

Dissolved organic carbon and trihalomethane formation potential removal during coagulation of a typical UK upland water with alum, PAX-18 and PIX-322

Rachel Gough, Peter J. Holliman, Terence R. Heard and Christopher Freeman

ABSTRACT

This paper considers the removal of dissolved organic carbon (DOC) from a typical UK upland reservoir water using three different coagulants; aluminium sulphate/alum ($\text{Al}_2(\text{SO}_4)_3(\text{aq})$), polyaluminium chloride/PAX-18 ($\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}(\text{aq})$) and ferric sulphate/PIX-322 ($\text{Fe}_2(\text{SO}_4)_3(\text{aq})$). A comparison of DOC quality including fractional character, colour, specific ultraviolet absorption (SUVA) and molecular weight was made between the source water and the supernatants obtained following its coagulation in each case. Trihalomethane formation potential (THMFP) was compared before and after treatment to assess which coagulant performed best in terms of THM amelioration. The conditions (coagulant dose and pH) required to obtain optimal DOC removal were established using bench-scale jar tests. Statistically significant differences in DOC removal rates were observed between the different coagulants. THMFP removal was linked to a combination of high net DOC removal and the preferential removal of THM precursors. This selectivity may also be responsible for the increase in brominated THM species (BrTHMs) observed following treatment.

Key words | coagulation, dissolved organic carbon, trihalomethanes, water treatment, XAD fractionation

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INTRODUCTION

Natural organic matter (NOM) is present in all natural surface and ground waters and comprises biogenic material at various stages of biological and chemical degradation (Hope *et al.* 1994). Although not currently regulated as a water quality parameter, NOM can compromise the taste, colour and odour of potable water and stimulate bacterial growth within water distribution systems (Matilainen *et al.* 2010). Furthermore, dissolved organic carbon (DOC) (operationally defined as organic matter which passes through a 0.45 µm filter) (Thurman 1985) can act as a precursor to potentially harmful disinfection by-products (DBPs) including trihalomethanes (THMs), formed during chlorination (Rook 1974; Symons *et al.* 1975). The World Health Organization (WHO) has

published guideline maximum drinking water concentrations for the four main chlorinated and brominated THMs: 300 µg L⁻¹ for CHCl₃, 100 µg L⁻¹ for CHBr₃ and CHBr₂Cl and 60 µg L⁻¹ for CHBrCl₂ (WHO 2011). In the UK the Water Supply (Water Quality) Regulations 2010 (DWI 2010) stipulate a stricter limit of 100 µg L⁻¹ total THMs for water samples taken from consumers' taps.

Removal of DOC prior to disinfection is considered to be the most effective means of minimising THM formation and is typically achieved by coagulation using iron or aluminium salts (O'Melia *et al.* 1999). However, a trend of increased DOC concentrations in waters draining upland catchments in Northern and Western Europe and North

America has been widely reported in recent decades (Freeman *et al.* 2001; Hejzlar *et al.* 2003; Stoddard *et al.* 2003; Worrall *et al.* 2003; Monteith *et al.* 2007). Traditionally coagulation-flocculation is designed to attain target levels of colour and turbidity (Iriarte-Velasco *et al.* 2007). However removal of colour/turbidity does not necessarily correlate with optimal DOC removal (Yan *et al.* 2008a). Enhanced coagulation refers to the optimisation of organic carbon removal, beyond what would be expected if coagulation was applied solely for colour/turbidity removal (White *et al.* 1997; Boyer & Singer 2005). This technique has been recognised as the best available technology for minimising THM and other DBP formation in chlorinated drinking water (USEPA 1999). Jar testing is the industry standard method for establishing optimum coagulation conditions (pH, coagulant dose and sequence of chemical addition) to achieve the desired quality of treated water. It is necessary to regularly establish these conditions experimentally, since the quality of raw water entering most water treatment works (WTW) is highly variable.

The aim of this study is to compare DOC concentration and characteristics between a typical upland reservoir water and the supernatants obtained following coagulation using three commercial coagulants (aluminium sulphate/alum ($\text{Al}_2(\text{SO}_4)_3(\text{aq})$), polyaluminium chloride/PAX-18 ($\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}(\text{aq})$) and ferric sulphate/PIX-322 ($\text{Fe}_2(\text{SO}_4)_3(\text{aq})$)), each widely used in the potable water treatment industry. Bench-scale jar testing was carried out in order to establish optimum conditions (coagulant dose and pH) for DOC removal using each of the three coagulants. Specific ultraviolet absorption (SUVA), colour and molecular weight (MW) measurements were used to compare DOC character between samples. DOC was also partitioned using XAD fractionation to investigate potential selectivity in the removal of DOC during coagulation. Zeta potential measurements were used to evaluate the extent of charge neutralisation. Since THM amelioration is a key objective in the coagulation process, this study also compares trihalomethane formation potential (THMFP) and THM speciation between the coagulated and raw water samples. These parameters were also compared between DOC fractions obtained following XAD fractionation to investigate potential differences in reactivity relating to character.

