Impact of extracted algogenic organic matter on coagulation performance

Linan Xing, Christopher W. K. Chow, Jiane Zuo, Dongsheng Wang, Rolando Fabris, John van Leeuwen and Mary Drikas

ABSTRACT

Understanding coagulation behaviour and treatability of waters impacted by algogenic organic matter (AOM) is important for waters with frequent algal blooms. Physico–chemical characteristics of AOM spiked into a water sample, before and after coagulation, were investigated using high-performance size exclusion chromatography (HPSEC) with UV and fluorescence detection, three dimensional-fluorescence excitation emission matrix (3D-FEEM) measurement and resin fractionation in which three fractions were determined including very hydrophobic acid (VHA), slightly hydrophobic acid (SHA) and hydrophilic fractions. Release of AOM from algal cells with consequential increases in dissolved organic carbon and UV absorbance led to changes in 3D-FEEM spectra indicative of increased aromatic protein presence. Changes in disinfection by-product formation potential after the AOM spiking indicated possible interactions between natural organic matter and AOM. A study of the treatability of the AOM spiked water using two coagulants, alum and a polyaluminum composite coagulant, was conducted with the relative percentages of UV absorbance values of both the SHA and hydrophilic fractions higher in the post coagulated AOM spiked water than in the coagulated water, with corresponding reductions in the VHA proportion. It was found that the increased SHA and hydrophilic components in the AOM spiked natural water were recalcitrant to removal by both coagulants.

Key words | 3D-FEEM, algogenic organic matter (AOM), HPSEC-fluorescence, HPSEC-UV, natural organic matter (NOM), resin fractionation

Linan Xing
School of Biological Engineering,
Beijing Polytechnic, Beijing, China

Jiane Zuo
State Key Joint Laboratory of Environment
    Simulation and Pollution Control,
School of Environment, Tsinghua University,
Beijing, China

Christopher W. K. Chow (corresponding author)
Rolando Fabris
Mary Drikas
Australian Water Quality Centre, SA Water
    Corporation,
SA Water House, 250 Victoria Square/
    Tarntanyangga, Water House SA 5000, Australia
E-mail: chris.chow@sawater.com.au

Christopher W. K. Chow
Dongsheng Wang
John van Leeuwen
Mary Drikas
Centre for Water Management and Reuse,
University of South Australia, Australia
and
State Key Lab of Environmental Aquatic Chemistry,
RCEES, CAS, Beijing, China

John van Leeuwen
Barbara Hardy Institute,
University of South Australia,
101 Currie Street, Adelaide SA 5000, Australia

INTRODUCTION

The presence of algae in source water is a worldwide problem for the drinking water industry. During algal bloom seasons, the increase of algae cells and their excreted metabolic substances can significantly impact water quality (Huang *et al.* 2009; Ghernaout *et al.* 2010). This algogenic organic matter (AOM) may impact the treatability of water (Chow *et al.* 1999).

AOM originates from cyanobacteria and algae as extracellular organic matter, and more significantly from their decay as intracellular organic matter (Pivokonsky *et al.* 2006). AOM is known to comprise a wide range of organic compounds including proteins, nucleic acids, amino sugars, neutral and charged polysaccharides (Henderson *et al.*

2008). Similar to other natural organic matter (NOM), it is frequently characterised using specific UV absorbance (SUVA), hydrophobic/hydrophilic composition, and by charge density and zeta potential (Edzwald 1993; Henderson *et al.* 2010). In recent years, resin fractionation (RF) and molecular weight distribution (MWD) have also been used to characterise AOM. It has been found that the relative abundance of hydrophilic organic constituents of AOM is higher than that of the other organic constituents (Henderson *et al.* 2008). Also reported by Henderson *et al.* (2008) is that the high molecular weight fraction of the AOM is comprised of mostly carbohydrates and proteins. Low molecular weight compounds of AOM cannot be characterised easily by existing methods.

The use of three dimensional-fluorescence excitation emission matrix (3D-FEEM) measurement can provide organic character information specifically on protein and humic/fulvic-like substances in NOM (Baker 2002; Her *et al.* 2004; Nguyen *et al.* 2005).

