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Abstract

Increased regulatory pressure to meet THM standards with the possible introduction of HAA regulations means that organic matter, the predominant DBP precursor needs to be removed effectively from site whilst coping with increased economic and environmental drivers for change.

Organics are typically removed via coagulation / flocculation which can be optimised by operating in the correct zeta potential range (-10mV and +8mV) and the correct DOC:FE coagulant dose ratio (1:1). However, due to spatial and temporal changes in bulk NOM and its fractional character there are no standard operating conditions, consequently sites have to respond to changing conditions.

Seasonal trends in DOC and THMFP levels were measured under optimised and current operational conditions. Results indicated that UV_{254} could be used to predict coagulant dose and zeta potential could be used to indicate optimum coagulation conditions for DBP precursor removal across 16 sites. Under optimised condition improved organics removal and floc properties was observed across all source waters however the degree to which this occurred depended on the source water. Understanding of the fractional make up is thus important to assess the potential for optimisation of the coagulation process. Providing the electrostatic forces are minimised, increasing the NOM content of the floc matrix will lead to an increase in floc strength. One of the implication of optimised coagulation conditions were that flocs could be created at lower retention time then quoted by best practice guidelines. As such a 66% decrease in flocculation energy could be achieved without any detrimental impact to floc quality or removal efficiency.

One of the important findings is that due to the inherent difference in source waters, optimisation for a site can vary in terms of cost and clarified water quality, hence each site needs to be evaluated before schemes are carried out.

Executive Summary

Natural organic matter (NOM) is ubiquitous in all natural waters, varying in composition and character on both a temporal and spatial basis (Scott *et al.*, 2001; Parsons *et al.*, 2007). Elevated NOM levels can lead to a multitude of detrimental impacts to the process train and has been linked to poor water quality, colour, taste and odour, as well as corrosion and biological growth within distribution (Eikkebrokk *et al.*, 2004). Residual organics have been shown to react with chlorine and form carcinogenic disinfection-by-products (DBPs) such as Trihalomethanes (THMs) and Haloacetic acids (HAAs), as a result THMs are currently regulated to 100µg/l and HAA standards could be imposed in the future.

NOM is typically treated via the utilisation of a metal based coagulant, usually derived from iron or aluminium (Fearing, 2004), which incorporates NOM in to flocs via a combination of charge neutralisation, entrapment, adsorption and complexation (Vilge-Ritter *et al.*, 1999; Dennett *et al.*, 1984). These flocs can then be removed from water during clarification (Jarvis *et al.*, 2005).

A recent increase in organic material (DBPPs) of surface waters in Europe and United States has been observed, in some cases as high as 300% (Skjelkvaale, 2003). As a consequence, water companies must adapt to deteriorating raw water quality, increasingly stringent regulatory obligations and the drive to reduce costs. This makes process optimisation a key parameter in meeting future social, economic and environmental demands.

Optimisation of the coagulation/flocculation in terms of organic removal is therefore paramount to maintaining acceptable water quality standards. This can be achieved by operating at a -10mV and +8mV (Sharp *et al.*, 2005; Gregory and Carlson 2003; Ratnaweera *et al.*, 1999) and a DOC:Fe coagulant ratio is 1:1 (Jarvis *et al.*, 2005). UV₂₅₄ could be used to predict coagulant dose and zeta potential could be used to indicate optimum coagulation conditions for DBP precursor removal across 16 sites. Under optimised condition improved organics removal and floc properties were

observed across all source waters however the degree to which this occurred and how much this cost depended on the source water.

Sites were evaluated for optimisation via a combination of improved clarified water quality and cost. These were then prioritised to identify where schemes were best suited (table below)

Parameter	Top six priority sites
Water quality Improvements	Whitacre , Melbourne, Ogston , Campion Hills, Churchwilne, Draycote
Economic	Bamford, Frankley, Mitcheldean, Ogston , Cropston, Whitacre
Water quality and economics	Ogston , Whitacre , Cropston, Bamford, Melbourne, Churchwilne

Ogston and Whitacre were deemed most suitable for coagulant optimisation representing good water quality improvements at a reasonable cost.

Under the current STW low pH coagulation scheme Whitacre, Melbourne, and Strensham were identified as waters that would be suitable for acid dosing to achieve optimum zeta conditions. This study is partly in accordance with Whitacre and Melbourne being suggested sites, however Strensham is a poor choice. Strensham is not recommended as its optimisation only increases removal by 0.8mg/l yet would cost an additional £18 MI¹ (£23.21 KG DOC⁻¹). An alternative treatment is suggested to reduce the risk of breaching THM standards at this site.

Evaluated of the flocculation process at Frankley, a site that typically operates under optimised conditions was conducted. Under optimised conditions results indicated that the flocculation retention time could be reduced by 66% without any detrimental impact to the floc size distribution or removal efficiency. This suggests that the current hydraulic conditions for flocculation cited under best practice are out of date. Under the new mixing regime energy costs could be reduced by £51,000 pa equating to approximately a 280t reduction in CO₂.

Table of Contents

Abstract	i
Executive Summary	ii
Table of Contents	iv
List of Figures	vii
List of Tables	ix
Abbreviations and Notation	x
Acknowledgments	xii
1. Introduction	1
2. Literature Review	3
2.1 Introduction	3
2.2 Bulk NOM Characteristics	4
2.3 NOM characterisation	9
2.3.1 Resin Fractionation	10
2.3.2 Mineral Adsorption	13
2.3.3 HPSEC	14
2.3.4 Membranes	16
2.3.5 Charge Density	19
2.4 Coagulation	20
2.4.1 Coagulant Types	21
2.4.2 Coagulation pH	22
2.5 Flocculation	23
2.5.1 Growth	24
2.5.2 Measuring floc size and shape	25
2.5.3 Measuring floc strength	28
2.5.4 Optimisation	29
2.5 Conclusion	31
3. Long Term Organics Monitoring	32
3.1 Executive Summary	32
3.2 Introduction	34
3.3 Do we need to consider changing current operation?	36
3.4 Can UV be used as a surrogate for DOC through the works?	39

3.5 Is it possible to determine if coagulation has been optimised?.....	42
3.6. Can dose requirements be predicted	44
3.7 Can you predict residual levels after optimised treatment?	46
3.8 Are there any other benefits gained from of optimising coagulation?.....	48
3.8.1 Clarification	48
3.8.2 Filters	49
3.8.3 Manganese removal	50
3.8.4 GAC	51
3.9 What sites are good for low pH coagulation?	52
3.10 How robust is the optimised process to changes in water quality?.....	56
3.11 What Next?	60
3.12 References	61
4. The impact of water sources on the characteristics of natural organic matter flocs formed during drinking water treatment	63
4.1 Abstract	63
4.2 Introduction.....	64
4.3 Methods and Materials.....	65
4.3.1 Coagulation jar tests.....	65
4.3.2 High size exclusion chromatography	66
4.3.3 Fractionation	66
4.3.4 Surface Charge	66
4.3.4 Floc diagnostics	66
4.4 Results	67
4.4.1 Characterisation	67
4.4.2 Removal	69
4.4.3 Floc properties.....	70
4.5 Discussion	74
4.6 Conclusions	77
4.7 Acknowledgements	77
4.8 References	78
5. Flocs off the bench on to the field: The scope for potential energy savings in the flocculation process.....	82
5.1 Abstract	82
5.2 Introduction.....	82

5.3 Materials and Methods.....	84
5.3.1 Floc diagnostics	85
5.3.2 Surface Charge	85
5.3.3 Dissolved Organic Carbon and High size exclusion chromatography	85
5.4 Results	85
5.5 Discussion	88
5.5 Conclusion	89
5.6 References	90
6. Synthesis	93
7. References	96

List of Figures

Figure 2-1: Schematic representation of COD and DOC measurements (Page and Dillon, 2007)	6
Figure 2-2: Relationship between DOC and UV absorption for 38 source waters	6
Figure 2-3 Relationship between DOC and THM for 60 source waters	7
Figure 2-4 Relationship between THM-FP and SUVA for 44 source waters (Goslan, 2003)	8
Figure 2-5 NOM classification via analytical technique (Goslan, 2003., Parsons <i>et al.</i> , 2007)	9
Figure 2-6 NOM classification via NOM properties	10
Figure 2-7 Proportions (mole fractions) of dissolved hydrolysis products in equilibrium with amorphous hydroxides. (Duan and Gregory, 2003)	22
Figure 2-8 Electrophoretic mobility (EM) and residual turbidity for kaolin suspensions (50 mg/l) with low dosages of aluminium sulfate ('alum') at pH 7 (Duan <i>et al.</i> , 1997)	23
Figure 2-9 Two proposed mechanisms for floc breakage under different shear conditions (Jarvis <i>et al.</i> , 2005; Parsons <i>et al.</i> , 2007)	25
Figure 2-10 Zeta vs. removal for iron and aluminium salts (Sharp <i>et al.</i> , 2005).....	30
Figure 3-1 Site mean DOC residual and clarified THMFP	38
Figure 3-2 Site mean UV residual and clarified THMFP	38
Figure 3-3 Raw water DOC vs UV absorbance	40
Figure 3-4 Raw Water HPI fraction vs UV absorbance	40
Figure 3-5 Raw Water HPINA fraction vs UV Absorbance.....	40
Figure 3-6 Clarified water DOC vs UV absorbance	40
Figure 3-7 Mean Raw and treated UV and DOC values for differing source waters ..	41
Figure 3-8 Seasonal change in raw and treated UV and DOC values	41
Figure 3-9 Zeta potential vs DOC residual (lowland waters)	42
Figure 3-10 Zeta potential vs UV residual (lowland waters).....	42
Figure 3-11 Zeta potential vs clarified water turbidity (lowland waters) (site data only)	43
Figure 3-12 Comparison between DOC and UV	44

Figure 3-13 Site DOC residuals and HPI fraction46

Figure 3-14 Mean UV residuals and HPI fraction46

Figure 3-15 Mean treated THMFP and HPI fraction.....47

Figure 3-16 Mean treated HAAFP and HPI fraction47

Figure 3-17 Turbidity removal vs. zeta potential during the flotation of a high turbidity water (Jefferson, 1997).....49

Figure 3-18 Post filter turbidity residual vs. zeta potential for high and low turbidity waters (Parsons, 2004)50

Figure 3-19 Bamford 2006 demonstrating autumn flush in total organic56

Figure 3-20 Frankley Water stable.....56

Figure 3-21 Relationship for Mythe and Strensham 200657

Figure 3-22 Relationship for Mythe and Strensham 200757

Figure 3-23 Bamford 2006 HPSEC Autumn flush (Upland).....58

Figure 3-24 Frankley HPSEC autumn flush58

Figure 3-25 Mythe (low-DA) HPSEC autumn flush58

Figure 3-26 Strensham (LOW) HPSEC autumn flush.....58

Figure 4-1 Raw water fractionated DOC68

Figure 4-2 Raw water HPSEC profile69

Figure 4-3 Treated water HPSEC69

Figure 4-4 Breakage profile for lowland water.....71

Figure 4-5 Breakage profile for upland water.....71

Figure 4-6 Breakage profile for moorland water71

Figure 4-7 Floc size distribution profile for lowland water72

Figure 4-8 Floc size distribution profile for upland water72

Figure 4-9 Floc size distribution profile for moorland water72

Figure 4-10 Comparison of floc breakage rates for all three sources at optimum zeta potentials.73

Figure 4-11 Relationship between floc DOC content and stable floc size exponent..74

Figure 5-1 Site Schematic84

Figure 5-2 Jar test; response to shear87

Figure 5-3 Floc response to different mixing regimes87

Figure 5-4 d50 floc size distribution for different mixing regimes(volume).....87

Figure 5-5 Removal response to different mixing regimes87

Figure 5-6 HPSEC Curves for raw and clarified water88

List of Tables

Table 2-1 Bulk NOM measurements	5
Table 2-2 Application of wavelengths to NOM quantification	8
Table 2-3 Amberlite® Resin Properties	10
Table 2-4 Comparison between XAD-8 and DAX-8 (Chow, 2006)	11
Table 2-5 Review of some recent reports utilising resin fractionation	12
Table 2-6 Review of recent literature utilizing HPSEC	14
Table 2-7 Review of recent literature utilizing HPSEC	17
Table 2-8 Review of recent literature measuring charge density	19
Table 2-9 Review of recent literature measuring floc characteristics	26
Table 2-10 Review of floc strength tests (Jarvis <i>et al.</i> , 2005)	28
Table 3-1 Priority site ranked via various parameters	32
Table 3-2 Techniques used to measure various water parameters	35
Table 3-3 THMFP of SevernTrent Sites	37
Table 3-4 THM of SevernTrent Sites	37
Table 3-5 Prioritisation of sites ranked by various parameters	52
Table 3-6 Prioritisation via water quality improvements	53
Table 3-7 Prioritisation by cost	54
Table 3-8 Prioritisation based on water quality improvements and cost	55
Table 3-9 Relative organic stability	59
Table 4-1 Characterisation and monitoring techniques.	65
Table 4-2 Raw water characteristics.	68
Table 4-3 Performance data.	70
Table 4-4 Floc properties	73
Table 5-1 Best practice guidelines for flocculation	83
Table 6-1 Project review	93

Abbreviations and Notation

AMW	Apparent molecular weight
CFD	Computational fluid dynamics
COD	Chemical oxygen demand
DAF	Dissolved air flotation
DBP	Disinfection by product
DBPFP	Disinfection by product formation potential
DOC	Dissolved organic matter
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EEM	Excitation emission matrix
FAF	Fulvic acid fraction
GC- μ ECD	Gas Chromatograph(y) - Electron Capture Detector
GWh	Gigawatt hour
HAA	<i>Haloacetic</i> acids
HAA5	Monochloroacetic Acid, Dichloroacetic Acid, Trichloroacetic Acid, Monobromoacetic Acid and Dibromoacetic Acid.
HAAFP	<i>Haloacetic</i> acid formation potential
HAF	Humic acid fraction
HIA	Hydrophilic acid
HIB	Hydrophilic base
HIN	Hydrophilic neutral
HMW	High molecular weight material
HMW OC	High molecular weight organic carbon
HPIA	Hydrophilic acid
HPINA	Hydrophilic non acid
HPO	Hydrophobic
HPOA	Hydrophobic acid
HPOB	Hydrophobic base
HPON	Hydrophobic neutral
HPSEC	High performance size exclusion chromatography
KWh	Kilowatt hour

LMW	Low molecular weight material
LMW OC	Low molecular weight organic carbon
MF	Micro filtration
NF	Nano filtration
NOM	Natural organic matter
RO	Reverse osmosis
SEC	Size exclusion chromatography
SEM	Scanning electron microscope
SUVA	Specific UV absorbance
THM	Trihalomethane
THMFP	Trihalomethane formation potential
TOC	Total organic carbon
TTHM	Total trihalomethane
UF	Ultra filtration
UV	Ultraviolet absorbance at 254nm
WTW	Water treatment works

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1. Introduction

Natural organic matter (NOM) is a heterogeneous mix of compounds, ubiquitous in all natural waters, varying in composition and character on both a temporal and spatial basis (Scott *et al.*, 2001; Parsons *et al.*, 2007). Elevated NOM levels can lead to a multitude of detrimental impacts to the process train and has been linked to poor water quality, colour, taste and odour, as well as corrosion and biological growth within distribution (Eikkebrokk *et al.*, 2004). Residual organics have been shown to react with chlorine and form disinfection-by-products (DBPs) such as Trihalomethanes (THMs) and Haloacetic acids (HAAs) on site as well as in distribution. These DBPs are deemed to be hazardous to health with trihalomethanes displaying carcinogenic properties at concentrations as low as 49µg/l (Villanueva *et al.*, 2006a; Villanueva *et al.*, 2006b).

An increase in the total organic level of surface waters in Europe and United States has been observed over the past 10-12 years, with the vast majority of this originating from humic sources. In some case this increase has been as high as 300% (Skjelkvaale, 2003). This increase is believed to be a combination of shifting temperature and precipitation patterns, coupled with changes in catchment land use and management practise (Skjelkvaale *et al.*, 2001; Liltvid *et al.*, 2002). As a consequence, water companies must adapt to this growing challenge or face a decrease in water quality with a risk of breaching regulations.

NOM is typically treated via the utilisation of a trivalent metal ion based coagulant, usually derived from iron or aluminium (Fearing, 2004). Coagulation removes NOM through a combination of charge neutralisation, entrapment, adsorption as well as complexation with the metal coagulant ions (Vilge-Ritter *et al.*, 1999; Dennett *et al.*, 1984). Initially, insoluble particle aggregates form, which agglomerate further during the flocculation process, which can then be removed from water during clarification (Jarvis *et al.*, 2005).

Optimisation of the coagulation/flocculation in terms of organic removal is therefore paramount to maintaining acceptable water quality standards. Increases in bulk NOM concentrations have been demonstrated to increase coagulant consumption by up to 60% (Eikkiebrokk *et al.*, 2004). This is believed to be as a result of extra coagulant being needed to neutralise the high negative charge exerted by the hydrophobic humic and fulvic acids which make up the majority of the organic material of surface waters (Sharp *et al.*, 2006). Previous research in to upland waters has demonstrated that optimum removal condition are found between zeta potentials between -10mV and +8mV (Sharp *et al.*, 2005; Gregory and Carlson 2003; Ratnaweera *et al.*, 1999) and that the DOC:Fe coagulant ratio is 1:1 (Jarvis *et al.*, 2005). These studies went on to comment on the floc characteristics, whereby under these conditions flocs grew to a large stable floc size with a high resistance to shear, which is in contrast to previous studies that indicated the presence of NOM in the flocs resulted in a decrease in size and strength (Bach *et al.*, 1997). Floc strength has also been indicated to be heavily influenced by the hydraulic conditions under which they are created (Li *et al.*, 2006), however the hydraulic optimisation of the flocculation process has been less readily researched in comparison to chemical optimisation.

The combination of deteriorating raw water quality, increasingly stringent regulatory obligations and the drive to reduce costs makes process optimisation a key parameter in meeting future social, economic and environmental demands.

2. Literature Review

2.1 Introduction

Natural organic matter is ubiquitous to natural waters from both ground and surface sources and represents one of the major components that WTWs have to treat. The composition of NOM is complex, comprising of a great number of organics compounds which can simplistically be split in to two molecular groups: identified biopolymers and humic substances (Humbert *et al.*, 2007). The identified biopolymers are derivatives from microbial process (autochthonous) such as extracellular releases and leachate from bacteria and algae, which can include polysaccharides, amino sugars and proteins. Humic substances are terrestrially derived (allochthonous) and have been identified as yellow to black high molecular weight molecules which stem from the decomposition and leaching of plant and soil matter through the process of humification.

Elevated NOM levels can be deemed a health hazard as it is a precursor to disinfection by-products (DBP's) (Eikebrokk *et al.*, 2004). This is a result of organic residuals reacting with chlorine to produce carcinogenic trihalomethanes (THM's) and haloacetic acids HAA's (Singer, 1999; Wang *et al.*, 2007). In light of this, THM concentrations in UK drinking water are regulated to 100 µg/l limit (New Drinking Water Regulations in the UK, 1998, www.dwi.gov.uk), with future legislation expected to be tighter (Crozes *et al.*, 1995). Further regulations could also encompass HAA's, which are currently unregulated in the UK (Colbourne, 2003). Regulation in the states is tighter, with the USEPA (United States Environmental Protection Agency) imposing a regulation of 80 µg/l limit on THMs as well as a 60 µg/l consent on a total of 5 Haloacetic acids (HAA5: monochloro-, dichloro-, trichloro-, monobromo-, and dibromo-acetic acids). Like in the UK, regulations are expected to get tighter with consents of 40 µg/l for TTHM and 30 µg/l for HAA5. In light of current reports associating THM levels above 49µg/l with an increased cancer risk (Villanueva *et al.*, 2006a; Villanueva *et al.*, 2006b), the tightening of regulations could be seen as likely.

Natural organic matter (NOM) has a multitude of impacts within the treatment process train (Duguet and Mallevalle, 1998). It is responsible for a number deleterious effects with regards to coagulation, flocculation, disinfection, membrane filtration (Drikas *et al.*, 2002) and activated carbon treatment (Hopman *et al.*, 1998; Ding *et al.*, 2006.). Additionally NOM is detrimental to water quality through taste and odour (Jegatheesan *et al.*, 2004), bacterial growth and corrosion in distribution systems and colour (Drikas *et al.*, 2002).

To reduce the impact of organics on process and DBP formation, NOM is typically removed via the conventional water treatment process train of coagulation flocculation, clarification (DAF or sedimentation) and filtration. Coagulation removes NOM through a combination of charge neutralisation, entrapment, adsorption as well as complexation with the metal coagulant ions (Vilge-Ritter *et al.*, 1999; Dennett *et al.*, 1984). Initially, insoluble particle aggregates form which agglomerate further to form flocs which can then be removed from water during clarification (Jarvis *et al.*, 2004). The significance of floc structural properties with regards to the efficiency of the clarification process means that it is important to optimise the coagulation/flocculation process in terms of organics removal as well as floc strength. Both of these factors are strongly linked to zeta potential (Sharp *et al.*, 2006) and the coagulant dose to NOM ratio (Jarvis *et al.*, 2005), both of which are strongly influenced by changes in the source water.

This review aims to provide further understanding on the character, measurement and process implication of NOM from various sources. Comparison of different bulk NOM measurements against other water parameters will be conducted, which will include its relationship with its various fractions derived via various procedures. Bulk and fractional NOM characteristics can also be linked to coagulation and flocculation performance. With optimum condition for organics removal being determined through the various methods of measuring floc size and strength.

2.2 Bulk NOM Characteristics

For natural waters, the most commonly used parameters to quantify bulk NOM concentrations are TOC (total organic carbon) or DOC (Dissolved organic carbon).

Other popular parameters (Table 2-1) include: elemental ratios (C/N, C/O, C/H, C/S), particulate ratios (OC/TOC), isotopic ratios ($^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$), different spectroscopic parameters (UV absorption, EEM fluorescence), various disinfection by-product total and formation potentials (THM, THMFP, HAA5, HAAFP) (Filella, 2008).

Table 2-1 Bulk NOM measurements

Parameter	What it measures	Mesured With	Methodology
TOC	Total organic carbon (TC-IC=TOC)	TOC analyzer	APHA (1998)
DOC	Carbon content of TOC particles <0.45 μm in diameter	TOC analyzer	APHA (1998)
Permanganate Index: $\text{COD}_{(\text{Mn})}$	Chemical oxygen demand (oxidisation via permanganate)		APHA (1998)
THM	Actual THMs formed	GC- μECD	EPA Method 551.1 (USEPA, 1990).
THMFP	Maximum THMs formed	GC- μECD	Standard Methods of 5710B (APHA, 1998)
HAA	Actual HAAs formed	GC- μECD	EPA Method 552.3 (USEPA, 2003a,b).
HAAFP	Maximum HAAs formed	GC- μECD	Standard Methods of 5710B (APHA, 1998)
UV absorption	UV absorbed at 254nm	UV/Vis spectrophotometer	APHA (1998)
SUVA	UV absorbance per mg of DOC	TOC analyzer & UV-Vis spectrophotometer	APHA (1998)
Fluorescence spectroscopy (EEM)	Intensity at various emission-excitation wavelengths	luminescence spectrometer	Smith and Kramer (1999)

Both the DOC and permanganate index are used to quantify organic matter within natural systems. Whilst DOC is the more commonly used parameter, $\text{COD}_{(\text{Mn})}$ can act as a surrogate for NOM in situations where a limiting monitoring capacity exists. This is particularly evident for Chinese waterworks, where the permanganate index has been proposed as a surrogate parameter for NOM in the 2006 National Standards for Drinking Water Quality (NSDWQ) (Sun *et al.*, 2008). Considering the $\text{COD}_{(\text{Mn})}$ index measures oxidisable inorganics, changes in water quality outside the range of the carbon pool spectrum could significantly alter results (Figure 2-1) This highlights why no expected correlation between DOC and $\text{COD}_{(\text{Mn})}$ truly exists (Viraraghavan, 1976).