METHODS

Works description

The water used in this study was taken from the raw water inlet of a potable WTW in an upland area of the UK. Raw water for the works is abstracted from a reservoir whose catchment includes an extensive area of woodland plantation (30%) consisting mainly of coniferous species. The remainder of the catchment is described as grassland (38%) and peatland (32%) (Cohen 2009). Existing treatment consists of coagulation ($\text{Al}_2(\text{SO}_4)_3$) and flocculation followed by dissolved air floatation for clarification, primary filtration using rapid gravity sand filters (RGF), secondary RGF for manganese removal and finally chlorine dosing for disinfection. Average works output is 38–40 ML d⁻¹. During the study period raw water colour ranged from 75 to 80 Hazen, pH values from 6.0 to 6.2, UV absorbance at $\lambda = 254$ nm from 0.560 to 0.570 UV a.u. and typical alkalinity was 3 mg L⁻¹ as CaCO₃. At the time of testing, raw water DOC concentration was 9.3 mg L⁻¹.

Reagents

The experimental design included three coagulants: aluminium sulphate/alum ($\text{Al}_2(\text{SO}_4)_3(\text{aq})$), polyaluminium chloride/PAX-18 ($\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}(\text{aq})$) and ferric sulphate/PIX-322 ($\text{Fe}_2(\text{SO}_4)_3(\text{aq})$), all supplied by Kemira. Working solutions of 0.84 g L⁻¹ (as Al) for alum, 0.9 g L⁻¹ (as Al) for PAX-18 and 1.18 g L⁻¹ (as Fe) for PIX-322 were made. These were freshly prepared before each set of jar tests in order to minimise hydrolysis prior to dosing.

Jar test procedure

A Stuart SW6 variable speed, programmable, six paddle flocculator was used for jar testing. 5 × 1 L aliquots of raw water were measured into 1 L beakers and placed on the flocculator. The water was dosed with lime (100% Ca(OH)₂) for pH adjustment followed by the coagulant while stirring at 240 rpm. pH was measured using a Mettler Toledo portable pH/conductivity meter calibrated daily with pH 4, 7 and 10 buffer solutions (Reagecon). The

volume of lime required for pH adjustment had been predetermined experimentally. Samples were then mixed at 240 rpm for 1 min after addition of the coagulant followed by 19 min at 20 rpm. Floc size at 5 and 20 min was measured by eye and recorded. The stirring paddles were removed and the floc allowed to settle for 30 min. Treated water samples were then filtered through a Whatman No. 1 filter paper (11 μm pore size) to simulate the clarification stage at the WTW. These samples were analysed for colour (Hazen) using a Cecil 2020 spectrophotometer at $\lambda = 400\text{ nm}$ and residual coagulant (mg L^{-1} as total Al/Fe). Both residuals were measured using a standard Palintest[®] colorimetric test and a Palintest[®] 7100 automatic wavelength selection photometer. Eriochrome cyanide R indicator was used for Al and PPST in combination with a decomplexing/reducing agent was used for Fe. Samples were then filtered through a 0.45 μm Nylon membrane (Whatman) before off-site analyses. These included determination of DOC concentration with a Thermalox TOC/TN analyser equipped with a non-dispersive infrared CO_2 detector, UV absorbance measurements using a Molecular Devices SpectraMax M2e multi-detection spectrophotometer and high pressure size exclusion chromatography (HPSEC) using a Varian PL-GPC-50 DataStream unit detecting at $\lambda = 254\text{ nm}$. The HPSEC unit was interfaced to Cirrus software and equipped with a Bio Sep 2000 column. Calibration standards consisted of sodium polystyrene sulfonate polymers with MWs of 150,000, 77,000, 32,000, 13,000 and 4,300 Da (Fluka) and cyanocobalamin (1,340 Da). For the mobile phase Milli Q water was buffered with phosphate ($0.002\text{ M KH}_2\text{PO}_4 + 0.002\text{ M K}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$) to pH 6.8. XAD fractionation and THMFP tests were also conducted.