Microcystins are the most prevalent class of cyanotoxins and the most widely studied (Westrick *et al.* 2010). Research into treatment of microcystins has mostly concentrated on cells and AOM removal (Nguyen *et al.* 2005; Gao *et al.* 2010). The impact of conventional water treatment processes on *Microcystis aeruginosa* cells has been previously investigated (Chow *et al.* 1999). It was found that conventional treatment using alum did not damage *Microcystis aeruginosa* cells and therefore did not result in release of cell organic matter above background concentrations. The impact of AOM from *Microcystis aeruginosa* cells released into raw water on the treatability of NOM has not been well characterised. It has been found that AOM has a different character to allochthonous NOM (Henderson *et al.* 2008). Understanding the impact of AOM derived from an algal bloom on the overall character of NOM present in aquatic environments should provide useful information on the treatability of raw water of resources used for potable supply. In this paper, we report the results of an investigation conducted to assess the impacts of AOM derived from *Microcystis aeruginosa* on water quality and treatability using alum and HPAC (a polyaluminum based composite coagulant).

MATERIALS AND METHODS

AOM extraction

An isolate of *Microcystis aeruginosa* was laboratory cultured in ASM-1 medium (Chow *et al.* 1999). The cells were harvested on the 16th day of culture (in the exponential growth phase). The AOM sample was prepared by separation of the cells from the growth medium by filtration through a 5 μm MF-Millipore membrane filter followed by lysing of the cells. The separated cells were mixed with 100 mL Milli-Q® water (Millipore Corporation, Molsheim, France) and cell lysis was performed using a freeze and thaw procedure (Chow *et al.* 1999). After four freeze and thaw cycles, the cell culture was sonicated using a dip-in ultrasonic homogeniser (HD 3200, 20 kHz,

60 W) probe. The efficiency of cell lysis was confirmed by inspection using an optical microscope (B4, Optech Technology Co., Ltd, Taipei, Taiwan) and the residual cellular materials were removed using a 0.22 μm membrane filter. Dissolved organic carbon (DOC) and UV absorbance at 254 nm (UV_{254}) of the AOM filtrate were measured and then the filtrate stored at $-18\,°C$ prior to experimentation.

Water source and preparation of water samples

Raw water sourced from the River Murray, South Australia, was taken from the inlet of the Mount Pleasant (MP) water treatment plant. This water source varies markedly over time depending on climatic conditions, with DOC concentrations ranging from $\sim$4 to 18 mg L^{-1} and turbidity ranging from $\sim$20 to 250 NTU between 2000 and 2013.

The AOM spiked into MP water (AMPW) was prepared by the addition of concentrated AOM solution into the MP water (MPW). 300 mL of concentrated AOM solution (DOC: 40.4 mg L^{-1}, UV_{254}: 0.360 cm^{-1}, SUVA: 0.89 L mg^{-1} m^{-1}) were added to 6.5 L MP raw water. Water quality parameters of the AMPW were measured after thorough mixing. This was done to test the effects of the AOM as an overall contribution of NOM after mixing with the natural water.

A comparative test water (CW) was prepared by adding the same volume (300 mL) of concentrated AOM solution to 6.5 L Milli-Q® water (Millipore Corporation, Molsheim, France) and the DOC and UV_{254} were measured. The preparation of the CW is considered as diluting the concentrated AOM solution with Milli-Q® to the same dilution factor as AOM in MPW and it can be used to provide a simple assessment based on the mass balance of $AMPW = MPW + CW$. This test water was prepared to investigate and compare the treatability of the AOM without the influence of the NOM present in the River Murray sourced water.

Coagulation study

Chemicals

Alum stock solution (20,000 mg L^{-1} as $Al_2(SO_4)_3.18H_2O$) was prepared in Milli-Q® water from liquid aluminium sulphate (approximately 7.5% as Al_2O_3) used for commercial water treatment. High-performance poly aluminium

chloride (HPAC) is a composite aluminium based coagulant developed by the Research Centre for Eco-Environmental Sciences. The aluminium concentration of the stock solution was measured using an inductively coupled plasma-mass spectrometry method. Sodium hydroxide and hydrochloric acid were analytical grade chemicals.