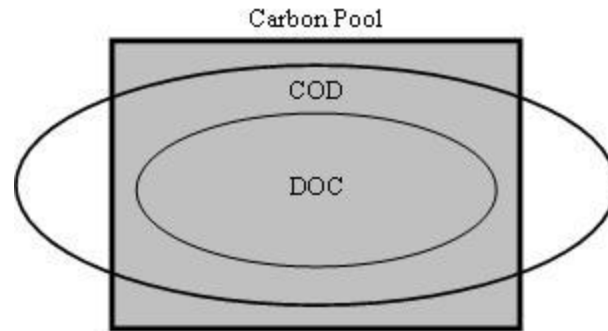


Figure 2-1: Schematic representation of COD and DOC measurements (Page and Dillon, 2007)

Goslan, (2003) showed a strong trend between UV and DOC for 88 source waters, however this does not strike an accordance with a recent comparison of 38 source waters (Mergen *et al.*, 2006; Jarvis *et al.*, 2004; Hua *et al.*, 2007; Sharp *et al.*, 2004; Humber *et al.*, 2007; Wei *et al.*, 2008) which demonstrated a much weaker trend (Figure 2-2). Discrepancies between UV_{254} and DOC have been observed (Uyak *et al.*, 2008) where a 2 fold increase in DOC corresponded to a 3 fold increase in UV absorbance. A study by Volk *et al.*, (2005) demonstrated a similar disproportionality where a 12 fold increase in UV absorbance corresponded with a 5.5 fold increase in DOC. This demonstrates a change not only in total NOM but in NOM composition. A higher UV:DOC ratio indicates a change in SUVA and a corresponding change in the aromatic C content (Liang and Singer, 2003).

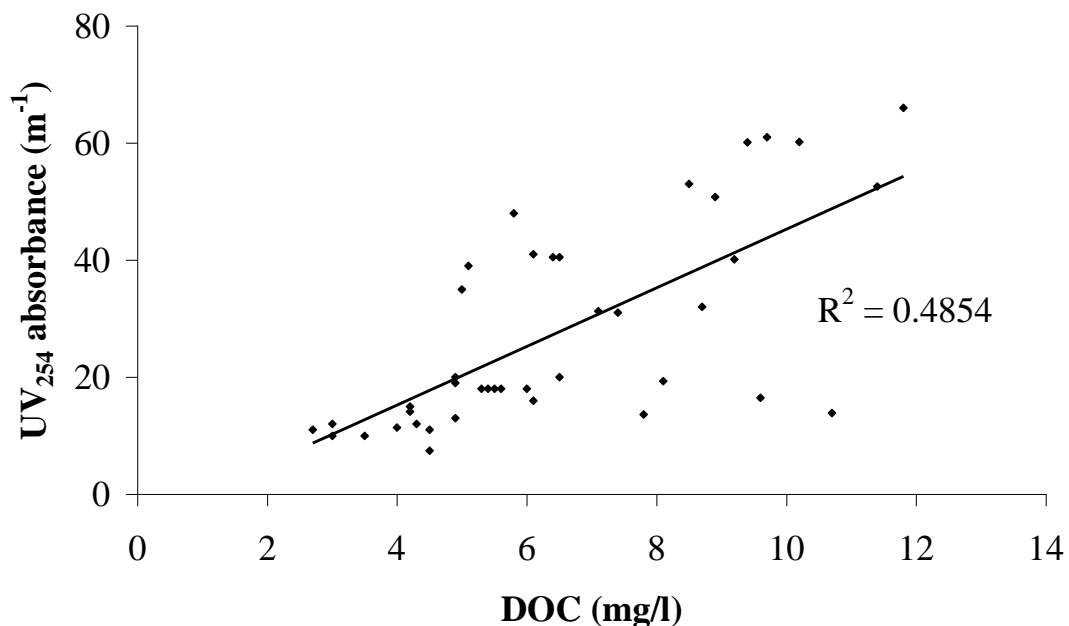


Figure 2-2: Relationship between DOC and UV absorption for 38 source waters

A study of DOC and THMFP was compiled by Goslan, (2003) (Allgeier and Summers 1995; Amy *et al.*, 1987; Afcharian *et al.*, 1997; Collins *et al.*, 1986; Kitis *et al.*, 2001; Nokes *et al.*, 1999; Pomes *et al.*, 1999; and Singer *et al.*, 1995) was expanded to 61 source waters (Uyak *et al.*, 2007; Teksoy *et al.*, 2007; Wei *et al.*, 2007) and demonstrated a weak relationship between the DOC and THM (Figure 2-3). A relationship is expected between DOC and THMFP, due to THMs being formed by the reaction of organic matter with chlorine. This trend is weak however, due to differences in the character of the source water, which influence the reactivity of the organic material with the chlorine (Uyak *et al.*, 2008), in addition to differences in chlorination dose, dosing regime and temperature.

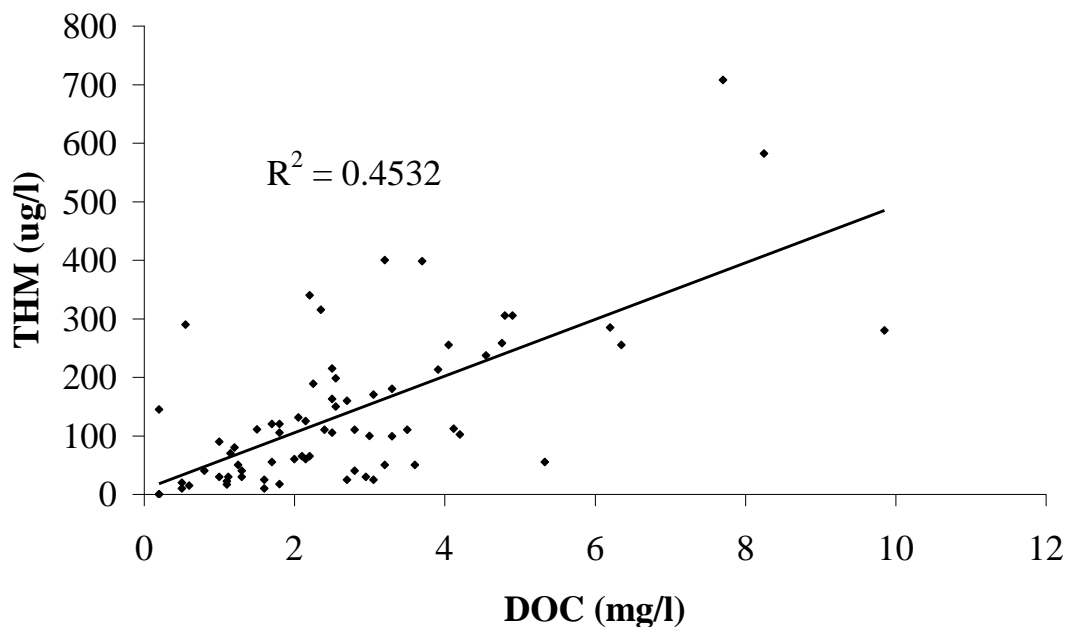


Figure 2-3 Relationship between DOC and THM for 60 source waters

SUVA indicates changes in the characteristics of the bulk water, often this is related to the aromatic carbon content of the water, of which the humic fraction plays a significant role (Volke *et al.*, 2005). The hydrophobic, humic acids are shown to have a greater THM yield in comparison to that of the hydrophilic fraction (Reckhow and Singer, 1990). However the poor correlation between THMFP and SUVA (Figure 2-4) indicates the importance of other raw water characteristics, with regards to THM formation.

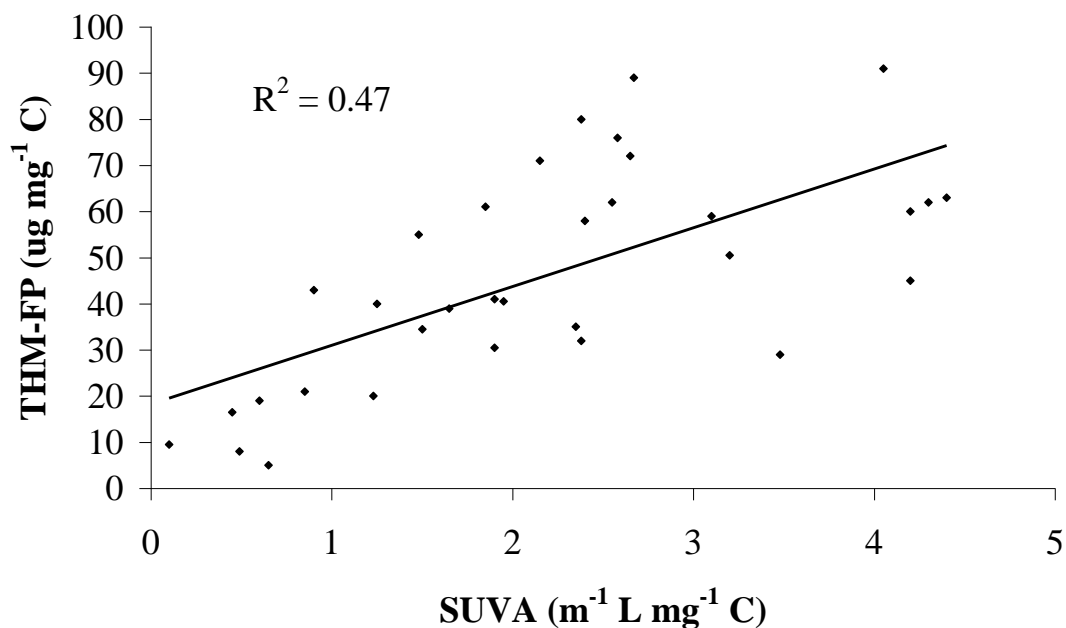


Figure 2-4 Relationship between THM-FP and SUVA for 44 source waters (Goslan, 2003)

UV-Vis at single wave lengths or at wave length ratios can be used to identify alterations in bulk NOM concentrations as well as changes in its fractional characteristics (Table 2-2). Due to the sensitivity of fluorescence to many environmental factors (type of solution, pH, ionic strength, temperature, redox potential of the medium and interactions with metal ions and organic substances), it is less commonly used in comparison to absorbance (Senesi, 1990). This is due to absorbance responding better to factors influenced by the organic material such as pH, aromaticity, total carbon content and molecular weight (Chen *et al.*, 1977).

Table 2-2 Application of wavelengths to NOM quantification

Wave Length	Proxy for	Reference
272nm	Aromaticity&molecular weight	Traina <i>et al.</i> , 1990
$\alpha_{465} / \alpha_{665}$	aromaticity	Chen <i>et al.</i> , 2002
$\alpha_{254} / \alpha_{410}$	molecular weight	Andersen <i>et al.</i> , 2000; Andersen and Gjessing, 2002
$\alpha_{254} \text{m}^{-1} / \text{DOC mg/l}$	SUVA (linked in to aromacity)	Weishaar <i>et al.</i> , 2003
254nm	DOC concentration	Allpike <i>et al.</i> , 2005
400-465nm	DOM concentration	Hautala <i>et al.</i> , 2000
250nm, 330nm, 350nm	DOC TOC	Moore, 1985; Edwards and Cresser, 1987
Ex380, Em450	humic	Ma and green., 2008 Baker <i>et al.</i> , 2002
Ex320, Em420	fulvic	Baker <i>et al.</i> , 2002
Ex275, Em350	Tryptophan	Baker <i>et al.</i> , 2002; Nakashima <i>et al.</i> , 2008

Bulk measurements of NOM provide an indication of how a source water is likely to respond in a water treatment work, this is due to 100% of the NOM being present during the measurement, allowing for interactions between the constituent NOM fractions present. However, bulk measurements have the limitation of not being able to take in to account changes in the fractional make-up of the water which can strongly influence removal efficiencies, floc characteristics and THM-FP.

2.3 NOM characterisation

Bulk NOM measurements have demonstrated the ability to display trends in raw water character (section 2.2). These trends however, are not particularly strong ($R^2 < 0.48$) as a result of alterations in the fractional make up of the NOM, which are not clearly portrayed via bulk NOM tests. Investigation of NOM fractions can offer a greater understanding of how a raw water is likely to respond to treatment, it should be noted that this approach reduces the synergistic effects of the multitude of chemicals that NOM comprises of (Hwang *et al.*, 2001). Complete splitting of the NOM in to its constituent parts is currently not possible, so the NOM is split in to groups which display similar characteristics. As of yet there is no official classification system for the grouping of NOM categories, however they are often a function the analytical technique used or by the constituent properties (Ma and Green, 2008).

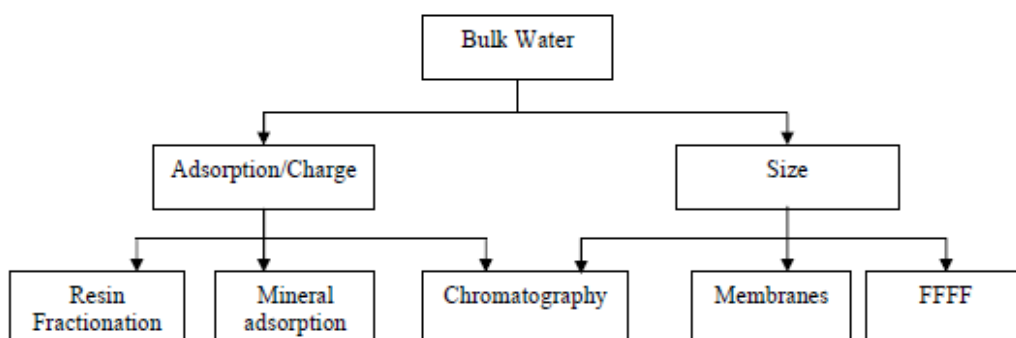


Figure 2-5 NOM classification via analytical technique (Goslan, 2003., Parsons *et al.*, 2007)

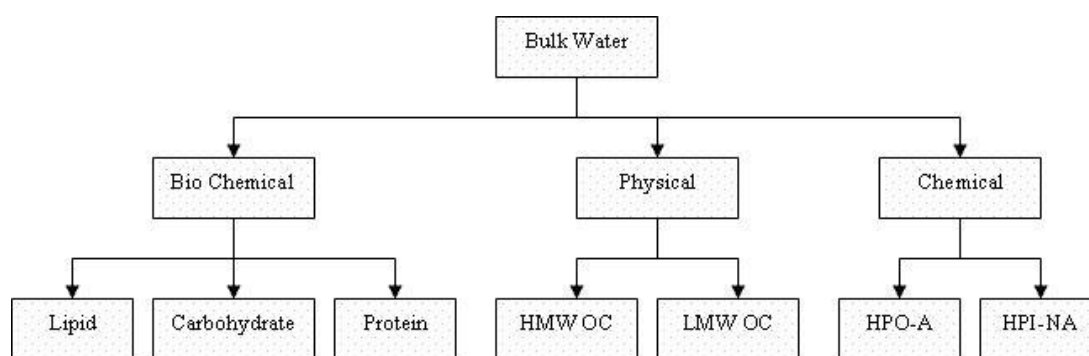


Figure 2-6 NOM classification via NOM properties

For the purpose of this study NOM will be classified with regards to the analytical tests utilised.

2.3.1 Resin Fractionation

Isolation of chemically distinct fractions of NOM can be achieved through the utilisation of non-ionic macroporous resins (XAD resin) (Leenheer, 1981; Thurman and Malcolm, 1981). Where by weak acids are protonated and absorbed on the resin at low pHs and are subsequently ionised and desorped at higher pHs. The characteristics of the weak organic acids adsorbed on to resin is influenced by variations in resin pore size, surface area and chemical composition. Properties of the current XAD resins are shown below (Table 2-3 Amberlite® Resin Properties), previous resin properties can be found in Aitken, (1979) and Goslan (2003).

Table 2-3 Amberlite® Resin Properties

XAD resin	Type	Surface Area (m ² /g)	Porosity (ml/ml)	Particle Size (mm)	Pore Envelope(Å)
4	Aromatic	750	≥0.50	0.3-1.2	55-80
16	Aromatic	800	≥0.55	0.3-1.2	200-250
16HP	Aromatic	800	≥0.55	0.3-1.2	200-250
1180	Aromatic	500	≥0.60	0.2-1.9	400-450
1600	Aromatic	800	≥0.55	0.4	80-120
7HP	Acrylic	450	≥0.50	0.3-1.2	450-500

A previous resin (XAD-8) was used to extract humic substance from acidified bulk water samples (Leenheer, 1981; Thurman and Malcolm 1981). This set up later included the use a second resin (XAD-4), which removed organic matter of a higher hydrophilic nature from the XAD-8 filtrate (Aiken *et al.*, 1992; Malcolm and MacCarthy, 1992). Following the discontinuation of Amberlite® XAD-8, replacement resins were produced; Superlite™ DAX-8 (Sigma Aldrich Co) and Amberlite® XAD-7HP (Rohm and Haas Co). These are chemically and physically similar (Table 2-3 & Table 2-4) with both resins being used for removal of humic and fulvic acids and similar compounds up to either 60,000MW (XAD-7HP) or 150,000 (DAX-8).

Table 2-4 Comparison between XAD-8 and DAX-8 (Chow, 2006)

Resin	Type	Surface Area (m ² /g)	Specific Pore volume (cm ³ /g)	Particle Mesh	Pore Envelope (Å)
Amberlite XAD 8	Acrylic	140	0.82	20-50	250
Superlite DAX 8	Acrylic	160	0.89	40-60	225

Despite the chemical and physical similarities, discrepancies exist between removal performance from DOC from aquatic (Peuravuori *et al.*, 2001, 2002b) and terrestrial (Chow *et al.*, 2006) origins, with regards to the XAD-8 and the DAX-8. A relationship between the XAD-8 and XAD-7HP removal efficiencies has yet to be shown. A review of current literature (Table 2-1, Table 2-5) has demonstrated the continued use of the XAD-8 resin (despite not being commercially available), as well as the XAD-7HP and DAX-8.

Recent literature has demonstrated a great temporal and spatial variation in the composition of NOM from natural sources as well as in the DBP yield from each of these fractions, making a general characterisation of source waters challenging. The characteristics of the source water can significantly alter the operational parameters of certain processes. This emphasises the importance of water characterisation studies prior to process selection.

Table 2-5 Review of some recent reports utilising resin fractionation

Reference	Resins Used	Fractional Data	Main Points of study
Kim <i>et al.</i> , 2006	XAD 7HP	Humic fraction represents 47% & 56% of total DOC & UV respectively	Natural and commercial humic substances differ in terms of characterisation
Kenichi <i>et al.</i> , 2005	XAD 7HP XAD 4	Humic substances represented 60% of DOC in river but only 25% in lake. HPO content contributed 70% of THM from river but only 30% from Lake. Lake hydrophilic content 20% but contributes to 40% of THM.	Source waters can differ in fractional composition. Fractions can differ in THM yield depending on source water.
Chen <i>et al.</i> , 2008	XAD 8 XAD4	HPOA represented 35.6% of DOC and HPIA represented 26.5% HPOA contributed 61% towards THMs whilst HPIA contributed 23.5	HPOA highest fraction & highest yield. Highest DBP yield was in autumn, this corresponds to highest DOC and highest HPOA content.
Rangsivek & Jekel 2008	XAD 8 XAD4	Tin roof run off Autumn: HPO = 65% HPI = 16% TPI = 18% After drought HPO = 8% HPI = 70% TPI = 22%	Roof run off from same roof differs greatly in character, this will influence the type of treatment greatly. NOM is high in summer and low in winter
Zhang <i>et al.</i> , 2008	XAD 8 XAD 4	HPOA = 49.6% HPON = 46.1% HPOB = 0.4% HIA = 2.5% HIN = 0.2% HIB = 1.2%	The percentages of HPOB and HI fractions were low in contrast to a similar report by Swietlik <i>et al.</i> (2004) for a filtered water. The HPON content of the water is quite high compared to that reported by other researchers such as Swietlik <i>et al.</i> (2004) and Korshin <i>et al.</i> (1997). Catalytic ozonation improves the break down of hydrophilic material
Gray <i>et al.</i> , 2007	DAX 8 XAD4 Amberlite IRA-958	HPO = 44%, 39% HPIC = 22%, 26% HPIA = 19%, 19%	Neutral and charged hydrophilics foul membrane the greatest by forming an organic gel. Hydrophobic material caused less fouling however fouling was limited to inside the pores.

The predominant fraction to be removed via conventional treatment is hydrophobic in nature, whilst removal for the hydrophilic material is much lower and almost no

removal is observed for the hydrophilic non-acid (Fearing *et al.*, 2004). As such good correlations between hydrophilic material and DOC residuals have been observed (Sharp *et al.*, 2004). Application of this knowledge can therefore be used to predict residual DOC levels on site (Sharp *et al.*, 2006). Consequently knowledge of the hydrophobic fraction could be used as a rough prediction for optimum DOC removal.

2.3.2 Mineral Adsorption

Fractionation via adsorption on to minerals such as goethite (α -FeOOH), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and montmorillonite ($(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$) is possible, however this is a much less investigated tool.

For a NOM solution Meier *et al.*, (1999) identified a decrease in molecular weight (MW) whilst in the presence of clay minerals. From this it was suggested that the larger molecular weight organics and those with aromatic functional groups had a greater propensity for adsorption on to goethite and kaolinite. This is in contrast to (Specht *et al.*, 2000) who demonstrated that HMW organics showed the greatest affinity towards clay minerals, whilst smaller aromatic structures with a high content in carboxylic functional groups show little adsorption. Further studies demonstrated that phenolic groups may be more significant than carboxylic groups for the chemical adsorption of NOM on minerals Guan *et al.*, (2006).

Investigation of pH conditions on the adsorption of fulvic acid onto goethite demonstrated that at low pH, high MW fractions were adsorbed whilst at high pH, intermediate MW fractions were adsorbed. (Zhou *et al.*, 2001). With regards to a bulk NOM solution SEC chromatograms indicated pH controls the amount of NOM adsorbed but does not reflect the quality of the adsorption (Specht *et al.*, 2000).

As fractionation by mineral adsorption gives an indication of the high molecular weight, aromatic content of a water (which tends to be more hydrophobic by nature) it could be used to indicate DOC removal and residuals on site. Application mineral adsorption has generally been used to investigate the sorption of pollutants to humic substances (Loar *et al.*, 1998; Specht *et al.*, 2000) rather than for water treatment purposes.

2.3.3 HPSEC

High performance size exclusion chromatography (HPSEC) is a technique that has been employed to fractionate NOM into groups of similar molecular weight. Rather than providing an absolute molecular weight values, this technique is best suited for comparative studies of waters from the same source. This is primarily due to the indefinite chemical structure of the humic standards used to calibrate the HPSEC column (Conte and Piccolo, 1999). In addition the HPSEC gels might have charge repulsion effects (Peuravuori and Pihlaja, 1997) and adsorption interactions with humic compounds (Myllykangas *et al.*, 2002).

The principal of Size Exclusion Chromatography (SEC) is based on the differential permeation rates of molecules into a porous matrix. Smaller molecules traverse the HPSEC column to a greater degree resulting in larger materials eluting first and the smaller material last (Hongve *et al.*, 1996). Parameters that can influence this procedure include the mobile phase, column packing and the standards used for the molecular size calibration, which are summarised below (Table 2-6).

