Operational Paper

A case study of treatment performance and organic character

Christopher W. K. Chow, Rolando Fabris, Mary Drikas and Michael Holmes

ABSTRACT

Two South Australian drinking water treatment plants (WTPs), Happy Valley and Myponga, with different source water supplies, were selected for an 18-month natural organic matter (NOM) characterisation case study. During this study (January 2001 to July 2002), the raw water dissolved organic carbon (DOC) concentration increased near the end of 2001; however, the applied alum dose required to maintain treated water DOC concentration decreased for both WTPs. This observation linked well with the results obtained from the rapid fractionation. It was found that the increase in organic carbon at the end of the year was mainly an increase of the very hydrophobic acids (VHA) fraction. This fraction typically has the characteristic of being easily removed by alum treatment. The use of the rapid fractionation technique to study the impact of organic character on disinfection was also very successful. The chlorine demand correlated well with the VHA fraction ($r^2 = 0.75$ for Happy Valley and Myponga combined) while the r^2 values of chlorine demand with DOC and UV were 0.55 and 0.58, respectively.

Key words | alum, disinfection, DOC, NOM, rapid organic matter characterisation, water treatment

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INTRODUCTION

Natural organic matter (NOM) is an important topic in drinking water treatment. Considerable research effort has occurred worldwide to link NOM character to treatability. Reduction in NOM before disinfection can minimise the formation of disinfection by-products and reduce the chlorine dose required to control bacterial regrowth in the distribution system, resulting in water of higher quality for consumers.

The removal of NOM by conventional water treatment utilising inorganic coagulants is affected by the character of the NOM and factors such as the pH and alkalinity of the raw water (Krasner & Amy 1995; Owen *et al.* 1995). A number of characterisation techniques have been developed to enable a better understanding of the impact of organic compounds on the treatment processes. General

analytical techniques, such as dissolved organic carbon (DOC) and UV absorbance measurements have been used as surrogate parameters to monitor the concentration of NOM and they are widely accepted by water treatment operators as parameters to assess treatment plant performance. UV absorbance measurement is one of the simplest characterisation methods and there are also several advanced analytical techniques developed to characterise NOM based on humic/non-humic fractions, the hydrophobic/hydrophilic character and molecular weights of the constituents (Edzwald *et al.* 1985; Wang *et al.* 2000).

NOM can be isolated based on either the chemical or the physical properties of the compounds. Commonly used isolation techniques include ion-exchange resins or

ultrafiltration membranes with different nominal molecular weight cutoffs. In general, organic fractionation is used as an isolation procedure (Croue *et al.* 1994). As such, this technique is not commonly used as an analytical technique in the drinking water industry to optimise treatment processes. In an earlier alum flocculation study using isolated organic fractions from two Australian reservoirs, it was established that the removal efficiency was highly influenced by the character of the fractions (Chow *et al.* 2000; van Leeuwen *et al.* 2002).

A rapid fractionation (analytical) technique based on measuring the organic carbon concentrations before and after contact with the resins (DAX-8, XAD-4 and IRA-958) has been reported recently (Chow *et al.* 2004). The concentration of four NOM fractions, very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU), in the sample can be determined based on subtraction of the organic carbon concentrations of subsequent resin effluents. This technique was successfully applied in a jar test experiment and the results showed that particular NOM fraction removal was dependent upon treatment conditions, such as applied alum dose, pH etc., and these can be optimised based on the character of the organic matter present in the source water (Chow *et al.* 2004).

In this paper, the impact of organic character on treatment plant performance (coagulation and disinfection) due to seasonal variation is reported. The organic character of water sources for the Happy Valley and Myponga water treatment plants (WTPs) was monitored using the rapid fractionation technique over an 18-month period together with DOC, UV_{254}, colour and molecular weight distribution measurement using high performance size exclusion chromatography (HPSEC). The results were then used to establish a link between organic character and treatment plant operation conditions such as applied alum dose and DOC removal performance.

The organic characterisation work was then extended to study the impact of organic character on disinfection. Disinfection is the final phase of the treatment process and the presence of a disinfectant residual can assist greatly in the maintenance of water quality throughout the distribution system. Chlorine is the most widely used disinfectant for the supply of potable water. It is highly reactive with organic and inorganic compounds found in bulk water and on distribution system infrastructure surfaces. The organic characterisation results obtained were linked with the disinfection process, which included chlorine demand and trihalomethane (THM) formation.

RESERVOIRS AND TREATMENT PLANTS

The Happy Valley Water Treatment Plant is situated 15 km south of Adelaide and is the largest water treatment plant in South Australia with the design capacity of 850 Ml per day. The plant employs coagulation/flocculation, sedimentation and filtration processes. The source is primarily from the River Murray and is supplemented by the Mt Bold catchment. The Myponga Water Treatment plant is located about 50 km south of Adelaide. It has a production capacity of 50 Ml per day and employs the dissolved air flotation-filtration (DAFF) process. The source water is only from natural catchment. The water is generally high in colour and organic content and low in turbidity. Both treatment plants use alum $(Al_2(SO_4)_3 \cdot 18H_2O)$ and a cationic polymer for coagulation and chlorine as the disinfectant.

