The impact of alum coagulation on the character, biodegradability and disinfection by-product formation potential of reservoir natural organic matter (NOM) fractions

Yeow Chong Soh, Felicity Roddick and John van Leeuwen

ABSTRACT

Natural Organic Matter (NOM) from Myponga Reservoir, South Australia, was separated into four organic fractions based on their hydrophobic and hydrophilic properties using a sequence of non-ionic and ionic resins. NOM fractions were isolated for the purpose of determining the impact of alum coagulation on removal of these fractions in conventional water treatment, and their potential as precursors in the formation of disinfection by-products (DBP) and in supporting microbial growth. The NOM comprised VHA (very hydrophobic acids), SHA (slightly hydrophobic acids), CHA (charged hydrophilics) and NEU (neutral hydrophilics) fractions. These fractions were then jar tested with alum using low (50 mg/L), operational (100 mg/L) and very high (200 mg/L) doses to assess the removal capacities for these fractions in a conventional treatment plant. High-performance size exclusion chromatography-UV-DOC (HPSEC-UV-DOC) revealed that alum removed more of the hydrophobic and higher molecular weight components of NOM, but less of the NEU fraction and lower molecular weight components of NOM. Determination of biodegradable dissolved organic carbon (BDOC) indicated that the NEU fraction had the highest biodegradability, followed by the CHA, SHA and VHA fractions. The VHA fraction had the highest total-trihalomethane formation potential (t-THMFP), followed by NEU, SHA and CHA. The NOM not removed by alum coagulation had the potential to support microbial growth (NEU fraction), and disinfection by-product (DBP) formation (VHA and NEU fractions). To obtain treated water with lower overall residual NOM, other treatment methods would need to be applied in addition to alum coagulation in order to reduce the concentration of the neutral fraction.

Key words | alum coagulation, biodegradable dissolved organic carbon, high-performance size exclusion chromatography, natural organic matter, resin fractionation, trihalomethane formation potential

INTRODUCTION

Natural organic matter (NOM) is a mixture of organic compounds derived from plants and animals present in soils and aquatic systems such as lakes, rivers and reservoirs. It plays a significant role in aquatic food webs as it mediates the bioavailability of nutrients and metals, and modifies the optical properties of water bodies. Its role in aquatic ecosystems is important as it acts as a source of carbon for the metabolism of living things found within it. Its heterogeneity and complexity is not well understood, but changes in its character depend on source of input (allochthonous and autochthonous) and its transformation and consumption (by bacterioplankton) within the water body.

Inorganic metal coagulants are commonly used for the conventional treatment of drinking water, primarily for the
removal of colour and turbidity. In recent years, there has been increased focus in drinking water treatment to remove NOM to reduce disinfectant demand, disinfection by-product (DBP) formation and bacterial growth in the distribution system. Much research is currently being conducted on NOM to understand its heterogeneous nature and to develop techniques to minimize its impacts on water treatment and water quality.

Due to the heterogeneous nature of NOM, a combination of methods has been applied to better understand its character (Leenheer & Croue 2003). Resin fractionation, developed by Leenher (1981), has recently become a common method to characterise NOM (Marhaba et al. 2003; Buchanan et al. 2005). This method enables the separation of NOM into its humic/non-humic, and hydrophobic/hydrophilic components. Chow et al. (2004) developed a Rapid Fractionation technique to simplify the fractionation process for NOM characterisation and to study water treatment processes. In this method, the sequential use of non-ionic and ionic resins resulted in four fractions, consisting of very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilics (CHA) and neutral hydrophilics (NEU). The Rapid Fractionation method is so-named because it takes less time as NOM fractions adsorbed onto the resins are left on them. Elution of the fractions from the resins, allows further experiments to be conducted to determine their impact on water treatment processes (eg., in removal by alum coagulation) and water quality (THMFP and BDOC).

The work reported here was an investigation of how NOM fractions from reservoir water influence coagulant and disinfectant demand. Further to work performed previously (van Leeuwen et al. 2002; Chow et al. 2005), HPSEC-UV-DOC, BDOC and THMFP of the eluted fractions were studied to further understand the changes of NOM in the water. The aim was to determine the removal of each fraction by alum coagulation during conventional treatment, and the potential of the residual fractions for DBP formation and biofilm formation in the distribution systems. This should allow water utilities to have a better understanding of water quality and therefore the ability to customise water treatment techniques for improved drinking water quality for different water sources.