Table 2-6 Review of recent literature utilizing HPSEC

Reference	Study	Packing material	Solution	Standard	Findings
Vuorio <i>et al.</i> , (1998)	Assessing relative changes of NOM size distribution throughout a water treatment works	TSK-G 3000SW	0.01M Sodium acetate	No standards used	HPSEC proved to be a reproducible method in determining NOM size distribution. Results were derived using UV detection only
Conte and Piccolo (1999)	(HPSEC) of Humic Substances and Column Performance.	TSK-G 3000SW & Biosep S2000	0.05M sodium nitrate	Polysaccharide	Both columns were deemed suitable for monitoring changes in the molecular size of NOM. These values gave approximations of the hydrodynamic radius and provide only nominal MW values, not absolute values.
Matilainen <i>et al.</i> , (2002)	Removal of NOM in the different stages of the water treatment process	TSK-G 3000SW	0.01 M Sodium acetate	None stated	HMW matter was easier to remove by coagulation and clarification in comparison to the LMW matter. Activated carbon was able to remove some of the larger LMW material, however this was dependant on its regeneration. Significant correlation was established among HPSEC, KMnO ₄ , UV254 absorbance, and TOC.
Lee <i>et al.</i> , (2008)	Natural organic matter (NOM) fouling in membrane filtration	Shodex KW802. 5 packed silica column	Not stated	Not stated	Medium to low MW NOM (300–1,000 Da) is responsible for the initiation of fouling. The subsequent bulk of the fouling is a result of high MW ‘colloidal’ NOM (>50,000 Da). Hydrophilic membranes

					foul less.
Her <i>et al.</i> , (2007)	Identification of nanofiltration membrane foulants	TSK-50S	Not stated	Not stated	Most of the dissolved foulants were in a high-MW range (21,000–24,000 Da) that exhibited high DOC and low SUVA value (0.18–0.25 L/mgm). Whilst the components between 1000 and 5000Da exhibited a low DOC and a relatively high SUVA value, (2.20–5.83 L/mgm). Lower-MW components (400 and 600 Da) do not contain chromophoric or fluorophoric components. Therefore, they show a low SUVA and almost no fluorescence intensities even with relatively high DOC levels, indicating that the components are mostly composed of aliphatic components.
Fabris <i>et al.</i> , (2007)	Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes	Shodex KW802. 5 packed silica column	Phosphate buffer (0.1 M) with 1.0M NaCl	Poly-styrene sulphonate MW standards of 35, 18, 8 and 4.6 kDa	Pre-treatments reduce the majority of bulk water DOC of all MW ranges, including colloidal (very high MW) material successfully prevented short-term fouling of MF. Treatments that removed most of the DOC but failed to remove the colloidal components were unable to prevent fouling.
Sharp <i>et al.</i> , (2006)	Impact of fractional character on the coagulation of NOM	Not stated	Not stated	Not stated	Post coagulation organic residuals, were predominantly <3000 Da, indicating that the coagulation process is far more effective at removing the larger MW compounds. Evaluation of different NOM fractions in terms of hydrophobicity is relatively easy. Where as the comparison of humic and fulvic acids is less clear as they are both hydrophobic and have similar MW distributions.
Matilainen <i>et al.</i> , (2006)	Efficiency of the activated carbon filtration in the natural organic matter removal	TSK-G 3000SW	0.01 M Sodium acetate	Not stated	Coagulation/flocculation removes HMW matter almost completely, MMW material was reduced considerably but the LMW matter was hard to remove. In general, the MW fractions that remained after the coagulation/flotation process were removed by GAC dissimilarly. The amount of the HMW matter did not reduce any further. GAC was the most effective in the removal of MMW organic material. LMW organics were hard to remove even by GAC.
Humbert <i>et al.</i> , (2005)	Performance of selected anion exchange resins for the treatment of a high DOC content surface water	Protein-Pak Diol (OH)	0.02 M Na ₂ HP O ₄	Polystyrene sulfonate MW standards of 1400, 4300, 6800, 13000 and 17000 kDa	AERs were able to eliminate both HMW and some LMW UV absorbing NOM. HMW organic molecules were preferentially removed by coagulation/flocculation. HPSEC analysis with fluorescence detection helped to identify low molecular weight proteinaceous moieties as part of the refractory DOM.

HPSEC has been shown to be a useful tool for monitoring the quantity and quality of organic matter during the water treatment process, particularly with regards to removal efficiency. Removal values can be determined with relative ease and quickness, provide more information than some traditional methods and aid with

process performance follow-up Matilainen *et al.*, (2002). Application of monitoring techniques could be applied to coagulation/flocculation (Sharp *et al.*, 2006), GAC (Matilainen *et al.*, 2006), membranes (Fabris *et al.*, 2007) and AERS (Humbert *et al.*, (2005).

2.3.4 Membranes

Membranes can be utilized for the removal of NOM from source waters, however they can also be used to fractionate organic matter physically based on apparent molecular weight (AMW). Investigation regarding NOM have been conducted on a range of membranes MF (0.1 μ m), UF (0.01 μ m), NF (0.001 μ m) and RO (0.0001 μ m). One of the major operational issues that reduces membrane performance is that of fouling which has been demonstrated to reduce flux (Fabris *et al.*, 2007). NOM, in its particulate, colloidal and dissolved state have shown to contribute significantly to fouling of MF and UF membranes (Crozes *et al.*, 1993), with some studies suggesting it is the most important foulant (Yuan *et al.*, 2002). The myriad of issues surrounding contamination and adsorption of organic material means that only results from studies where rigorous cleaning and determination of DOC mass balances are performed can be considered reliable Fiella (2008).

Isolation of NOM from bulk waters is possible using RO, which is deemed favourable as it can extract large quantities of organics relatively quickly, without exposing the sample to harsh conditions (Fiella, 2008). This process concentrates the NOM but does not split it in to its constituent fractions (Maurice *et al.* 2002)., however as well as the NOM, it concentrates the other solutes as well as the (Aiken, 1985).

Typically porous UF membranes are used for fractionation of NOM. There is no general size criteria for the NOM fractions due to differences in filter material, pore size, molecular charge and configuration, as such the nominal AMW cut off point of the membrane is cited (Fiella, 2008).

Table 2-7 Review of recent literature utilizing HPSEC

Reference	Study	Membrane material	MWCO (KDa)	Findings
Kim <i>et al.</i> , 2005	Characterization of NOM in the Han River and evaluation of treatability using UF–NF membrane	Polysulphone	1 30 100	Fractionation of raw water in to AMW groups of greater than 100K, 100–30K, 30–1K, and less than 1K Da were 20%, 14%, 28%, and 38%, respectively for a raw water. Raw water contained a higher percentage of the lower molecular weight material (<30K DA = 66%). This compares to a HPI content of the water of 61%.
Margit <i>et al.</i> , 2002	A new concept for the fractionation of DOM as a basis for its combined chemical and biological characterization	Fluoropolymer	3 10 30	Multistage UF is considered to provide better conditions for further investigations on the fractions than preparative SEC because both a fractionation and concentration of the sample can be achieved, and no eluent is required. It is also, by nature, less prone to microbiological contamination than a SEC column when membranes are replaced on a regular basis
Kittis <i>et al.</i> , 2002	Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation	Not Stated	1 3 5 10 30 100	Utilization of UF to isolation and/or fractionation organic material does not alter either the SUVA or the reactivity of DOM in terms of DBP formation and speciation. Correlations were observed between SUVA and both THM and HAA ₉ yields, independent of the fractionation process employed (UF or XAD-8). There was no consistent trend between the MW and DBP formation for the UF fractions, this implies that aromaticity of DOM components is more important than the size for predicting DBP formation.
Wei <i>et al.</i> , 2008	Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study	Not Stated	1 3 10 30	The properties of UF fractions appeared less stable in contrast to the chemical fractions (isolated by RA) throughout the sampling period, with large seasonal changes observed in MW in relation to DOC, UV ₂₅₄ and THMFP. MW of material was predominantly in the of 10–30 kDa and 1 kDa range relatively speaking. With the HPO and HPI matter dominating the chemical fractions.
Cai, 1999	Size distribution measurements of dissolved organic carbon in natural waters	Regenerated cellulose	3 10	Concentrations of DOC in low molecular weight size classes may be underestimated if membrane rejection is neglected
Chiang <i>et al.</i> , 2002	NOM characteristics and treatabilities of ozonation processes	Cellulose derivative	1 5 10 30	Pre-ozonation effectively reduces HMW organics (>10 kDa) converting them to smaller ones, resulting in increases in the MW fraction <5 kDa. Coagulation is able to remove large MW fractions (>30 kDa) with about 59% DOC reduction, compared to 7% elimination for the MW fraction <1 kDa. The coagulation processes can provide efficient reduction of DOC and DBPFP

				only for large MW organics; moreover, ozonation can convert large MW compounds to small ones.
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Fractionation using UF to provide size distribution analysis has shown that that in the majority of cases that organic material is predominantly below 30k DA (mainly between 10-30). This has been shown to be especially true of surface waters (Amy et al, 1990, 1991), despite research showing that MW characteristics display a great deal of spatial variations (Amy *et al.*, 1992; Newcombe *et al.*, 1997). However these values could be even higher in some instances if DOC values are not adjusted because to reflect the rejection of molecules smaller than the MWCO (Cai, 1999).

The trends observed between the physical and chemical fractions were largely site dependant. The more hydrophobic waters which predominantly had organic material >1KDa, demonstrated an amplification in SUVA as MW increased, with all material >1KDa having a high SUVA (>4). This strongly suggests a link between size and aromatic content (Chin *et al.*, 1994; Kittis, 2002) which is would be expected from hydrophobic waters which contain high proportions of pedogenic humic substances (Wilkinson et al, 1997). In retrospect, the hydrophilic waters which mainly comprised of LMW material (<1KDa), had low SUVA values (<3) with the small amount of HMW present having the lowest SUVA value (<1), indicating the presence of low aromatic compounds including HMW proteins and carbohydrates which are indicative of alogenic source waters (Kitis, 2002)

Application of membrane fractionations can be applied to the operational capacity of ion exchange resins (Mergen et al, 2008). HMW organics have been shown to block the outer pores, which prevents the adsorption of LMW material in the smaller pore spaces reducing the adsorption capacity, both in resins (Mergen *et al.*, 2008) and carbon (Ding et al., 2006). Further application can be directed to predict the extent of membrane fouling, where LMW material (0.3-1 KDa) is responsible for the initiation of fouling, whilst HMW material (>50 KDa) contributes to the bulk of membrane fouling. (Lee *et al.*, 2007).

2.3.5 Charge Density

NOM can be fractionated on the basis of charge density due to inherent differences observed in the organic matters functional group. Typically a negative charge is associated with NOM at ambient pHs (Duan *et al.*, 2002) which is as a result of the dissociation of carboxylic functional groups on the surface of the NOM. However in some instances (aliphatic waters) surface confined groups can be less acidic, as a result of the electrostatic interactions of surface groups of the monolayer and a reduced permittivity at the surface (Schweiss *et al.*, 2001).

Table 2-8 Review of recent literature measuring charge density

Reference	Subject	Source	Charge density (meq/g _{DOC})	Findings
Mergen <i>et al.</i> , 2008	Magnetic ion-exchange resin treatment: Impact of water type and resin use	Algae laden water	1.9	Trends existed between the charge density and the hydrophobicity of the raw waters, with the more hydrophobic waters containing more highly charged material per mass of organic in the water.
		Hydrophobic Water	0.3	
		Hydrophillic water	6.4	
Henderson <i>et al.</i> , 2006	Identifying the linkage between particle characteristics and understanding coagulation performance	NOM Kaolin Algae	10–15 0.1-1 Variable	NOM particles required a colloid to coagulant weight ratio of 1–10 mg/mg to reach the i.e.p. In contrast, kaolin required a ratio 100 times greater. This difference can be attributed to the NOM having a greater specific surface area (SSA) and charge density. However, with respect to algae, the relatively low SSA (1.09 mg/mg) does not fit the observed data despite the high charge density, which is likely to be due to the excretion of extracellular organic matter (EOM).
Sharp <i>et al.</i> , 2006	Seasonal variations in natural organic matter and its impact on coagulation in water treatment	HAF FAF HPIA HPINA	6.8 4.2 0.006 not detected	Hydrophobic HAF and FAF have a significantly greater charge density than the HPI and HPINA fractions. The negligible charge density of HPINA fraction may explain the reduced interaction with iron and the poor removal of this fraction with conventional coagulation methods. The largest proportion of the total charge comes from the FAF fraction, which also exerts the greatest influence on coagulation conditions. The charge density of the FAF fraction has also shown some variation throughout the sampling period.
Mikkelsen, 2003	Applications and limitations of the colloid titration method for measuring activated sludge surface charges	Humic acid	1.5 ± 0.04	Surface charges of particle suspensions are lower than the limit of detection in colloid titration. Total sludge charge may be divided into the “inner floc charge” and the “surface charge”, which are inaccessible and accessible to surface reactions with polymers, respectively
Kam and	The interaction	Humic acid	5–5.6	Removal of organic matter from water by

Gregory, 2001	of humic substances with cationic polyelectrolytes			coagulation/flocculation processes is greatly dependent on neutralisation of charge, either by hydrolysing metal coagulants or cationic polymers. Thus fractions with higher charge densities will require a higher dose to fully neutralize the charge
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Literature has demonstrated a link between the charge density and water hydrophobicity for a range of waters, with organic material such as humic and fulvic acids displaying a greater charge density per mass of organic in the water in relation to hydrophilic material, by at least one order of magnitude (Sharp *et al.*, 2006; Edzwald, 1993). Charge densities for hydrophobic humic and fulvic acids have typically ranged from 5-15 meq/g_{DOC}, with HPIA under 0.1 meq/g_{DOC} and HPINA remains mostly undetectable (Sharp *et al.*, 2006; Edzwald, 1993). This is due to the hydrophobic humic and fulvic acids having a higher concentration of dissociable functional groups that impart negative charge on the organic material (Ussiri and Johnson, 2004). Due to the dominance of the hydrophobic fractions in raw waters (Malcolm, 1985) in combination with its high charge density, the hydrophobic fractions has strong influence on the charge balance of the colloidal system (Sharp *et al.*, 2006).

The predominant mechanism for organics removal is charge neutralisation, which is achieved through the addition of multivalent hydrolysing metal compounds and/or cationic polymers. Due to this, the charge density (and in turn hydrophobic content) of a source water is often closely linked with coagulant demand, thus making it an important parameter to measure with regards to process optimisation investigations (Jefferson *et al.*, 2004).

2.4 Coagulation

Organic material needs to be removed in water treatment to a sufficient level, to ensure THM regulations are not breached, this is conventionally achieved through the coagulation/flocculation process (Uyak *et al.*, 2008). Due to the charge imparted on the system by organic matter (predominantly the hydrophobic fraction), raw waters tend to be anionic under ambient conditions, which provides them with a high affinity for cationic coagulants and polymers. The addition of a tri-valent metal coagulant or

cationic polymer reduces the colloidal stability of the water and thus promotes the aggregation of colloidal and dissolved organic material in to loosely bound structures referred to as flocs (the coagulation process). These flocs are then allowed to grow in size, via gentle mixing/agitation of the dosed raw water (flocculation) before they are removed via sedimentation or flotation (clarification). Factors such as coagulant type/dose and pH are considered key parameters to the coagulation process.

2.4.1 Coagulant Types

Coagulants typically used in industry include metal salts such as ferric Sulphate (Jarvis *et al.*, 2006), ferric Chloride (Rizzo *et al.*, 2008), aluminium Sulphate (Gertrig, 2000) and aluminium chloride (Yan *et al.*, 2008). Cationic polymers can also be dosed as coagulants, either independently or in conjunction with metal salts and can include poly(DADMAC) (Bolto *et al.*, 2002), magnafloc LT22 (Ismail *et al.*, 1987) and chitosan (Rizzo, 2008). These polymers have high charge densities and have shown to help in removing NOM (Kam and Gregory, 2001).

A general trend has shown that iron salts have a greater propensity for removing organic material in comparison to aluminium salts (Parsons *et al.*, 2007; Volk *et al.*, 2000). This is thought to be due to iron salts (ferric chloride) having approximately two times more active positive charges per dry weight per coagulant, in addition to it being more acidic, which enables it to consume twice as much alkalinity in comparison to alum (Crozes *et al.*, 1995). This is not conclusive, as for some source waters aluminium has been determined to be a better coagulant (Lind, 1995).

There have been concerns regarding the residual Al and Fe concentrations in drinking water supply due to the harm they could cause to humans (Wen and Fung, 2002), as a result there has been an interest in using organic polymers, such as chitosan (Rizzo *et al.*, 2008). Despite expecting high residual Al and Fe concentrations even under high coagulant doses, metal concentrations were frequently remained low and were not deemed an issue (Mesdaghinia *et al.*, 2005). In addition to this, post-chlorination toxicity on site was shown to increase via the use of an organic cationic polymer, in comparison to conventional metal coagulants (Rizzo *et al.*, 2008).

2.4.2 Coagulation pH

Coagulation pH is a key parameter, both in terms of dictating the dominant removal mechanism as well as influencing process optimisation.

The four primary mechanisms involved between coagulants and particles are; double layer compression, bridge-aggregation, sweep-flocculation and charge-neutralization (Wu *et al.*, 2008). With regards to hydrolyzing metal coagulants, sweep flocculation and charge neutralization are deemed the primary mechanisms, determination of the dominant mechanism is based on the dosed raw water pH (Cheng *et al.*, 1995). This is due to the influences that pH exerts on the end point hydrolysis products and the corresponding charge of these species (Figure 2-7). Bridging is more commonly associated with the addition of polymers.

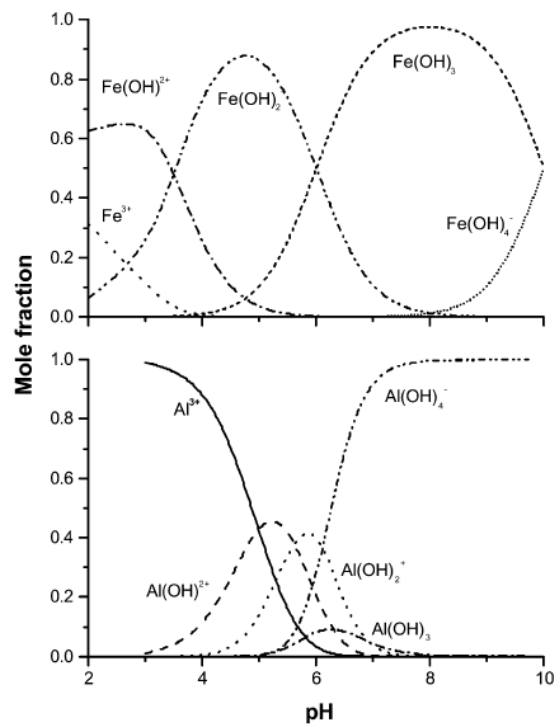


Figure 2-7 Proportions (mole fractions) of dissolved hydrolysis products in equilibrium with amorphous hydroxides. (Duan and Gregory, 2003)

Charge neutralisation destabilises the colloidal system through an increase in cationic species (such as $\text{Al}(\text{OH})^{2+}$), which strongly adsorb on to the negative surfaces of the organic matter, reducing the zeta potential and in turn the thickness of the diffuse part

of the electrical double layer (Matijevic, 1973). This is demonstrated by a decrease in turbidity residuals when the electrophoretic mobility is around $0 \mu\text{m s}^{-1}\text{V}^{-1}\text{cm}$ (Figure 2-8). Figure 2-8 shows Electrophoretic mobility (EM) and residual turbidity for kaolin suspensions (50 mg/l) with low dosages of aluminium sulfate ('alum') at pH 7 (Duan *et al.*, 1997).

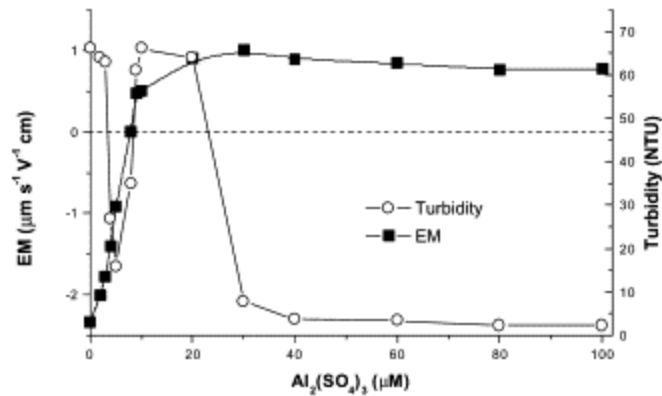


Figure 2-8 Electrophoretic mobility (EM) and residual turbidity for kaolin suspensions (50 mg/l) with low dosages of aluminium sulfate ('alum') at pH 7 (Duan *et al.*, 1997)

In contrast, the specific adsorption of counterions to neutralise the particle charge causes the destabilisation in sweep flocculation. This results in the natural contaminants being enmeshed and removed from the suspension by the hydroxide precipitate caused when EM is around $1 \mu\text{m s}^{-1}\text{V}^{-1}\text{cm}$ (Figure 2-8).

2.5 Flocculation

The properties of flocs, formed from the gentle mixing of colloiddally destabilised dosed raw water, are a key parameter in the performance of clarification process, both in terms of removal efficiency and cost (Jarvis *et al.*, 2005; Parsons *et al.*, 2007; Bridgeman *et al.*, 2008). Solid-liquid separation can be predominantly split in to two categories, sedimentation and flotation. The removal mechanisms for these processes are inherently different, and this needs to be reflected in the properties of the floc created both in terms of size and strength.

Small particles are deemed to be less efficiently removed via sedimentation due to them having a slower settlement rate (Boller and Blaser, 1998). Areas of localised high shear such as weirs, the impeller region, or even interaction with the surface can

lead to floc breakage (Kilander *et al.*, 2006). Thus, flocs also need to be strong, otherwise breakage will increase the amount of small particles and reduce process efficiency. Ideally flocs would be engineered to be strong, large and dense, however non of these parameters have been quantified.

With regards to DAF, the best flocs are advocated to be small (10-30 μm) and strong (Edzwald, 1995; Valade, *et al.*, 1996; Bache and Rasool, 2001). Sheer gradients within DAF cells are extremely high and are suggested to have a G value of around 1000 s^{-1} , this corresponds to Kolomorgorov length of 40 μm (Bache *et al.*, 2001). The creation of large flocs under low shear environments is thus not productive as flocs will most certainly break, which will reduce removal efficiency.

2.5.1 Growth

The growth of flocs in a colloiddally destabilised system, arising from the addition of multivalent coagulant, is based up on two independent steps (Gregory, 1988) of particle transport and particle attachment (Armirtharajah and O'Meila, 1990). This is based upon the number of particle collisions as well as their attachment efficiency. Flocs grow to reach a steady state size, where the growth rate of the floc is equal to the breakage rate, which is determined by shear conditions within the vessel (Ducoste and Clark, 1998; Biggs and Lant, 2000). This can be summarised in Equation 2-1 (Jarvis *et al.*, 2005; Parsons *et al.*, 2007).

$$R_{\text{floc}} = \alpha R_{\text{col}} - R_{\text{br}}. \quad \text{Equation 2-1}$$

Where the floc size (R_{floc}) is related to the rate of particle collisions (R_{col}) the efficiency of these collisions (α) and the breakage rate (R_{br}). As this process is dynamic floc growth is in a permanent state of flux of either growth ($\alpha R_{\text{col}} > R_{\text{br}}$) or breakage ($\alpha R_{\text{col}} < R_{\text{br}}$).

The degree of floc breakage at a given sheer rate is dependant up on floc strength, which is influenced by the number and strength of individual inter-particle bonds within the floc structure (Bache *et al.*, 1997). Different mechanisms have been shown to have the following hierarchy with regards to floc strength: bridging > charge

neutralization>sweep flocculation (Li *et al.*, 2006). A further finding was that the hydraulic properties had a great role in determining the floc strength, with smaller compact flocs being strongest due to an increase in the number of bonds relative to its weight.

Flocs breakage is heavily influenced by the type of stress it is placed under, tensile stress or shearing stress (Yeung and Pelton., 1996). Tensile stress (across the whole floc) results in large scale fragmentation, where flocs are cleaved in to aggregate of similar size without an increase in primary particle concentration. Shearing stress (tangential to floc surface), results in surface erosion where small particles are removed from the flocs surface thus increasing the particle numbers in the lower size range (Jarvis *et al.*, 2005).

