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Characterisation of dissolved organic matter to optimise powdered activated carbon and clarification removal efficiency†

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The character of dissolved organic matter (DOM) present in drinking water treatment systems greatly impacts its treatability by coagulation–flocculation. Powdered activated carbon dosing has been suggested to enhance DOM removal when combined with coagulation–flocculation. However, optimising powdered activated carbon (PAC) dosing requires further research. In this study, fluorescence spectroscopy combined with parallel factor analysis (PARAFAC) and liquid chromatography with organic carbon detection (LC–OCD) has been used to characterise DOM removal in three ways: (a) coagulation–flocculation–sedimentation without PAC dosing, (b) PAC dosing prior to- and (c) PAC dosing during coagulation–flocculation–sedimentation treatment. It was shown that only coagulation–flocculation–sedimentation preferentially removed biopolymer and humic substance chromatographic fractions and fluorescent DOM, whereas dosing PAC preferentially removed building blocks and low molecular weight neutral chromatographic fractions. The DOM treatability that was achieved when PAC was dosed both prior to- and during coagulation–flocculation–sedimentation was comparable, but higher than what was achieved without any PAC dosing. Introduction of PAC to the coagulation–flocculation–sedimentation process significantly improved DOM removal, with fluorescent components removed by 97%. This study also highlights that a combination of fluorescence spectroscopy and LC–OCD is essential to track the removal of both, fluorescent and non-fluorescent DOM fractions and understand their impacts on DOM treatability when using different treatment processes. Overall, lower residual DOM concentrations were obtained in the treated water when PAC adsorption and the coagulation–flocculation–sedimentation processes were combined when compared to treating the water with only one of the processes, despite differences in source water character of DOM.

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Water impact

This study showed that a combination of fluorescence spectroscopy and liquid-chromatography with organic carbon detection is beneficial in tracking the fate of different organic matter (OM) fractions that impact traditional treatment processes, especially during extreme weather events in catchments. By monitoring OM removal during different treatment processes, it was established that treatment plant operators could use powdered activated carbon in combination with coagulation–flocculation to ensure that periodic, elevated OM events are adequately managed despite varying OM character, thereby lowering the risk of disinfection by-product production.

1. Introduction

The clarification process, which typically includes coagulation–flocculation followed by sedimentation or

flotation, is commonly used for drinking water treatment. This process can be optimised for turbidity or dissolved organic matter (DOM) removal by altering the coagulation–flocculation operating conditions. However, the character of the DOM present greatly impacts its treatability by coagulation–flocculation because coagulation–flocculation predominantly targets high molecular weight (MW), highly charged hydrophobic materials (typically 40–60% of overall DOC), in contrast to lower MW and hydrophilic fraction of DOM.^{1,2} During high DOM events such as those caused by heavy rainfall following extended drought periods, changes to DOM character have been observed resulting in fluctuating

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DOM removal.^{3,4} The variations DOM removal combined with downstream disinfection can cause periodically elevated disinfection by product (DBP) concentrations.⁵ Hence, optimisation of coagulation–flocculation has been recommended to minimise the formation of DBPs in the treated water.⁶

Powdered activated carbon (PAC) has been investigated as an adsorbent that can be added as required for enhanced DOM removal during unusually high DOM events either on its own,⁷ or before, during or after coagulation.^{8,9} Knowledge on which of these PAC dosing methods is more effective is limited. For instance, PAC dosing post-coagulation is not efficient as subsequent removal of PAC is challenging and leads to increases in operating costs.^{10,11} Dosing PAC prior to, rather than during coagulation–flocculation greatly improved the DOM separation efficiency in source waters that had high specific ultraviolet absorbance ($SUVA > 4 \text{ L mg}^{-1} \text{ m}^{-1}$) and high dissolved organic carbon (DOC) concentrations ($>20 \text{ mg C per L}$).^{8,12} In contrast, dosing PAC during alum-based coagulation of OM (DOC $< 4 \text{ mg L}^{-1}$) resulted in high removal efficiencies of DOM.¹³ Another important consideration is that the adsorption of low molecular weight DOM fractions onto PAC can take up adsorption sites that would otherwise remove micropollutants such as taste and odour compounds, reducing its capacity to treat these chemicals which is typically another important objective of activated carbon dosing.^{14–16} Hence, if PAC is to be applied to enhance DOM removal, an improved understanding of how to optimise this process is required.

There is abundant evidence demonstrating that coagulation is sensitive to changes in DOM character, which can occur relatively quickly as a consequence of vast spatial and temporal distributions of DOM.^{1,2,17,18} Therefore, DOM treatment processes need to be closely monitored to ensure that they are properly optimised because monitoring techniques can give information on whether the fractions of DOM that are being removed are of interest. There are several methods available to monitor DOM. DOC analysis is a concentration measurement only and gives no information on DOM character. Specific UV absorbance at 254 nm (SUVA) is frequently measured; however it only gives an indication of the relative aromaticity of the total OM,¹⁹ although it has been correlated with DOM treatability.²⁰ Fluorescence excitation–emission matrix (EEM) spectroscopy in combination with parallel factor analysis (PARAFAC) has been widely used for DOM characterisation,^{17,21} due to its increased selectivity and sensitivity in comparison to UV spectroscopy.²² The resultant PARAFAC components have been linked to different DOM fractions based of their source of origin; for example terrestrially- or microbially-delivered organic matter.^{21,23,24} Furthermore, the PARAFAC components can be used for tracking DOM concentrations and changes during water treatment as well as for assessing DOM treatability when using PAC.^{25–27} It is possible to undertake this technique in the field to provide rapid, *in situ*

diagnoses of influence of DOM character and treatment performance.^{25,28–33}

Another popular DOM characterisation technique is liquid chromatography with organic carbon, UV₂₅₄ and nitrogen detection (LC–OCD).^{34,35} While it cannot be undertaken in the field, it can provide important complementary data to the field-based techniques previously described. LC–OCD separates components according to their size ranging from higher to lower, providing a molecular weight distribution. The resultant peaks can be classified as biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight acids and low molecular weight humics, and low molecular weight neutrals (LMWN).³⁴ These fractions have also been linked to treatability; for instance, a 60% reduction in high MW HS was observed in comparison to a 10% decrease in the LMWN fractions when treating a Canadian river water with alum.³⁶ In a West Australian water treatment plant (WTP), it was demonstrated that the removal of BP (80%) and HS (60%) was higher than LMWN (20%) when treating the water with FeCl₃.³⁷ Therefore, a combination of LC–OCD and fluorescence EEMs–PARAFAC data would provide insights into the DOM character during treatment using PAC and coagulation.