Jar tests

Jar tests were performed at pH 6 using alum and HPAC. The coagulation pH was controlled by addition of NaOH or H_2SO_4 and determined prior to the addition of coagulant. A six paddle gang stirrer with 7.6 cm diameter flat paddle impellers and Gator jars were used. 2 L water samples were placed on the gang stirrer and the jar tester operation procedure was as follows: rapid mixing at 230 rpm for 1 minute, slow mixing at 20 rpm for 14 minutes and settling for 15 minutes. The settled water samples were gravity filtered using pre-rinsed 11 μm pore-size paper filters (Whatman International Ltd, Maidstone, UK). Six doses of 20, 60, 90, 110, 150 and 200 mg L^{-1} as alum equivalent were used and the optimum dose for both coagulants was found to be 90 mg L^{-1}. The water samples were filtered through 0.45 μm membranes (Microscience, MicroAnalytix, New South Wales, Australia) before determining the parameters of colour, DOC and UV_{254}. Samples (500 mL) were collected for subsequent RF. Samples collected for high-performance size exclusion chromatography (HPSEC) were filtered through 0.22 μm membranes (Microscience, MicroAnalytix, New South Wales, Australia).

Analytical methods

DOC, UV_{254}, SUVA and turbidity

DOC was measured using a total organic carbon analyser (Model 900, Sievers General Electric Analytical Instruments Inc., Boulder, CO, USA) after water samples were filtered through 0.45 μm filters. UV_{254} was measured using a UV-visible Shimadzu Model 1201 spectrophotometer (Japan). SUVA was determined by using the UV_{254} absorbance × 100 divided by the DOC concentration of the sample. Turbidity was measured using a turbidity meter (2100AN, HACH, Redding, CA, USA).

3D-FEEM spectroscopy

3D-FEEM spectra of test waters before and after coagulation were acquired using a fluorescence spectrophotometer (PLS55, Perkin Elmer Instruments, Norwalk, USA). Emission spectra were scanned from 280 to 540 nm at 0.5 nm increments and excitation spectra scanned from 250 to 400 nm with 5 nm increments (Baker 2002). The slits for excitation and emission were 5 nm.

MWD determination by HPSEC

HPSEC is a method used to determine the MWD of dissolved organics, specific to the detector types incorporated. In this study, a Shodex KW 802.5 glycol-functionalised silica gel packed column (Shoko Co. Ltd, Kurashiki, Japan) and two detectors: (1) UV detector: A Waters 996 Photodiode Array Detector at 254 nm; and (2) Fluorescence detector: Waters 2475 multi wavelength fluorescence detector, were used. Wavelengths selected for detection of humic acid-like compounds were 320 nm for excitation and 430 nm for emission, and for protein-like compounds, 280 nm for excitation and 330 nm for emission detection. The flow rate in the Shodex column was 1 mL min^{-1} and the injection volume was 100 μL. The retention time was calibrated for AMW using polystyrene sulfonate standards (Polysciences Inc., Warrington, PA, USA) of molecular weights 35, 18, 8 and 4.6 kDa. HPSEC for molecular weight analysis was conducted based on the procedure reported earlier (Chow *et al.* 2008).

Resin fractionation

Chemical fractionation was performed based on the method described by Chow *et al.* (2004) for determination of the concentrations of three fractions, very hydrophobic acid (VHA), slightly hydrophobic acid (SHA) and hydrophilic. DAX-8 and XAD-4 resins (Supelco, Bellefonte, PA, USA) were used to adsorb hydrophobic proportions while the compounds that remained in the solution were determined as the hydrophilic proportion.

Feed and effluent samples (after passing both resins) were collected for DOC analysis. The organic carbon concentration of each fraction was calculated by subtraction (feed DOC–effluent DOC).

Disinfection by-product (DBP) formation potential

Samples were adjusted to pH 7 by HCl before chlorination and buffered with 0.1 M phosphate buffer to maintain the pH at 7.4. An excessive chlorine dose of approximately 20–30 mg L^{-1} was added. After incubation at 35 °C for 4 hours, the samples were quenched with excess ascorbic acid (Chow *et al.* 2002). Trihalomethanes (THMs) were determined by gas chromatography and electron capture detection (GC/ECD) according to Standard Method 552 (USEPA 2006).

RESULTS AND DISCUSSION

The impact of AOM on raw water character

The impact of AOM on raw water character was investigated by comparing the parameters of AMPW, MPW and AOM only water (CW). Table 1 shows that after the addition of AOM to MPW, the turbidity level increased slightly by 9% and pH increased by 0.6. UV$_{254}$ and DOC increased by 10% and 33%, respectively, which contributed to a SUVA decrease of 17%. The decrease of SUVA was expected because CW has a much lower SUVA value than MPW.