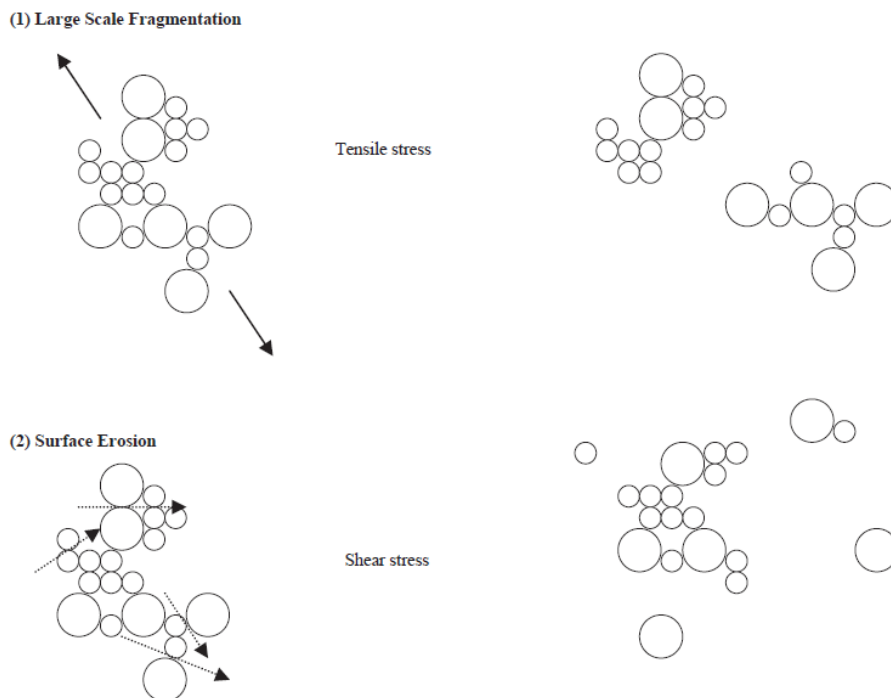


Figure 2-9 Two proposed mechanisms for floc breakage under different shear conditions (Jarvis *et al.*, 2005; Parsons *et al.*, 2007)

2.5.2 Measuring floc size and shape

Measurements of flocs are considered challenging as they are highly irregular three-dimensional structures, which vary in size, shape, and density. Due to the inherent differences in analysis techniques, each measurement portrays flocs characteristics in

a slightly different way, which is why it is important to cross checked by independent means (Bache and Gregory, 2007).

Table 2-9 Review of recent literature measuring floc characteristics

Measurement type	Reference	Measuring	Findings
Microscopy	Fukasawa and Adachi 2006	temporal evolution of the number concentration of flocs	The growth of floc structures is included in a modified expression for the Smoluchowski solution. In the later stage of coagulation, the growth rate increases remarkably, in accordance with the substantial increase of number concentration of flocs due to the increase of the effective volume of flocs.
	Yoong and Deng (2004)	Dynamic floc size	SLM was used to investigate flocculation and reflocculation of a clay solution with polymer. Large flocs can be obtained by effective polymer bridging, but high reflocculation can only be induced by high electrostatic attractive forces between suspended particles.
	Sato <i>et al.</i> , 2004	Fractal dimension temporal evolution of the number concentration of flocs	The reason for the gradual increase in coagulation rate in the later stage is that the increase of effective volume fraction of dispersed phase overcomes the decrease of floc diameter.
Photography and image analysis	Droppo and Stafford (2008)	Dynamic floc size and settlement	Polyacrylamide flocculants produced the largest flocs with the highest settling velocity. Flocs remained larger than those formed with alum or chitosan but ruptured more easily. All flocs ruptured via the fracture mechanism rather than by microscale erosion.
	Kilander <i>et al.</i> , 2007	Localised floc size distribution and fractal dimension	Scale-up behaviour of floc size distribution showed large spatial differences in the mean size and size distribution of flocs. Spatial variation decreased as tank size increased from 5 to 281, yet increased when the tank size reached 5601 increases. This indicates a change in the dynamics of the flocculation between different parts of the tank as size changes.
	Bouyer <i>et al.</i> , 2005	Floc size distribution and fractal dimensions	The floc size during ortho-kinetic flocculation is controlled by a balance between hydrodynamic stress and aggregate strength. Strength of the aggregate was influenced by the flocculation history and physicochemical conditions that control the cohesion forces between primary particles.
Light Scattering	Rasteiro <i>et al.</i> , 2008	Floc size distribution, aggregation kinetics and fractal dimensions	Floc size and fractal dimension determined by light scattering (Mastersizer 2000) were validated by image analysis. Light scattering was demonstrated to be a better tool to determine flocs characteristics in comparison to image analysis or settling. Comparison of two polymers with high molecular weight shows that for medium charge density the flocculation process occurs by bridging mechanism while when the charge density is very high the patching mechanism becomes important and occurs simultaneously with bridging. As the flocculant

			concentration increases the flocculation rate decreases. The flocculation concentration also affects the flocs size stabilization rate.
	Lin <i>et al.</i> , 2008	Floc size distribution, aggregation kinetics and fractal dimensions	Floc size and fractal dimension determined by light scattering (Mastersizer 2000) were validated by SEM. Coagulation with a low dose of PACI- Al_3 at a high alkaline pH (10) is destabilized as a result of electrostatic patches. This results in aggregates with high fractal dimensions. Interparticle bridging becomes the major mechanism under high doses, leading to flocs with low fractal dimensions, even though the zeta potential has been reduced
	Li <i>et al.</i> , 2006	Floc size distribution, aggregation kinetics and fractal dimensions	Different flocs characteristics were generated by various coagulation mechanisms, the floc strength had the following hierarchy: bridging > charge neutralization > sweep. For each mechanism there was a strong relationship between fractal dimensions and strength, with the Floc strength being determined predominantly by hydraulic conditions.
photometric dispersion analyser (PDA)	Xiao <i>et al.</i> , 2008	Flocculation kinetics	Microscopy had to be used to analyse floc size. Low temperature were shown to influence different phases of the coagulation process. Low temperatures are shown to impedes the slow coagulation, whilst do not exert a significant influence on the fast coagulation.
	Liu <i>et al.</i> , 2007	Flocculation kinetics	Coagulation can be enhanced by pre-ozonation if the positive effect of desorption of organic material from particles is larger than the negative effect of reducing the hydrophobicity of the particles.
	McCurdy <i>et al.</i> , 2004	Flocculation kinetics	Floc size was determined with image analysis. Bench-scale differences in floc morphology, zeta potential and reflocculation may be indicative of pilot-scale and full-scale filtration performance.
Settlement	Jarvis <i>et al.</i> , 2006	Settling velocity/fractal dimension	The precipitate flocs had higher settling velocities in comparison to similar sized organic flocs. The relationship between floc size and terminal settling velocity is indicative of the of the degree of aggregate.
	Sharp <i>et al.</i> , 2006	Settling velocity/floc size	FAF fraction produced the most compact flocs whilst HAF produced the most open flocs. This is believed to be the result of different flocculation mechanisms.

From the literature it has been shown that the physiochemical and hydraulic systems have a strong influence on floc size, shape and density. As each of these studies have different raw waters, coagulants, coagulating conditions, mixing vessels and mixing regimes floc characteristics from each study would not be comparable.

Previous reviews have suggested that there is no ideal method for measuring floc size (Jarvis *et al.*, 2005; Bache *et al.*, 2007). Photo analysis has the benefit of being non-intrusive, however it is time consuming and can not detect small flocs (under 30 μ m) and can be problematic in concentrated floc suspensions.(Bache et al, 1999). However

with modern techniques and cameras can greatly increase the number and speed of speed of measurements (Wang et al., 2002). In contrast Rasteiro *et al.*, (2008) and Lin *et al.*, (2008) demonstrated that a light scattering instrument (Malvern Mastersizer 2000) produces similar results to image analysis and microscopy respectively. Thus reducing the concerns that all PDA or light scattering instrument can cause shearing of flocs during measurements (Bache et al, 2007). Light scattering is also quicker than image analysis, has a larger sample size (Rasteiro *et al.*, 2008) and can analyse a greater range of particles 20nm-3mm (Parsons *et al.*, 2007).

2.5.3 Measuring floc strength

Just as there is no standard method for measuring floc size, there is no standardised floc strength test. This is primarily due to differences in floc properties. The energy required to break a floc either by tension, compression or shear is indicative of floc strength (Zahng *et al.*, 1999), as such a range of tests have been developed to measure these parameters both on a microscopic and macroscopic level. These tests have been summarised by Jarvis *et al.*, (2005) as illustrated in Table 2-10. Due to the inherent differences in the techniques used to determine floc strength, comparisons can not be made. Comparisons floc strength using the same methodology but in a system can not truly be compared due to differences in localised sheer gradients as well as scaling up factors (Li *et al.*, 2006; Kilander *et al.*, 2007). As such floc strength values are best used comparatively within the same system.

Table 2-10 Review of floc strength tests (Jarvis *et al.*, 2005)

Strength Technique	Description	Strength calculation
Macroscopic		
Impeller	Exposure of floc to single level of increased shear within a containing vessel and compare the ratio of the floc size before and after breakage (Francois, 1987; Fitzpatrick et al, 2003).	$\text{Strength factor} = \frac{d(2)}{d(1)} \times 100$ where d(1) is the average floc size of the plateau before breakage (m) and d(2) is the floc size after the breakage period.
	Exposure of the floc to increased levels of shear at a controllable rate within a containing vessel and measure the energy input for floc breakage (Leentvaar and Rebhun, 1983; Francois, 1987).	$\log d_{\max} = \log C - \gamma \log G,$ where dmax is the maximum floc diameter (m); C is the floc strength co-efficient; G is the average velocity gradient (s ⁻¹) and g is the stable floc size constant, an exponent dependent upon floc break-up mode and the size of eddies that causes the breakage. A plot of the maximum floc size remaining against the average velocity gradient gives a line with a characteristic slope indicative of floc strength and

		break-up mode.
Ultrasonics	Application of a controllable ultrasonic field to a floc suspension and observe floc erosion (Wen and Lee, 1998; Chu et al., 2001).	$\frac{\delta}{\phi} = \frac{-0.78k^{0.5}\Delta\tau}{d_{f0}^{-D/3}D(dy/dj) _{j \rightarrow 0}}$ <p>where δ is the floc binding strength (Jm^{-2}); Φ is the power of the ultrasonic field per floc's volume and time ($\text{Wm}^{-3} \text{s}$); $\Delta\tau$ is the ultrasonic time (s); d_{f0} is the floc size before sonification (m); d_f is the floc size after sonification (m); k is the proportionality constant (the ratio of the floc's crosssectional area and $d_f^{2D/3}$); D is the floc fractal dimension and j is the time of ultrasonification (s).</p>
Multigrid mixer	Flocs exposed to hydrodynamic stress from a controllable oscillatory mixer (Bache et al., 1999). Flocs placed in a vibrating column and subjected to varying amounts of oscillation. The vibration is converted into an energy input for the system.	$s \approx \frac{\rho_w \varepsilon^{3/4} d^{1/3}}{v^{1/4}}$ <p>where s is the floc strength (Nm^{-2}); ρ_w is the density of water (kg m^{-3}); ε is the energy dissipation at height of floc rupture ($\text{m}^2 \text{s}^{-3}$) and d is the floc diameter (m).</p>
Microscopic micromechanics	The breaking force required to pull apart a single floc in the tensile mode (Yeung and Pelton, 1996).	$s = \frac{F}{(\pi/4)d^2}$ <p>where s is the floc strength (Nm^{-2}); d is the floc diameter (m) and F is the floc rupture force (N).</p> <p>$F = C_s D$, where F is the floc rupture force (N); C_s is the cantilever stiffness (Nm^{-1}) and H is the cantilever deflection (m).</p>
Micromanipulation	The squeezing of a single aggregate in suspension between a glass slide and a fibre optic probe until floc breakage using a force transducer (Zhang et al., 1999).	$F = K(W_0 - W)$ <p>where F is the floc breaking force (N); K is the sensitivity of the force transducer (NV^{-1}); W is the voltage output (V) and W_0 is the baseline voltage of the force transducer (V).</p>

2.5.4 Optimisation

The coagulation/flocculation process can be optimised with regards to cost, removal efficiency, floc characteristics and down stream process performance. Optimisation in terms of organics removal is significant, as these are the main source of DBP precursors (Eikebrokk *et al.*, 2004). In addition it is also relevant to see if these conditions coincide with those needed to create strong flocs. Exposure of weak flocs to high shear gradients would increase the number of particles in the low size range

(Jarvis *et al.*, 2005), increasing the carry over of organic matter on to subsequent process which could ultimately result in increased DBPs.

The predominant mechanism for organics removal is charge neutralisation, where the negative charge associated with NOM at ambient pHs (Duan *et al.*, 2002) is reduced via the addition of a metal coagulant. The degree to which this charge has been neutralised and thus the stability of the colloidal system can be quantified through the use Zeta potential measurements. Several studies (Sharp *et al.*, 2006; Gregory and Carlson 2003; Ratnaweera *et al.*, 1999) have demonstrated that maintaining a zeta potential between -10mV and +8mV during the coagulation and flocculation processes has lead to the production of low and steady residual values for a number of waters with differing coagulants (Figure 2-10). Advantageously, optimal conditions occur a wide range of zeta potentials, hence surface charge does not need to be totally neutralised. (Ratnaweera *et al.*,1999).

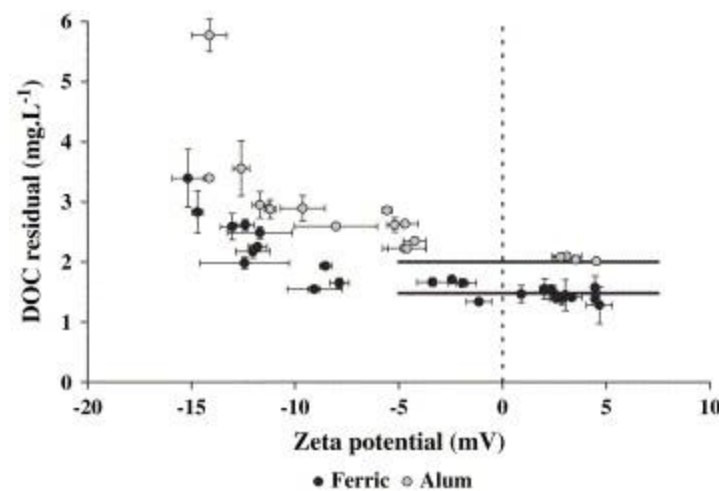


Figure 2-10 Zeta vs. removal for iron and aluminium salts (Sharp *et al.*, 2005)

This strikes accordance with previous work by Duan *et al.*, (1997) who demonstrated that reducing the electrophoretic mobility of a water (a function of the zeta potential) increased turbidity removal (Figure 2-8).

This diminution of charge within the system, allows particles within a closer proximity of one another, thus increasing the prospect of agglomeration and in turn, removal. The closer proximity of particles also suggests that an increase in the number of bonds is possible, which in turn would increase floc strength (Bache *et al.*, 1997). This notion is supported by Sharp *et al.*, (2006) where zeta potential strongly

influenced the flocs response to shear and contributed towards its steady state size over a range of Fe:DOC ratios for upland waters.

2.5 Conclusion

The complexity and variability of total NOM and its constituent fractions makes quantify it problematic, as such a variety of parameters and tools have been developed to characterise it. The two major fractions, both in terms of characterisation and relevance to the coagulation/flocculation process are hydrophobic NOM and hydrophilic NOM. Hydrophobic waters can generally be categorized to be; aromatic, have phenol based functional groups, carry a high negative charge density, comprise of HMW material, have a high SUVA and are more readily removed via conventional treatment. In contrast hydrophilic material is; aliphatic, has carboxylic based functional groups, carries no or little charge, comprise of LMW material, have a low SUVA and less readily removed via conventional treatment. The THM yield from these fractions can vary both temporally and spatially and as such is difficult to categorise.

Indications of process performance in terms of organic removal can be predicted to some extent by residual levels, however this does not provide an indication of floc quality. Floc quality can be measured in terms of floc size and strength, however there is no one standard tool or methodology to do this as such there is limited capacity to compare floc characteristic between different systems. Optimisation of the floc process, as well as organics removal is heavily influenced by zeta potential (-10mV and +8mV) and DOC:FE ratio (1:1).

3. Long Term Organics Monitoring

3.1 Executive Summary

Current operation needs to be changed as there is a strong chance of some sites failing the 100 µg/l TTHM standard. The predominant precursor to THMs and HAAs is NOM, thus operations needs to be optimised in terms of organics removal in order to reduce the risk of breaching THM standards.

Sites should be aiming for a 1:1 dose of Fe:DOC as it has been determined as the optimum dose for improving floc properties. Absorbance of UV at a wave length of 254nm can be used as proxy for the raw water DOC content and thus can be utilised in coagulation control. A UV monitor fed forward with a control loop can be used to give a rough dose requirement, however dose does not indicate if coagulation is occurring under optimised conditions. A zeta potential between $-8 < \zeta > 5+$ mV indicates optimised coagulation conditions for organics removal. Down stream clarification and filtration have similar optimum zeta potential ranges to coagulation. Consequently, optimisation of coagulation zeta can also improve the efficiency of subsequent processes including, clarification, filtration, manganese removal and GAC adsorption.

The cost / benefits of optimisation vary on a site by site basis and were influenced by the current THM levels, the water quality improvements and cost (Table 3-1). Whitacre and Ogston (bold) were deemed the top two priority sites overall and were deemed high priorities for all parameters.

Table 3-1 Priority site ranked via various parameters

Parameter	Top six priority sites
THM levels	Cropston, *Whitacre, Churchwilne, Bamford, Ogston , Campion Hills
Water quality Improvements	* Whitacre , *Melbourne, Ogston , Campion Hills, Churchwilne, Draycote
Economic	Bamford, Frankley, Mitcheldean, Ogston , Cropston, * Whitacre
Water quality and economics	Ogston , * Whitacre , Cropston, Bamford, *Melbourne, Churchwilne

Current STW schemes have identified *Whitacre, *Melbourne and Strensham as sites designated to operate under low pH coagulation. Whitacre and Melbourne are deemed to be suitable for this scheme based on current risk and the increased removal of DOC for a relatively cheap price. Although Strensham suffers from elevated THM levels findings suggest that alternative treatments are better suited.

3.2 Introduction

In the past decade, the removal of NOM has become increasingly important for water utilities in the UK. Operational problems are now being reported during periods of elevated organic levels in the water. These include the formation of fragile flocs, a greater particulate carryover onto downstream processes and increased DBP formation.

Increasing regulatory standards for THM formed when residual organics react with chlorine, have become a particular concern for the water industry. Furthermore, it is known that UK waters also have the potential to form HAAs, currently regulated in the US, at levels that may pose troubles for particular sites if UK regulations are brought in for their control. Current removal strategies typically involve conventional coagulation methods. However, traditional approaches to coagulation control tend to focus solely on coagulation pH and coagulant dose as these tend to be the main operational variables. Consequently, such an approach does not adequately respond to changes in organic concentrations and composition. Continuing research into the removal of organics from drinking water is important, especially with regards to the formation of potentially carcinogenic DBPs.

The current project involves long term monitoring of various water parameters using a number of analysis tools (Table 3-2) related to organics and DBP formation from various sites to highlight site that are at risk of exceeding target residual organic concentrations and associated DBP levels. In addition, the increased understanding of NOM composition and character will aid in the optimisation of the coagulation process, to reduce the risk of breaching DBP standards. The work will be set out as a series of questions with the corresponding answer and evidence. This format was chosen as they were key questions by the sponsoring company and it made the findings easier to apply on site.

Table 3-2 Techniques used to measure various water parameters

Technique	What it measures	Parameter	Equipment
HPSEC High Performance Size Exclusion Chromatography	Molecular Weight of organic material	(UV ₂₅₄ abs m ⁻¹)	Shimadzu HPLC
DOC Dissolved organic carbon	Raw and Clarified water organic content	(DOC mg.L ⁻¹)	TOC analyser
UV absorbance	Raw and Clarified water organic content	UV ₂₅₄ abs (m ⁻¹)	UV meter
Raw Water Fractionations	HPO and HPI content of raw waters	Dissolved organic carbon (DOC mg.L ⁻¹)	XAD Ion Exchange Resins
Zeta potential	Surface charge	Zeta Potential (mV)	Malvern Zetasizer (Nano)
THMFP	Maximum concentration of THMs that can be produced	Total THM levels (ug/l)	GC-μECD
HAAFP	Maximum concentration of HAAs that can be produced	Total HAA levels (ug/l)	GC-μECD

3.3 Do we need to consider changing current operation?

Answer: Yes

There is a strong chance of some sites failing the 100 µg/l TTHM standard. Current operations need to be optimised to remove NOM, the predominant precursor for THMs, in order to reduce the risk of failing compliance.

Evidence:

Ranking of the THMFPs (Table 3-3) and actual THMs (Table 3-4) provides an indication of sites that are currently at risk of breaching THM standards.

Ranking is based on the risk of the THMFP breaching the 100 µg/l consent, which is obtained by spot sample. A green ranking indicates sites in which the combined mean and standard deviation is less than 100ug/l, this only comprises of 4 waters. The bulk of the sites (10) fit in to the amber category which indicates that THMFPs are likely to deviate under/over this 100 µg/l threshold, posing a potential risk for breaching standards. Four of the sites THMFP levels deviate at ranges that are consistently over the 100 µg/l limit and pose the greatest risk.

The ranking system for Table 3-4 is based on the Severntrent internal THM standard of 50 µg/l leaving the works. Rankings were based on sites maximum deviation under the 50 µg/l threshold. Green represents the 4 sites that are under 30 µg/l, amber represents 30-40 µg/l, which consists of 3 sites. The majority of the sites (9) deviates over 40 µg/l. This can represent a high risk in THM standard failure due to increased THM production in distribution.

A comparison between the two tables indicates 5 sites that are consistently in the same risk category. Mitcheldean is considered low risk and Campion Hills, Cropston, Whitacre and Draycote considered high risk sites on both accounts.

Table 3-3 THMFP of SevernTrent Sites

	Mean THMFP Optimum (µg/l)	Standard Deviation (µg/l)
Little Eaton	58.26	9.42
Mitcheldean	64.13	25.34
Frankley	72.99	21.19
Frankley Bartley	80.18	16.93
Shelton	84.07	19.66
Bamford 1	86.47	30.47
Churchwilde	81.76	41.36
Trimpley	105.14	22.17
Strensham	102.28	29.94
Mythe	106.21	30.37
Tittesworth	114.14	37.22
Melbourne	119.07	34.62
Ogston	113.22	48.14
Bamford 3	117.07	68.34
Campion Hills	173.19	75.34
Cropston	138.13	-
Whitacre	142.85	33.25
Draycote	186.94	61.24

Table 3-4 THM of SevernTrent Sites

Preliminary results indicate a positive trend ($R^2=0.84$) between THMFP and residual organics both with reference to DOC and UV₂₅₄ absorbance (Figure 3-1 & Figure 3-2). This indicates that sites that have been designated to be at risk from breaching THM standards should aim to be optimised in terms of DOC and/or UV removal.

