinity, there was no correlation found between turbidity and river flow rate. The highest turbidity levels that we found occurred during the pre-flood period. The basis for this is unclear but might be due to low volume, channelled river flow within the river bed area, drying of river banks, their destabilization and subsequent collapse into low flow waters and growth of algae. Continued high turbidity of Murray River waters in South Australia during and after the flood periods was due to sediment transport into Murray–Darling Basin waterways following inundation of catchments, and contribution of flow from the Darling River. The
Table 1 – River water qualities before (Mar–July 2010), during (Dec 2010–May 2011) and after (Apr–Dec 2012) a major flood associated with a strong La Niña event.

<table>
<thead>
<tr>
<th>Location</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Palmer</th>
<th>Mannum</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Morgan</th>
<th>Morgan</th>
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<tbody>
<tr>
<td>Month</td>
<td>Mar</td>
<td>Apr</td>
<td>July</td>
<td>July</td>
<td>July</td>
<td>Dec</td>
<td>Feb</td>
<td>Mar</td>
<td>Apr</td>
<td>May</td>
<td>Apr</td>
<td>July</td>
<td>Sept</td>
<td>Nov</td>
</tr>
<tr>
<td>Average SOI a</td>
<td>−5.2</td>
<td>−4.6</td>
<td>−1.4</td>
<td>−1.4</td>
<td>−1.4</td>
<td>9.8</td>
<td>15.4</td>
<td>18.1</td>
<td>18.9</td>
<td>18.2</td>
<td>6.6</td>
<td>4.2</td>
<td>2.9</td>
<td>1.7</td>
</tr>
<tr>
<td>In Flow rate (ton/day × 10^6)b</td>
<td>3.1</td>
<td>4.2</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>62</td>
<td>85</td>
<td>77</td>
<td>62</td>
<td>30</td>
<td>59</td>
<td>30</td>
<td>46</td>
<td>16</td>
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<td>pH</td>
<td>7.7</td>
<td>7.9</td>
<td>7.4</td>
<td>7.4</td>
<td>7.3</td>
<td>7.5</td>
<td>7.5</td>
<td>7.6</td>
<td>7.2</td>
<td>7.9</td>
<td>7.8</td>
<td>7.5</td>
<td>7.6</td>
<td>7.6</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>214</td>
<td>133</td>
<td>115</td>
<td>124</td>
<td>130</td>
<td>90</td>
<td>20</td>
<td>53</td>
<td>82</td>
<td>109</td>
<td>58</td>
<td>52</td>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>Colour (HU)</td>
<td>17</td>
<td>20</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>112</td>
<td>86</td>
<td>68</td>
<td>27</td>
<td>29</td>
<td>37</td>
<td>49</td>
<td>45</td>
<td>27</td>
</tr>
<tr>
<td>Alkalinity (mg/L CaCO3)</td>
<td>37</td>
<td>55</td>
<td>48</td>
<td>52</td>
<td>56</td>
<td>85</td>
<td>128</td>
<td>168</td>
<td>78</td>
<td>104</td>
<td>62</td>
<td>54</td>
<td>42.5</td>
<td>N.A</td>
</tr>
<tr>
<td>UV254 nm (cm⁻¹)</td>
<td>0.12</td>
<td>0.16</td>
<td>0.13</td>
<td>0.17</td>
<td>0.14</td>
<td>0.52</td>
<td>0.61</td>
<td>0.51</td>
<td>0.39</td>
<td>0.27</td>
<td>0.24</td>
<td>0.22</td>
<td>0.26</td>
<td>0.25</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>4.2</td>
<td>5.2</td>
<td>4.9</td>
<td>5.1</td>
<td>5.4</td>
<td>10.5</td>
<td>12.6</td>
<td>15.9</td>
<td>10.6</td>
<td>10.1</td>
<td>8.1</td>
<td>7.9</td>
<td>8.4</td>
<td>7.1</td>
</tr>
<tr>
<td>SUVA c</td>
<td>2.76</td>
<td>3.14</td>
<td>2.59</td>
<td>3.27</td>
<td>3.25</td>
<td>4.93</td>
<td>4.80</td>
<td>3.23</td>
<td>3.74</td>
<td>2.64</td>
<td>3.00</td>
<td>2.82</td>
<td>3.14</td>
<td>3.58</td>
</tr>
<tr>
<td>Specific colour d</td>
<td>4.05</td>
<td>3.88</td>
<td>2.65</td>
<td>2.77</td>
<td>2.80</td>
<td>10.67</td>
<td>8.10</td>
<td>5.41</td>
<td>6.42</td>
<td>2.67</td>
<td>3.59</td>
<td>4.68</td>
<td>5.83</td>
<td>6.34</td>
</tr>
<tr>
<td>% VHA</td>
<td>N.A</td>
<td>N.A</td>
<td>52.8</td>
<td>55.4</td>
<td>58.9</td>
<td>72.2</td>
<td>72.5</td>
<td>76.9</td>
<td>70.6</td>
<td>69.8</td>
<td>N.A</td>
<td>74.2</td>
<td>77.1</td>
<td>N.A</td>
</tr>
<tr>
<td>Mn (Da)</td>
<td>N.A</td>
<td>N.A</td>
<td>740</td>
<td>762</td>
<td>796</td>
<td>1009</td>
<td>1163</td>
<td>1121</td>
<td>967</td>
<td>968</td>
<td>N.A</td>
<td>906</td>
<td>967</td>
<td>758</td>
</tr>
<tr>
<td>Mw (Da)</td>
<td>N.A</td>
<td>N.A</td>
<td>1138</td>
<td>1148</td>
<td>1167</td>
<td>1284</td>
<td>1558</td>
<td>1453</td>
<td>1216</td>
<td>1229</td>
<td>N.A</td>
<td>1158</td>
<td>1282</td>
<td>964</td>
</tr>
</tbody>
</table>