Treatment is required to ensure water quality compliance with the Australian Drinking Water Guidelines (NHMRC/AWRC 1996) as well as satisfying various contractual targets. Coagulation at both treatment plants was optimised for DOC removal by adjusting alum dose and coagulation pH. The coagulation pH used at Happy Valley WTP ranged from 6.6 to 6.9. A lower coagulation pH was used at Myponga WTP, 6.1 ± 0.1, to achieve a higher DOC removal. Dose rates for alum and chlorine are reviewed monthly and adjusted in light of process and network water quality trends (Holmes & Oemcke 2002).

EXPERIMENTAL

Analytical methods

Ultrapure water used in these experiments was obtained from a Milli-Q® purification system (Millipore, France). Water samples were 0.45 μm filtered prior to analyses except pH and turbidity measurements. General water quality parameters, pH (pH 320, WTW, Germany), turbidity

(2100AN, Hach, USA) and dissolved organic carbon (DOC) (820, Sievers Instruments Inc., USA) were determined using the methods described in *Standard Methods* (1998). The UV absorbance at 254 nm (UV_{254}) was measured using a UV/VIS spectrophotometer (Model 918, GBC Scientific Equipment Ltd, Australia) with a 1 cm quartz cell (*Standard Methods* 1998). Colour was determined using the method described in Bennett & Drikas (1993) with a 5 cm cell.

The apparent molecular weight of the UV absorbing compounds was determined using high performance size exclusion chromatography (HPSEC). A Shodex KW 802.5 packed column (Shoko Co. Ltd, Japan) was used with a Waters 2690 separation module and 996 photodiode array detector. The carrier solvent was a 0.1 M phosphate buffer solution (pH 6.80) adjusted to an ionic strength of 1.0 M with sodium chloride. The flow rate was $1 \, ml \, min^{-1}$. Calibration was performed using polystyrene sulfonate (PSS) standards (Polysciences Inc. Massachusetts) of molecular weights 35,000, 18,000, 8,000 and 4,600 Daltons. Detection was based on UV absorbance ($260 \, nm \, cm^{-1}$). The procedure was based on the method described by Chin *et al.* (1994). The chromatogram can also be used to determine average molecular weight based on the weight average (Mw) formula:

$$M_w = \frac{\sum_{t=1}^{n} UV_{260t} \times MW_t}{\sum_{t=1}^{n} UV_{260t}} \tag{1}$$

The rapid fractionation technique was reported in Chow *et al.* (2004), which was modified from the method published by Croue *et al.* (1994) and Bolto *et al.* (1999) and resulted in determining the concentration of four fractions: VHA (adsorbed by DAX-8), SHA (adsorbed by XAD-4), CHA (adsorbed by IRA-958) and NEU, which was not adsorbed on any of the ion exchange resins. Three 20 cm (length) × 13 mm internal diameter (ID) glass columns for DAX-8, XAD-4 and IRA-958 resins, respectively, were set up in series. DAX-8, XAD-4 and IRA-958 resins were supplied by Supelco (Belefonte, Pennsylvania). Sodium hydroxide, hydrochloric acid and sodium chloride solutions used for pH adjustment and cleaning/regeneration of resins were prepared from AR grade chemicals.

Chlorine decay was determined by dosing an appropriate volume of saturated chlorine solution into 1 litre of (plant or jar test) treated water stored in an amber bottle.

The dose selection criterion was to achieve $0.5 \, mg \, l^{-1}$ chlorine residual at the end of 72 hours (3 day). At predetermined times 100 ml samples were taken for chlorine analysis over a period of 72 hours. Samples were incubated at $20 \pm 2°C$. Chlorine residual was determined using the N,N-diethyl-p-phenylenediamine (DPD) ferrous titration method. DPD is used as an indicator in the titration procedure with ferrous ammonium sulfate (FAS) (*Standard Methods* 1998).

A THM formation test was performed by chlorinating 60 ml of treated water at appropriate chlorine dose (selection criteria mentioned in previous section) in a glass-stoppered amber bottle filled to the brim with no headspace. After incubation at $20 \pm 2°C$ for 72 hours the sample was immediately quenched with ascorbic acid and analysed for THMs. THM components were determined using a gas chromatograph with a headspace autosampler, coupled with an electron capture detector (*Standard Methods* 1998).

Experimental procedures

Raw (plant inlet) and product water (prior to chlorination) samples were collected over an 18-month period on a monthly basis (January 2001 to July 2002). Raw water samples were analysed for turbidity, colour, DOC and UV_{254} and treated water samples were analysed for DOC, UV_{254}, chlorine decay and THM formation. Specific UV absorbance (SUVA) and specific colour were used for simple organic characterisation of the raw water samples. SUVA was determined by (UV_{254}/DOC) × 100 while specific colour was determined by colour/DOC. Selected samples were characterised using HPSEC (molecular weight distribution and average molecule weight measurement) and rapid fractionation.