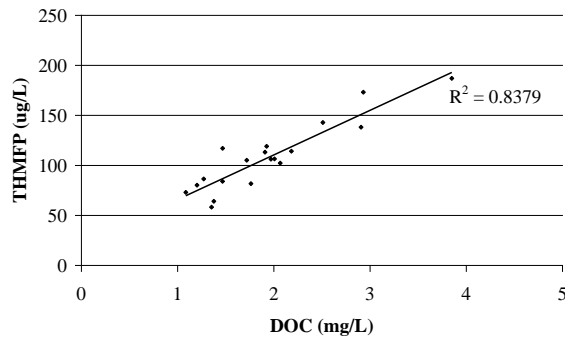


Figure 3-1 Site mean DOC residual and clarified THMFP

	Mean THM operational (ug/L)	Standard Deviation (ug/L)
Mitcheledean	12.96	4.62
Trimpley	13.99	4.58
Mythe	15.71	8.04
Shelton	17.90	7.15
Little Eaton	20.27	9.83
Frankley	22.61	7.70
Tittesworth	24.76	9.04
Melbourne	30.40	11.39
Draycote	31.07	8.94
Strensham	32.10	13.74
Campion Hills	32.62	9.23
Ogston	34.20	11.97
Bamford	34.84	12.97
Church Wilne	35.74	15.81
Whitacre	36.15	11.00
Cropston	43.51	12.93

Figure 3-2 Site mean UV residual and clarified THMFP

3.4 Can UV be used as a surrogate for DOC through the works?

Answer: No

UV detects compounds which absorb light at a wavelength of 254nm. These compounds are predominantly associated with colour. UV₂₅₄ does not detect other types of organic compound. As NOM is made of both coloured and uncoloured compounds, UV absorbance is unable to detect all of the organics. It does however act as a suitable surrogate for coloured compounds which means it can be utilised for coagulant control.

Evidence:

A clear relationship between the raw water DOC and UV₂₅₄ absorbance is apparent for a range of source waters (Figure 3-3). Despite a similar range in DOC concentration values and trend line gradients the impact on UV₂₅₄ absorbance is predominantly site specific. To illustrate, an increase in DOC from 4.6mg/l to 8.9mg/l for Mythe (lowland direct abstraction) showed an increase in UV from 10.96m⁻¹ to 35.03 m⁻¹, whilst a similar increase in DOC (4.49 mg/l to 8.97 mg/l) for Bamford demonstrated an increase in UV₂₅₄ absorbance from 26.69 m⁻¹ to 51.33 m⁻¹.

Whilst UV acts as a useful proxy for the raw water DOC content of individual sites it has limited use for providing an accurate dosing algorithm as it gives no indication of the fractional make up of the water (Figure 3-4 and Figure 3-5). In comparison to total DOC trends, a decrease in R² values is observed for all source waters when the HPO fraction is plotted against UV₂₅₄ absorbance. This is unexpected as the hydrophobic fraction is the predominant source of coloured organics, this indicates that there is a fractional variation in the UV absorbing functional groups between different sites. This is supported by figure 2.3 which shows no correlation (0.009) for Champion Hills, in comparison to a rough trend (0.49) for Mythe.

With regards to clarified water, a poor relationship between DOC and UV₂₅₄ absorbance exists (Figure 3-6). The removal of DOC is highly dependant on the fractal nature of the raw water, as this is not detected by the UV₂₅₄ absorbance it could

help explain why the relationship between UV and DOC deteriorates when it is used for clarified waters.

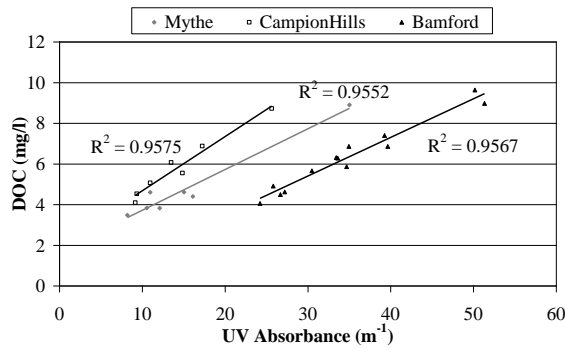


Figure 3-3 Raw water DOC vs UV absorbance

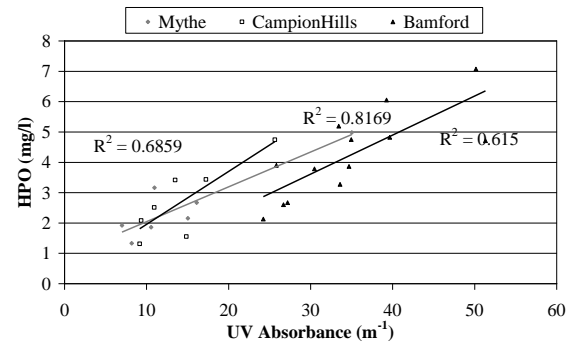


Figure 3-4 Raw Water HPI fraction vs UV absorbance

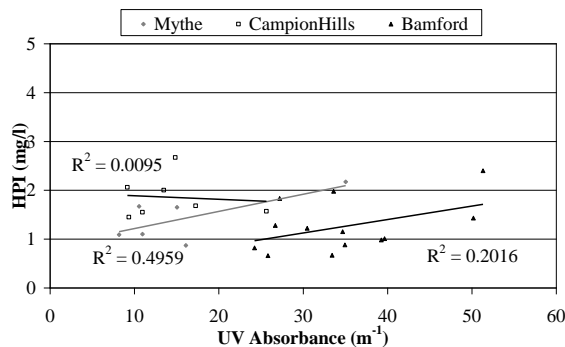


Figure 3-5 Raw Water HPINA fraction vs UV Absorbance

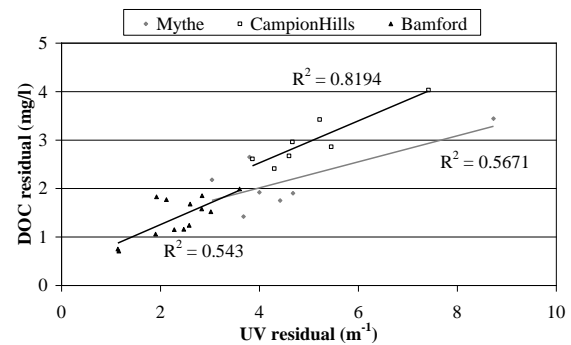


Figure 3-6 Clarified water DOC vs UV absorbance

Differences in the relationship between UV_{254} and DOC exist spatially and are heavily influenced by the character of the source water. The moorland water in Figure 3-7 shows a higher raw UV_{254} value ($30m^{-1}$) in comparison to that of the lowland water ($16.4m^{-1}$). This is in contrast to the raw DOC content where the moorland water is $1.1mg/l$ lower than that of the lowland water. Differences in the source water, such as the fractal makeup and charge density also exhibit an influence on removal values, hence why the UV_{254} and DOC removal values are greater for the moorland water in comparison to the lowland water.

As the charge density and fractal make up of individual source waters changes throughout the year, differences in the relationship between UV_{254} and DOC also change temporally, both in terms of raw and clarified waters (Figure 3-8). Between

the months of July and October a 51% increase in UV 254 absorbance is observed, this however corresponds to 6% in DOC. During this time period, a 92% removal of UV254 absorbing material is observed, however July showed a 60% removal DOC in contrast to the 78% DOC removal shown in October.

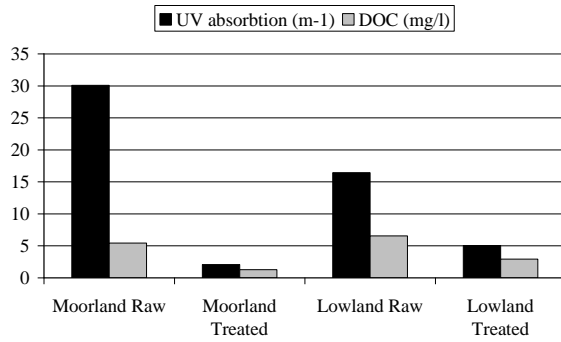


Figure 3-7 Mean Raw and treated UV and DOC values for differing source waters

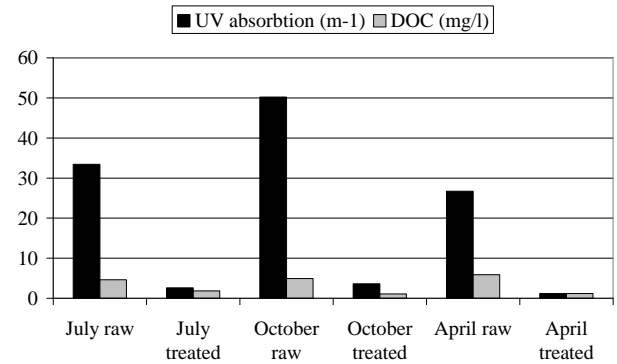


Figure 3-8 Seasonal change in raw and treated UV and DOC values

3.5 Is it possible to determine if coagulation has been optimised?

Answer: Yes

A zeta potential between $-8 < \zeta > 5+$ mV indicates optimised coagulation conditions.

Evidence:

To reduce the risk of breaching THM standards coagulation has to be optimised in terms of organics removal (Section 3.2). The majority of the lowest DOC residuals (3mg/l) occurred when coagulation conditions were inside the of $-8 < \zeta > 5+$ mV range. Outside of this range, residuals sharply increase, with concentrations >5 mg/l being commonly observed (Figure 3-9). In addition, this trend is also strongly apparent with UV_{254} residuals (Figure 3-10), with a sudden reduction in the number of residuals above $5m^{-1}$ observed within this $-8 < \zeta > 5+$ mV zeta range. This indicates that zeta potential measurements can be used to determine if coagulation conditions are optimised for organics removal, striking accordance with work by Sharp *et al.*, (2006)

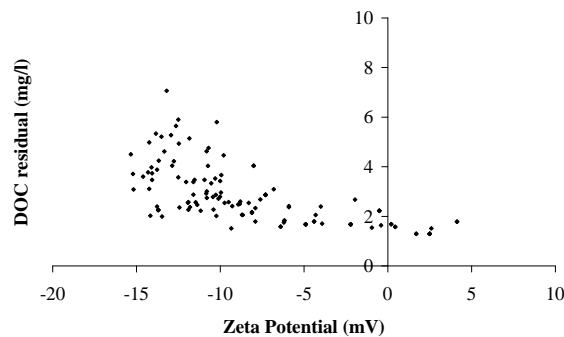


Figure 3-9 Zeta potential vs DOC residual (lowland waters)

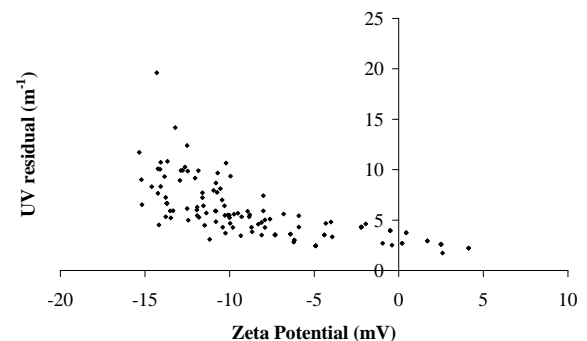


Figure 3-10 Zeta potential vs UV residual (lowland waters)

Optimisation of coagulation by zeta potential also offers other removal benefits as illustrated in Figure 3-11, which depicts improved clarified residual turbidities under a similar zeta range. Zeta conditions under 7mV were shown to reduce the number of instances where clarified turbidity exceeded 1 NTU, however this trend is not as apparent as that compared to organics removal

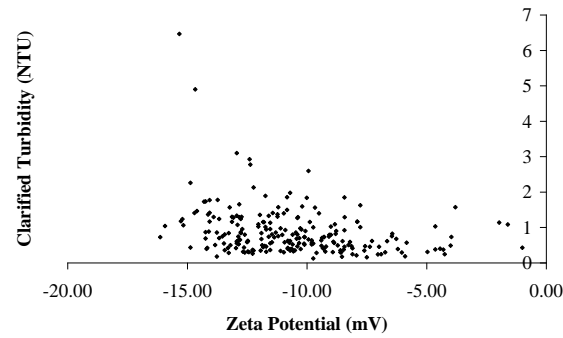


Figure 3-11 Zeta potential vs clarified water turbidity (lowland waters) (site data only)

Optimised coagulation conditions with regards to organics removal can be determined via zeta potential. Charge neutralisation is the predominant removal mechanism for organic material, reducing the charge of a colloidal system allows NOM particles to come in to closer proximity of one another, as such more particles can be incorporated in to the floc. As Zeta potential measures the charge of the colloidal system it provides an indication of how readily NOM can be removed and thus the efficiency of the coagulation process.

3.6. Can dose requirements be predicted

Answer: Yes

A rough dose requirement can be predicted with a feed forward UV monitor, which would provide a 1:1 dose of Fe:DOC.

Evidence:

Previous research has determined that the optimised coagulant dose has a DOC: Fe ratio of 1:1 (Jarvis *et al.*, 2005a). As such, monitoring or prediction of the DOC can be used as a proxy for coagulant dose.

Results indicate that UV can act as a proxy for DOC for a wide range of source waters (Figure 3-12). Although DOC concentrations remain similar for all sites, there are great variations in the amount of UV absorbing material. For example Bamford was shown to have the highest UV absorbance per mg of DOC, ranging from around 20-50m⁻¹, this is in contrast to other waters which ranged from around 10-30m⁻¹. As such trends have to be calculated on a site by site basis.

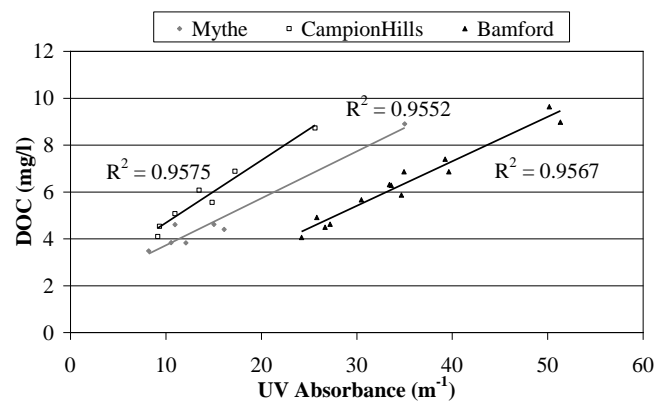


Figure 3-12 Comparison between DOC and UV

UV₂₅₄ monitoring, acting as a proxy for DOC could be fed forward via a control loop to alter coagulant dose. This approach has the benefit of taking in to account some of the alterations in charge density which also influences the amount of coagulant dose (Jefferson *et al.*, 2004). UV absorbing materials tend to be hydrophobic in nature, so an increase in UV absorbance indicates an increased amount of this fraction. One characteristic of these hydrophobic fractions is that they have functional groups that

readily dissociate and impart a negative charge on the system. As such an increase in UV absorbance could indicate an increase in the negative charge and an associated increase in coagulant demand.

3.7 Can you predict residual levels after optimised treatment?

Answer: Yes

Coagulation removes charged components and does not removed uncharged ones. Consequently monitoring the level of uncharged organics in the raw water provides a good indication of the residual achievable under optimum coagulation conditions.

Evidence:

Due to the low charge, the hydrophilic fraction is typically harder to remove with conventional coagulation methods. As such, a strong trend exists between it and the DOC residual (Figure 3-13), however the overall trend is site specific. The lowland waters display an approximate 1:1 relationship with the HPI fraction and DOC residual, whilst the Bamford trend indicates a lower residual per mg of HPI. This suggests that the upland water includes charged hydrophilic material to some degree. Due to chemical variations in source water characteristics residual levels of DOC can be predicted after optimisation on a site by site basis. In contrast a more general trend is apparent with regards to UV₂₅₄ residual (Figure 3-14), treated THMFP (Figure 3-15) and treated HAAFP (Figure 3-16) when compared against HPI. The THMFP and HAA have a slightly weaker trend and higher deviation in comparison to DOC,

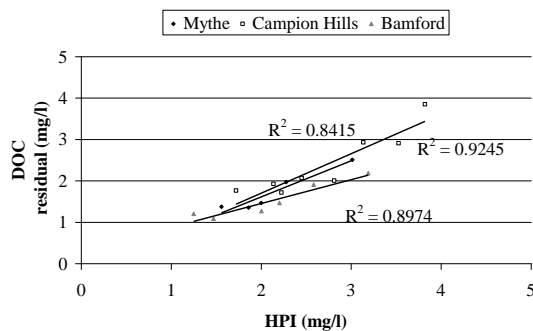


Figure 3-13 Site DOC residuals and HPI fraction

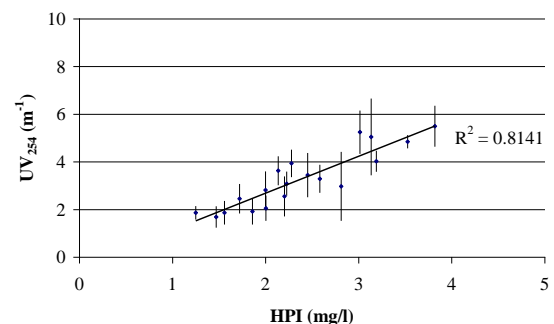


Figure 3-14 Mean UV residuals and HPI fraction

this is as a result of seasonal variations in the DBP (Uyak *et al.*, 2008)

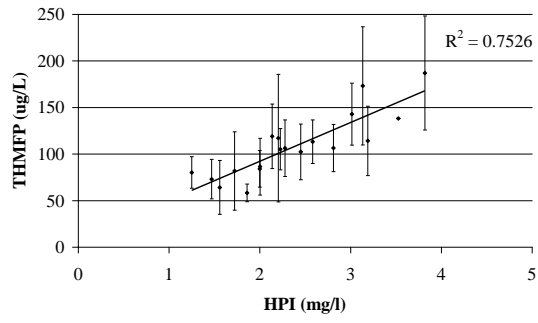


Figure 3-15 Mean treated THMFP and HPI fraction

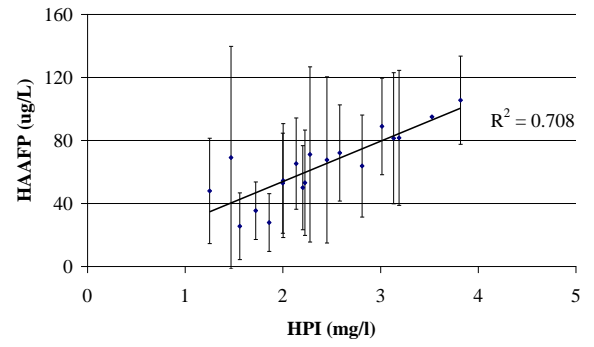


Figure 3-16 Mean treated HAAFP and HPI fraction

3.8 Are there any other benefits gained from of optimising coagulation?

Answer: Yes

The two main impacts of un-optimised coagulation is

- 1) Elevated NOM residuals leading to elevated DBPs
- 2) Down stream clarification and filtration have similar optimum zeta potential ranges to coagulation. Consequently, an elevated zeta outside of optimised range can lead to reduced clarification and filtration performance.

The current project did not directly investigate these issues but evidence from the literature can illustrate the impacts.

Evidence:

3.8.1 Clarification

NOM flocs are deemed to be weaker in comparison to Kaolin flocs (Bache *et al.*, 1997). The introduction of a weak floc to an elevated shear environment could lead to the exposure of newly fragmented surfaces altering the surface charge of the floc and lead to partial re-stabilisation of the colloidal system reducing removal efficiency (McCurdy *et al.*, 2004). Floc breakage, particularly via surface erosion can lead to increases in the small particle size range (Jarvis *et al.*, 2005b) and in turn lower removal efficiencies (Boller and Blaser, 1998). Due to this optimisation of the Zeta potential and coagulant dose are essential to improving removal.

Optimised coagulation conditions have been shown to correspond closely with those of DAF clarification, with a range of $-4 \text{ mV} < \zeta < +7 \text{ mV}$ for kaolin particles (Han *et al.*, 2001) and $-15 \text{ mV} < \zeta < +13 \text{ mV}$ for humic acid (Zouboulis *et al.*, 2003). Removal efficiencies have been shown to increase the closer the system is to optimum conditions (Figure 3-17)

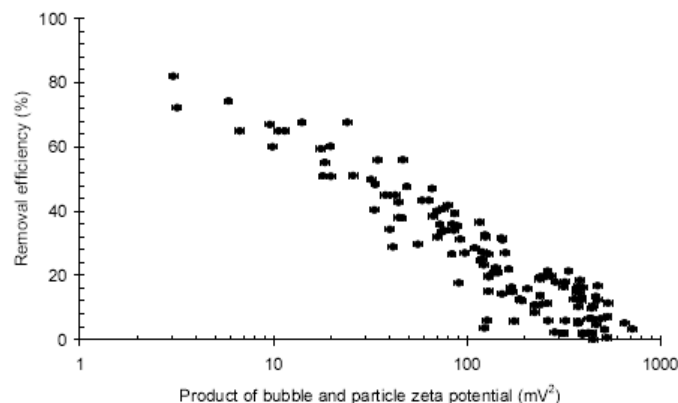


Figure 3-17 Turbidity removal vs. zeta potential during the flotation of a high turbidity water (Jefferson, 1997)

Utilising a high pH (7.4) and high alum dose (97 mg/l) to achieve optimum zeta conditions (1.0-1.2mV) has been shown to reduce clarified turbidity by 60%, in comparison to pH of 6.1 and a lower alum dose (26mg/l) which produced a turbidity of 1.0NTU. DOC removal remained constant Gregory and Carlson (2003). This is thought to be as a result of a more equal distribution in charge at a higher pH (Amal et al., 1997)

Operational experience has suggested that poor clarification can have detrimental impacts on filter performance due to a greater carryover of particles,

3.8.2 Filters

Optimisation has been shown to reduce particle loading, turbidity breakthrough and increase filter run times. Similarities exist between optimised coagulation conditions and those observed in filtration (Figure 3-18), with filtration having a slightly greater zeta range of $-16 \text{ mV} < \zeta < 0 \text{ mV}$, in comparison to that of coagulation ($-10 \text{ mV} < \zeta < +3 \text{ mV}$). Optimisation of the filtration process from $>-17\text{mV}$ to $<-15\text{mV}$ showed a drop in filtered turbidity from $>1\text{NTU}$ to $<0.2\text{NTU}$ for high turbidity waters and 0.2NTU to 0.07NTU for low turbidity waters.

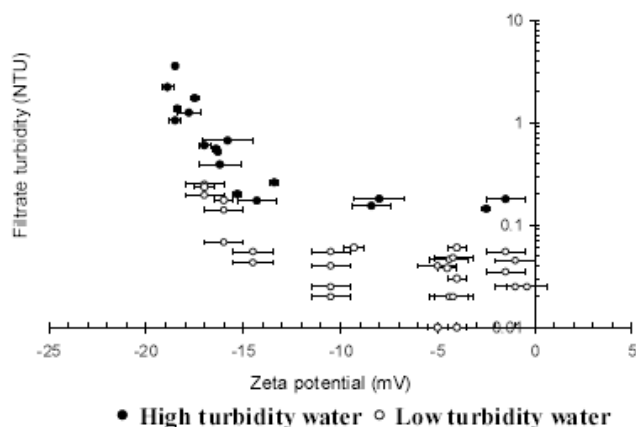


Figure 3-18 Post filter turbidity residual vs. zeta potential for high and low turbidity waters (Parsons, 2004)

In an un-optimised system an increase in the humic fraction lead to an increase in raw water colour from 20 to 35 mg/L⁻¹ and resulted in increased TOC residuals by 26%-87% and a significant increase in the number of backwashes per day. An associated decrease in the plants hydraulic capacity was observed and filters run times decreased by 10% to 47% (Eikebrokk et al., (2004).

3.8.3 Manganese removal

NOM has shown to display negative impacts upon manganese removal, with the adsorbtion of the humic, ferric and manganese complex decreasing the effect of filtration for manganese removal. The concentration of the organic material is a primary factor with regards to manganese removal (Sheng *et al.*, 2006). Increasing the chlorine dose (as hypochlorite) has shown to reduce the detrimental impact that elevated NOM levels have on manganese removal (Sheng *et al.*, 2006), however this is liable to dramatically increase the amount of THM's produced onsite.

Sites prone to Manganese issues, such as Cropston, would thus benefit from optimising coagulation. A reduction in post clarified DOC, would reduce the amount of hypochlorite needed to precipitate out the manganese, both of these factors would aid in reducing final THM levels.