For each coagulant under investigation, a series of jar tests were conducted to determine the optimum coagulant dose and coagulation pH for DOC removal. A range of coagulant doses were tested initially, with pH maintained at a constant level. pH was then varied over subsequent tests by adjusting the lime dose to determine optimum pH at that coagulant dose. A final set of replicate tests was conducted using the optimum conditions (pH and coagulant dose) in order to test the repeatability of the procedure and to obtain sufficient quantities of supernatant to perform XAD fractionation and THMFP tests. On-site analysis of supernatant colour provided an indication of DOC removal

but direct DOC measurements of clarified samples quantified this. Where colour removal under different conditions was similar, turbidity and residual coagulant content of the clarified sample were used to decide the optimum. Satisfactory clarification was considered to have been achieved with colour measurements of <5 Hazen. Zeta potential was measured on the supernatants derived from each optimised test. These measurements were supplied by Cranfield University with analysis conducted using a Malvern Zetasizer 2000HSA.

Fractionation

Fractionation of DOC was achieved by resin adsorption using a method adapted from Thurman & Malcolm (1981) and Marhaba *et al.* (2003). Samples were separated into five fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophobic neutral (HPON) according to their adsorption onto a series of macroporous resin adsorbents (Superlite[™] DAX-8 resin and Amberlite[™] XAD-4 resin (both Supelco)).

THMFP method

THMFP analyses were conducted on composite samples, made by combining equal volumes from five replicates. THMFP_{7d} denotes the quantity of THMs formed ($\mu\text{g L}^{-1}$) following chlorination of a water sample after a 7 d incubation period at 25 °C. The method used was adapted from the Standing Committee of Analysts (1981) procedure. In this study samples were diluted to 1 mg L^{-1} DOC in order to derive a standardised THMFP_{7d} (STHMFP_{7d}) value which provides a measure of DOC reactivity. A THMFP_{7d} value was then calculated by multiplying STHMFP_{7d} by DOC concentration. For the chlorination procedure, 97.5 mL of diluted sample was dosed with 2.0 mL of 0.5 M $\text{KH}_2\text{PO}_4(\text{aq})$ to buffer the solution to pH 6.8. Samples were then dosed with 0.5 mL of $\text{NaOCl}(\text{aq})$ to provide 5 mg of free Cl per mg of DOC. After 7 d incubation in the dark at 25 °C, the reaction was quenched using 0.4 mL of 0.8 M $\text{Na}_2\text{SO}_3(\text{aq})$. Extraction of the four chlorinated and brominated THM species (CHCl_3 , CHBrCl_2 , CHBr_2Cl and CHBr_3) was achieved using direct immersion SPME

followed by quantification using a Varian 450 GC coupled with an electron capture detector. In addition to analyses of raw and coagulated samples, THMFP_{7d} was also determined for the isolated XAD fractions.

Statistical analysis

Depending on the conditions satisfied by the data, Analysis of Variance (ANOVA) and Kruskal-Wallis tests were performed to identify statistically significant differences in water quality parameters between raw water and coagulated samples using alum, PAX-18 and PIX-322 coagulants. Statistical analyses were also conducted to compare characteristics of HPOA, HPIA and HPON fractions across all sample types. The HPOB and HPIB fractions were not included in these analyses since their contribution to total DOC was negligible. Significant results for ANOVA were further investigated using the Tukey HSD post-hoc test. Post-hoc analysis for Kruskal-Wallis was the rank-based test described by Siegel & Castellan (1988). Statistical analysis was carried out using version 18 of the SPSS Statistics package (IBM).

RESULTS AND DISCUSSION

Optimum coagulation conditions

Optimum coagulant dose was similar for the two aluminium-based coagulants (4.2 and 4.5 mg L⁻¹ as Al for alum and PAX-18, respectively) and higher for the ferric-based coagulant (9.4 mg L⁻¹ as Fe for PIX-322) (Table 1). Optimum coagulation pH was also similar for the two aluminium-based coagulants, (6.0 and 6.1 for alum and PAX-18, respectively). The optimum pH recorded for

PIX-322 was lower (4.6), consistent with data reported previously (Matilainen *et al.* 2010). This is due to the lower pH at which the preferred hydrolysed products (Fe(OH)₃) of the coagulant are formed. Ferric-based coagulants are also effective over a wider pH range than aluminium-based coagulants, which is advantageous in a water treatment context where coagulation conditions can be controlled less precisely than in a laboratory context.