Excitation emission matrices (EEM) can provide semi-quantitative characterisation information on dissolved organic matter (Her *et al.* 2004). EEM results were analysed according to Chen (2003a) and EEM peak positions were determined as humic-like organic compounds, fulvic acid-like organics, soluble microbial protein-like material, or aromatic proteins. The MPW contained mostly humic acid and fulvic acid-like compounds (Figure 1(a)) and for the CW sample (Figure 1(b)), EEM peaks were mainly representative

Table 1 | Water quality of MPW, AMPW and CW

	MPW	AMPW	CW
Turbidity (NTU)	55	60 (+9%)	N.A.
pH	7.2	7.8 (+8%)	N.A.
UV$_{254}$ (cm^{-1})	0.127	0.140 (+10%)	0.018
DOC (mg L^{-1})	5.2	6.9 (+33%)	2.02
SUVA (L mg^{-1} m^{-1})	2.45	2.03 (-17%)	0.89

Note: (%) is the percentage increase of the parameter in AMPW following addition of AOM to MPW.
N.A: Not analysed.

of aromatic protein regions. There were no other peaks in the AMPW (Figure 1(c)) compared with peaks of MPW and CW, as was to be expected. Four components, humic-like, fulvic-like, microbial protein-like and aromatic protein-like substances were identified from fluorophores described in the literature (Chen *et al.* 2003b; Henderson *et al.* 2008). Fluorescence emission intensity at 426 nm from excitation at 235 nm (Peak A) reflects the concentration of humic-like substances, Peak C (Ex: 325 nm Em: 426 nm) indicates the presence of fulvic-like substances, Peak T1 (Ex: 300 nm Em: 350 nm) indicates the presence of microbial protein-like substances and Peak T2 (Ex: 225 nm Em: 350 nm) indicates the presence of aromatic protein-like substances. Figure 1(d) compares peak intensities of the four peaks and it can be seen that they all increased after addition of AOM to MPW. Peaks A, C, and T1 intensities increased in AMPW matching the intensities of MPW plus CW. However, the change in Peak T2 did not follow this trend. The increase of intensity in AMPW was lower than the intensity of aromatic protein-like substances in CW. This indicates an interaction between AOM and NOM in AMPW with some aromatic protein-like substances with fluorescence responses removed.

Chemical fractionation

MPW and AMPW were fractionated using resins as detailed above in 'Resin fractionation'. Percentages of hydrophobic (VHA and SHA) and hydrophilic fractions as DOC in MPW were 63% and 37%, respectively (Table 2), while in the AMPW, the DOC percentage of the hydrophilic fraction increased to 49%. However, for the hydrophobic fraction, the DOC percentage of the SHA fraction increased by 8%, and the VHA fraction decreased. This indicates that the AOM contributed to the increase of DOC concentrations of the hydrophilic and SHA-like portions. For both MPW and AMPW, UV$_{254}$ absorbing compounds were predominant in the VHA fraction, consistent with hydrophobic compounds usually having higher UV absorbance than hydrophilic compounds (Parsons *et al.* 2004). It is noteworthy that in the AMPW, the percentages of UV$_{254}$ of SHA and hydrophilic fractions increased only slightly, despite the large increase in DOC concentration. This shows that the AOM of *Microcystis aeruginosa* contains a high proportion of hydrophilic
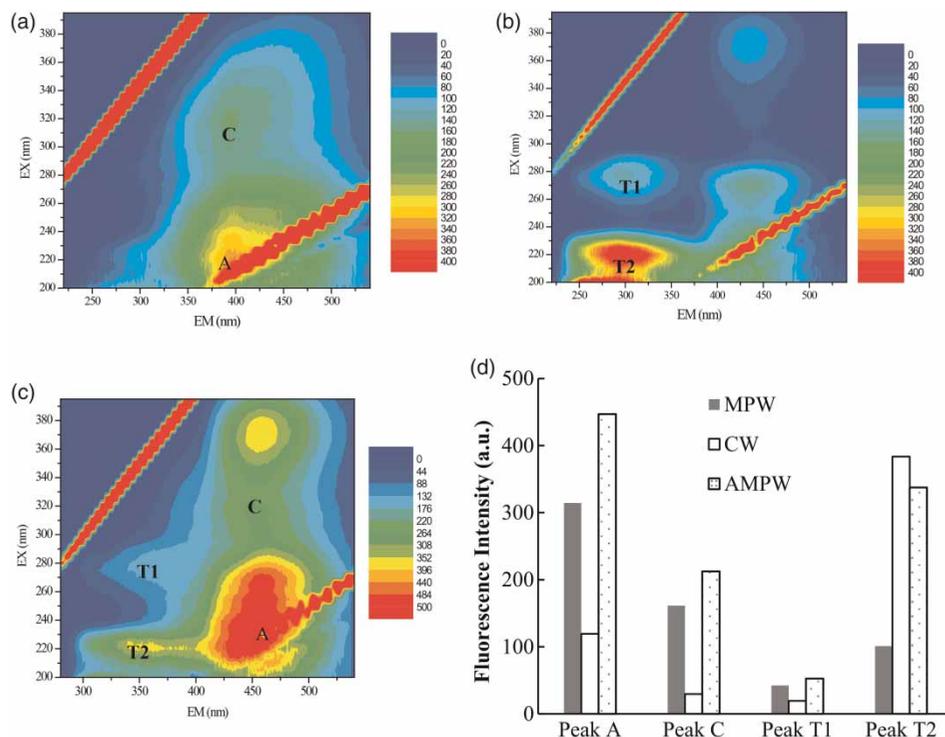
Figure 1 │ Fluorescence excitation–emission matrix spectra for (a) MPW, (b) CW and (c) AMPW, and (d) fluorescence intensities of the four peaks: Peak A (Humic-like) Ex: 235 nm Em: 426 nm, Peak C (Fulvic-like) Ex: 325 nm Em: 426 nm, Peak T1 (Microbial protein-like) Ex: 300 nm Em: 350 nm, Peak T2 (Aromatic protein-like) Ex: 225 nm Em: 350 nm.