3.8.4 GAC

NOM has been shown to compete for adsorption sites within GAC, reducing the life time of the media and decreasing the removal efficiency of pesticides, hardness, colour as well as taste and odours. With regards to pesticide removal, GAC lifetime was shown to be extended by over 100 times by using nanofiltration as a pre-treatment and by 30-70% when an ozone dose of 1.4 mg/l was applied in the presence of 2 mg DOC per litre (Hopman et al., 1995).

3.9 What sites are good for low pH coagulation?

Answer:

Sites change depending on the basis of prioritisation (Table 3-5)

Table 3-5 Prioritisation of sites ranked by various parameters

Parameter	Top six priority sites
Water quality Improvements	Whitacre , Melbourne, Ogston , Campion Hills, Churchwilde, Draycote
Economic	Bamford, Frankley, Mitcheldean, Ogston , Cropston, Whitacre
Water quality and economics	Ogston , Whitacre , Cropston, Bamford, Melbourne, Churchwilde

Evidence:

Sites were evaluated in suitability for low pH ($-10 \text{ mV} < \zeta < +3 \text{ mV}$) coagulation based on the improvements seen in clarified water quality, the cost to implement such a scheme as well as a combination of the two.

Water quality improvements were ranked based off the percentage increase in organic material that could be removed via optimised treatment in contrast to current operation (Table 3-6). The red category represents high priority waters sites in which optimisation can increase organics removal by over 20%. It includes 7 source waters with sites such as Whitacre and Melbourne showing a 35% increase in the amount of DOC removed via optimisation. The amber category represents source waters where a 10%-20% increase in organics material can be achieved and consists of 6 source waters, these are deemed a medium priority. The green category is for waters that show less than a 10% increase in organic material removal, however the majority of these waters are already optimised and show no significant increase in removal performance. As such they are deemed low priority sites.

Table 3-6 Prioritisation via water quality improvements

	Mean DOC residual Operational (mg/l)	Mean DOC residual Optimum (mg/l)	Mean DOC removal % Operational	Mean DOC removal % Optimum	Mean THMFP Optimum (µg/l)
Whitacre	4.53	2.60	18	53	142.85
Melbourne	3.70	1.97	24	59	119.07
Ogston old	3.20	1.82	28	59	113.22
Campion Hills	4.76	3.13	22	48	173.19
Churchwilne	2.60	1.70	18	44	81.76
Ogston new	3.17	1.90	37	62	113.22
Draycote	5.44	3.93	17	40	186.94
Trimpley	2.62	1.58	51	70	105.14
Cropston	3.94	2.84	50	64	138.13
Strensham	2.78	1.98	40	54	102.28
Little Eaton	1.91	1.39	42	56	58.26
Shelton	2.09	1.53	50	63	84.07
Mythe	2.85	2.17	40	50	106.21
Tittesworth	2.40	2.21	66	69	114.14
Bamford 1	1.43	1.29	78	79	86.47
Bamford 3	1.36	1.45	81	80	117.07
Frankley Bartley	1.24	1.49	56	48	80.18
Frankley	1.25	1.27	57	57	72.99
Mitcheldean	1.46	1.51	51	51	64.13

The suitability of sites for optimisation was also investigated in terms of economics (Table 3-7). This parameter was based off the increase in cost to remove a Kg of DOC. Increase in coagulant, initial and secondary pH correction (based off the optimised jar tests) were used to calculate the cost. A linear trend between chemical addition and DOC was also assumed. The red category indicates sites that would be cheapest to optimise, and thus economically more appealing to solve first. It should be noted that the five priority sites best suited for the scheme are already considered optimised (previous table) hence why there is no associated cost increase. The bulk of the sites (11) are considered medium priority, with costs ranging from 9.54-15.22 £/Kg DOC. Whilst the sites Strensham, Mythe and Little Eaton are deemed low priority sites due to their extremely high costs, at over £23 per Kg DOC removed

Table 3-7 Prioritisation by cost

	Initial DOC removed	Extra DOC removed (Kg/ML)	Increased Cost (£/ML)	£/Kg DOC removed
Bamford 1	1.43	0.14	-0.03	-0.21
Bamford 3	1.36	0	-0.03	-
Frankley B	1.25	0	0.37	-
Frankley F	1.24	0	0.37	-
Mitcheldean	1.46	0	10.26	-
Ogston old	3.2	1.38	13.16	9.54
Cropston	3.94	1.1	10.95	9.95
Ogston new	3.17	1.27	13.16	10.36
Whitacre	4.53	1.93	21.08	10.92
Tittesworth	2.4	0.19	2.36	12.42
Trimpley	2.62	1.04	13.22	12.71
Churchwilne	2.6	0.9	12.98	14.42
Shelton	2.09	0.56	8.1	14.46
Draycote	5.44	1.51	22.62	14.98
Melbourne	3.7	1.73	26.21	15.15
Campion Hills	4.76	1.63	24.81	15.22
Strensham	2.78	0.8	18.57	23.21
Mythe	2.85	0.68	18.22	26.79
Little Eaton	1.91	0.52	19.87	38.21

It was deemed necessary to prioritise site on a basis of both economics and improvements in organics removal. As even if raw waters saw vast improvements in water quality a high cost of pH correction would render the scheme economically unfeasible. Just as though cheap easy fix options may be considered pointless if no significant increase in water quality is observed. Some of the low cost schemes would not be worth doing as the improvements in water quality are not significant enough.

The top 5 priority waters that represent quality investments with regards to optimisation solutions were identified as Ogston, Whitacre, Cropston, Bamford,

Melbourne, these sites had a combined (Table 3-8). The lowest priority sites were deemed to be Mythe, Little Eaton, Strensham and Shelton.

Table 3-8 Prioritisation based on water quality improvements and cost

	Rank based on risk of failure	Rank based on lowest cost	Priority (highest failure + lowest cost)
Ogston old	3	6	9
Whitacre	1	9	10
Ogston new	6	8	14
Cropston	9	7	16
Bamford 1	15	1	16
Melbourne	2	15	17
Churchwilne	5	12	17
Bamford 3	16	2	18
Trimpley	8	11	19
Campion Hills	4	16	20
Frankley Bartley	17	3	20
Draycote	7	14	21
Frankley	18	4	22
Tittesworth	14	10	24
Mitcheldean	19	5	24
Shelton	12	13	25
Strensham	10	17	27
Little Eaton	11	19	30
Mythe	13	18	31

Under the low pH coagulation scheme, Whitacre, Melbourne, and Strensham have been identified as sites that will be optimised. The current study has identified Whitacre as a priority site due to its high THMFP/THM levels, shows large benefits in organics removal and relatively low cost. Melbourne too has high THMFP/THM levels and shows benefits from optimisation, but not to the extent as Whiacre. Strensham has medium risk THMFP levels and high risk THM levels, this is expected as it shows a poor organics removal (40%). However it does not respond well to optimisation with only a 14% increase in organics removal as such it is considered a high cost option (23£/Kg DOC removed). This indicates that an alternative treatment is better suited rather than low pH coagulation.

3.10 How robust is the optimised process to changes in water quality?

Answer:

Evidence:

Sites were monitored on a monthly basis, showing temporal variations in DOC. Elevated DOC levels are expected around September/October time as a result of increased precipitation events flushing through higher amounts of organic matter. Bamford, a moorland sourced water demonstrates this (Figure 3-19) with a 73% and 82% increase in total DOC between the months of August and October. However this is not the case for all waters. Frankley, an upland water demonstrated an annual variation of only 1.02mg/l for Bartley reservoir and 1.89mg/l for the Frankley reservoir, with no evidence of an autumn flush period (Figure 3-20). Other sites were shown to display a greater degree of monthly variation (Figure 3-21 and Figure 3-22), with only the sites Mythe and Strensham demonstrating any sort of trend between monthly DOC's ($R^2=0.88$). The large peak in July 2007 (Figure 3-22) corresponds with the major flood events in the West Midlands and Gloucester.

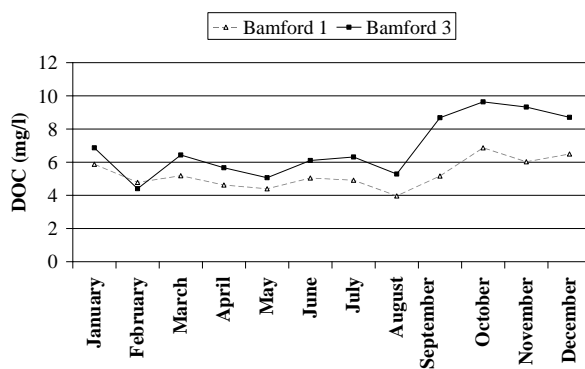


Figure 3-19 Bamford 2006 demonstrating autumn flush in total organic

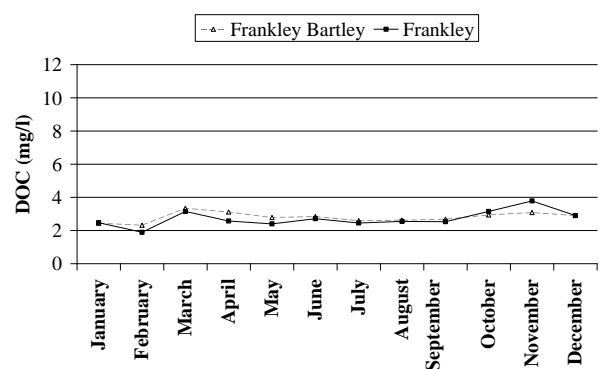


Figure 3-20 Frankley Water stable

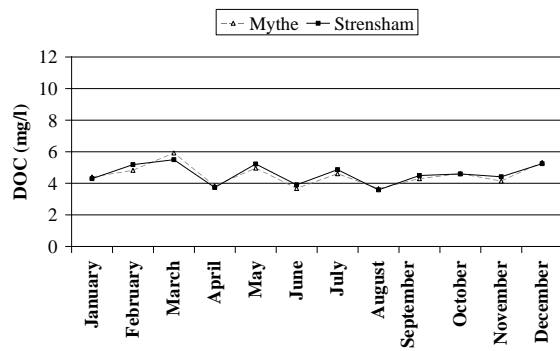


Figure 3-21 Relationship for Mythe and Strensham 2006

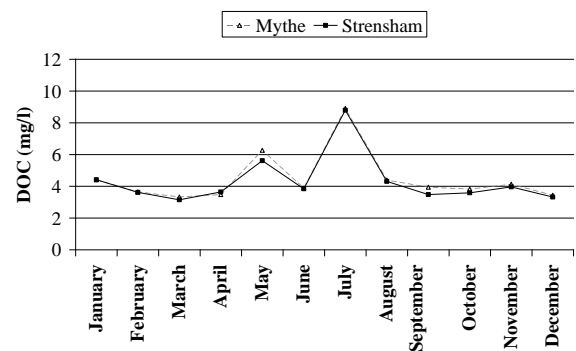


Figure 3-22 Relationship for Mythe and Strensham 2007

Despite differing variations of total DOC over time, a much more prominent trend was spotted when investigating changes in molecular size of the source water material. HPSEC traces determined that an increase in larger molecular weight material occurred over the autumn period for a variety of different source waters (Figure 3-23 - Figure 3-26.). This is demonstrated by an increase in the absorbance units around the elution times of 6-8 minutes between the months of August and October; an autumn flush. In addition a flush of low molecular weight material is observed in the months following the period of elevated HMW material, this primarily occurs in November for the upland sources (Figure 3-23 & Figure 3-24) and December for the direct abstraction (Figure 3-25) and lowland (Figure 3-26) sources.

Higher molecular weight material is often associated with hydrophobic organics such as humic and fulvic acids, which have been demonstrated to increase coagulant demand (Sharp et al., 2006). If a site does not respond to this increase in demand it can lead to fragile flocs, increased filtered turbidity values and ultimately a greater production of THMs. With regards to OPEX, it is important to be able to identify when this coagulant demand reduces otherwise the site could be significantly overdosing.

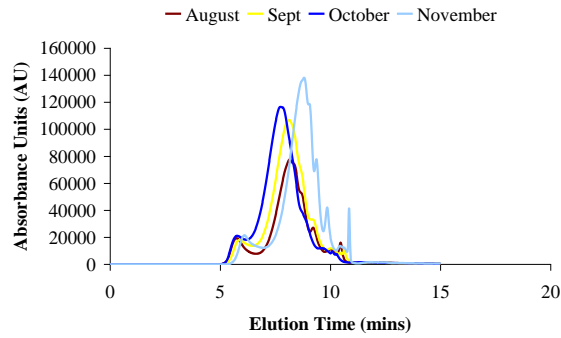


Figure 3-23 Bamford 2006 HPSEC Autumn flush (Upland)

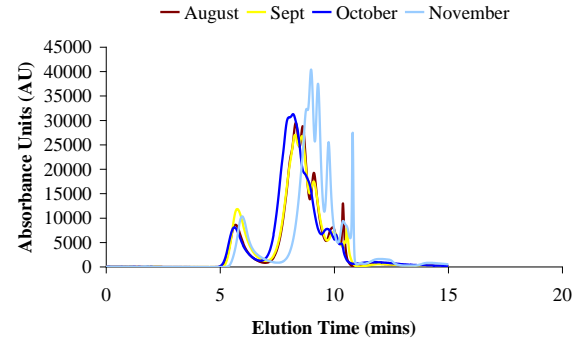


Figure 3-24 Frankley HPSEC autumn flush (Upland)

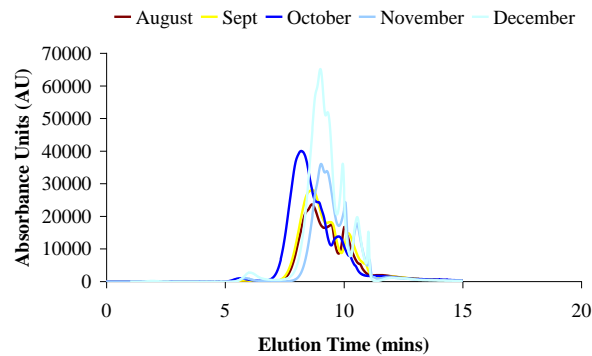


Figure 3-25 Mythe (low-DA) HPSEC autumn flush

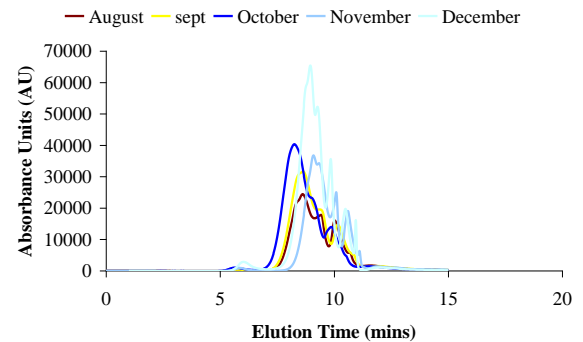


Figure 3-26 Strensham (LOW) HPSEC autumn flush

Sites have been ranked in terms of relative organic concentration stability (Table 3-9). Optimisation of the sites in the top bracket (green) is deemed to be robust with regards to changes in water quality. From this list Draycote is seen to be particularly stable in combination with it ranking highly in the sites likely to fail THM standards as well as in the sites benefiting from optimisation.

Table 3-9 Relative organic stability

	Mean DOC (mg/l)	DOC STDEV	Peak DOC concentration (mg/l)
Draycote	6.44	0.33	7.10
MelbourneF	4.11	0.40	4.94
FrankleyB	2.83	0.46	3.54
FrankleyF	2.76	0.61	3.80
Church Wilne	3.19	0.61	5.09
Ogston	4.84	0.77	6.68
Trimpley	4.68	0.84	6.97
Tittesworth	6.93	0.88	8.46
Mitcheldean	2.89	0.96	5.22
Little Eaton	2.96	0.96	5.73
MelbourneS	4.48	1.04	5.41
Whitacre	5.95	1.10	9.09
Strensham	4.45	1.17	8.79
Campion Hills	5.53	1.20	8.72
Mythe	4.49	1.20	8.90
Shelton	4.08	1.27	7.48
Bamford1	5.69	1.27	8.57
Cropston	7.58	1.32	9.72
Bamford3	6.96	1.69	9.63

It should be noted that the monthly changes in the HPI are only known on a seasonal basis in comparison to that of the DOC, which was recorded monthly. Due to the importance of the HPI fraction influencing the clarified water residuals the stability of each of the sites is not completely understood.

3.11 What Next?

Answer:

This study can be used by the company on a strategic, programme and operational level to improve performance and reduce DBPs.

Evidence:

At a strategic level this work could contribute to influencing a DBP reduction scheme. The work highlights sites that pose a risk to breaching THM standards and whether DBP levels can be met via optimisation or by alternative technologies. It also indicates if currently optimised sites need further treatment. The prioritisation in terms of both improved water quality and costs indicates whether capital investment schemes are needed and the urgency they are needed in relation to other sites.

The grouping of sites in to upland surface waters, lowland surface waters, and lowland direct abstractions provides some programme level implications. The study indicates that sites face challenges varying in severity and occurrence that are dependant on their source water categories. Monitoring and preventative measures can thus be arranged to reduce the impact of changing source water characteristics on DBP formation.

Operational level applications include. fine scale tuning with regards to coagulant dose and zeta potential for optimal floc properties and organics removal. This could be used to indicate sites that are currently over dosing or utilised as a diagnostic tool to see if poor process performance of subsequent processes stems from deteriorating water quality and coagulation conditions.

3.12 References

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4. The impact of water sources on the characteristics of natural organic matter flocs formed during drinking water treatment

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4.1 Abstract

Over the past decade an increase in NOM fluxes has been observed across Europe and the U.S leading to an increase in charged organics and in turn, the colloidal stability of the aqueous system. Natural organic matter (NOM) is present in surface waters, varying in character and composition on both a temporal and spatial basis. As a result, water treatment facilities have experienced periods of operational difficulties including the production of fragile flocs and poor organics removal. Previously, a zeta potential range of $-10 \text{ mV} < \zeta > +3 \text{ mV}$ has been utilised to identify a sufficiently destabilised system which provides optimum coagulation conditions for organics removal for moorland waters. Using this zeta potential range, the physical floc characteristics of three NOM rich waters from contrasting sources were investigated. Results indicate that through the reduction of the systems charge to that of the previously given optimum range that NOM removal for lowland waters is significantly improved and that for all waters incorporation of NOM in to the floc matrix increases their resistance to shear.

KEYWORDS

Coagulation; Flocs; Fractionation; Natural organic matter (NOM), Zeta potential.

4.2 Introduction

Natural organic matter (NOM) is a poorly defined mix of compounds found in natural waters and is known vary spatially as well as temporally (Scott *et al.*, 2001; Parsons *et al.*, 2007). These variations not only occur in bulk concentrations but also in the physical and chemical fractional composition of the NOM (Sharp *et al.*, 2006). Fractionation of NOM can be conducted in a multitude of ways including resin absorption, membrane separation, HPSEC and charge density (Fiella, 2008). These techniques have all been utilised to show differences in fractional composition from different source waters. Upland waters tend to be hydrophobic in nature, comprising of high molecular weight (HMW) molecules which are more readily removed from treatment due to its high negative charge. In contrast low land waters consist of more aliphatic material which is more hydrophilic in nature. This material is harder to remove via conventional treatments due to it having little or no charge (Sharp *et al.*, 2006; Jarvis *et al.*, 2005).

Removal of NOM is typically via a combination of coagulation and flocculation (Uyak *et al.*, 2008). The addition of a tri-valent metal coagulant or cationic polymer reduces the colloidal stability of the water and thus promotes the aggregation of NOM in to loosely bound structures known as flocs (the coagulation process). Gentle mixing/agitation of the dosed raw water promotes the growth of these aggregates (flocculation) before they are removed via sedimentation or flotation (clarification). As such, floc characteristics play a significant role in the performance of subsequent processes (Bridgeman *et al.*, 2008). Poor operational performance has been linked to seasonal increases in bulk NOM concentration and the hydrophobic component of the source water (Eikebrokk *et al.*, 2004). This is demonstrated by a reduction in filter run time till break through and an increased number of backwashes per unit time, suggesting that the change in raw water characters has altered floc characteristics.

Previous floc studies have investigated the temporal variations of NOM for moorland waters (Sharp *et al.*, 2006; Jarvis 2005) or have looked at flocs created by individual fractions (Jefferson *et al.*, 2004). This study aims investigate the spatial variation of NOM by comparing flocs from different water sources.

4.3 Methods and Materials

Bulk raw water samples were collected from three different UK surface waters all rich in NOM, comprising of waters from moorland, upland, and lowland sources, with the moorland water being from one of the sources used in previous studies (Sharp *et al.*, 2004, 2006; Jarvis *et al.*, 2004; Jefferson *et al.*, 2004). Moorland and upland sources were characterised as low turbidity (<2 NTU), low alkalinity (<20 mg.L⁻¹ as CaCO₃) waters, in comparison to the lowland source which was relatively hard (175 mg.L⁻¹ as CaCO₃) and significantly more turbid (17 NTU). Samples were coagulated under optimum conditions, to a zeta potential within the previously identified optimum range of -10 mVζ+3 mV (Parsons *et al.*, 2007). NOM character, floc properties and treatment performance were assessed based on a set of standard techniques (Table 4-1). Coagulated jar tests were subsequently performed under operational conditions and analysed using the same standard techniques.

Table 4-1 Characterisation and monitoring techniques.

Technique	Parameter	Equipment
High Performance Exclusion Chromatography (HPSEC)	Size UV ₂₅₄ abs (m ⁻¹)	Shimadzu HPLC
Raw water fractionation	Dissolved organic carbon (DOC mg.L ⁻¹)	XAD Ion Exchange Resins
Surface charge	Zeta Potential (mV)	Malvern Zetasizer (Nano)
Floc diagnostics	Size (µm), growth and breakage	Malvern Mastersizer (2000)

4.3.1 Coagulation jar tests

Coagulation jar tests were undertaken at an ambient temperature (20°C) using a six paddle programmable jar tester (*Phipps and Bird, USA*), coagulating with ferric sulphate (*Feripol Xl, EA West*) and pH adjustment with NaOH solution. The

procedure included a 1.5 minute rapid mix stage at 200 RPM and a 15 minute flocculation stage at 30 RPM followed by a 20 minute settlement period.

4.3.2 High size exclusion chromatography

All samples were filtered (0.45 μm membrane filters, PALL, UK.) to remove suspended solids before DOC (*ppm LABTOC analyser*) and high performance size exclusion chromatography (HPSEC) analysis (*Shimadzu VP series, Shimadzu, UK*). The HPSEC analysis used a TSK gel, GW3000SW column, 7.5mm internal diameter and 30cm in length. The guard column was also TSK, 7.5mm internal diameter and 7.5cm in length (*Tsoh Biosep GmbH, Stuttgart, Germany*).

4.3.3 Fractionation

Raw water samples were fractionated by XAD resin adsorption techniques into their hydrophobic acid (HPOA) and hydrophilic acid (HPIA) constituents using an adapted methodology from Malcolm and MacCarthy (1992). These components were extracted through utilisation of an Amberlite XAD-7HP and Amberlite XAD-4 resin pair (*Rohm and Haas, PA, USA*). The non-adsorbed fraction was categorised as hydrophilic non acid (HPINA).