Overall, the aim of this study was to relate the advanced DOM characterisation data from fluorescence EEMs–PARAFAC and LC–OCD techniques to DOM removal *via* three different approaches (no PAC dosing, PAC dosing prior to and during coagulation–flocculation–sedimentation) to gain an improved understanding of how to optimise PAC dosing. To achieve the aim, the following objectives were set: (a) determine source water character using fluorescence EEM spectroscopy combined with PARAFAC and LC–OCD, (b) study the impact of PAC dosing and coagulation–flocculation–sedimentation process on DOM removal *via* three different approaches, and (c) monitor the effluent to identify fluorescent and size-fractionated DOM remaining post-treatment in order to link them to DOM treatability. In doing so, this paper demonstrates that LC–OCD and advanced fluorescence analysis combined with PARAFAC can provide significant insights when studying the fate of fluorescent, non-fluorescent and size-fractionated DOM fractions during treatment *via* PAC adsorption and coagulation–flocculation–sedimentation processes.

2. Materials and methods

2.1. Sample collection

Source water was collected from Grahamstown Dam (GD) in New South Wales and Leslie Harrison Dam (LHD) in Queensland and couriered to the laboratory within 20 h where it was kept in the dark in a refrigerator at +4 °C to minimise water quality changes during the experiments. The sites were selected in order to maximise potential DOM variability due to location, the associated catchment and reservoir type, and climate zone. For example, the dams were located in both subtropical and temperate climate zones and

included both unprotected and protected reservoirs and river systems.

2.2. Chemicals

A 10% solution of aluminium sulphate (Sigma-Aldrich, Australia) was used as the coagulant. The PAC used for experiments was coal based Acticarb PS1300 (Activated Carbon Technologies Pty Ltd, Australia). Sodium hydroxide (Ajax Finechem Pty Ltd, Australia) and hydrochloric acid (32%, Ajax Finechem Pty Ltd, Australia) diluted to 2 M, 1 M and 0.2 M concentrations were used for pH control of the coagulated water during jar tests. MilliQ water was used for the dilution of all chemical solutions.

2.3. Jar test method

Jar tests were performed using a Velp Scientifica (Italy) jar tester using beakers of 1 L capacity. Three experiments were performed using the two source waters (Fig. S1†):

- Experiment 1: coagulant (aluminium sulphate) was dosed at various concentrations from 1.6 mg Al per L to 62 mg Al per L without PAC addition and the pH was adjusted to 6.5. The mixing conditions for experiment 1 were as follows: rapid mixing at 200 rpm for 2 min, flocculation at 30 rpm for 20 min, and sedimentation with no mixing for 30 min.

- Experiment 2A: PAC was dosed at various concentrations from 2 mg L⁻¹ to 160 mg L⁻¹ as a slurry to the jar prior to coagulant dosing and mixed at 200 rpm for 2 min followed by 15 min mixing at 30 rpm, after which sampling was conducted at 15 min intervals.

- Experiment 2B: the sample from experiment 2A after 30 min was dosed with aluminium sulphate (doses similar to experiment 1) and pH was adjusted to 6.5. The sample was stirred at 200 rpm for 2 min, following by flocculation at 30 rpm for 20 min, after which the paddle flocculators were halted to allow 30 min of sedimentation.

- Experiment 3: PAC and coagulant were dosed simultaneously (doses similar to experiment 2). The mixing procedure for experiment 3 was the same as for the experiment 1.

Note that the alum and PAC dose ranges were selected to determine the optimum DOM removal values, and the PAC adsorption period in the experiments was to replicate the limited PAC contact time within WTP feed by the studied sources in a WTP. Treated water was collected after the sedimentation stage for analysis. All feed water and treated water samples were filtered through a 0.45 µm filter and analysed for DOC, fluorescence EEMs and UV absorbance. The samples were also collected for LC-OCD analysis and to determine aluminium concentrations.

2.4. Analytical methods

DOC concentrations. DOC concentrations were determined using a Shimadzu TOC_{CSH} total organic carbon analyser (Shimadzu, Australia) *via* the non-purgeable organic

carbon (NPOC) determination method. The full procedure has been described previously.³⁸

UV absorption. UV absorption data was obtained using a Cary 50 Bio UV-vis absorption spectrophotometer (Varian, Australia). The data was collected in triplicate using a 1 cm path length quartz cuvette (Starna, Australia) for an absorption range of 200–600 nm at an increment of 1 nm and a scan speed of 600 nm min⁻¹. Using this, the SUVA was calculated by dividing the UV absorbance of the sample (in cm⁻¹) at 254 nm by the DOC of the sample (in mg L⁻¹) and then multiplying by 100 cm m⁻¹. SUVA is reported in units of L mg⁻¹ m⁻¹. The full procedure has been described previously.³⁸

Fluorescence EEMs. Fluorescence EEMs were obtained using a 1 cm path length quartz cuvette (Starna, Australia) and a Cary Eclipse fluorescence spectrophotometer (Varian, Australia). Fluorescence intensities were measured in triplicate at excitation wavelengths of 200–400 nm in 5 nm increments and emission wavelengths of 280–500 nm in 2 nm increments. The full procedure has been described previously.³⁸

Inductively coupled plasma – optical emission spectrometry (ICP-OES). Inductively coupled plasma – optical emission spectrometry (ICP-OES) (Agilent Varian vista pro) was used to determine the initial and residual concentrations of aluminium in raw and treated water samples to consider the potential interference of the increased aluminium concentrations and fluorescence spectra. The analyses were conducted from solutions filtered through 0.45 µm filters and acidified with 2% nitric acid.

LC-OCD. LC-OCD (DOC Labor, Germany) was used to identify fractions of organic compounds in the water samples before and after treatment. Biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight acids and low molecular weight humics (LMW-AH), and low molecular weight neutrals (LMWN).³⁴ A Toyopearl TSK HW-50S column was used and the mobile phase was phosphate buffer at a flow rate of 1.1 mL min⁻¹. The example of raw water and treated water LC-OCD chromatogram and identified fractions is shown on Fig. S2.† The full procedure has been described previously.³⁸

2.5. Data processing

Spectral correction of the fluorescence EEMs was undertaken. EEMs were corrected for inner filter effect (IFE); instrument specific correction factors were applied; Rayleigh–Tyndall and Raman scatter lines were removed; and EEMs were normalised to RU. Examples of corrected EEMs are shown on Fig. S3.† The full procedure has been described previously.³⁸

A PARAFAC model of 375 samples was generated using Solo 7.5 (Eigenvector Research, Inc.). Non-negativity constraints were applied for the model which was validated with split-half analysis. To further validate the model, the dataset was split into two site specific datasets, where LHD EEMs and GD EEMs were modelled separately as well.