Note:
- SA: South Australia; N.A: Not available; SOI: Southern Oscillation Index; SUVA: specific UV absorbance; VHA: Very hydrophobic acid.
- a Average of previous 12 months.
- b Into South Australia.
- SUVA = \(\frac{\text{UV absorbance at 254 nm/cm} \times 100}{\text{DOC mg/L}}\).
- d Specific colour = \(\frac{\text{Colour HU}}{\text{DOC mg/L}}\).
Darling River is recognised for having characteristic high turbidity waters (De Rose et al., 2004).

### 2.2. Assessment of treatability of NOM

With increases in UV absorbance of raw waters, the predicted alum dose needed for maximizing removal of organics only (not including the dose needed for turbidity removal) also increased (Table 2). Predicted alum dose demands based on DOC (alum/DOC) varied but were lowest during the flood period, inferring that the organics were then most treatable by coagulation. Calculated average alum/DOC (mg/mg) values for the three consecutive periods were 9.1, 8.0 and 8.5, respectively. There was variation in SUVA and specific colour between each period, indicating changes in the characters of the organics (Table 1). Highest variation occurred within the La Niña period studied.

The results of jar tests conducted at coagulation pH 6 are shown in Table 3. Enhanced coagulation doses (EnCD) provided for near maximum removal of organics, when compared to removals attained by application of very high alum doses, used to differentiate between removable (coagulable) and non-removable (non-coagulable) organics as measured by DOC. For the mEnCo model, the enhanced dose is based on established jar test data of a range of water
qualities where near maximum removal refers to a DOC decline rate with alum dosing at 0.15 mg DOC/10 mg alum (a gradient of −0.015) (van Leeuwen et al., 2005). The application of the high coagulant dose at controlled pH has no practical relevance other than to enable differentiation of coagulable from non-coagulable DOC and characterization of the organics that are recalcitrant to removal at a specified coagulation pH. The approach of using high coagulant doses for this purpose has been previously reported (Kastl et al., 2004; Chow et al., 1999). For organics remaining in post-treated waters, a range of characterization methods can be used, including those applied in this study, as well as Pyrolysis–GC/MS, resin fractionation and $^{13}$C NMR (Chow et al., 1999; Gadel and Bruchet, 1987; Wong et al., 2002).

### 2.3. Characterization of NOM using HPSEC-UV and HPSEC-fluorescence

The characters of dissolved organic matter (DOM) present in raw waters and after alum treatment were investigated by HPSEC-UV (before, during and after the flood period) and by HPSEC-fluorescence (during and after the flood period). Figs. 2, 3, and 4 show the AMW distributions obtained by HPSEC-fluorescence and UV absorbance. The chromatographs of organics in waters collected in the flood period show presence of higher AMW (to 3.4 kDa) compounds than those in waters collected before and after the flood period. High molecular weight, hydrophobic compounds are more amenable to removal by coagulation (Stephenson and Duff, 1996; Randkte, 1988) consistent with the flood period organics having the overall lowest calculated alum/DOC value at the enhanced coagulation dose. For the three samples collected in July 2010, the AMW distributions were similar, as might be expected for samples collected from the river at the same time. These variances ranged from $5 \times 10^{-3}$ to $6.6 \times 10^{-3}$ for the raw water 1–2 kDa fraction (Fig. 2) and indicate analytical variation or error when compared with UV absorbance 254 nm data (Table 1). In contrast, samples collected from the same location (Morgan) at different times of the year within the flood period and afterwards showed comparatively high variation (Figs. 3 and 4). For example, in July 2012, there was a much higher relative abundance of UV absorbing organics of AMW 1–2 kDa than for subsequent months. This indicates significant differences in the character of organics seasonally, as reported by Sharp et al. (2006) even though DOC concentrations clustered distinctly for each of the three separate climate periods studied.