MATERIALS AND METHODS

Characterisation of Myponga reservoir water

The water used in this study was collected from Myponga Reservoir, South Australia, in March 2007. Water was sampled at the dam wall before chlorination, and was stored at 4°C after collection. Water samples were filtered through a 0.45 μm hydrophilic membrane (Durapore PVDF) before dissolved organic carbon (DOC) measurement using a Sievers 820 TOC analyzer. A double beam UV/vis spectrophotometer (Unicam UV2) was used for all spectrophotometric readings. A 1 cm quartz cell was used for absorbance readings at 254 nm (A254) and a 4 cm glass cell was used to measure colour in Hazen units (HU) at 446 nm (A446). Specific UV absorbance (SUVA), a measure of the aromaticity of organic compounds, was determined as the ratio of A254 to DOC concentration [(A254/DOC) × 100]. A Hach Sension 156 pH meter was used for pH measurements. Alkalinity was determined using sodium carbonate and sulphuric acid titration (Standard Methods 2320 B) (APHA 1998). Turbidity was measured using a Hach spectrophotometer (DR/4000) and a formazin standard. Table 1 summarizes the characteristics of Myponga reservoir water.

High-performance size-exclusion chromatography–UV–DOC (HPSEC-UV-DOC)

The method for HPSEC-UV-DOC was based on work performed by Allpike et al. (2005). Size-exclusion chromatography (SEC) was performed using a TSK HW-50S gel column (length 250 mm, inner diameter 20 mm, particle size 30 μm, void volume (V0) 21 mL, permeation volume (Vp) 47 mL). Calibration of standards to determine apparent molecular weight (AMW) was with a series of polystyrene sulfonates of MW 840 to 35,300 Da. A phosphate buffer eluent was used (10 mM KH2PO4 + 10 mM Na2HPO4, pH 6.80) at a flowrate of 1 mL/min with online A254 and DOC detection. A cylindrical thin film reactor with a rotating...
inner cylinder and a low-pressure mercury lamp was used to oxidise DOC to CO₂ which was quantified by a Balzers Thermostar GSD 300 mass spectrometer operating in single ion mode (m/z 44) at a sampling frequency of 0.8 Hz, dwell time 1 s, and source voltage 1,500 V.

**Fractionation of water samples**

Rapid Fractionation of NOM was based on the method developed by Chow *et al.* (2004) and uses a sequence of non-ionic resins (DAX-8, Supelite and XAD-4, Amberlite) and a strong anionic exchange resin (IRA-958, Amberlite) to separate dissolved NOM into four fractions. After adjusting the pH of water sample to 2, the VHA fraction was adsorbed by the DAX-8 resin and the SHA fraction in the resultant effluent was adsorbed by the XAD-4 resin. Effluent from the XAD-4 resin was adjusted to pH 8 for the CHA fraction to be adsorbed by the IRA-958 resin. The effluent from the IRA-958 resin contained the NEU fraction.

For the Adsorption/Desorption method, the Rapid Fractionation method was first followed using 1 L of raw water. The fractions were then desorbed by elution of each of the non-ionic resins (DAX-8 and XAD-4) with 100 mL of 0.1 M NaOH, and the strong anionic exchange resin (IRA-958) with 100 mL 0.1 M NaOH/0.1 M NaCl (Wong *et al.* 2002). Each of the three resins was washed with 900 mL Milli-Q water to make up 1 L of VHA, SHA and CHA fractions respectively from each column. The pH of all fractions was adjusted to 7 before further experiments.

**Jar test procedure**

Alum (aluminium sulphate, Al₂(SO₄)₃.18H₂O) was used in jar test experiments (Phipps and Bird PB-700). A range of alum concentrations (50, 100 and 200 mg/L, pH 6) was used to test each water sample. The 100 mg/L dose is near to the operational dose applied for Myponga Reservoir water. Water samples (1 L) were flash mixed at 150 rpm for 1 minute, then slow mixed at 30 rpm for 15 minutes. Flocs were allowed to settle for 60 minutes before filtration (Whatman No.1). The pH of treated water was adjusted to 7 before further experiments.

**Biodegradable dissolved organic carbon (BDOC)**

The BDOC method (Joret *et al.* 1989) using biologically active sand from the Yarra River, Lilydale, Victoria was followed. Jar tested water samples (500 mL) were each incubated with the sand (125 g wet weight) for a period of 10 days under aerobic conditions. DOC concentrations were monitored daily and the greatest reduction in DOC observed during this time was taken as the BDOC concentration.

**Trihalomethane formation potential (THMFP)**

THMFP was determined using Standard Methods 5710 B (APHA 1998) and test method T0050-03 from the Australian Water Quality Centre, Adelaide, South Australia. Samples were buffered (phosphate buffer, pH 7.4), dosed with excess sodium hypochlorite (approximately 20 mg/L of residual free chlorine) and allowed to react for 4 hours at 35°C. The sample was then quenched with ascorbic acid and the THM components concentrated by liquid-liquid extraction before headspace analysis by gas chromatography with an electron capture detector.