To evaluate DOC removal performance, a calculated parameter 'specific alum demand' was used. Specific alum demand is defined as alum dose required to remove 1 mg of DOC. It is calculated as the required alum dose divided by the DOC concentration removed by the process (inlet DOC concentration – treated water DOC concentration). The required alum dose ($mg \, l^{-1}$) is the plant alum dose subtracted by the dose required to remove turbidity (turbidity compensation). A simple mathematical relationship reported by van Leeuwen *et al.* (2001) was employed to

compensate the turbidity contribution to alum consumption. Dose required to remove turbidity was calculated on the basis that $1 \, mg \, l^{-1}$ alum removes 0.4775 NTU.

During the experimental period, jar tests were performed on selected samples using the conditions of (i) $20 \, mg \, l^{-1}$ alum less than plant alum dose achieving a coagulation pH of approximately 7.0–7.2 (without pH adjustment) and (ii) $30 \, mg \, l^{-1}$ alum more than the plant dose with coagulation pH 6.2, to simulate under and over dosing conditions, respectively. The same analyses as above were performed for the treated water (jar test) samples.

RESULTS AND DISCUSSION

Water quality, plant operation and performance

The two WTPs were selected based on different source water supply. Happy Valley Reservoir obtains water from the local catchment supplemented with River Murray water. Past water quality data indicate that turbidity is usually higher with a larger variation compared with Myponga. During the experimental period turbidity varied between 3.9 and 23.4 NTU with an average of 11.0 NTU. Alkalinity varied considerably ranging from 70 to $110 \, mg \, l^{-1}$ (as $CaCO_3$) with an average of $83.3 \, mg \, l^{-1}$. The pH ranged from 7.6 to 8.2 with an average of 7.9. DOC concentration was stable over the studied period around $10 \, mg \, l^{-1}$, with a peak of $11.8 \, mg \, l^{-1}$ in January 2002. Colour and UV_{254} both increased slightly towards the end of 2001. Myponga Reservoir is a primary catchment that is fed solely from runoff in the surrounding areas. The water quality is low in turbidity (range 1.8 to 4.0 NTU) with an average of 3.1 NTU during the studying period, high colour and high DOC water. Alkalinity was relatively stable (range of 51 to $63 \, mg \, l^{-1}$ as $CaCO_3$) with an average of $57.9 \, mg \, l^{-1}$. The pH ranged from 7.4 to 7.8 with an average of 7.6. Most of the rainfall occurs during the winter months (May–August) when fresh organic matter is flushed into the reservoir. DOC concentration, colour and UV_{254} all increased progressively towards the end of 2001. DOC concentration reached a peak of $15.8 \, mg \, l^{-1}$ in December 2001 (Figure 1b).

Treated water DOC concentration was maintained within the range of 4.3 to $6.1 \, mg \, l^{-1}$ (Happy Valley) and 4.7 to $5.7 \, mg \, l^{-1}$ (Myponga) with an average of $5.0 \, mg \, l^{-1}$ and $5.2 \, mg \, l^{-1}$, respectively (Figure 1). The percentage DOC removal during the period was between 36 and 57% (47% average) and 56 and 65% (62% average) for Happy Valley and Myponga, respectively.

Jar tests were performed on Happy Valley and Myponga raw water using alum doses $20 \, mg \, l^{-1}$ less than the plant dose and $30 \, mg \, l^{-1}$ more than the plant dose. Results showed that when the lesser dose was used, DOC removal was reduced by an average of 8.7% and 8.2% compared with the plant treated water for Happy Valley and Myponga WTPs, respectively. When dosing above the plant dose, DOC removal increased by an average of 3.6 and 3.0% for Happy Valley and Myponga, respectively, when compared with the plant. This confirmed that the selected plant doses were very close to the maximum DOC removal.

It is interesting to note that the DOC removal performance for both WTPs increased at the end of 2001; that is, for Myponga WTP, 16.6 mg of alum was required to remove 1 mg of DOC in March, while in November only 8.9 mg of alum was required (Figure 1). In addition, the DOC removal performance was found to be better for Myponga WTP than Happy Valley; that is, less alum was required to remove the same concentration of DOC. Differences in specific alum demand may be explained by the fact that Myponga WTP was optimised at a lower coagulation pH.