4.3.4 Surface Charge

Samples were extracted from the coagulation jar tests 5 minutes in to the slow mix stage. The Zetasizer Nano (*Malvern Instruments, UK*) was then utilised to calculate the zeta potential (ζ). determine the zeta potential of the coagulated jar test under operational conditions and also to ensure the maintenance of a zeta potential between -10mV and +3mV when coagulating under optimum conditions (Parsons *et al.*, 2007)

4.3.4 Floc diagnostics

An identical methodology to Jarvis *et al.* (2005) was implemented to calculate floc size and strength. Coagulation jar tests were conducted as mentioned previously,

however, following the 15 minute flocculation phase there was an additional 15 minute phase of elevated shear. Each experiment was repeated at elevated shear conditions at RPM's of 30, 50, 75, 100, 150 and 200. The dynamic floc size was measured during the growth and breakage of the flocs by drawing water through the optical unit of a laser diffraction instrument (*Malvern Mastersizer 2000, Malvern Instruments, UK*). Floc sizes were expressed as an equivalent volumetric diameter derived from light scattering intensity distribution. Floc strength was measured in terms of energy required to break flocs under shear (Zhang *et al.*, 1999). This was determined through the application of the following empirical constant derived by Jarvis *et al.*, (2005) where RPM represents shear in terms of paddle speed.

$$\log d = \log (C') - (\gamma') \log \text{RPM} \quad (1)$$

where d is the floc diameter, C' is the floc strength constant, γ' is the stable floc size exponent and RPM represents the shear in terms of paddle speed. The G value, which is a measurement of the energy transferred in to the water via paddle was also calculated.

$$\log d = \log (C) - (\gamma) \log G \quad (2)$$

Comparisons of both the stable floc size exponents (γ and γ') from the breakage profiles were made to calculate relative floc strength terms of RPM and G value.

4.4 Results

4.4.1 Characterisation

Analysis of raw water indicated that the highest concentration of DOC was found in the lowland source at 7.2 mg.L^{-1} , compared to 4.7 mg.L^{-1} and 2.3 mg.L^{-1} for the moorland and upland sources respectively (Table 4-2). The DOC values for the moorland water corresponds with that of values in the lower range identified in previous studies, whilst the DOC content of the lowland source and upland source is

typical for those particular site as determined through long term organics monitoring (Sharp *et al.*, 2005.).

Subsequent DOC tests of the raw water fractions revealed that all three sources were predominantly hydrophobic in nature, ranging from 52% for the lowland source to 56% for that of the moorland water (Figure 4-1). This in accordance with previously published work which indicates that the hydrophobic content of a raw water is characteristically the largest NOM fraction constituting approximately 50% of the DOC concentration Owen *et al.* (1993). The hydrophilic fraction can be split further in to the hydrophilic acid (HPI-A) and hydrophilic non acid fraction (HPI-NA) where by the lowland water is the only source to have the majority of its hydrophilic organics as the non-acid fraction at 61% (30% of total DOC) in comparison to moorland and upland water at 20% and 18% of total DOC respectively. The moorland source analysed by Sharp *et al.*, (2006) had a similar HPI-NA content throughout the year at $18\pm 6\%$, although it has been shown that moorland waters can have a much HPI-NA at 30% (Jefferson *et al.*, 2004) which is similar to that of lowland water source analysed for this paper.

Table 4-2 Raw water characteristics.

Source	pH	Alkalinity (mg.L^{-1} as CaCO_3)	Turbidity (NTU)	DOC (mg.L^{-1})	UV ₂₅₄ abs (m^{-1})	SUVA* ($\text{m}^{-1}.\text{L.mg}^{-1}$)
Lowland	8.1	175	17.0	7.2	17.3	2.4
Upland	6.3	13	0.8	2.3	9.5	4.1
Moorland	5.6	8	1.5	4.7	27.3	5.8

*Specific UV₂₅₄ absorbance

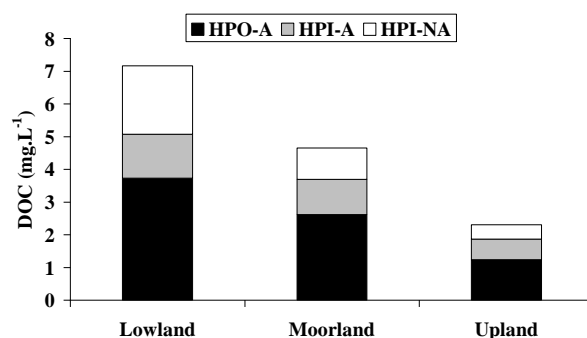


Figure 4-1 Raw water fractionated DOC

Hydrophobic waters, such as these, are typically associated with high molecular weight organics such as humic and fulvic acids which are coupled with high specific UV₂₅₄ absorbance (SUVA) values (>4) (Edzwald and Tobiason, 1999). The moorland source (SUVA 5.8) and upland water (SUVA 4.1) strike an accordance with this. However the lowland water with a similar hydrophobic fraction percentage, has a much lower SUVA (2.4), indicative of a lower hydrophobic to hydrophilic fraction ratio. The SUVA values are further supported by raw water HPSEC profiles (Figure 4-2), indicating the presence of predominantly low molecular weight molecules in the lowland water compared to upland and moorland sources which have a higher percentage of >5KDa molecular sized material.

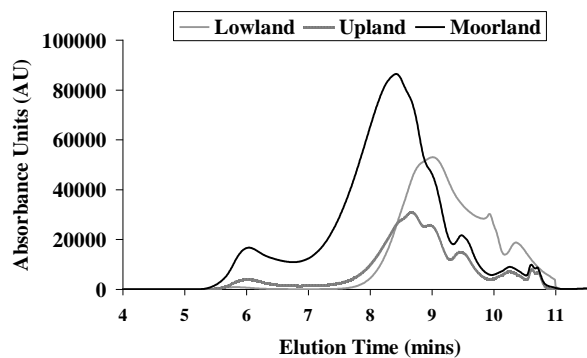


Figure 4-2 Raw water HPSEC profile

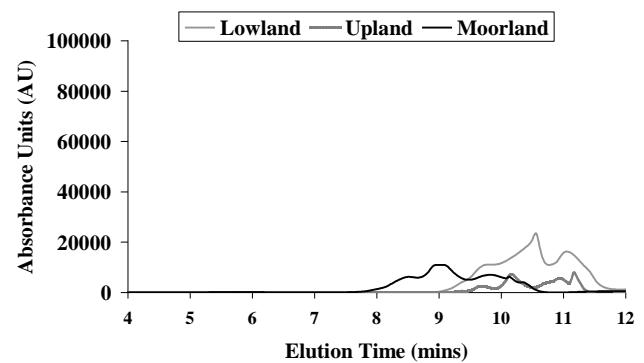


Figure 4-3 Treated water HPSEC

4.4.2 Removal

DOC removal efficiencies varied significantly from a low of 56% (upland water) to 80% (moorland water), the removal for the lowland water was slightly higher than that of the upland water at 63% (Table 4-3). The removal efficiency for the moorland water is in accordance with those tested by Sharp *et al.*, (2004, 2006) who demonstrated a removal efficiencies of 73%-84% whilst coagulating under similar zeta potentials (-10 mV ζ +3 mV). The upland water achieves a comparatively low DOC removal at 56%, outside of the range given in previous studies.

With regards to UV₂₅₄ absorbance, the lowland water achieved the lowest removal percentage at 73%, whilst removal for the upland and moorland waters under optimum zeta conditions was greater than this at 84% and 94% respectively, which is similar to values determined from other studies (Sharp *et al.*, 2006). HPSEC analysis

supports this notion (Figure 4-2 & Figure 4-3), showing a predominant removal of large molecular weight molecules for all three waters, with a peak area reduction of 89% observed for both the moorland and upland water, with the lowland water only achieving a 67% decrease.

No clear link between raw water source characteristics and removal efficiencies could be determined. The upland water had a DOC removal percentage (56%) which was comparative to that of the hydrophobic fraction (53%), however this did not hold true for the lowland and moorland waters which demonstrated some removal of the hydrophilic fraction.

Table 4-3 Performance data.

Source	Coagulation pH	Coagulant dose (mg.L ⁻¹ as Fe)	Coagulation Zeta potential (mV)	UV ₂₅₄ abs removal (%)	DOC removal (%)
Lowland	4.5	7.2	-8.4 ± 0.3	73	63
Upland	5.3	2.8	-1.1 ± 0.8	84	56
Moorland	4.5	4.6	-0.3 ± 0.5	94	80

4.4.3 Floc properties

The floc growth profiles for differing source waters illustrate differences in steady state floc size and response to sheer (Figure 4-4 – 4-6). There is a large range of d_{50} floc sizes ($333 \pm 29 \mu\text{m}$), with the lowland source achieving the largest floc size of $968 \pm 9 \mu\text{m}$ in comparison of that of $826 \mu\text{m}$ and $635 \mu\text{m}$ for the upland and moorland waters respectively (table 4-4). The d_{50} floc size of the moorland flocs from Sharp *et al.*, (2006) displayed a similar steady state size ($603 \pm 24 \mu\text{m}$) under similar zeta conditions as the moorland source in this study. However these were around 70-170 μm smaller than those shown in Jarvis *et al.*, (2005).

All waters were shown to have a similar overall growth rate 64-70 ($\mu\text{m}\cdot\text{min}^{-1}$). The moorland water was shown to reach a steady size first, growing at $70 \mu\text{m}\cdot\text{min}^{-1}$, the lowland water grew to steady conditions at a similar rate ($69 \mu\text{m}\cdot\text{min}^{-1}$), however its initial growth rate was much quicker ($132 \mu\text{m}\cdot\text{min}^{-1}$) than that of the moorland water ($111 \mu\text{m}\cdot\text{min}^{-1}$).

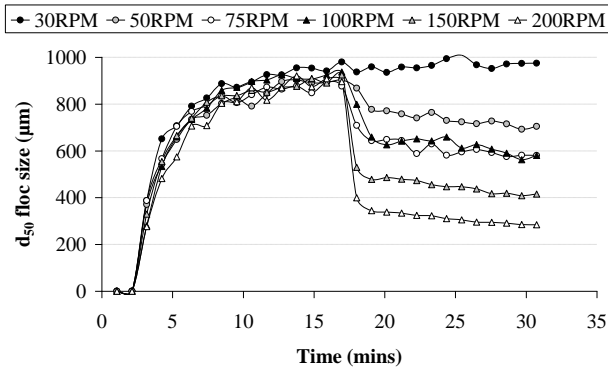


Figure 4-4 Breakage profile for lowland water

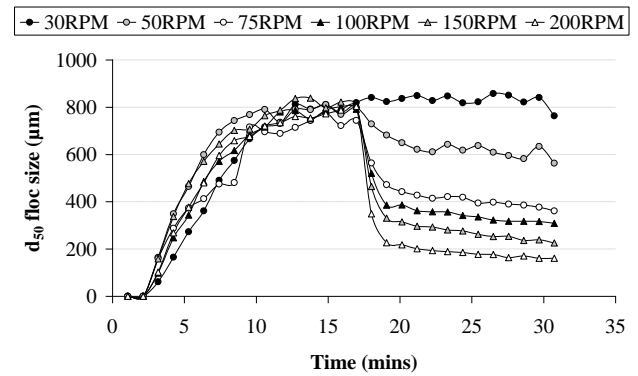


Figure 4-5 Breakage profile for upland water

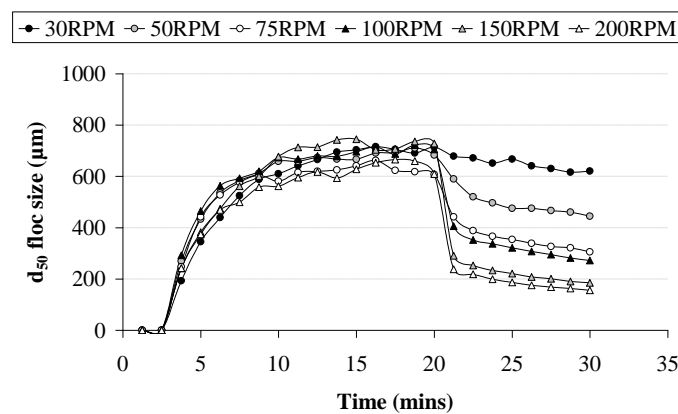


Figure 4-6 Breakage profile for moorland water

Floc size distribution (Figures 4-7 – 4-9) revealed similar profiles for the lowland and upland waters, despite having a 300µm difference in floc size. A slight increase in shear caused a reduction in the mean floc size, combined with a small increase in peak height and associated decrease in distribution width for all waters. A higher increase in shear, caused a large reduction in mean floc size and size distribution, with a much larger percentage of flocs being found in the sub 400µm. This trend was most prominent for the moorland water, with the low land water being the least effected. These changes in distribution are very similar to those observed on both a bench scale (Sharp *et al.*, 2006) and field scale Kilander *et al.*, (2007). In both these case an increase in smaller particle numbers was observed with an associated decrease in the floc size distribution.

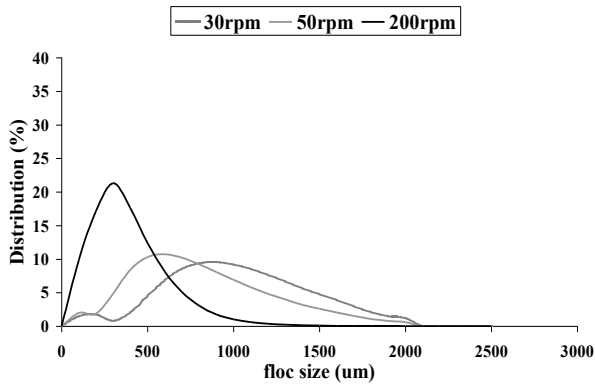


Figure 4-7 Floc size distribution profile for lowland water

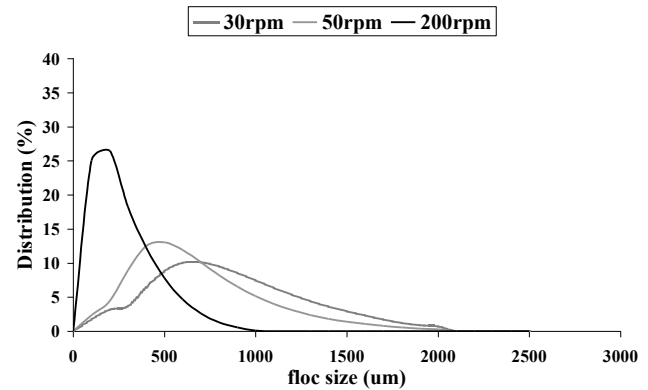


Figure 4-8 Floc size distribution profile for upland water

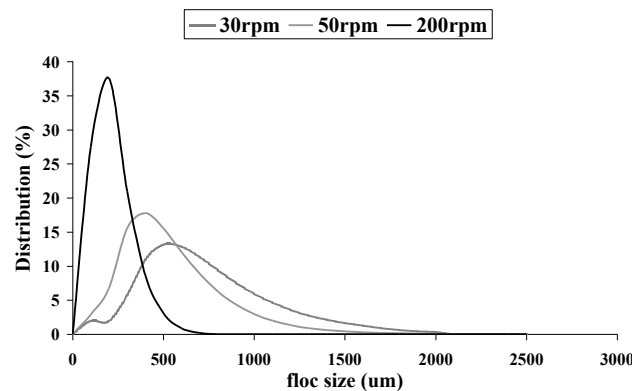


Figure 4-9 Floc size distribution profile for moorland water

The stable floc size exponents (γ' / γ), derived from the breakage profiles were compared to analyse floc strength. In this instance results indicate that lowland sources produced flocs with an increased resistance to shear (Table 4-4 and Figure 4-10) as a result of the lower floc size exponent for the lowland source (0.58' / 0.38) in comparison to that of the upland (0.78' / 0.51) and moorland (0.85' / 0.56) waters. Despite this difference, the flocs created in this study were found to be particularly strong in comparison to previous studies. The associated γ value derived from the G value has been previously used to identify the weakness of the charge neutralisation mechanism. Li *et al.*, (2006) indicated that the stable floc size exponent for various mechanisms had the following hierarchy: charge neutralisation (0.61)>sweep (0.56)>bridging (0.36) for kaolin flocs, which are deemed stronger than NOM flocs (Bache *et al.*, 1999a).

With the inclusion of previously published work, (Jarvis *et al.*, 2005; Mergen *et al.*, 2006; Sharp *et al.*, 2006) a correlation ($R^2 = 0.7$) between DOC removal and the stable floc size exponent (γ') was observed, indicating that stronger flocs can be produced if increased levels of NOM are incorporated in to the floc structure under optimum conditions (Figure 4-11). Where by an approximate increase of 2mg/l DOC incorporated in to the floc matrix leads to 0.2 reduction in the stable floc size exponent.

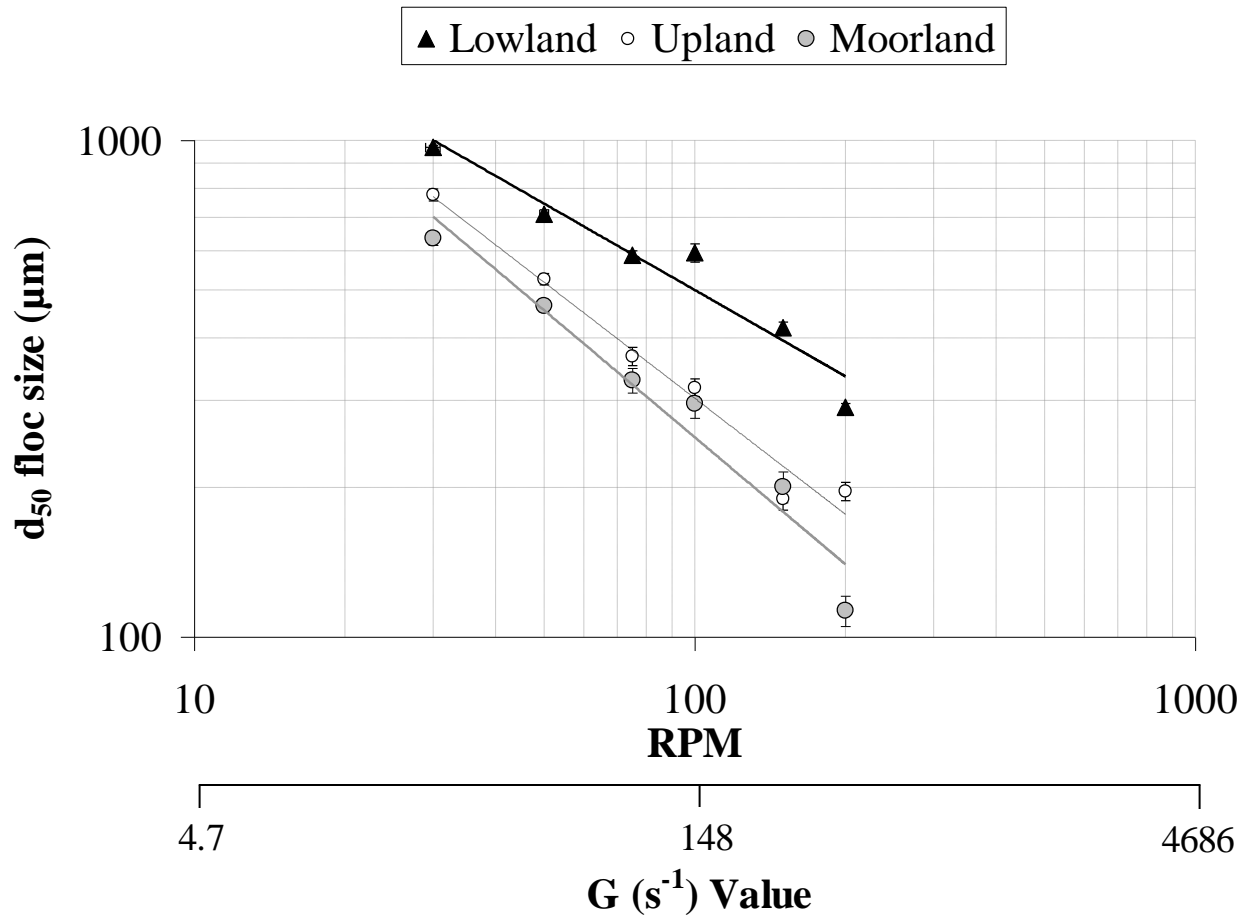


Figure 4-10 Comparison of floc breakage rates for all three sources at optimum zeta potentials.

Table 4-4 Floc properties

Source	Coagulation pH	Coagulation potential (mV)	Zeta	Growth rate ($\mu\text{m}\cdot\text{min}^{-1}$)	Steady state d ₅₀ (μm)	Stable floc size exponent (γ')	Stable floc size exponent (γ)
Lowland	4.5	-8.4 ± 0.3	69		968 ± 9	0.58	0.38
Upland	5.5	-1.1 ± 0.8	64		826 ± 38	0.78	0.51
Moorland	4.5	-0.3 ± 0.5	70		635 ± 20	0.85	0.56

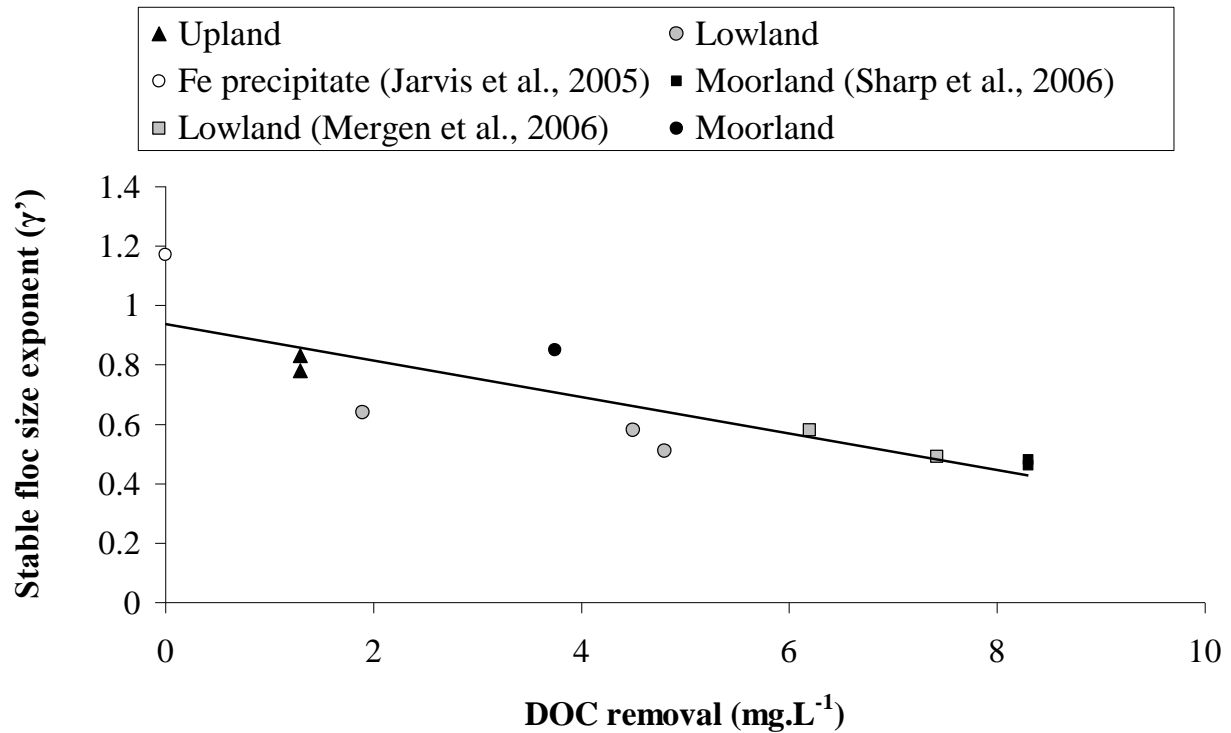


Figure 4-11 Relationship between floc DOC content and stable floc size exponent.

4.5 Discussion

Results indicate a clear difference in the three source waters apart from with regards to the split between the hydrophobic and hydrophilic fractions, which is similar for all the source waters with the hydrophobic fraction constituting just over 50% of the DOC concentration, as highlighted by Owen *et al.* (1993). As the hydrophilic fraction is deemed a good indicator of the likely residual concentration achieved via coagulation (Sharp *et al.*, 2006), a similar DOC residual would have been expected for the three different source waters, however the 3% difference in hydrophilic fraction concentrations led to a 26% difference in residuals. Also, for all of the sources, the percentage DOC removal was greater than that of the hydrophobic indicating the removal of some hydrophilic organics. With previous studies showing significant removal of the hydrophobic fractions and almost completely no removal of the hydrophilic non-acids (Fearing *et al.*, 2004) this suggests varying removals of the

hydrophilic acid fraction occurred for the different sources. Mechanisms involved in the competitive NOM:coagulant interactions include charge neutralization, complexation/precipitation and ligand exchange (McKnight *et al.*, 1992), such that the larger MW and a greater charge density of the hydrophobic material provides a greater propensity for removal (Gu *et al.*, 1995). Due to the inherent size characteristic of the hydrophilic acids, the variation in the removal of the hydrophilic acid fraction is likely to be a result of its particles carrying a negative charge, as observed in some moorland waters (Parsons *et al.*, 2007.) An understanding of the fractions as well as their charge is therefore needed to be able to indicate residual concentrations. Fractionation data can only provide so much information on DOC removal, therefore the scope for projects investigating optimisation for organics removal should look at hydrophobic/hydrophilic split, whilst taking in to account charge.