3. Results and discussion

3.1. PARAFAC modelling

A three component (C1–C3) PARAFAC model was developed using source and treated water samples for both water sources. Similar modelling results were obtained when modelling both site-specific datasets and the entire dataset. As there was no difference in the composition of the components, the use of the “combined water sources” model was preferred. Component loadings are shown in Fig. 1. According to classification,^{21,38,39} C1 consisted of a combination of peak A and peak C, at the optical location where terrestrial, non-processed DOM has been observed to fluoresce and this region is associated with the presence of aromatic, hydrophobic, charged material that is usually treatable by coagulation;^{21,38,40} C2 was also a composite of peak A and peak C but was shifted to shorter wavelengths as compared to C1, and thus linked to terrestrial, processed DOM; C3 was a combination of peak T and A fluorescence, linked to microbial protein-like DOM and terrestrial DOM. It is suggested that since the variation of these substances in the dataset were similar, C3 was not distinguished as two separate components by PARAFAC. Since the Tucker congruence coefficients were higher than 0.95 for C1 and C2 components (C1 excitation 0.99/emission 0.99 and C2 excitation 0.99/emission 0.98) in this study, C1 and C2 component changes were comparable with previous research.³⁸ Thus, the terrestrially delivered, unprocessed component C1 is anticipated to have a higher treatability than C2 on coagulation–clarification.⁴¹

3.2. Source water characterisation

Water sources were specifically selected with highly contrasting water quality and, potentially, treatability (Table 1). Source water quality for LHD and GD, was comparable to a previous study, where samples were collected over a one year period.³⁸ LHD water had the highest

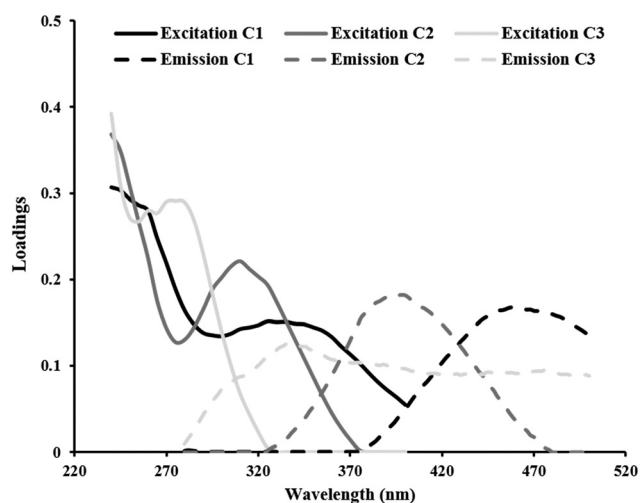


Fig. 1 PARAFAC components C1, C2 and C3 loadings.

Table 1 Source water quality as characterised via LC–OCD and fluorescence EEMs–PARAFAC

Parameter	Units	Grahamstown Dam (GD)	Leslie Harrison Dam (LHD)
DOC	mg C per L	7.2	13.8
Fluorescence C1	RU	12.0	47.8
Fluorescence C2	RU	6.1	18.0
Fluorescence C3	RU	5.3	8.7
HS	mg C per L	3.5	7.7
BP	mg C per L	1.3	2.1
LMWN	mg C per L	0.8	0.5
HS MW	g mol ⁻¹	0.9	1.3
HS SUVA	L mg ⁻¹ m ⁻¹	462	608
UV ₂₅₄	cm ⁻¹	2.5	4.6
SUVA	L mg ⁻¹ m ⁻¹	0.12	0.6
C1/C2	—	1.6	4.3
C1/C3	—	2.0	2.7
C1:DOC	RU L per mg C	2.2	5.5
C2:DOC	RU L per mg C	1.7	3.5
C3:DOC	RU L per mg C	0.9	1.3
		0.7	0.6

DOM concentration as detected using DOC measurements, fluorescence component intensities and UV absorbance (Table 1). LHD source water also had the highest proportion of terrestrially-delivered C1 fraction of fluorescent DOM (64%) and higher HS content (56%) in comparison to GD water with only 51% of C1 and 49% of HS. Furthermore, LHD raw water DOM had more aromatic, hydrophobic, charged material since the HS molecular weight (608 g mol⁻¹), SUVA (SUVA > 4 L mg⁻¹ m⁻¹) and fluorescent PARAFAC component score ratio C1:C2 (2.7) was higher in LHD water in comparison to GD water that had lower charge and more hydrophilic components (Table 1); the data indicates higher DOM treatability in LHD in comparison to GD raw water due to the presence of greater concentrations of aromatic, charged and relatively hydrophobic groups.^{25,42,43} However, GD water had the highest BP proportion of DOC (11%) in comparison to LHD water (4%) (Table 1). DOM present in GD and LHD water had contrasting treatability, where GD water had lower DOC removal of 37 ± 3% and lower C1:C2 ratio in comparison to LHD site with DOC removal of 51 ± 11% and the higher source water C1:C2 ratio.³⁸ Hence, it was established that GD and LHD source waters could be used to determine the influence of DOM concentration and character on enhanced treatment that incorporated PAC adsorption.

3.3. Determination of optimal dosing points

3.3.1. Coagulation–flocculation followed by sedimentation (experiment 1). Experiment 1 included coagulation–flocculation treatment for both GD and LHD water followed