**RESULTS AND DISCUSSION**

**Rapid fractionation versus adsorption/desorption**

Before using the fractions eluted from the resins for further experiments, it was important to determine whether the characteristics of the fractions were the same for both the Adsorption/Desorption and Rapid Fractionation methods. Comparison of the DOC, A₂₅₄ and colour of the fractions (Table 2) shows that the values are sufficiently close to indicate that the eluted fractions have similar characteristics to those determined by Rapid Fractionation. With the exception of the CHA fraction, the DOC of fractions from both methods are very comparable. The A₂₅₄ values of the VHA and CHA fractions and the colour for the SHA and NEU fractions for both methods differ slightly, but they follow the same trend where values for VHA > SHA > CHA > NEU. NOM from Myponga Reservoir is of predominantly hydrophobic character, with the VHA and SHA fractions making up nearly 70% (8.94 ppm) of the...
NOM compared with the hydrophilic fractions CHA and NEU (3.90 ppm, 30%). The effect of treatment of the eluted fractions by alum coagulation and the impact on water quality was then investigated.

**Effect of alum coagulation on NOM fractions**

Alum concentrations of 50, 100 and 200 mg/L were used in the jar tests to simulate low, near operational, and very high doses, respectively. With increasing alum dose from low to operational doses, the removal of whole NOM increases (Figure 1a). However at very high doses, NOM removal is not significantly improved, suggesting the presence of components of NOM recalcitrant to removal by coagulation. This phenomenon is also evident in the VHA, SHA and CHA fractions. Most significantly, little NEU fraction was removed with the addition of alum at any concentration. Similar trends were observed for A254 reduction (Figure 1b), where higher alum concentrations reduced the A254 of treated water. When the DOC and A254 for the four fractions were added together and compared with whole NOM, the values were comparable (Table 3). The application of the same alum dose to the fractions as to whole NOM gave little difference in the removal of DOC and A254.

Changes in the characteristics of the NOM fractions were investigated by HPSEC-UV-DOC (Figure 2). UV detection shows only the UV-absorbing components of NOM, whilst HPSEC-DOC provides quantitative analysis of all of the components and so gives a more accurate representation of the NOM present in each sample (Her et al. 2002; Allpike et al. 2005). HPSEC-DOC detected more of the lower MW species, including those <0.6 kDa representing the low MW neutrals (such as sugars, alcohols, aldehydes, ketones and amino acids), and the 4 humic/fulvic peaks between 0.6 and 10 kDa. A peak considered to be of polysaccharides and proteins from 20 to 60 kDa (Her et al. 2003) was only detected by HPSEC-DOC, as this component of NOM is not strongly UV-absorbing.

### Table 2

<table>
<thead>
<tr>
<th>Rapid fractionation</th>
<th>Adsorption/desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>DOC (ppm)</td>
</tr>
<tr>
<td>Whole NOM</td>
<td>12.67</td>
</tr>
<tr>
<td>VHA</td>
<td>6.36</td>
</tr>
<tr>
<td>SHA</td>
<td>2.59</td>
</tr>
<tr>
<td>CHA</td>
<td>1.65</td>
</tr>
<tr>
<td>NEU</td>
<td>2.07</td>
</tr>
<tr>
<td>Total</td>
<td>12.67</td>
</tr>
</tbody>
</table>

Figure 1 | Jar test results for whole NOM and fractions comparing low, operational and very high alum doses showing (a) DOC and (b) A254.
HPSEC-UV and HPSEC-DOC chromatograms for whole NOM and its four fractions are presented in Figure 3a and b, respectively. As observed previously, HPSEC-UV chromatograms have poorer resolution and under-represented peaks. However, HPSEC-DOC chromatograms have a region of negative detector response between 0.1 and 1 kDa probably due to salt interference. Nevertheless, HPSEC-DOC provides improved total MW distribution information compared with HPSEC-UV and hence is used in further discussion. The VHA fraction comprised about 50% of whole NOM and included the polysaccharide/protein (55 kDa) and the humic/fulvic peaks (5.5, 3.8, 2.1 and 1.2 kDa). The SHA fraction has a significantly reduced polysaccharide/protein peak and about 20% of the humic/fulvic peaks when compared with whole NOM. This is congruent with the fractionation results where the hydrophobic component makes up 70% of whole NOM. The remaining 30% of NOM, including the hydrophilic CHA and NEU fractions, has significantly reduced peaks in the humic/fulvic region, and no detectable polysaccharide/protein peak. The appearance of an apparent polysaccharide/protein peak in the VHA instead of the NEU fraction is unlike what has been reported elsewhere (Kennedy et al. 2005); this could be due to the nature of this NOM sample as the fractionation procedures used were similar to those previously reported.