HPSEC-fluorescence data were acquired of organics present in waters collected during and after the La Niña cycle. During the flood period, relative abundances of humic-like compounds of 1–2 kDa (Fig. 3) varied markedly over the 5 month period and were higher than for the following period (Fig. 4). In the post-flood period, relative abundances of these compounds in river waters were greater in the lower AMW ranges of <0.5 and 0.5–1 kDa. Also, in the postflood period, the relative abundances of humic-like organics of 1–2 and 0.5–1 kDa showed greater similarity between months (July–December 2012) than during the flood period studied (December 2010–May 2011). Generally, reductions in humic-like and protein-like compounds with alum treatment were comparatively greater for organics with higher AMW than lower AMW. For the AMW 0.5–1 kDa humic-like fraction, removals were more than 80% for all doses while for the AMW <0.5 kDa fraction, about 50% was removed. Both types of organics, as determined by HPSEC-fluorescence demonstrated recalcitrance to removal by coagulation using alum.

Despite the detection of UV absorbing compounds of >2 kDa using HPSEC-UV in raw waters collected during the flood period, compounds >2 kDa were not detected using HPSEC-fluorescence for these waters. The basis for this might be that compounds other than those as defined as humic-like and protein-like in this study, and with UV absorbing properties were present in these waters. In this study, two sets of excitation and emission

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**Table 3 – Average DOC concentrations in raw and treated waters, with percentage removals ($n = 15$).**

<table>
<thead>
<tr>
<th>La Niña</th>
<th>Raw DOC</th>
<th>0.75 EnCD</th>
<th>EnCD</th>
<th>4 EnCD or VHD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre</td>
<td>4.9 mg/L</td>
<td>3.2 mg/L (36.2%)</td>
<td>2.4 mg/L (50.2%)</td>
<td>2.2 mg/L (55.8%)</td>
</tr>
<tr>
<td>During</td>
<td>11.9 mg/L</td>
<td>5.8 mg/L (51.0%)</td>
<td>5.4 mg/L (54.2%)</td>
<td>4.7 mg/L (59.6%)</td>
</tr>
<tr>
<td>Post</td>
<td>7.7 mg/L</td>
<td>3.8 mg/L (49.8%)</td>
<td>3.4 mg/L (55.2%)</td>
<td>3.1 mg/L (58.0%)</td>
</tr>
</tbody>
</table>

%: Percentage removal of DOC after coagulation at various doses, VHD: very high coagulant dose.

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![Fig. 2](image-url) – AMW peak areas of UV absorbing compounds detected in River Murray raw waters collected before (July 2010) the La Niña event and post-alum treatment.
Fig. 3 – AMW peak areas of UV absorbing compounds, humic-like and protein-like materials detected in River Murray (at Morgan S.A.) raw waters collected during a La Niña event (December 2010 to May 2011) and post-alum treatment.

Fig. 4 – AMW peak areas of UV absorbing compounds, humic-like and protein-like compounds detected in River Murray (at Morgan S.A.) raw waters collected following (July 2012, September 2012, December 2012) the La Niña event and after alum treatment.
wavelengths were used, i.e., λex 280 and λem 330 nm for protein-like and λex 320 and 430 nm for humic-like compounds. Bridgeman et al. (2011) reported other excitation wavelengths for humic-like compounds (237–260 nm for Peak A) and for protein-like compounds (λex 225–237, λem 309–321 nm for Peak B1 [Tyrosine], λex 225–237, λem 340–381 nm for Peak T2 [tryptophan]). In this study, the two techniques were principally applied on the basis of enabling comparisons of AMW (and characters) between samples collected in each of the distinct climate periods.

3. Conclusions

Water quality and treatability of organics by conventional processing were investigated for water samples collected from the River Murray, in three distinct climate cycles, being (1) prior to (2) during and (3) after a strong La Niña event that occurred in late 2010 and early 2011. Significant changes occurred in river DOC concentrations and in the character of dissolved organic matter, as determined by UV–visible spectroscopy and apparent molecular weight distributions, over the three periods studied. Strong correlations were found between DOC concentration and the character of DOM with river flow rates. Increased flows, with a corresponding increase in DOC, SUVA, specific colour, very hydrophobic acid fraction and AMW, reflected input of organics from allochthonous, terrestrially derived sources. Although these organics increased substantially in concentrations, they were overall more treatable than organics in waters before or after the flood period. The increased treatability correlated with higher AMWs of UV absorbing compounds, and of humic-like and protein-like compounds. River flow rate data can potentially provide early warning not only of higher DOC concentrations in waters but also of changes in the character of organics that then impact water treatment processing for drinking water supply.

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