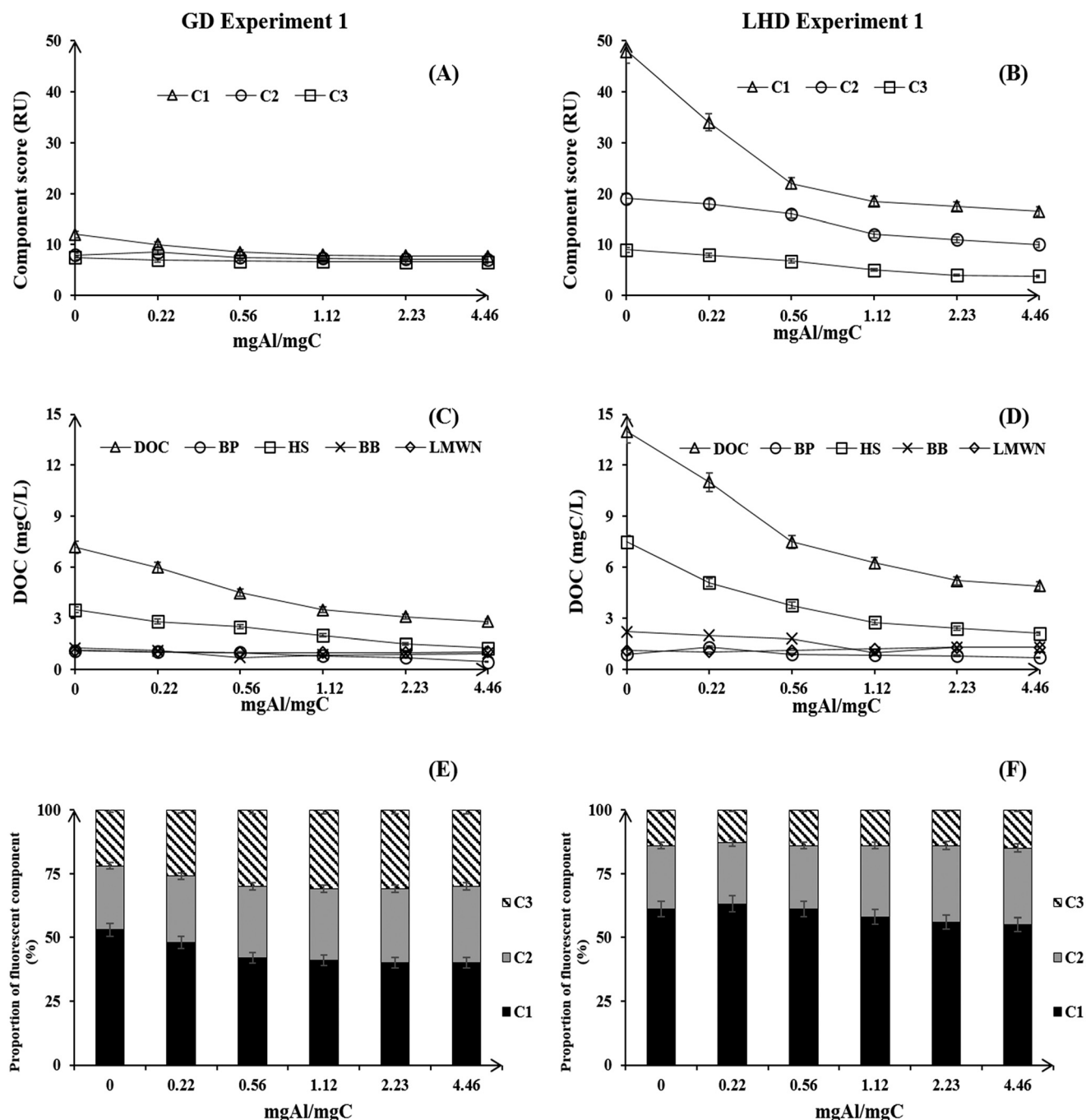


Fig. 2 Changes to fluorescence components C1, C2 and C3, DOC, and organic matter fractions: humic substances (HS), building blocks (BB), biopolymers (BP) and low molecular weight neutrals (LMWN) during coagulation–flocculation followed by sedimentation in GD (A, C and E) and LHD (B, D and F) experiments 1. Zero point represents raw water quality. Aluminium sulphate concentrations varied from 1.6–62 mg Al per L and the pH was 6.5. Rapid mixing was conducted at 200 rpm for 2 min, flocculation at 30 rpm for 20 min, and sedimentation with no mixing for 30 min.

by sedimentation at a range of coagulant (aluminium sulphate) doses. Fig. 2A–D illustrates the impact of aluminium sulphate dose on DOM removal by coagulation of DOC, HS, BB, BP, LMWN fractions and fluorescence PARAFAC components C1, C2 and C3.

In general, there was a gradual decrease of DOC with increased doses of alum during experiment 1 (Fig. 2A–D) in

both GD and LHD experiments. Despite greater than 65% DOM removal, the residual DOC in the LHD jar tests at the optimum dose of coagulant was still significant at 4.8 mg C per L, while in equivalent GD jar tests (DOM removal was >50%), the residual DOC was 3.5 mg C per L. As coagulation typically targets high molecular weight, charged and relatively hydrophobic components, it could be possible that the

components that remained in the residual DOC pool were relatively hydrophilic, uncharged and had low molecular weight.^{40,44} Analysis of the results from this experiment also demonstrates that maximum DOM removal from water (based on experiment 1) does not guarantee minimal residual DOC concentrations in the treated water and could still lead to DBP formation at the chlorination stage.⁴⁵ However, the DBP formation is not only dependent on DOC concentrations, but also on other parameters such as pH, temperature, disinfectant concentration and reaction time, and therefore these parameters should be collectively analysed for DBP formation potentials.⁵

When using coagulation–flocculation followed by sedimentation (experiment 1), it was observed that the proportion of DOM removal was inconsistent across fractions. In GD experiments, maximum median DOC removal was 53%, C1 removal 58%, C2 removal was 35% and C3 removal was 43%. Maximum observed removal of LC–OCD fractions was 86% for BP, 64% for HS, 43% for BB, and 26% for LMWN. In LHD experiments, the maximum DOC removal was 67%, while maximum removals of 74%, 56% and 68% were observed for C1, C2, and C3, respectively. The maximum LC–OCD fraction removals were 84% for BP, 81% for HS, 70% for BB, and 27% for LMWN. These results are in agreement with previous research, where LMWN and BB fractions were characterised to be recalcitrant fractions with lower treatability by coagulation than the BP or HS fractions.^{7,17,46,47}

In the treated GD and LHD water, the proportion of fluorescent components C1 and C2 varied over the coagulant dose range whereas the proportion of C3 remained within the same range, indicating that C3 was the least treatable component (Fig. 2A, B, E and F). While the proportion of C1 in treated water gradually decreased, that of C2 increased until the DOM fractions stabilised at the optimum coagulant dose, indicating that there was no further DOM removal possible (Fig. 2E and F). There are two standpoints from which these results can be perceived: (a) impact of metal ions such as aluminium, and (b) influence of DOM character and the treatment process. The impact of aluminium was questionable because the pH during coagulation was maintained at 6.5, while the presence of aluminium has been observed to impact fluorescence predominantly at pH 4–6.²² Furthermore, since the residual aluminium was lower in the treated water than in source water, it is suggested that the presence of aluminium in the treated water samples had minimal effect on fluorescence EEM changes. In terms of DOM character, the fluorescence in the C1 area is typically associated with high molecular weight hydrophobic humic-like material (*e.g.* high SUVA material), which is easy to remove *via* coagulation–flocculation,^{1,29} and therefore, would explain the decrease of this component with increasing coagulant dose (Fig. 2E and F). As C1 is preferentially removed, the DOC decreases and, consequently, there is an increase in the overall proportion of C2.³⁸ Thus, the variation in fluorescent component removal was attributed

predominantly to the character of DOM and the influence of treatment process rather than the presence of metal ions such as aluminium.

The optimum doses of aluminium sulphate were identified as 16 mg Al per L and 32 mg Al per L for GD and LHD water, respectively. When converted to normalised optimum coagulant dose, the values obtained for the same samples (2.2 and 2.3 mg Al per mg C) were comparable to those observed previously for alum-based coagulation of OM.⁴⁸

3.3.2. DOM adsorption onto PAC (experiment 2A).

Experiment 2A was conducted for both GD and LHD waters (Fig. S1†). This section analyses only the preceding PAC adsorption part of experiment 2A.