Table 2 │ The UV_{254}, DOC and TTHMP results of each resin fraction

		Raw	VHA	SHA	Hydrophilic
MPW	UV_{254} (cm^{-1})	0.127	0.101 (80%)	0.020 (16%)	0.006 (4%)
	DOC (mg L^{-1})	5.2	2.4 (46%)	0.9 (17%)	2.0 (37%)
	SUVA (L mg^{-1} m^{-1})	2.45	4.21	2.22	0.30
	TTHMP (µg L^{-1})	238	169 (71%)	50 (21%)	19 (8%)
	Specific TTHMP (µg mg^{-1} DOC)	46	70	56	10
AMPW	UV_{254} (cm^{-1})	0.140	0.105 (75%)	0.024 (17%)	0.011 (8%)
	DOC (mg L^{-1})	6.9	1.8 (26%)	1.7 (25%)	3.4 (49%)
	SUVA (L mg^{-1} m^{-1})	2.03	5.83	1.41	0.32
	TTHMP (µg L^{-1})	188	108 (57%)	37 (20%)	43 (23%)
	Specific TTHMP (µg mg^{-1} DOC)	27	60	22	13

Note: (%) is the percentage of the total concentration.

compounds that comprised the majority of DOC with low UV_{254} absorbance. The presence of AOM did not impact the SUVA of the hydrophilic fraction, but the SUVA of VHA in the AMPW was found to be higher than that of the MPW itself. UV_{254} absorbance of VHA in the AMPW increased to slightly more than that of MPW. However, the DOC concentration of the VHA fraction of the AMPW decreased. The DOC percentage of the VHA fraction of AMPW was 20% lower than that of the MPW.

DBP formation potential of MPW and AMPW

NOM and AOM are precursors of THMs (Huang *et al.* 2009) and total concentrations of THMs (TTHM) produced per milligram of DOC of MPW and APMW are shown in Table 2. It was found that both TTHM and Specific TTHM in AMPW were lower than in MPW. As excess chlorine was used during the TTHM formation test, the change in DOC/chlorine ratio should not be a factor and the slight

dilution (300 mL of concentrated AOM to 6.5 L MP raw water) when preparing AMPW, would also not contribute significantly to this variation. The only possible explanation of this finding is that there was some character change of organics in AMPW which led to the results of the Specific TTHM values of the fractions. The THM formation potential (TTHMP) of the hydrophilic fraction of AMPW was higher than that of the same MPW fraction. The Specific TTHMP of the combined hydrophobic fraction (VHA and SHA) of the AMPW was lower than that of MPW. It has been reported that THMs are mainly generated from hydrophobic compounds of NOM in natural water (Hyun-Chul & Yu 2007; Chen *et al.* 2008) and our results are consistent with these reports, i.e. the VHA fraction generated the highest TTHMs. The TTHM of the VHA fraction significantly decreased in the AMPW compared with the MPW. It can also be seen from Table 2 that the hydrophilic fraction of the AOM contributes to DBP formation. The decrease in

specific TTHM in the VHA and SHA fractions of the AMPW appears to be due to changes in the character of MPW after AOM was added, consistent with findings reported above in 'Chemical fractionation'.