The optimum coagulant doses correspond to 100, 50 and 80 mg L⁻¹ as neat product for alum, PAX-18 and PIX-322, respectively. The associated lime doses required for pH correction were 12.3, 7.8 and 12.5 mg L⁻¹ of 100% Ca(OH)₂ (Table 1). Based solely on coagulant cost (£189, £207 and £162 per tonne of alum, PAX-18 and PIX-322, respectively), a cost saving of 45% was calculated for the replacement of alum with PAX-18, and a saving of 31% calculated for the replacement of alum with PIX-322. Lime dose also affects the sustainability of the coagulation process as high doses can lead to deposition within the WTW or distribution system, necessitating costly remediation. On this basis also, PAX-18, which required the lowest lime dose, represents the most cost-effective option for this system.

Mean residual coagulant concentration was also similar for the aluminium-based coagulants (26 and 20 µg L⁻¹ as Al for alum and PAX-18, respectively). The residual coagulant concentration was relatively higher for PIX-322 (108 µg L⁻¹ as Fe) and floc size after 20 min was greater (2.25–3.00 mm diameter) (Table 1).

Zeta potential values for supernatants treated under optimal conditions using the three coagulants were -10.9, -5.1 and -9.5 mV for alum, PAX-18 and PIX-322, respectively (Table 1). Charge neutralisation mechanisms are believed to be most important where coagulation conditions have been optimised for maximum DOC removal (Yan *et al.*

Table 1 | Optimum conditions (pH, coagulant dose and lime dose) and residual coagulant, floc size and zeta potential measurements under optimum conditions for DOC removal using alum, PAX-18 and PIX-322 coagulants

	Optimum coagulant dose (mg L ⁻¹ /µmol L ⁻¹ as Al or Fe)	Optimum coagulation pH	Lime dose (mg L ⁻¹ as 100% Ca(OH) ₂)	Residual coagulant (µg L ⁻¹ as Al/Fe)	Floc size after 20 min (mm)	Zeta potential (mV)
Alum	4.2/156	6.0 ± 0.02	12.3	26 ± 4	1.50–2.25	- 10.9
PAX-18	4.5/81	6.1 ± 0.02	7.8	20 ± 0	1.50–2.25	- 5.1
PIX-322	9.4/168	4.6 ± 0.02	12.5	108 ± 6	2.25–3.00	- 9.5

Where applicable results given as mean ± standard error of the mean (*n* = 5).

2008a). However, zeta potential at optimal coagulation conditions is reported to deviate from zero, suggesting that other mechanisms such as complexation, adsorption and co-precipitation may also occur. Indeed, zeta potential values ranging from -10 to $+3$ mV have been cited for different source waters optimised for DOC removal (Sharp *et al.* 2006b). The values obtained in this study are therefore comparable to those reported previously.

Comparison of raw and coagulated samples

Mean DOC concentration in the raw water was 9.3 mg L^{-1} . Mean DOC concentration in samples treated with alum, PAX-18 and PIX-322 were 3.4 , 3.1 and 2.4 mg L^{-1} , respectively. These values correspond with % DOC removal levels of 63, 67 and 74%, respectively (Table 2). DOC concentration in the raw water was significantly higher than in the samples treated with each of the three coagulants ($p < 0.01$). In addition, DOC concentration in samples treated with alum was significantly higher than in samples treated

with PAX-18 ($p < 0.05$) and PIX-322 ($p < 0.01$) and samples treated with PAX-18 had significantly higher DOC concentrations than those treated with PIX-322 ($p < 0.01$).

The large number of variables affecting coagulation, not least variability in raw water and DOC characteristics, mean that reported DOC removal rates can differ considerably. Under conditions optimised for DOC removal, Qin *et al.* (2006) reported a removal rate of 45% at pH 5.2 using alum from a Singapore reservoir water containing 3.27 – 7.45 mg L^{-1} DOC. Uyak & Toroz (2007) reported DOC removal rates of 66, 71 and 43% at pH 5.25 for three different Istanbul reservoir waters using FeCl_3 , and 52, 67 and 34% at pH 5.25–5.50 using alum on the same three source waters. They attributed the higher removal levels observed for one water source to its higher alkalinity and DOC concentration (135 mg L^{-1} as CaCO_3 and 4.22 mg L^{-1} , respectively). Chow *et al.* (2009) cited DOC removal levels of $>50\%$ at pH 5–6 using alum for water from four reservoirs in south-eastern Australia, when optimised for DOC removal. These waters contained between 5.0 and

Table 2 | Results of raw and coagulated water quality analysis showing statistically significant differences