3.3.2.1. *Changes to effluent water quality upon PAC dosing (experiment 2A).* Analysis of the results from 15 min sampling intervals demonstrated that the DOC reached steady state at 30 min sampling time and therefore, results from the 30 min sampling time point will be presented in Fig. 3. Poor removal (<45%) of DOC was observed upon applying PAC without any coagulation to both water sources. As with coagulation–flocculation followed by sedimentation (experiment 1), DOM removal by PAC was influenced by the DOM character. Changes in the fluorescent DOM fractions were similar for both sites, where C1 and C2 had the highest removal (in GD and LHD water C1 removal was 71–77%, C2 was 68–71%) followed by C3 (in GD water C3 removal was 48–54%) (Fig. 3A and B). However, the DOM fraction changes, such as BP, HS, and BB, were higher in GD than in LHD water (Fig. 3C and D), suggestive of the fact that the results from the DOM characterisation techniques do not always point to one type of behaviour. The removal of BP was 83% in GD water, while there was no BP removal observed in LHD experiments. Humic substances removal was 77% in GD jar tests when compared to 39% in LHD jar tests; BB removal was 82% in GD and 61% in LHD waters; the removal of LMWN was 79% in GD and 77% in LHD waters (Fig. 3C and D). Previously, PAC treated water was found to have the lowest ultrafiltration membrane fouling potential because it preferentially adsorbed BB and LMWN compounds.^{27,49} In another study investigating treatment of micropollutant-laden domestic wastewater, >80% and <40% removal of low MW compounds and BP, respectively, were observed at a PAC:DOC ratio of 8.9 mg PAC per mg C,⁵⁰ demonstrating the preferential adsorption of low MW compounds by PAC. Overall, there was a gradual decrease in the DOC across all DOM fractions, which was apparent at increased doses of PAC for both GD and LHD experiments, except for BP in the LHD experiments which had negligible removal (Fig. 3C and D).

3.3.2.2. *Mechanisms by which PAC adsorption influences DOM treatability.* It is suggested that during PAC adsorption (experiment 2A), high MW DOM with chromophoric moieties adsorb to the external surface of activated carbon particles, while low MW non-chromophoric DOM can be adsorbed onto internal adsorption sites of PAC.^{7,16,51,52} Hence, when PAC

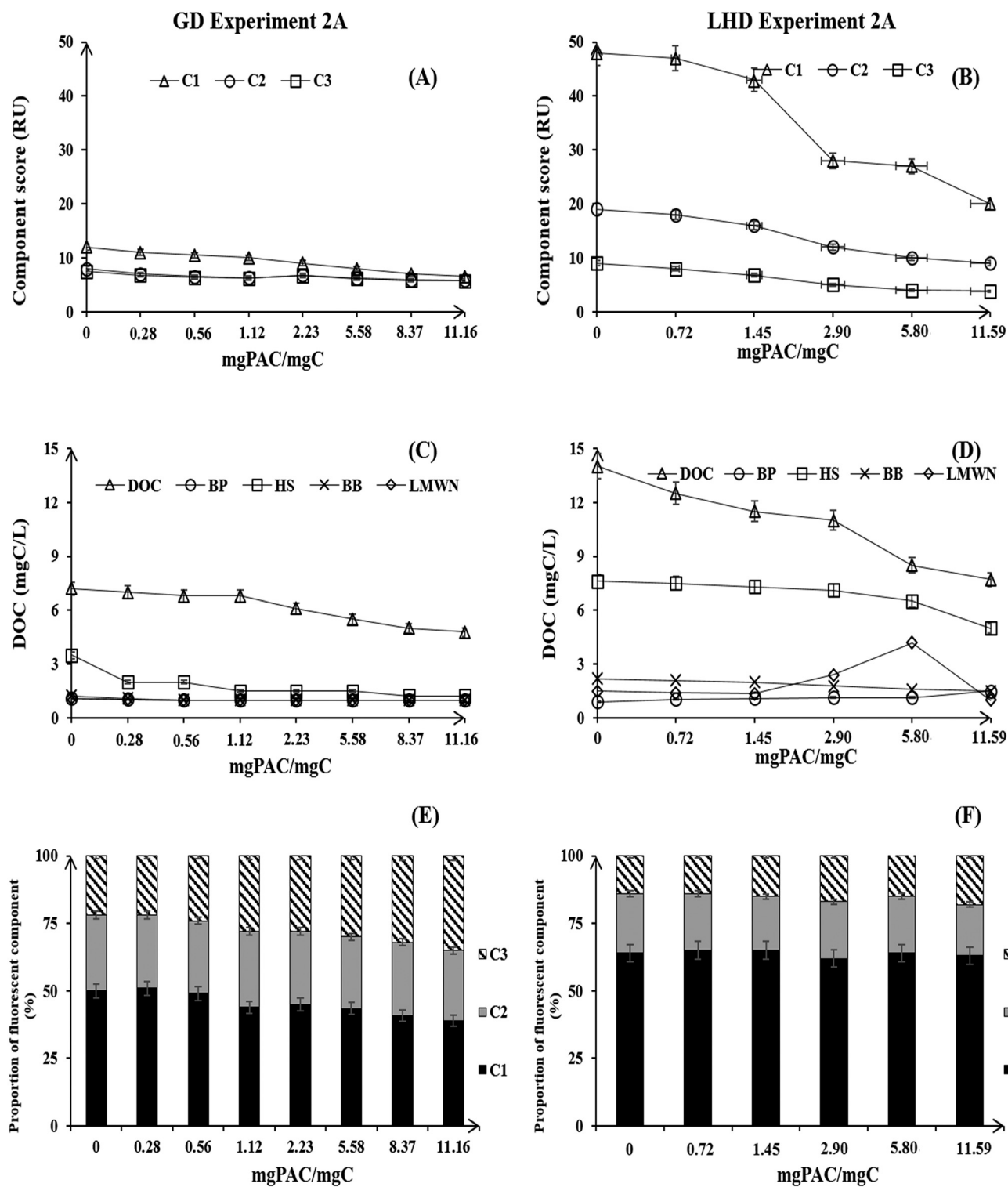


Fig. 3 Changes to fluorescence components C1, C2 and C3, DOC, and dissolved organic matter fractions: humic substances (HS), building blocks (BB), biopolymers (BP) and low molecular weight neutrals (LMWN) during PAC adsorption in GD (A, C and E) and LHD (B, D and F) experiment 2A. PAC was dosed from 2–160 mg L⁻¹ as slurry to the jar and mixed at 200 rpm for 2 min, followed by 15 min mixing at 30 rpm, during which time sampling was conducted at 15, 30, 45, 60 min. Analysis of the results from 15 min sampling intervals demonstrated that the DOC reached steady state at 30 min sampling time and therefore, results from the 30 min sampling time point will be presented.

was added to the system: (a) the removal of both BB and LMWN fractions was greatly improved at both sites

(Fig. 3C and D), and (b) the removal of BB, LMWN and fluorescent component C2 was higher in both the waters

when compared to experiment 1 (Fig. S6†). Despite the finding that experiment 2A preferentially removed the same DOM fractions in both water experiments, the removal of other components was variable. For instance, a greater

removal of HS was achieved for GD water when compared to LHD water *via* PAC dosing (experiment 2A) (Fig. S6†). This is attributed to the: (a) shorter adsorption time per DOC concentration of raw water in LHD experiments when