Molecular weight profile determination by HPSEC

The MWDs of MPW, AMPW and CW determined by HPSEC analyses are shown in Figure 2. HPSEC data showed that the MWD of organics of the CW (AOM only) covered a wide distribution range but with very low UV_{254} absorbance (Figure 2(a)). Comparing MPW with AMPW, the proportion of compounds of molecular weight of 0.5–4 kDa decreased and that of compounds of low molecular weight (<0.5 kDa) increased. Fluorescence detection was used to further investigate the molecular weights of constituent organics. The fluorescence responses of humic acid-like and protein-like compounds in the three samples are shown in Figure 2(b) and 2(c),
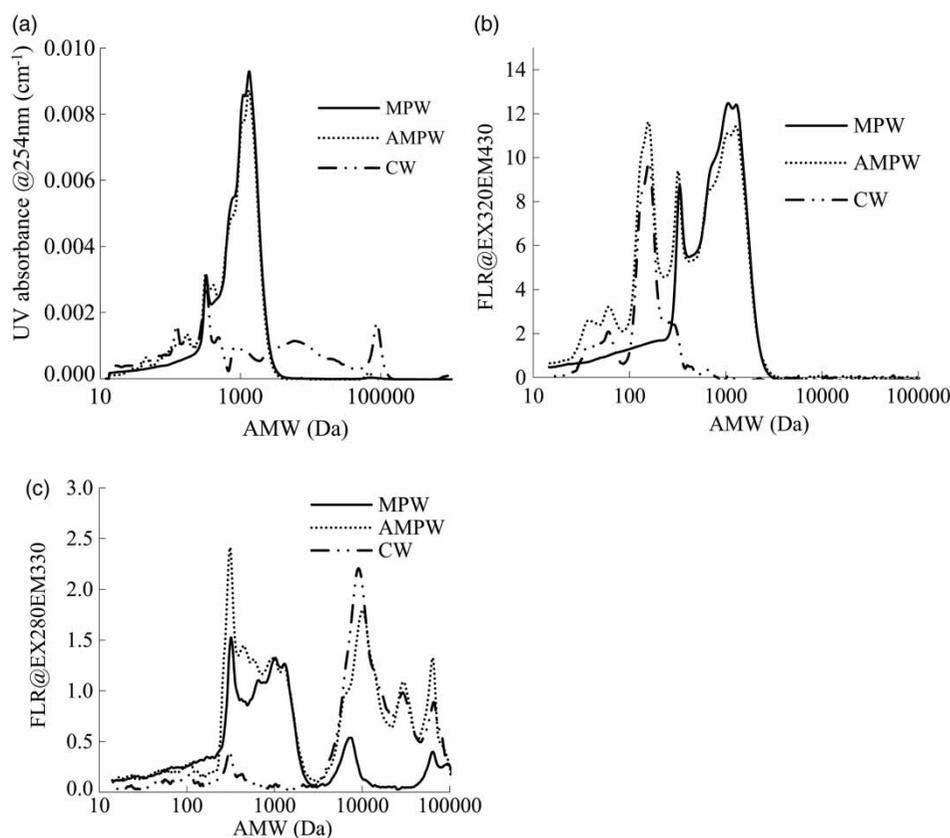