The link between source water organic character and treatment performance

DOC, UV_{254}, colour and molecular weight measurements

An attempt was made to correlate source water organic characterisation information with alum usage and NOM removal. Figure 2a shows the corresponding alum dose (turbidity compensated) plotted against the inlet DOC concentration for both WTPs. Moderate correlation was established with r^2 values of 0.51 and 0.66 for Happy Valley and Myponga WTP, respectively. It is generally assumed that an increase in raw water DOC concentration will require an increase in alum dose to maintain treated water DOC concentration. However, the result suggests that this is not the case as indicated by the negative relationship between alum dose and DOC concentration. It is worth noticing that the interpretation of this negative relationship is rather complex; the graph should not be used as a
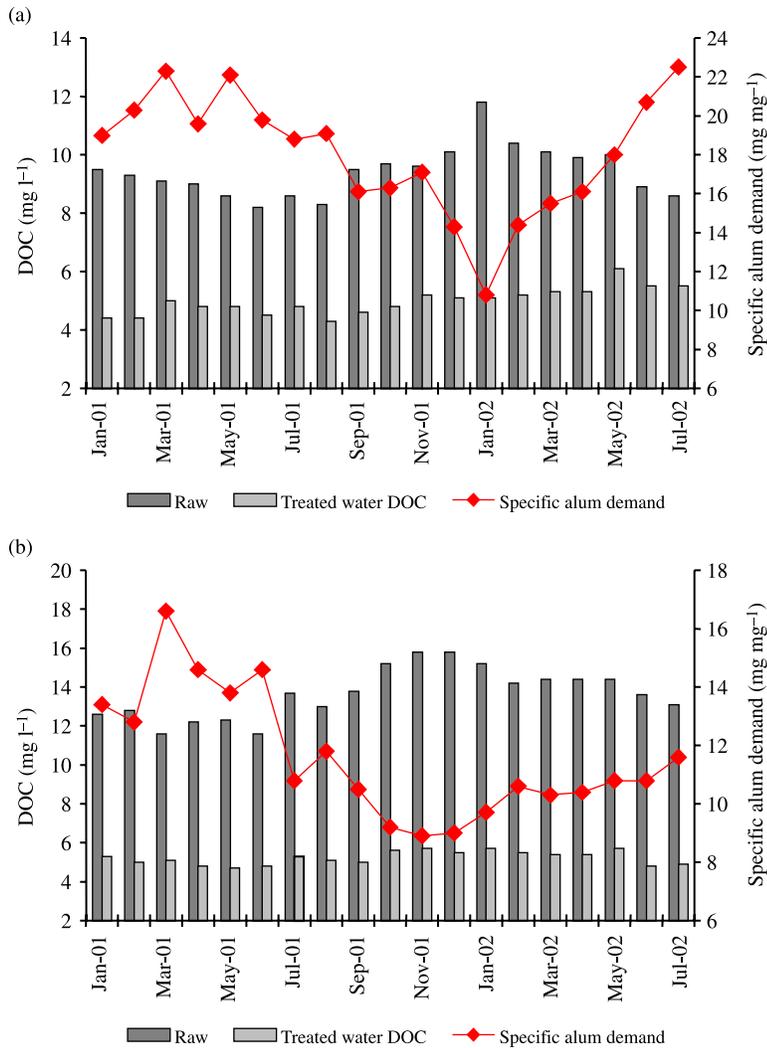
Figure 1 │ Seasonal variation of water quality, raw and treated water DOC concentration and specific alum demand: (a) Happy Valley and (b) Myponga WTP. Specific alum demand was determined based on the required alum dose divided by the concentration of DOC removed by the treatment process.

calibration curve of alum dose against DOC concentration (source water) without taking into account the organic character. Figure 2b shows specific alum demand plotted against the inlet DOC concentration for both WTPs. The negative linear relationship indicated that DOC removal performance improved (as indicated by the decrease of the specific alum demand) with the increase of inlet DOC concentration. Additional organic characterisation techniques, HPSEC and rapid fractionation, were applied in an attempt to explain the above phenomenon.

During the period when DOC concentration reached its peak (seasonal variation), the UV_{254} and colour also reached

the peak of $0.388 \, cm^{-1}$ and 71 HU for Happy Valley and $0.595 \, cm^{-1}$ and 108 HU for Myponga, respectively. SUVA and specific colour are commonly used parameters to provide organic characterisation information. The organic character variation based on these two parameters for both reservoirs during the experimental period is shown in Figure 3a. SUVA values ranged from 2.6 to 4.7 with an average of $3.5 \, m^{-1} mg^{-1} l$ for Happy Valley, and 3.4 to 4.3 with an average of $3.7 \, m^{-1} mg^{-1} l$ for Myponga. Happy Valley specific colour ranged from 3.5 to 9.6 with an average of $5.8 \, HU \, mg^{-1}$; 5.4 to 8.0 with an average of $6.3 \, HU \, mg^{-1}$ for Myponga. In addition, a similar seasonal trend was observed for both
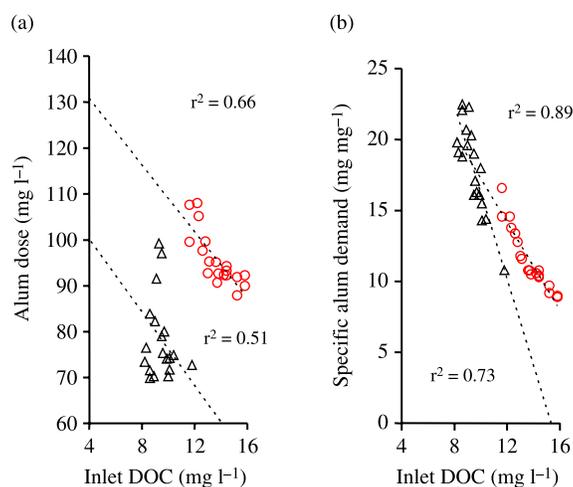
Figure 2 | Impact of treatment plant inlet DOC concentration on (a) alum dose and (b) specific alum demand; (Δ) Happy Valley and (o) Myponga. Alum dose used in Figure 2a and specific alum demand used in Figure 2b were turbidity compensated (refer to the equations described in the text).