Jar tests with 100 mg/L alum removed most of the polysaccharide/protein peak (55 kDa) of whole NOM, as well as most of the humic/fulvic peak at 5.5 kDa. The other humic/fulvic peaks at 3.8, 2.1 and 1.2 kDa were removed to decreasing extents. This portion of NOM not removed is considered to be recalcitrant to removal by alum coagulation. HPSEC-DOC shows that there was removal of the larger MW components from the VHA, SHA and CHA fractions and the lower MW components were resistant to removal. The NEU fraction was virtually unchanged before and after alum coagulation.

Biodegradability of NOM fractions

The BDOC component of NOM gives an indication of the potential of the water to support microbial growth in the distribution systems. Myponga Reservoir NOM treated with 100 mg/L alum had a BDOC of 0.72 ppm, compared with 1.80 ppm for untreated water (Figure 4). Hence, 60% of the BDOC was removed by alum coagulation, similar to the removal of DOC during coagulation. The BDOC of the NEU fraction was the highest (0.61 ppm), followed by the CHA, SHA and VHA fractions. The NEU fraction contributed 85% of the BDOC for the whole NOM sample. BDOC/DOC did not change with alum coagulation, but it is clear that the potential for BDOC is highest for the NEU fraction. It appears that the lower MW NOM in the NEU fraction more easily assimilated by the bacteria used in the BDOC determinations compared with the other three fractions, and hence the NEU fraction is most likely to contribute to microbial growth in distribution systems (Buchanan et al. 2005). Since alum coagulation did not reduce the concentration of the NEU fraction, a disinfectant residual is required to control microbial growth and biofilm formation in the distribution system.
Trihalomethane formation potential of NOM fractions

Total THMFP (t-THMFP) is the sum of the formation potential of the four trihalomethanes (chloroform, dichlorobromoform, dibromochloroform and bromoform). The coagulation of Myponga Reservoir water with 100 mg/L alum reduced t-THMFP by 66% (Figure 5). Of the four NOM fractions, the highest contributor to t-THMFP is VHA, followed by NEU, SHA and CHA, similar to observations elsewhere (Buchanan et al. 2006). The t-THMFP appears to correlate with the DOC and $A_{254}$ values for these fractions, where $R^2 = 0.9561$ and 0.9861, respectively. Alum treatment at 100 mg/L reduced the formation potential of chloroform, but increased that of dichlorobromoform, dibromochloroform and bromoform. The formation potential of chloroform and dichlorobromoform was lower for the fractions, where VHA > SHA > NEU > CHA. The formation potential for dibromochloroform was similar for all four fractions, however there was no formation potential for bromoform. As the VHA and SHA fractions had higher THMFP, alum coagulation removed a significant portion of these fractions and the t-THMFP was reduced. However, much of the NEU fraction

Figure 4 | BDOC of untreated and treated (100 mg/L alum, pH 6) whole NOM and fractions.

Figure 5 | THMFP of untreated and treated (100 mg/L alum, pH 6) whole NOM and fractions.
was not removed and so contributed a significant proportion of the total THMs.

**CONCLUSIONS**

The isolation of NOM fractions from Myponga Reservoir and the testing of these fractions resulted in an improved understanding of the characteristics of its NOM constituents, and their potential for affecting water treatment processes and water quality. Alum coagulation (100 mg/L) removed nearly 60% of NOM and HPSEC-UV-DOC revealed that most of the NOM components removed were of higher MW. At the near operational dosing condition, 72% and 59% of the VHA and SHA fractions were removed, compared with 58% and only 16% for the CHA and NEU fractions. The NEU fraction not removed by alum made the highest BDOC contribution to the treated water, and had the potential to support biofilm formation in distribution systems. The VHA and NEU fractions not removed during coagulation also have the potential to contribute significantly to THM formation.

Although alum coagulation removed a large proportion of NOM, a significant component of the NOM was found to be recalcitrant to this treatment. To prevent microbial regrowth in the distribution system, disinfection and a disinfectant residual are required to prevent deterioration of treated water quality. The high BDOC level of Myponga NOM requires a disinfectant residual to control the microbial quality of the water, although increased chlorine disinfectant use will also increase DBP formation. Other water treatment methods (ie. biological treatment, membranes) could be applied in addition to the existing treatment processes if further removal of NOM is required.

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**REFERENCES**