Figure 2 │ HPSEC MWDs for MPW, AMPW and CW. (a) UV absorbance, (b) the molecular weight profiles of humic acid-like compounds and (c) the molecular weight profiles of protein-like compounds.
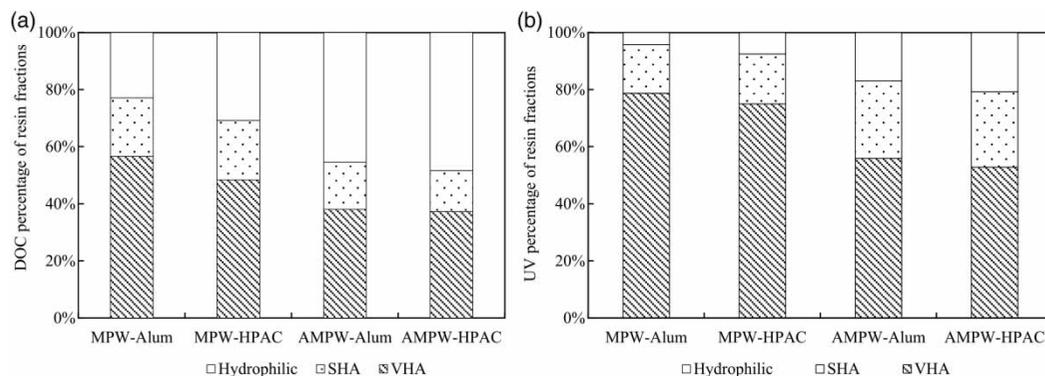
Figure 3 | Percentages of DOC and UV$_{254}$ absorbing compounds of resin fractions in coagulated water.

respectively. Protein-like compounds of 3 k–15 kDa were predominant in CW (Figure 2(c)). MPW had corresponding organic compounds with much wider MWD and very low fluorescence responses (Figure 2(c)). The fluorescence response of AMPW was much higher than that of MPW. As shown in Figure 2(b), the average molecular weight of CW was lower than the average molecular weight of MPW. It is interesting to see an additional dominant peak at around 500 Da in both AMPW and CW waters when comparing the results from UV and fluorescence detectors.

The efficiency of coagulation in removal of AOM

AOM released into natural water can affect coagulation performance (Sharp *et al.* 2006; Chen *et al.* 2009) and this was investigated in this study using a conventionally used coagulant (alum) and a newly emerging one, HPAC. Optimum doses for each were based on the DOC removal rate where the dose–response curve (residual DOC versus coagulant dose) began to level out, and where residual DOC was recalcitrant to removal by further coagulant dosing. The doses required to achieve optimum coagulation by each of the two coagulants were higher for AMPW than for MPW.

Percentages of DOC and UV$_{254}$ in resin fractions of coagulated waters are shown in Figure 3. For both MPW and AMPW waters, HPAC removed higher proportions of VHA and SHA than alum. After coagulation, the hydrophilic fraction of the AMPW was much higher than that of MPW and the removal efficiency was lower. The percentage of UV$_{254}$ absorbing compounds of SHA in the AMPW was higher than that in MPW, while the percentage DOC decreased. It

can be deduced that in the AMPW, some compounds with no UV absorbance were removed by coagulation.

CONCLUSIONS

The change in character of NOM in water sourced from the River Murray when AOM was added from *Microcystis aeruginosa* was investigated. The characteristics of organics were investigated through advanced characterisation techniques, including HPSEC with UV and fluorescence detection, 3D-FEEM and RF. From 3D-FEEM analysis, it was found that with AOM addition there was an increase in the relative abundance of aromatic protein-like components. Following addition of AOM to MPW, fluorescence spectroscopy indicated that the presence of humic acid-like compounds increased in the small molecular weight region. Three organic fractions of MPW and AMPW were isolated by RF, and the MWDs of each fraction were determined. The results showed that AOM released into surface water can increase the relative abundances of protein-like compounds and compounds of small molecular weight. Changes in DBP formation potential were also found with the addition of AOM to the MPW, with an overall decrease in TTHMP per mg of DOC.

The two coagulants used in this study, alum and HPAC, showed similar UV$_{254}$ and DOC removal efficiencies for MPW and AMPW. However, using RF, it was found that the efficiencies of the two coagulants for removal of DOC were slightly different. HPAC was found to be more efficient in removing the VHA fraction, than alum. The SHA and hydrophilic components in the AMPW were harder to remove by the two coagulants than those in the MPW.

ACKNOWLEDGEMENTS

REFERENCES

Baker, A. 2002 Fluorescence properties of some farm wastes: implications for water quality monitoring. Water Research 36 (1), 189–195.

Chen, W., Westerhoff, P., Leenheer, J. A. & Booksh, K. 2003a Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Environmental Science & Technology 37 (24), 5701–5710.

Chen, W., Westerhoff, P., Leenheer, J. A. & Booksh, K. 2003b Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Environmental Science & Technology 37 (24), 5701–5710.

Chen, C., Zhang, X. J., Zhu, L. X., Liu, J., He, W. J. & Han, H. D. 2008 Disinfection by-products and their precursors in a water treatment plant in North China: seasonal changes and fraction analysis. Science of the Total Environment 397 (1–3), 140–147.