	Raw (a)	Alum (b)	PAX-18 (c)	PIX-322 (d)
DOC concentration (mg L^{-1})	9.3 ± 0.1	3.4 ± 0.1	3.1 ± 0.1	2.4 ± 0.1
	BCD	AcD	AbD	ABC
% DOC removal	N/A	63 ± 1	67 ± 1	74 ± 1
SUVA ($\text{L mg}^{-1} \text{ m}^{-1}$)	4.1 ± 0.03	2.9 ± 0.10	2.6 ± 0.05	2.4 ± 0.09
	cd		a	a
Colour (Abs_{400}) (UV a.u.)	0.037 ± 0.0003	0.002 ± 0.0006	0.001 ± 0.0007	-0.001 ± 0.0011
	BCD	A	A	A
STHMFP _{7d} ($\mu\text{g THM mg DOC}^{-1}$)	86.6 ± 0.4	44.1 ± 1.4	40.9 ± 1.3	50.1 ± 1.5
THMFP _{7d} ($\mu\text{g L}^{-1}$)	806.6 ± 9.1	152.0 ± 10.4	125.4 ± 8.6	120.8 ± 8.2
% decrease STHMFP _{7d} from raw	N/A	49.1 ± 1.9	52.8 ± 1.7	42.2 ± 2.0
% decrease THMFP _{7d} from raw	N/A	81.2 ± 1.5	84.5 ± 1.2	85.0 ± 1.2
M_p (Da)	5760	4824	4711	4824
M_n (Da)	494	277	335	304
M_w (Da)	3658	2960	2770	2709
% HPOA DOC	50 ± 3	33 ± 1	36 ± 2	36 ± 1
	b	a		
% HPIA DOC	27 ± 1	29 ± 1	26 ± 2	29 ± 4
% HPON DOC	20 ± 2	32 ± 1	31 ± 3	29 ± 4

Where applicable results given as mean \pm standard error of the mean ($n = 5$ except for fraction percentage data where $n = 3$), except for THM results where measurements were conducted on composite samples and the standard error derived from detection repeatability experiments. Letter annotations denote significantly different means (lower case: $p < 0.05$, upper case: $p < 0.01$).

10.8 mg L⁻¹ DOC and alkalinity between 7 and 100 mg L⁻¹ as CaCO₃. In the context of previous studies, the removal levels observed in the present study are high, particularly for PIX-322. These data therefore suggest that high removal rates can be achieved under optimised conditions for low alkalinity water. Previous studies have reported improved DOC removal rates when ferric-based salts are used as opposed to aluminium-based salts (Edwards 1997; Uyak & Toroz 2005). This is thought to be due to the higher affinity for carboxylic groups associated with ferric ion (Sharp *et al.* 2006c). Furthermore, the flocs formed during ferric-based coagulation are reported to be more numerous and larger (Ratnaweera *et al.* 1999) as was observed in the present study, thus aiding their removal during clarification. The higher coagulation pH associated with the aluminium-based coagulants may also lead to lower-density, and hence less stable flocs. This has been explained by enhanced deprotonation of DOC molecules at higher pH values resulting in increased electrostatic repulsion within the floc (Slavik *et al.* 2012) and may lead to the return of DOC into solution. Typical DOC removal rates observed at this works, where alum is currently being used as a coagulant, are 72–83%, i.e. higher than the DOC removal rates observed in these jar tests using alum. However, past experience at this site suggests that removal rates tend to improve significantly when conditions established during jar testing are up-scaled and applied at the works. It should also be noted that the higher DOC removal rates associated with PAX-18 and PIX-322 will also increase sludge production and the costs associated with its de-watering and disposal.

The percentage contribution of individual fractions (HPOA, HPIA and HPON) to total recovered DOC concentration was compared between the raw water and the three treatments (alum, PAX-18 and PIX-322) (Figure 1). The percentage of HPOA in the sample treated with alum (mean: 33%) was significantly lower than the percentage of HPOA in the raw water (mean: 50%) ($p < 0.05$). Comparisons between other groups were not significant. No significant differences in the percentage contribution of HPIA or HPON were observed between samples (Table 2).

Previous studies have reported that DOC fractional character will affect the level of removal achieved by coagulation (Sharp *et al.* 2006a; Chow *et al.* 2009), with the hydrophilic, low MW fraction less amenable to removal