WTPs (Figure 3a). The trend shows that both SUVA and specific colour were lower in the winter period (May–July 2001) and increased in the summer months.

HPSEC has been widely used for NOM characterisation and is particularly well received by water treatment operators. The separation principle of HPSEC is based on the differences of molecular size and the ability of different molecules to penetrate the pores of the stationary phase to different extents (Lough & Wainer 1996). HPSEC has been reported to be an effective method for determining the molecular weight of NOM (Chin *et al.* 1994; Egeberg *et al.* 1999, 2002; O'Loughlin & Chin 2001). A series of samples collected from January 2001 to December 2001 were analysed using HPSEC. The chromatograms are shown in Figure 3b. The results confirmed that the profile shifted towards larger molecular weight towards the summer period. In order to quantify the chromatograms, the weight average apparent molecular weight (*Mw*) for both reservoirs was plotted in Figure 3b. The *Mw* values varied between 1,440 and 1,600 Da for Happy Valley and 1,200 and 1,500 Da for Myponga source water. The detection system used in this study is a UV detector that is commonly used in HPSEC systems. This type of detector is limited to the detection of UV sensitive materials, therefore it cannot detect all components of dissolved organic carbon (DOC), and the detector response is not quantitative even for the components that are detectable. Based on these results, the

organic material present in both reservoirs were found to be similar in character at the same period of time with only slight variation in some samples when characterised using *Mw*, SUVA and specific colour values (Figure 3).

SUVA values for raw water are generally between 1 and $5 \, m^{-1} mg^{-1} l$. A high SUVA value indicates that the organic compounds present are composed largely of aquatic humic substances which are higher in molecular weight having a relatively higher content of hydrophobic and aromatic components (Edzwald 1993). These fractions are preferentially removed by alum treatment (Krasner & Amy 1995; Goel *et al.* 1995). Organic compounds with lower SUVA values, which are recalcitrant to removal by alum treatment, have been suggested to be of lower molecular weight, relatively hydrophilic and less aromatic (Edzwald 1993). Highly coloured material is generally considered to be organic matter derived from humic substances with large molecular weight and is readily removed by alum treatment. Thus, the use of inlet SUVA or specific colour to predict DOC removal is feasible. However, regression analysis study did not show correlation between specific alum demand and SUVA ($r^2 = 0.02$ and 0.23 for Happy Valley and Myponga, respectively) and similarly for specific alum demand and specific colour ($r^2 = 0.13$ and 0.06 for Happy Valley and Myponga, respectively). This may be partially explained by the variation in raw water alkalinity, which had an impact on the specific alum demand but not on SUVA found at Happy Valley. The correlation between specific alum dose with molecular weight calculation using *Mw* showed mixed results with $r^2 = 0.11$ and 0.77 for Happy Valley and Myponga, respectively. Additional correlation analyses between alum dose with the three parameters showed similar results (SUVA: $r^2 = 0.62$ and 0.09, specific colour: $r^2 = 0.39$ and 0.01 and *Mw*: $r^2 = 0.33$ and 0.68 for Happy Valley and Myponga, respectively). The lack of correlation could be due to the relative stability of the SUVA, specific colour and *Mw* values during the experimental period. In most cases, better correlation is observed with wider range of variation.