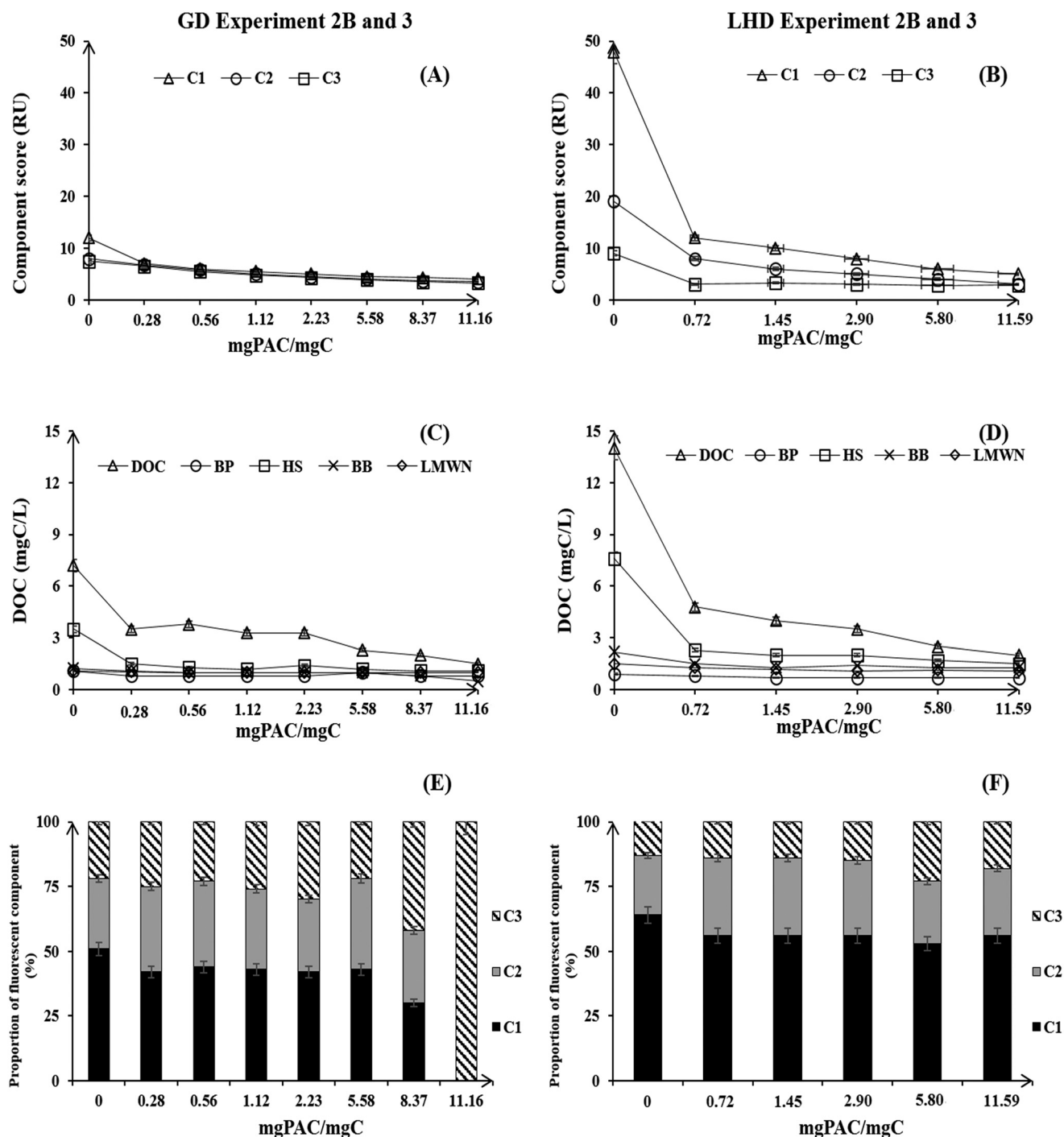


Fig. 4 Changes to fluorescence components C1, C2 and C3, DOC, and DOM fractions: humic substances (HS), building blocks (BB), biopolymers (BP) and low molecular weight neutrals (LMWN) during combined PAC adsorption and coagulation–flocculation sedimentation processes in GD (A, C and E) and LHD (B, D and F) experiments 2B and 3. In experiment 2B, PAC was dosed from 2–160 mg L⁻¹ as slurry to the jar and mixed at 200 rpm for 2 min, followed by 15 min mixing at 30 rpm. After 30 min PAC contact time, aluminium sulphate was dosed in varying concentrations from 1.6–62 mg Al per L and the pH was 6.5. Rapid mixing was conducted at 200 rpm for 2 min, flocculation at 30 rpm for 20 min, and sedimentation with no mixing for 30 min. In experiment 3, PAC and aluminium sulphate were dosed together at the same time under the same mixing conditions.

compared to the GD experiments, and (b) lower aromaticity and MW of the HS in GD water when compared to the HS in LHD water (Table 1), thereby suggesting that GD HS were adsorbed onto the internal PAC layers to a greater degree than the HS present in LHD water. This implies that the poor removal of BP from LHD water *via* PAC dosing (experiment 2A) was a result of the fouling of external PAC layers by the aromatic and high MW HS from LHD water. Overall, these results indicate that the process performance can be impacted by the DOM character of the source water.

Based on the results from Fig. 3, the optimum PAC dose to DOC ratio was selected as 8.4 and 5.8 mg PAC per mg C for the GD and LHD jar tests, respectively.

3.3.3. Combining PAC adsorption with coagulation-flocculation followed by sedimentation (experiments 2B and 3). There was no significant difference between treated water quality in experiments 2B and 3, and therefore, these will be reported together as a single set.

3.3.3.1. Influence on DOM removal and PAC-coagulant dose. The combination of PAC adsorption and coagulation processes greatly improved DOM removal across all DOM fractions (Fig. 4A–D). The DOC removal from LHD water was higher (86%) when compared to GD water (76%) (Fig. 4C and D). C1, C2 and C3 were removed at a similarly high range in both waters (91–97% in GD water and 85–92% in LHD water, Fig. 4A and B). The removal of HS and LMWN was almost the same in GD (92% HS and 91% low molecular weight neutrals) and LHD (89% HS and 89% LMWN) jar tests, while BB and BP removal was slightly lower in LHD jar tests (85% BB and 86% BP) than in GD jar tests (95% BB and 95% BP) (Fig. 4C and D). These results are in line with observations made previously where combination of PAC dosing and FeCl₃-based coagulation resulted in a decrease in concentrations of all fractions of micropollutant containing DOM obtained from several waste water treatment plants in Germany.⁵⁰ In another study, the combined effects of PAC adsorption and coagulation resulted in a low rate of irreversible and reversible fouling in ultrafiltration membranes due to >90% biopolymers and humics removal, while the removal of low MW compounds was approximately 80%.⁵³ Overall, these results indicate that combining PAC dosing and coagulation for the treatment of DOM containing waters can be beneficial for high DOM removal.