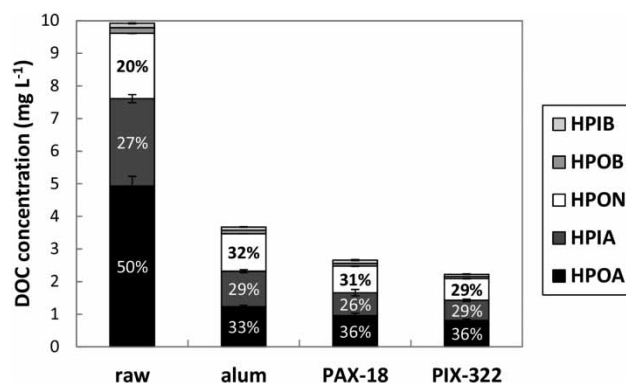


Figure 1 | Percentage contribution of HPOA, HPIA, HPON, HPOB and HPIB fractions to the total recovered DOC following fractionation for raw water and supernatants from optimised jar tests using alum, PAX-18 and PIX-322 coagulants. Error bars represent the standard error of the mean ($n = 3$).

than the high MW HPOA fraction (Krasner & Amy 1995; Edwards 1997; White *et al.* 1997). This has been attributed to the higher charge density associated with this fraction (Sharp *et al.* 2006c) and explains the lower mean HPOA percentage in the coagulated samples compared with the raw water in the present study. However, the degree of selectivity was less pronounced than anticipated and only the alum/raw HPOA percentage comparison was statistically significant. By contrast, Parsons *et al.* (2004) report >90% HPOA removal rate whilst the HPON fraction was almost unchanged. In the present study, mean percentage contribution of the HPIA fraction to total recovered DOC was fairly stable across all samples, with no significant differences observed. The contribution of the HPON fraction, however, was approximately 10% higher in each of the coagulated samples compared to the raw water (Figure 1), although this was not found to be statistically significant. This may simply be an artefact of the preferential removal of the HPOA fraction during coagulation. One possible explanation for the lower HPOA removal efficiency observed here could be the very low levels of alkalinity in the raw water, a typical feature of upland water sources (Parsons & Jefferson 2009). Wang *et al.* (2009) found a positive relationship between alkalinity and humic acid removal efficiency by coagulation with aluminium salts as a result of the charge neutralising effect of the Ca²⁺ ion on the surface of humic acid molecules. OH⁻ species are also consumed rapidly during hydrolysing reactions (Yan *et al.* 2008b), thus dynamically lowering pH. Alkalinity is therefore

required to buffer the solution and prevent the pH falling below the optimum for coagulation. However, given the addition of lime during the jar test procedure, it is difficult to relate coagulation efficiency to raw water alkalinity. Instead, removal rates for different fractions may be related to the distinct characteristics of the DOC for this water source. The precipitation of DOC during coagulation occurs in a competitive environment. Hence if the HPIA and HPON fractions in this water source are more amenable to removal than is normally the case, this will inhibit the removal of the HPOA fraction.

Coagulated samples had a lower mean SUVA value (2.9, 2.6 and 2.4 L mg⁻¹ m⁻¹ for alum, PAX-18 and PIX-322) than the raw water (4.1 L mg⁻¹ m⁻¹), though only the PAX-18/raw ($p < 0.05$) and PIX-322/raw ($p < 0.05$) comparisons were found to be statistically significant (Table 2). This observation has been reported previously and is also thought to relate to the preferential removal of the highly aromatic, high MW HPOA DOC during coagulation (Volk *et al.* 2000; Uyak & Toroz 2007). This selectivity also explains the dramatic and statistically significant reduction in colour observed in all of the coagulated samples (Table 2), since the HPOA fraction is reported to be associated with significantly higher colour than hydrophilic DOC (Oliver *et al.* 1983; Thurman 1985). Mean raw water colour was 0.037 UV a.u. and mean colour in the coagulated samples was <10% of this in each case. The reduction in MW following coagulation, as indicated by the decrease in all three MW averages (M_p , M_n and M_w) in the coagulated samples (Table 2), is also consistent with a fall in the proportion of HPOA in the coagulated water, since the HPOA DOC fraction constitutes higher MW molecules than the hydrophilic fraction (Edzwald & Tobiason 1999).

THMFP_{7d} was determined on composite samples of raw water and water treated with alum, PAX-18 and PIX-322 coagulants, hence the samples cannot be compared statistically. However, STHMFP_{7d} for the raw water (86.6 µg THM mg DOC⁻¹) was substantially higher than for the coagulated samples: 44.1, 40.9 and 50.1 µg THM mg DOC⁻¹ for alum, PAX-18 and PIX-322, respectively (Table 2). These values correspond with a 49.1, 52.8 and 42.2% decrease in STHMFP_{7d} for the three coagulants, respectively (Table 2). This indicates a preferential removal of THM precursors during coagulation. Differences