Rapid fractionation

Selected samples were analysed using the rapid fractionation technique. The variation in the percentage of the
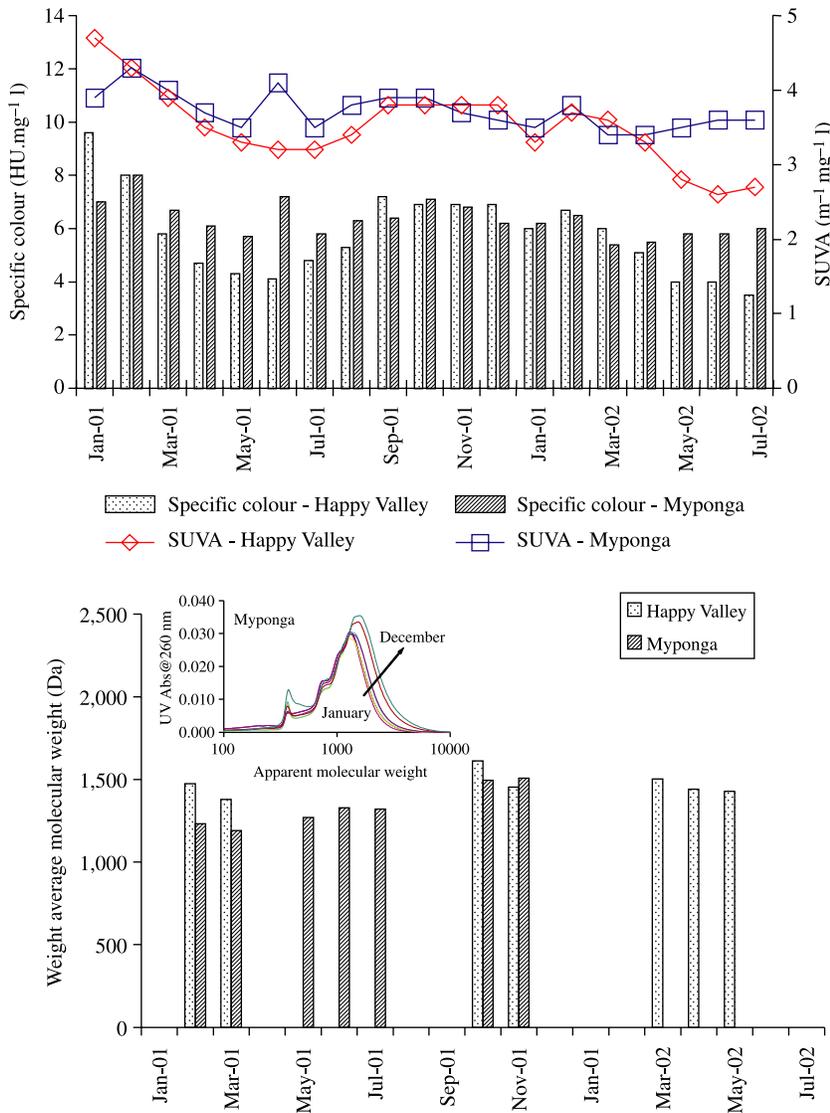
Figure 3 | Seasonal variation of organic character in Happy Valley and Myponga reservoirs measured by (a) specific UV absorbance (SUVA) and specific colour measurements and (b) molecular weight distribution using HPSEC (chromatograms of Myponga source water).

organic fractions which make up the total DOC can reflect differences in organic character. Figure 4 shows the concentrations of the VHA, SHA, CHA and NEU fractions in the inlet water for both reservoirs. The results indicated that the VHA fraction made up approximately half of the total DOC. It was also observed that the percentage VHA fraction increased towards the end of the year concomitant with the increase in DOC concentration. The concentrations of the other three fractions were relatively constant over the year. Therefore, the results suggest that the increase in DOC in the latter half of the year was mainly a result of

the increase in the VHA fraction. The increase of VHA coincides with the increase in SUVA, specific colour and *Mw*. Also worthy of mention is that the percentage of the four fractions was very similar for both reservoirs for samples collected over the same period of time (February, March, September and October 2001). This indicated that, at the time, the organic character in both reservoirs was similar. This supported the results obtained for SUVA, specific colour and *Mw*.

The variation of the distribution of the fractions over the year provided a good case study for organic character and
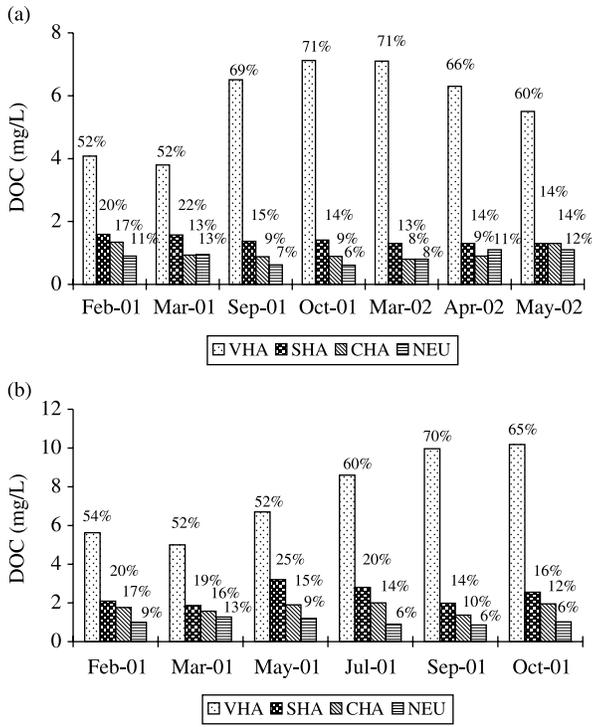
(a)