There were other also benefits that were observed when combining PAC dosing with coagulation. For instance, the optimum dose of the coagulant decreased to 8 mg Al per L for GD water and 16 mg Al per L for LHD water, reducing the optimum coagulant dose to DOC ratio to 1.1 and 1.2 mg Al per mg C in GD and LHD jar tests, respectively. Similar results have been observed previously in Polish waters where increasing the PAC dose from 30–75 mg PAC per L resulted in a 25% decrease in the optimum coagulant dose.⁵⁴ While there was a reduction in the optimum coagulant dose when using PAC, the optimum PAC dose for the GD water (PAC: DOC: 8.4 mg PAC per mg C, Fig. 4C) with the higher DOM treatability was almost 1.5 times higher than that obtained

for the more treatable DOM in the LHD experiments (PAC: DOC: 5.8 mg PAC per mg C, Fig. 4D), suggesting that the variations in the optimum PAC dose for both waters were driven by the differences in the DOM character between the source waters.

3.3.3.2. Comparison of combining PAC with coagulation-flocculation (experiments 2B and 3) with experiments 1 and 2A. In contrast to experiments 1 and 2A, there was no preferential removal of any DOM fractions when PAC adsorption and coagulation processes were combined (experiments 2B and 3) as all fractions had >75% removal at the optimum dose (Fig. S6†). DOC removal increased to 76% and 86% in GD and LHD jar tests, respectively (Fig. S6†), from only 53% and 65% in experiment 1 (Fig. S6†) and 38% and 44% in experiment 2A (Fig. S6†) for the same samples. The removal of C1, C2, C3, BP, HS and BB were also comparable or higher in experiments 2B and 3 when compared to experiments 1 and 2A (Fig. S6†). It was also observed that the LMWN removal was slightly higher in 2B and 3 for both waters (~87–91% in GD and LHD) when compared to experiments 2A (77–81% in GD and LHD), and almost three times higher than that observed in experiment 1 (Fig. S6†). During experiments 1 and 2A, increased DOM removal was initiated by an increased dose of the aluminium sulphate or PAC. In the combined process (experiments 2B and 3), increased removal of higher MW, highly treatable materials, such as C1, over less treatable reprocessed materials such as C2, was driven by increased PAC dose rather than coagulant dose (Fig. 5). For example, at a fixed dose of aluminium sulphate (*e.g.* 16 mg Al per L, Fig. 5), the C1 removal to C2 removal ratio decreased with increasing dose of PAC (Fig. 5), whereas at a fixed dose of PAC (*e.g.* 40 mg PAC L⁻¹), the proportion of the removal of highly treatable C1 to less treatable reprocessed fluorescent organic matter fraction C2 remained almost the same over the range of coagulant doses. Overall, in experiments 2B and 3, residual DOC concentrations of <2 mg C per L (Fig. 4C and D) were obtained for both water types at the optimised condition (GD: 1.7 mg C per L, LHD: 1.9 mg C per L) when compared to experiments 1 (GD: 3.6 mg C per L, LHD: 4.8 mg C per L) and 2A (GD: 4.4 mg C per L, LHD: 7.7 mg C per L). This indicated that from the perspectives of residual DOM concentrations, DBP formation could be expected to be reduced in experiments 2B and 3 when compared to experiments 1 and 2A.^{5,7,55}

3.3.3.3. Mechanisms by which DOM removal is enhanced by combining PAC with coagulation-flocculation. There are two underlying treatment mechanisms when the PAC adsorption was combined with coagulation-flocculation followed by sedimentation that can explain the improved and non-preferential DOM removal. Firstly, at the initial stage of the treatment, coagulant and PAC added into the source water compete and react with the DOM,^{12,51} with the coagulant targeting high MW HS, and terrestrially delivered fluorescent DOM fraction such as C1 (Fig. 4), and PAC adsorbing lower MW humic-like materials and LMWN (Fig. 4). Secondly, PAC

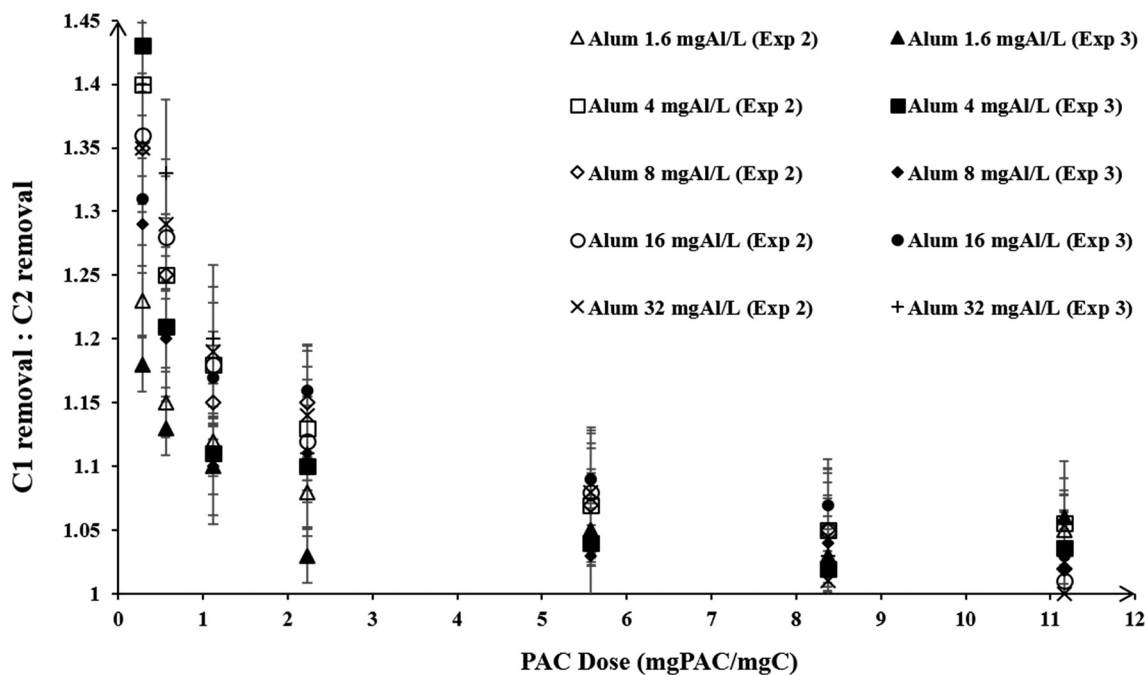


Fig. 5 Relative removal of fluorescent C1 and C2 fraction of organic matter during the experiments 2 and 3 in response to PAC dose per mg of DOC in source water.

could become a ballasting agent when it is incorporated into a floc matrix uniformly.^{56,57} During rapid mixing (in the presence of PAC in experiment 2B and 3), the number of

particles in the water increases, thereby increasing collision frequency. As PAC particles have a greater mass than the microflocs, PAC particles have a greater energy during the