between the raw water and coagulated samples were even more pronounced with regard to THMFP_{7d} which takes DOC concentration into account (Table 2). The THMFP_{7d} for the raw water sample was 806.6 µg L⁻¹ compared with 152.0, 125.4 and 120.8 µg L⁻¹ for samples treated with alum, PAX-18 and PIX-322, respectively (Table 2). This corresponds to an 81.2, 84.5 and 85.0% decrease in THMFP_{7d}, respectively. Although the STHMFP_{7d} of the PIX-322 sample was highest (50.1 µg THM mg DOC⁻¹) among the coagulated waters, as a result of its comparatively low DOC concentration, its THMFP_{7d} was the lowest. Reported THMFP removal rates following coagulation vary widely. Iriarte-Velasco *et al.* (2007) report 31–48% bulk removal of THMFP for a low DOC surface water under different alkalinity conditions using alum and polyaluminium chloride coagulants. Page *et al.* (2002) report a 55% THMFP removal on average across a range of reservoir waters and DOC concentrations using alum. Similarly, Uyak & Toroz (2007) report an average 56% precursor removal under optimum conditions averaged over three surface water sources using ferric chloride and alum coagulants. The high THMFP_{7d} removal shown in this study appears to be due to a combination of high bulk DOC removal levels and the selective removal of the HPOA fraction, which is generally thought to produce the highest THM yield upon chlorination (Chow *et al.* 2005; Zhang *et al.* 2009), though here, STHMFP_{7d} was not found to vary significantly as a function of DOC fraction (Table 3).

Comparing the speciation of THMs, the proportion of brominated THMs (BrTHMs) increased following coagulation from 3% in the raw water to 9, 10 and 12% in the alum, PAX-18 and PIX-322 samples, respectively (Figure 2). This increase is important because BrTHMs

Table 3 | Results of XAD fraction THMFP analysis showing statistically significant differences

	HPOA (a)	HPIA (b)	HPON (c)
STHMFP _{7d} (µg THM mg DOC ⁻¹)	104.6 ± 8.9	90.5 ± 5.2	89.0 ± 11.3
% BrTHMs	< 0.1 C	< 0.1 C	17.1 ± 1.6 AB

Where applicable results given as mean ± standard error of the mean ($n = 12$). Letter annotations denote significantly different means (lower case: $p < 0.05$, upper case: $p < 0.01$).

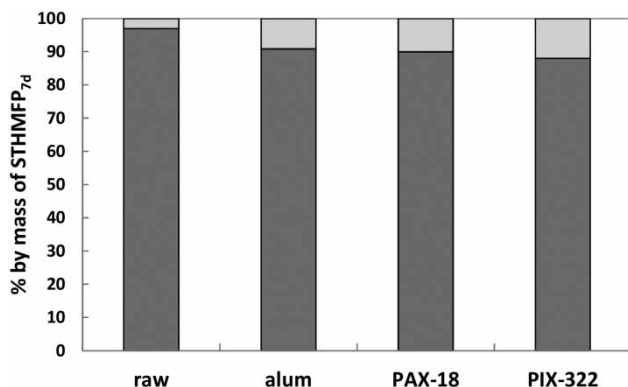


Figure 2 | Percentage contribution of THM species to STHMFP_{7d} (CHCl₃: dark grey, BrTHMs: light grey) for raw water and solutions derived from optimised jar tests using alum, PAX-18 and PIX-322 coagulants.

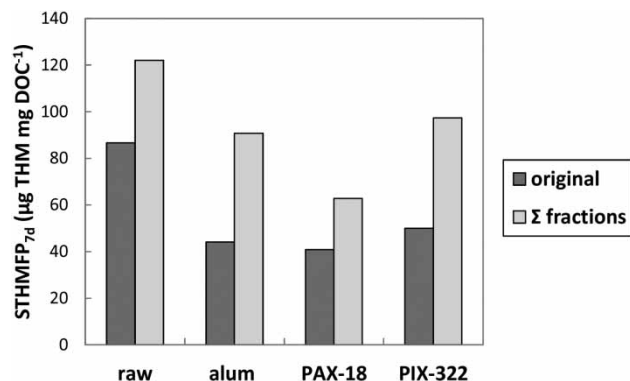


Figure 3 | STHMFP_{7d} for original, unfractionated sample and sum total STHMFP_{7d} for associated fractions for raw and coagulated samples.

are reported to be more genotoxic than their chlorinated analogues (Richardson *et al.* 2007). The increase in BrTHMs may reflect the preferential removal of aromatic DOC during treatment and the consequent increase in the proportion of aliphatic species which have been associated with the formation of higher proportions of BrTHMs (Heller-Grossman *et al.* 1993; Teksoy *et al.* 2008). Br⁻ occurs at trace levels in surface waters and commercial grade chlorine contains ca. 1% Br₂ as a production impurity. Interestingly, the proportion of BrTHMs also increased as DOC removal increased (alum <PAX-18 <PIX-322), most likely due to a successive increase in proportion of aliphatic DOC. Thus the enhanced removal of DOC during coagulation, whilst reducing THM precursors, may also shift their speciation towards more harmful BrTHMs.