(b)

Figure 4 │ Seasonal variation of organic fractions, VHA, SHA, CHA and NEU, in the inlet water supplied to (a) Happy Valley and (b) Myponga WTP. Both concentration and percentage total are presented.

treatability. Concentrations of each fraction were plotted against specific alum demand and alum dose: only the VHA fraction is shown (Figure 5). A good correlation was obtained between specific alum demand and VHA fraction (r^2 value of 0.93 and 0.83 for Happy Valley and Myponga,
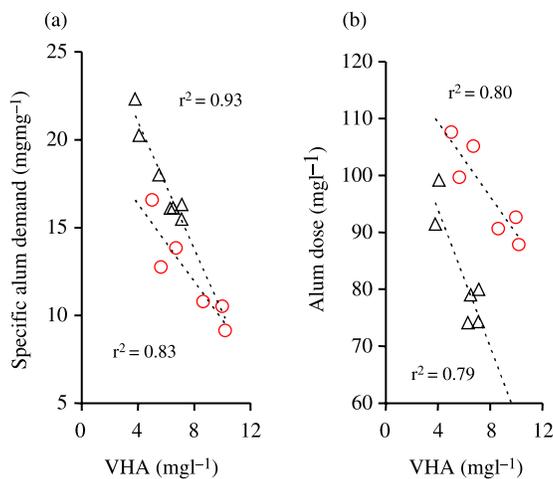

Figure 5 │ The correlation between (a) specific alum demand and (b) plant alum dose against VHA concentration; ∆: Happy Valley and o: Myponga WTP.

respectively). In contrast to the good and clear relationship found between VHA fraction and specific alum demand, the SHA, CHA and NEU fractions demonstrated either poor correlation or inconsistence between the two WTPs. The SHA fraction showed good correlation for one WTP with $r^2 = 0.72$ (Happy Valley) and poor correlation for the other with $r^2 = 0.05$ (Myponga). The CHA concentration did not have any correlation with specific alum demand for both WTPs. The NEU fraction showed good correlation with r^2 value of 0.67 and a positive slope for Myponga but no correlation for Happy Valley. The positive slope indicated that this fraction is harder to remove by alum treatment. When the NEU fraction concentration in the raw water increases, a higher alum dose is required; however due to the low concentration and small variation in NEU concentration over the monitored period ($\sim 0.1\,mg\,l^{-1}$ DOC), its contribution to a dose increase may not be significant.

The use of organic fractions to obtain a direct correlation with alum dose was attempted. A good correlation between VHA fraction and alum dose (r^2 value of 0.80 and 0.79 for Happy Valley and Myponga, respectively) was obtained. In contrast, the SHA, CHA, NEU fractions either did not correlate with alum dose or were inconsistent between the two WTPs, as reported for specific alum demand. The negative slope (Figure 5b) indicated that the alum dose required to achieve a mean treated water DOC concentration of $5\,mg\,l^{-1}$ decreased as raw water VHA concentration increased. For example, in March 2001, the percentage VHA in raw water was 52%, raw and treated water DOC concentration was $11.8\,mg\,l^{-1}$ and $5.1\,mg\,l^{-1}$, respectively, and alum demand was $16.3\,mg\,mg^{-1}$. In September 2001, the percentage VHA in raw water increased to 70%, DOC concentration in raw water increased to $13.8\,mg\,l^{-1}$, treated water DOC was slightly lower than in March ($5.0\,mg\,l^{-1}$) and the specific alum demand had reduced to $9.7\,mg\,mg^{-1}$.

The link between treated water quality and distribution system performance

In the previous section, the impact of organic character on treatment plant performance (DOC removal) was discussed

based on organic characterisation of raw water. By adopting a similar methodology, the impact of organic character on water quality following chlorination, including chlorine demand (consumption) and disinfection by-product formation can be evaluated.

Treatment using alum coagulation reduces DOC concentration and UV_{254}. Alum coagulation also changes the bulk water organic character and this can be studied using the techniques previously described in this paper. Further, changes in DOC character as a result of alum treatment also impact on disinfection and subsequent water quality in the distribution system, particularly disinfection by-product formation. Seasonal variation of organic character can also impact on THM formation as reported by Goslan *et al.* 2002. This further strengthens the value of organic characterisation in drinking water treatment.

The average treated water DOC concentration at the plant outlet during the experimental period was $5.0 \, \text{mg} \, l^{-1}$ and $5.2 \, \text{mg} \, l^{-1}$ for Happy Valley and Myponga, respectively. Considering both WTPs together, the treated water SUVA values ranged between 1.3 and $2.0 \, \text{m}^{-1} \text{mg}^{-1} l$ which was lower than the raw water SUVA which ranged from 2.6 to $4.7 \, \text{m}^{-1} \text{mg}^{-1} l$. Similarly the *Mw* of the treated water was in the range of $650 – 1,000 \, \text{Da}$ which was lower than the *Mw* of the raw water ($1,200 – 1,600 \, \text{Da}$).