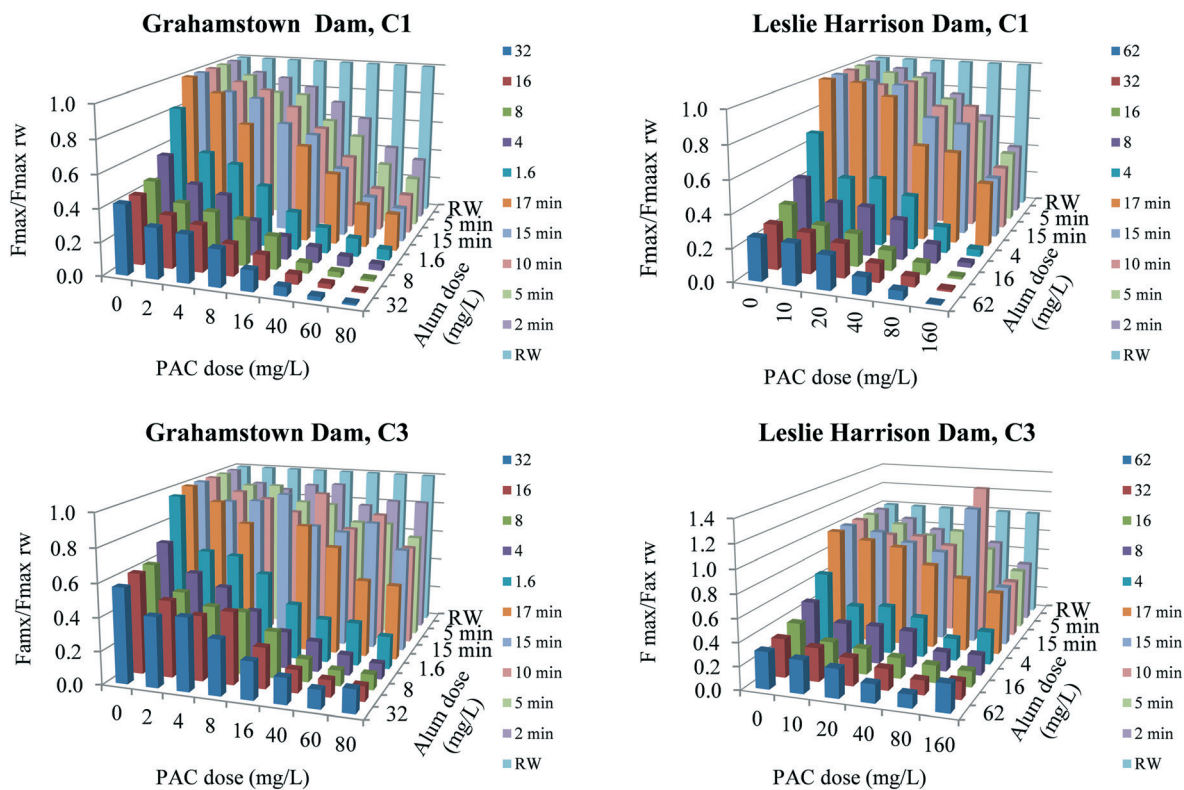


Fig. 6 Fluorescent DOM components removal following PAC and alum dosing assays (C1 and C2 patterns were statistically similar, thus only C1 is presented).

rapid mixing which allows the PAC particles to enter to the microfloc matrix by momentum. However, during slow mixing stage, flocs have a higher propensity to aggregate into larger ballasted flocs.⁵⁷ PAC is incorporated into flocs until the steady-state condition is reached, after which no more ballasted agent would be included into the floc as the floc would break up and aggregate again. The ballasted agent takes the place of the ballasted water in the floc matrix, causing the reduction of the amount of the water present in the floc, thereby increasing the floc density.^{56,58} Overall, the increased interaction of PAC and coagulant with OM and the increased floc density greatly improve the OM removal despite the differences in source water OM character. In conclusion, it can be stated that for effective DOM removal, the application of PAC dosing prior to- or during coagulation is beneficial.

3.4. Application of PAC and fluorescence measurements for OM monitoring

Changes in fluorescence components (C1, C2 and C3) followed the changing trends of DOC concentrations, where a gradual decrease in component scores was observed with increased PAC and coagulant doses (Fig. 6). PAC adsorption (experiment 2A) and PAC-coagulation-flocculation-sedimentation experiments (experiments 2B and 3) demonstrated similar trends for component removal for both types of source water. In the PAC adsorption experiments where PAC was dosed prior to the coagulation stage (experiment 2A), C1 and C2 removals were comparable (73% and 68% in GD water, and 59% and 63% in LHD water) and higher than C3 removal in both the water sources (52% in GD water and 44% in LHD water) (Fig. 3). In the experiments where the PAC and coagulation treatment were combined (experiment 2B and 3), there was no preferential removal of any component; all components were removed to a high degree (91–97% in GD water and 85–92% in LHD water) (Fig. 4). Overall, the dissimilar removal of fluorescence DOM fractions in experiment 1 indicates that the coagulation-flocculation-sedimentation process is highly influenced by DOM character, while combined PAC adsorption-coagulation-flocculation-sedimentation processes are less affected.

4. Conclusions

In this study, samples of DOM containing water were collected and analysed from two dams in two different states in Australia in order to maximise DOM variability due to location (which included both unprotected and protected reservoirs and river systems) and climate zone (subtropical and temperate climate zones). The study showed that a combination of fluorescence spectroscopy and LC-OCD was highly beneficial in tracking the fate of fluorescent, non-fluorescent and size-fractionated DOM fractions when different treatment processes are applied and to understand the mechanisms behind how these fractions impact DOM treatability. For instance, coagulation-flocculation-sedimentation without PAC dosing (experiment 1) had a

maximum DOM removal efficiency of 65% during which fluorescent DOM and biopolymer and humic chromatographic fractions (high-MW) were preferentially removed. Both, experiment 1 and 2A (PAC adsorption only) were affected by DOM character, resulting in high DOM concentrations in the effluent (3.5–9 mg C per L). In comparison, the combined PAC-coagulation-flocculation-sedimentation process (experiment 2B and 3) greatly improved the removal of all DOM fractions, with residual DOM concentrations of <2 mg C per L in the treated water, despite the difference in source water DOM character. Overall, the combination of advanced DOM characterisation and application of PAC-coagulation-flocculation-sedimentation process can be used to ensure that periodic, elevated DOM events are adequately treated, thereby lowering the risk of DBP production.

Future recommendations include evaluating the combined PAC-coagulation processes for dissolved organic nitrogen removal and its subsequent impact on DBP formation potentials. Other recommendations include analysis of micropollutants adsorbed onto the PAC and an assessment of the impact of PAC obtained from different sources on DOC removal.

Conflicts of interest

There are no conflicts to declare.

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