Fraction analysis

STHMFP_{7d} did not vary as a function of DOC fraction (HPOA, HPIA and HPON) (Table 3). Interestingly, however, when individual fractions were chlorinated to measure STHMFP_{7d}, it was found that the weighted sum of these values for the three prominent fractions (HPOA, HPIA, and HPON) was consistently higher than the values of the original samples (pre-fractionation). This was the case for all four samples (raw, alum, PAX-18 and PIX-322) (Figure 3). The amalgamated STHMFP_{7d} values were between 41% and 106% higher than the original STHMFP_{7d} values. This suggests that the fractionation of DOC using the

resin adsorption technique described above increased DOC reactivity with chlorine. It is possible that the extremes of pH used in the fractionation procedure may have hydrolysed some DOC functional groups such as esters, amides or ethers resulting in more reactive material. The potential for chemical change of DOC during fractionation has been reported previously (Gadmar *et al.* 2005).

The contribution of the four main THM species to STHMFP_{7d} in the different DOC fractions was also investigated. CHBr₂Cl and CHBr₃ measurements were consistently below LOQ. Mean percentage contribution of CHBrCl₂ to the HPOA and HPIA fractions was <0.1%. In the HPON fraction, however, the CHBrCl₂ species represented 17.1% of STHMFP_{7d} (Table 3). The percentage contribution of CHBrCl₂ to STHMFP_{7d} was significantly higher in the HPON fraction when compared with both the HPOA and HPIA fraction ($p < 0.01$), but the HPOA/HPIA comparison was not significant. The reaction of chlorine with DOC is a competitive process. Thus, when the isolated HPON fraction is chlorinated the reaction is not affected by competition from active sites on other DOC molecules. It is also possible that reaction with chlorine makes functional groups on the HPON DOC susceptible to bromination. In terms of its implications for the water treatment process, this result should however be treated with caution. First, this study has already shown that the chlorination reaction proceeds differently when DOC fractions are isolated from the original sample (Figure 3), which may simply be an artefact of the fractionation procedure. Secondly, when considering the chlorination of DOC, THMs

represent only a fraction of total chlorinated products. A fuller understanding of the nature of the reaction between chlorine and different DOC fractions would require the measurement of additional halogenated by-products.

CONCLUSIONS

This study has shown that relatively high DOC removal rates can be achieved in low alkalinity waters. Significant differences in DOC removal rates were observed under optimised coagulation conditions between alum, PAX-18 and PIX-322 coagulants (PIX-322 > PAX-18 > alum). The higher DOC removal rates for the ferric-based coagulant observed here have been reported elsewhere and are thought to be the result of the higher affinity of ferric ions for carboxylic groups in addition to their floc-forming characteristics. Although PIX-322 yielded the best results for DOC and THM precursor removal, due to its low required coagulant and lime dose, PAX-18 is likely to offer the most cost-effective solution.

Zeta potential measurements were consistent with those reported in previous studies where optimal DOC removal was achieved. No statistically significant differences in the fractional character of the coagulated samples were found, though mean HPOA levels were lower in the coagulated samples compared with the raw water, consistent with previous studies. Colour, SUVA and MW results also indicate the selective removal of DOC with high MW, hydrophobicity and aromaticity, during coagulation. This selectivity, in combination with effective bulk DOC removal resulted in a substantial decrease in THMFP_{7d} for all treatments. However, an increase in BrTHMs was also observed following coagulation, most likely due to the selective removal of aliphatic DOC. Furthermore, comparison of the different coagulants suggests that BrTHMs may increase as DOC removal efficiency is improved; an important consideration given the evidence that BrTHMs are more harmful than their chlorinated analogues.

Interestingly this study has also shown that the STHMFP_{7d} of DOC increases substantially following fractionation. This may be the result of the extremes of pH used during the fractionation procedure. In addition, a statistically significant difference in the proportion of CHBrCl₂ contributing to STHMFP_{7d} was found between the HPOA,

HPIA and HPON fractions with means of <0.1% calculated for the HPOA and HPIA fractions and 17.1% for the HPON fraction. Broadening this comparison to include other halogenated by-products may provide insight into the cause of this phenomenon.

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