Three-day chlorine demand (consumption) was determined for plant treated waters and waters generated using jar tests with a range of alum doses. This provided water

samples with different DOC concentration and character. In Figure 6, the correlation of treated water DOC, UV_{254} and VHA concentration were used to link organic character with chlorine demand. The 3-day chlorine demand data correlated best with VHA ($r^2 = 0.75$) followed by UV_{254} ($r^2 = 0.58$) and DOC ($r^2 = 0.55$). Poor correlation was found between the other fractions, SHA, CHA and NEU with chlorine demand showing an r^2 less than 0.2. This indicated that the character of these organic fractions did not show a clear relationship to chlorine demand. From an operational point of view, as these fractions comprise relatively small percentages of the bulk DOC concentration, they were not considered parameters of concern. Similarly, SUVA and *Mw* using HPSEC, were also evaluated and the r^2 values determined by regression analysis were found to be 0.35 and 0.06 for SUVA and *Mw*, respectively. From these results, VHA concentration was found to be the best parameter to correlate with chlorine demand.

The attempt to link organic character, DOC, UV_{254}, SUVA and VHA, SHA, CHA, NEU and *Mw*, with THM formation did not show a strong correlation. The best three correlating parameters were found to be UV_{254}, DOC and VHA with r^2 values of 0.48, 0.41 and 0.32, respectively. The lack of correlation with THM formation and only moderate correlation in the case of chlorine demand could be due to similarity of organic character of all the treated waters within this experimental set. Despite the fact that water treated using jar tests produced treated water with different
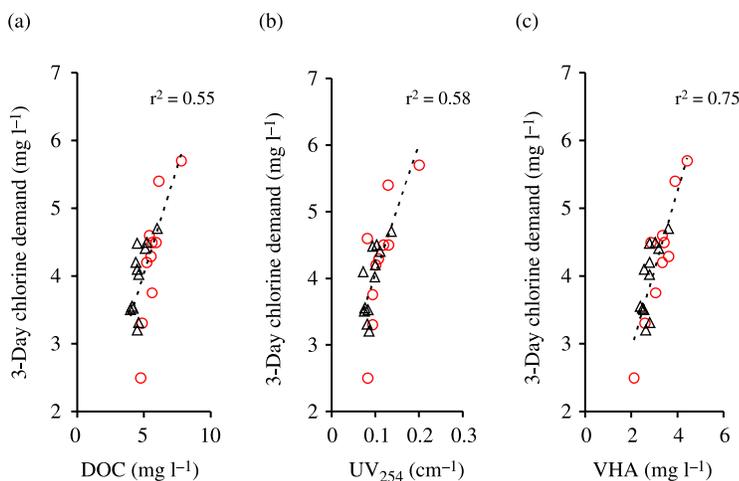

Figure 6 | The correlation between 3-day chlorine demand against (a) DOC, (b) UV_{254} and (c) VHA concentration; (Δ) Happy Valley and (o) Myponga WTP.

quality, they were still relatively similar in their reactivity with chlorine. Therefore no clear correlation was apparent in the regression study.

CONCLUSIONS

There has been an increasing emphasis on improved water quality and operators of water utilities have become more aware of the impact of NOM on their treatment processes. This study shows that, by improving the understanding of the NOM character, it is possible to optimise treatment. This can improve NOM removal and lead to reduced chlorine demand and disinfection by-products.

The use of a simple characterisation tool such as SUVA did not establish a link with DOC removal and applied alum dose. The use of the fractionation technique and HPSEC showed that the peak DOC concentration found during the summer of 2001 was mainly caused by the increase in concentration of the VHA fraction and consequently high molecular weight compounds as well. This correlated well with the performance of the treatment process which showed that applied alum dose decreased at the end of the year, owing to ease of removal of the VHA fraction.

The current water treatment practice to optimise alum dose for the two WTPs based on the treated water quality as feedback control worked well. However, in this work we have demonstrated the link between organic character and DOC removal performance. When applying this technique to characterise raw water NOM, the appropriate coagulant dose can be selected to remove the majority of the coagulable NOM based on the concentrations of the fractions. It is possible to employ these techniques as organic character indicators to fine-tune the treatment process and potentially customise the treatment conditions to address the particular water character, hence achieving the goal of maximum NOM removal.

When considering distribution system performance, the control of disinfectant residual is an important factor. The goal of many water quality managers is to maintain a residual disinfectant concentration throughout the distribution system to prevent microbiological contamination while being palatable to customers. This work demonstrated that the rapid fractionation technique can be used as a tool to predict chlorine demand, although the overall correlation

of the sample set was not significant enough to be considered ideal. However, the obtained r^2 figure for the correlation between VHA and chlorine demand is better than other commonly used parameters such as UV_{254} and DOC for the two studied WTPs.

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