Chen, J. J., Yeh, H. H. & Tseng, I. C. 2009 Effect of ozone and permanganate on algae coagulation removal - Pilot and bench scale tests. Chemosphere 74 (6), 840–846.

Chow, C. W. K., Drikas, M., House, J., Burch, M. D. & Velzeboer, R. 1999 The impact of conventional water treatment processes on cells of the cyanobacterium Microcystis aeruginosa. Water Research 33 (15), 3253–3262.

Chow, C., Cook, D. & Drikas, M. 2002 Evaluation of magnetic ion exchange resin (MIEX®) and alum treatment for formation of disinfection by-products and bacterial regrowth. Water Science and Technology: Water Supply 2 (3), 267–274.

Chow, C. W. K., Fabris, R. & Drikas, M. 2004 A rapid fractionation technique to characterize natural organic matter for the optimisation of water treatment processes. Journal of Water Supply: Research and Technology 2 (53), 85–92.

Chow, C. W., Fabris, R., Leeuwen, J. v., Wang, D. & Drikas, M. 2008 Assessing natural organic matter treatability using high performance size exclusion chromatography. Environmental Science & Technology 42 (17), 6683–6689.

Edzwald, J. 1993 Coagulation in drinking water treatment: particles, organics and coagulants. Water Science and Technology 27 (11), 21–35.

Gao, S. S., Yang, J. X., Tian, J. Y., Ma, F., Tu, G. & Du, M. A. 2010 Electro-coagulation-flotation process for algae removal. Journal of Hazardous Materials 177 (1–3), 336–343.

Ghernaout, B., Ghernaout, D. & Saiba, A. 2010 Algae and cyanotoxins removal by coagulation/flocculation: a review. Desalination and Water Treatment 20 (1–3), 133–143.

Henderson, R. K., Baker, A., Parsons, S. A. & Jefferson, B. 2008 Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms. Water Research 42 (13), 3435–3445.

Henderson, R. K., Parsons, S. A. & Jefferson, B. 2010 The impact of differing cell and algogenic organic matter (AOM) characteristics on the coagulation and flotation of algae. Water Research 44 (12), 3617–3624.

Her, N., Amy, G., Park, H.-R. & Song, M. 2004 Characterizing algogenic organic matter (AOM) and evaluating associated NF membrane fouling. Water Research 38 (6), 1427–1438.

Huang, J., Graham, N., Templeton, M. R., Zhang, Y., Collins, C. & Nieuwenhuijsen, M. 2009 A comparison of the role of two blue-green algae in THM and HAA formation. Water Research 43 (12), 3009–3018.

Hyun-Chul, K. & Yu, M. J. 2007 Characterization of aquatic humic substances to DBPs formation in advanced treatment processes for conventionally treated water. Journal of Hazardous Materials 143 (1–2), 486–493.

Nguyen, M. L., Westerhoff, P., Baker, L., Hu, Q., Esparza-Soto, M. & Sommerfeld, M. 2005 Characteristics and reactivity of algae-produced dissolved organic carbon. Journal of Environmental Engineering-ASCE 131 (11), 1574–1582.

Parsons, S. A., Jefferson, B., Goslan, E. H., Jarvis, P. R. & Fearing, D. A. 2004 Natural organic matter: the relationship between character and treatability. Water Science and Technology: Water Supply 4 (5–6), 43–48.

Pivokonsky, M., Kloucek, O. & Pivokonska, L. 2006 Evaluation of the production, composition and aluminum and iron complexation of algogenic organic matter. Water Research 40 (16), 3045–3052.

Sharp, E. L., Jarvis, P., Parsons, S. A. & Jefferson, B. 2006 Impact of fractional character on the coagulation of NOM. Colloids and Surfaces A: Physicochemical and Engineering Aspects 286 (1–3), 104–111.

USEPA 2006 Wadeable streams assessment: a collaborative survey of the nation's streams. EPA 841/B-06/002. Offices of Research and Development and of Water, US Environmental Protection Agency, Washington, DC, USA.

Westrick, J. A., Szlag, D. C., Southwell, B. J. & Sinclair, J. 2010 A review of cyanobacteria and cyanotoxins removal/inactivation in drinking water treatment. Analytical and Bioanalytical Chemistry 397 (5), 1705–1714.