The amount of DOC removal achieved by each of the source waters was also related to floc strength, whereby increasing the amount of DOC in the floc leads to a greater resistance to shear under optimum conditions, irrespective of source type. Work by Jarvis *et al.*, (2005) in to upland waters indicated that an increase in the NOM content of Fe-NOM flocs is detrimental to floc strength both in terms of size and resistance to shear. Hindrance of particle aggregation in this instance can be attributed to insufficient charge neutralisation of the system in which zeta potentials ranged from -11.6 mV to $+11.6$ mV. In this instance electrostatic repulsion and changes in the hydrodynamic layer thickness increased the separation distance between the particles and aggregates preventing agglomeration (Amal *et al.*, 1992). The model based on the previous study was further developed by Sharp *et al.* (2006) through the application of electrostatic theory in to gaining a greater understanding of both floc characteristics and removal efficiency. The study indicated that zeta potential was the dominant factor influencing removal efficiency and floc strength, in terms of resistance to shear. It was also a contributing factor to steady state floc size. Optimum conditions for the production of strong flocs and achieving low stable residual could be achieved via the maintenance of a zeta potential within the range of -10 mV $<\zeta>$ $+3$ mV.

The current paper extends the concept further, suggesting that under optimal zeta conditions an increase in the organic content of the floc will increase floc strength for a range of NOM dominated systems. Reduction of the zeta potential and thus charge density promotes the incorporation of NOM in to the floc matrix as a result of increased interaction energy between NOM particles and coagulant. A decrease in the electric double layer interactions reduces then separation distance between NOM particles allowing bonding to occur through van der waals forces. At higher NOM concentrations, an increased adsorbtion of organics on the primary floc occurs (Jarvis *et al.*, 2005), such that the increased amount of NOM incorporated in to the floc matrix would lead to an increase in the potential number of bonds and in turn floc strength (Bache *et al.*, 1999a). If this is the case then source water in terms of the total amount of removable DOC, will strongly influence the quality of the floc produced and thus the ability for that particular site to clarify the water

For the full range of waters floc size was shown to increase with floc strength, as supported by (Jarvis, 2005; Bache and Papavasilooulous, 2003) this is as a result of floc size being based on the equilibrium between growth and breakage (Biggs *et al.*, 2000). This however is not in accordance with Sharp *et al.*, (2006) who demonstrated for a moorland source water, that there was a poor correlation between floc size and floc strength. This further highlights the variable nature of a natural water, not only in terms of different source types, but also between different sources of the same type.

The low land water had a significantly higher turbidity in comparison to that of upland and lowland waters, this could have been a contributing factor towards the increase in floc strength displayed by the low land water. A study by Bache *et al.*, (1999a) commented that flocs produced from turbid waters were shown to produce a stronger flocs, as a result of the electrostatic bridging mechanism conferring greater attractive strength in comparison to that of the van der Waals forces which dominate the charge neutralisation mechanism (Bache *et al.*, 1999b). Li *et al.*, 2006 supported this, demonstrating that charge neutralisation had a higher stable floc size exponent (γ) in comparison to sweep flocculation and bridging mechanism, respectively. This is a possible explanation for why the lowland water coagulating under a sub-optimum zeta potential displayed a higher resistance to shear in comparison to that of the upland and moorland water under an optimum zeta potential. However it must be

noted that the previously mentioned journals did not monitor or optimise the zeta potential to which governs the potential strength of these van der Waals bonds. Work by Sharp *et al.*, (2006) takes in to account zeta potential, and for an upland water demonstrated that increased turbidity removal could be linked to increases in floc strength.

The paper demonstrated that optimising the zeta potential for a lowland water leads to increases in DOC removal, floc size and floc strength to an extent similar to previous studies in to moorland waters (Jarvis *et al.*, 2005; Sharp *et al.*, 2006). Despite the difference in the source, the essential charge neutralisation mechanism does not seem to have changed, hence why the improvement in water quality was still observed. Although this shows improved organics removal and floc characteristic for a lowland water can be achieved, due to the high alkalinity of the source water, this would be economically unfeasible as the cost of acid dosing to obtain the correct zeta potential would far out weigh the increased amounts of organics removed.

4.6 Conclusions

Removal efficiencies and floc characteristics can vary greatly for waters from different sources, irrespective of the type of source (moorland, upland or lowland).

Improved floc properties and organics removal can be achieved through optimisation of the zeta potential for lowland waters.

Understanding the fractional make up and their associated charges is important to assess the potential for optimisation of the coagulation process.

Providing the electrostatic forces are minimised, increasing the NOM content of the floc matrix will lead to an increase in floc strength.

4.7 Acknowledgements

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5. Flocs off the bench on to the field: The scope for potential energy savings in the flocculation process

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5.1 Abstract

Water treatment plants traditionally use coagulation/flocculation process to remove organics and turbidity particles in drinking water. Due to the chemical optimisation of the coagulation process having such a strong influence, it is believed that the current hydraulic conditions for flocculation cited under best practice are out of date. A 450Mld plant treating upland water was chemically optimised and it was observed that the total mixing energy input could be reduced by 66% without any detrimental impact upon the clarified water being observed. Under the new mixing regime energy costs could be reduced by £51,000 pa equating to approximately a 280t reduction in CO₂.

KEYWORDS

Floc engineering; Coagulation DAF; optimisation; pre-treatment

5.2 Introduction

Water companies are currently facing pressures to treat deteriorating source waters (Skjelkvaale, 2003) whilst meeting more stringent water quality regulations (Crozes *et al.*, 1995; Colbourne, 2003), coupled with escalating energy and chemical costs. These drivers apply heavily to the coagulation/flocculation process which has a high chemical and energy demand in addition to being the predominant removal mechanism for organic material.

Current research in to NOM removal and floc properties has focused primarily on the chemical optimisation on a bench scale to enable sufficient removal at minimum costs. Manipulation of the zeta potential between a range of $-10\text{mV} <\zeta> +3\text{ mV}$, has been shown to increase both turbidity and DOC removal and produce stronger flocs (Sharp *et al.*, 2006). Whilst a DOC:Fe ratio has shown to produce the strongest flocs (Jarvis *et al.*, 2005). In these reports, flocs reached steady state condition in around 6-10 minutes under optimised conditions.

In retrospect very little has been done with regards to investigating optimum hydraulic conditions needed. With reference to DAF clarification, Edzvald (1995) advocated the production of strong, small flocs ($10\text{-}30\mu\text{m}$), with no improvement in solids removal observed if larger flocs were created (Bache and Rasool, 2001). Small flocs created under high shear conditions ($G \approx 70\text{-s}$), for low retention times (5-10mins) have been shown under low pH conditions, to produce better post clarified water than that at shear rates and retention times advised under best practise (Valade, 1996). This ties in with recent chemical optimisation work, where flocs reach a stable size after 10 minutes (Sharp *et al.*, 2006., Jarvis *et al.*, 2005), further questioning the need for longer retention times ($>15\text{mins}$). Current flocculation regimes are based off best practice guidelines (Table 5-1 Best practice guidelines for flocculation), typically comprising of 2-3 stages flocculation which tends to focus on low G values and higher retention times ($<16\text{mins}$), contradicting the previous findings.

Table 5-1 Best practice guidelines for flocculation

Source	G (s^{-1})	t (mins)
Montgomery (1976)	10 - 75	30 (minimum)
AWWA / ASCE (1991)	10 - 60	16 - 25
Hammer (2004)		30 (minimum)
Sincero & Sincero (2000)	20 - 70	40 - 60
Camp (1955)	36 - 66	
Degremont (1991)	~100	

Analysis of the flocculation through a combination of image analysis and population balance models has demonstrated spatial and temporal alteration in localised shear gradients for different systems (Kilander *et al.*, 2006). The inherent differences in impeller-tank configuration would prevent the reproducibility of a full scale works on

a bench scale level which would mean that analysis of the hydraulic conditions on flocs needs to be conducted on a site level.

This paper aims to investigate potential energy savings that could be made through reducing the degree of mixing on a site down to the levels observed on a bench scale, without sacrificing post-clarified water quality.

5.3 Materials and Methods

Research was conducted at a 450 Mld water works treating upland water. The works (Figure 5-1) consists of lime dosing (dispersed via static mixers) prior to coagulant addition (blended via weir) and flow splitting subsequent to flocculation. Flocculation consists of 20 parallel streams of 3 stage tapered flocculation with G values of 77.5s^{-1} , 65.1s^{-1} , 58.7s^{-1} , with a total retention time of 30-36 minutes. Clarification is via DAF prior to dual media filtration and disinfection. Flocculation costs equated to 1.12GWh, costing approximately £78,000 pa (£0.07Kwh), this produces 480t of CO_2 a year.

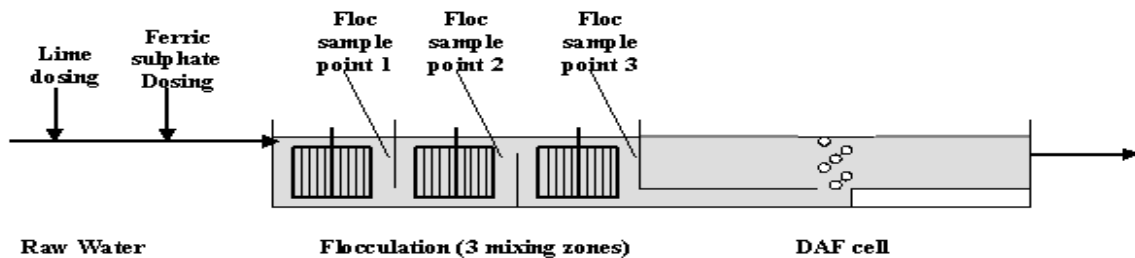


Figure 5-1 Site Schematic

Floc diagnostics were carried out at the designated sample points (Figure 5-1) whilst water characteristics were measured from the raw inlet to post DAF to ensure the site was operating under optimum chemical conditions (within the $10\text{mV} <\zeta> +3\text{ mV}$ range advocated by Sharp et al., 2006), that the correct Fe:DOC dose (Jarvis et al., 2005), as well as to measure removal efficiencies. Sample turbidity of the raw and post DAF clarified water were measured with the Hanche Lange e1720 turbidity meter and UV absorbance was measured at 254nm. A series of trials were conducted whereby different sequences of the mixing zones (MZ) of the flocculators were turned

off and the impact across the works observed. Flocs observed on site were compared to those created in the jar test procedure.

5.3.1 Floc diagnostics

An adapted method to Jarvis *et al.*, (2005) was implemented to measure floc size on site. Flocs were extracted directly from the flocculation cell utilising a peristaltic pump to draw water through the optical unit of the particle sizing instrument (*Malvern Mastersizer 2000, Malvern Instruments, UK*). Steady state floc sizes were expressed as an equivalent volumetric diameter derived through a measuring period of sufficient to ensure that the median floc size did not change by more than 15%. Bench scale floc tests were carried out as indicated in Jarvis *et al.*, (2005).

5.3.2 Surface Charge

The Zeta potential(ζ) of all the extracted samples were analysed with the Zetasizer Nano (*Malvern Instruments, UK*) to ensure that the plant was operating under the optimum zeta conditions of between -10mV and +3mV (Parsons *et al.*, 2007). A deviation outside of this range resulted in a change in floc characteristics and removal efficiencies.

5.3.3 Dissolved Organic Carbon and High size exclusion chromatography

Samples were filtered (0.45 μm membrane filters, PALL, UK.) to remove suspended solids before DOC (*ppm LABTOC analyser*) and high performance size exclusion chromatography (HPSEC) analysis (*Shimadzu VP series, Shimadzu, UK*). The HPSEC analysis used a TSK gel, GW3000SW column, 7.5mm internal diameter and 30cm in length. The guard column was also TSK, 7.5mm internal diameter and 7.5cm in length (*Tsoh Biosep GmbH, Stuttgart, Germany*).

5.4 Results

Floc characterisation in the laboratory revealed the median floc size to initially grow rapidly at a rate of $160\mu\text{m}\cdot\text{min}^{-1}$ reach a steady state size of $730\pm 36\mu\text{m}$ within 7-

12 minutes depending on the trial (Figure 5-2). Previous investigations in to floc growth have revealed that growth rate is dependant on the coagulant to DOC ratio with the growth rate ranging from 108.7 to 233 $\mu\text{m}\cdot\text{min}^{-1}$ as the DOC:Fe ratio increased from 0 to 0.75/1 $\text{mg}\cdot\text{mg}^{-1}$ (Jarvis *et al.*, 2005). In the current study the dose ratio was 1:1 corresponding to a growth rate of 160 $\mu\text{m}\cdot\text{min}^{-1}$ which is significantly less than that of Jarvis *et al.*, (2005). Application of elevated shear rates to the formed flocs resulted in breakage in two distinct ways. Initially a large scale decrease was observed followed by a more gradual decline (Figure 5-2). Similar observations have been previously reported as indicating floc rupture followed by erosion. The magnitude of each component was dependent on the applied shear rate. For instance, the initial decrease was 411, 305, 123 for elevated shear rates of 165 s^{-1} , 71 s^{-1} and 46 s^{-1} respectively. Similarly, the slow declining rate decreased from 12.57 to 6.4 $\mu\text{m}\cdot\text{min}^{-1}$ as the shear rate increased from 46 s^{-1} to 165 s^{-1} . Overall the median floc size, growth rates and breakage profiles indicate that the flocs under investigation in the current study are typical of many encountered during the flocculation of NOM rich waters from upland catchments (Sharp *et al.*, 2006a, 2006b; Jarvis *et al.*, 2005; Goslan, 2003).

Comparison of median floc sizes measured from the on line particle sizing equipment linked to the full scale site revealed a 57% decrease compared to the bench experiments with a median floc size of 337 μm (Figure 5-3). Similar floc sizes were observed in the bench experiments at shear rates 148 s^{-1} indicating that the mixing patterns in the two systems are very different and that average G is a poor indicator of the shear rate pattern observed in the flocculator (Kilander *et al.*, 2006; Bridgeman *et al.*, 2008). For instance CFD analysis of local g patterns reveal that even at low average G of 17 s^{-1} there are high local g zones of 150 s^{-1} which are likely to control actual floc sizes. Ultimately, current computational analysis of shear rate patterns in flocculators is still be refined and as such empirical measurement of the impact of changes in flocculator operation are still required.

Reduction of energy use by switching off mixing stages within the flocculator caused a maximum of 10% change in the median floc size. For instance switching off the first or last mixing zone caused the median floc size to decrease by 34 and 6 μm respectively (Figure 5-3). The least impact observed on the median floc size occurred

when both second and third stage mixers were shut off; in this case a reduction of 2.7 μm was observed (Figure 5-3). In all configurations a decrease in median floc size was observed through the flocculation process indicating that maximum flocculation had occurred within the first tank. To illustrate, with all mixing zone operating the median floc size decrease from 400 μm in tank 1 to 337 μm in tank 3. The maximum change was observed when 2 mixers were switched off whereby the floc size decreased by 87 μm across the flocculator. This is consistent with the growth profiles observed in the laboratory where steady state floc sizes were observed after no more than 12 minutes which is equal to the average retention time in the first tank and is equal to the 33.3 percentile of the residence time of the flow.

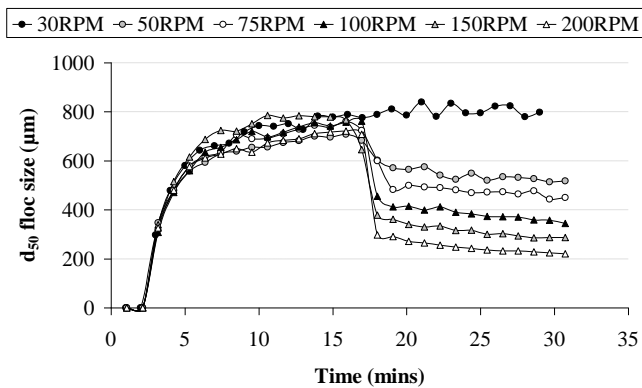


Figure 5-2 Jar test; response to shear

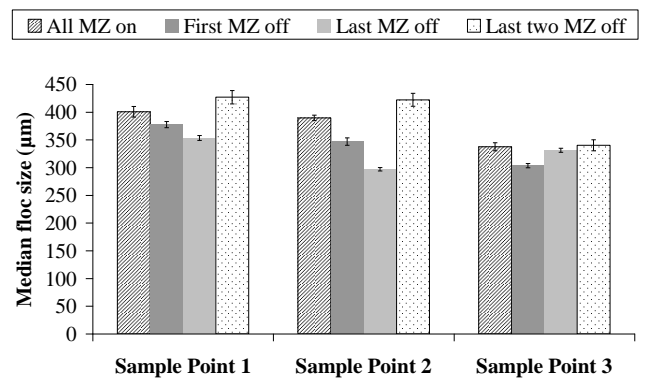


Figure 5-3 Floc response to different mixing regimes

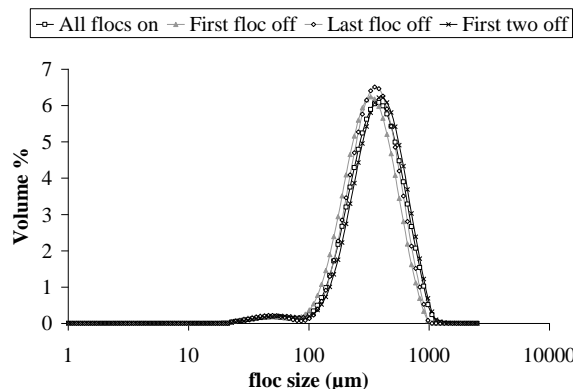


Figure 5-4 d₅₀ floc size distribution for different mixing regimes (volume)

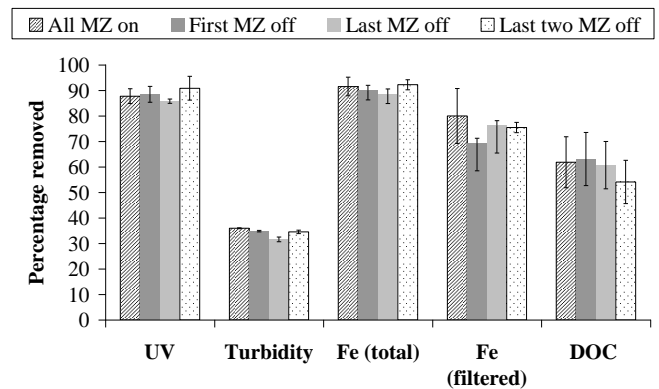


Figure 5-5 Removal response to different mixing regimes

The impact of the different operating regimes on overall removal observed on the plant was statistically insignificant at the 76% confidence level for all the measured parameters (Figure 5-5). To illustrate, residual turbidities of 0.48, 0.49, 0.48 and 0.54 NTU were observed for cases where all stages were on, the first stages is off, the last stage is off and the last two stages are off respectively (Figure 5-5). The maximum

observed difference between all four options was 5 % for UV, 4.3% for turbidity, 3.7% for iron and 8.9% for DOC. The largest observed difference was recorded in relation to DOC when the last two stages were switched off which resulted in an increase in residual DOC of 0.41 mg.L^{-1} compared to the base case. This trend was also demonstrated with HPSEC analysis (Figure 5-6) which showed similar removal values for the range of molecular weight materials for all mixing regimes. No observed differences in downstream operation were observed during the trial indicating that switching off the flocculators should not increase operational costs on either the DAF or depth filtration processes.

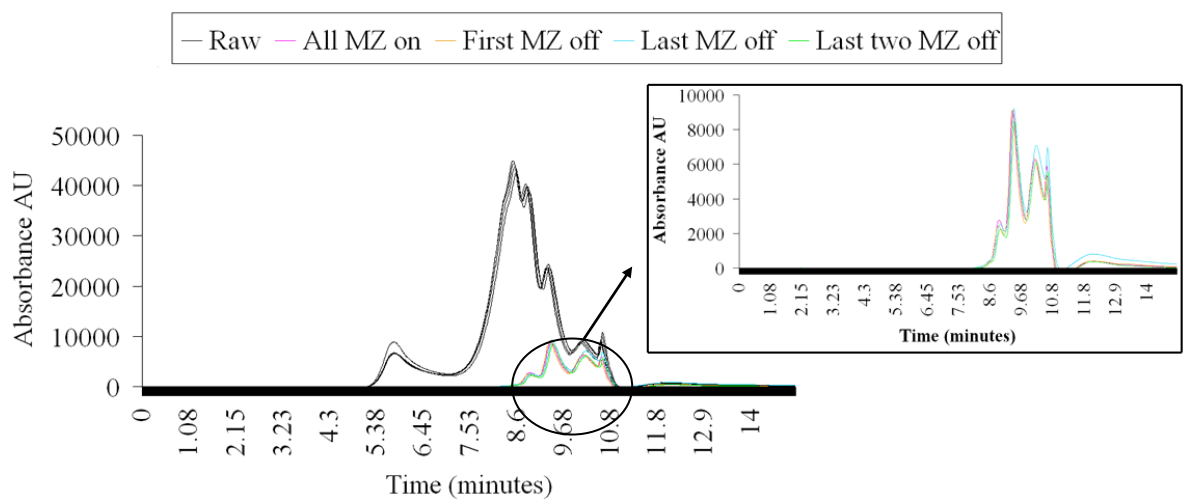


Figure 5-6 HPSEC Curves for raw and clarified water

5.5 Discussion

The present investigation has shown that under the conditions of the test that only one mixing stage of the flocculator is required. The additional mixing stages do not enhance the flocculation process and in fact deteriorate it slightly. Consequently, an operating saving of 66% can be achieved. In the case of the site used in the investigation this equates to an annual saving of £51,000 based on an electricity cost of 7p.KWh^{-1} . Given the upward trend in energy prices the saving is a conservative estimate of the potential savings. With the company having obligations to reduce its carbon footprint the 280t reduction in CO_2 will aid in contributing towards this. Rolling this scheme out across the company would provide a significant reduction in both costs and carbon.

The observed results are contrary to established operational practice where a 3 stage tapered flocculation system is believed to improve floc size (Yukselen *et al.*, 2006). In contrast, results presented here demonstrated a decrease of up to 18% in the final mixing stage irrespective of the operating regime. Previous reported investigations into tapered flocculation have also shown a decreasing floc size when operating at a constant shear rate. For example when flocculating a an aqueous suspension of monodisperse, spherical, polystyrene particles with Alum at a dose ratio of $1.68 \times 10^{-6} \text{cm}^{-3} \cdot \text{mg} \cdot \text{l}^{-1}$ Spicer *et al.*, (1998) reported a 53% decrease in median floc size across the system. The results were explained in terms of the increased density of the flocs after the first stage causing elevated breakage as they travelled through the later compartments. Both the current study and the others were a decrease in floc size have been observed all utilised relative long residence times of greater than 30 minutes. In contrast, during experiments with a shorter residence time of 10 minutes the tapered flocculation system was seen to increase floc size as a result of the decrease shear rate zones. Consequently, residence time appears to be a crucial factor in the impact of flocculator performance. Such an observation is supported by the growth profiles which suggest around 10 minutes to be required for flocs to reach a steady state size.

5.5 Conclusion

In this scenario, under optimum coagulation conditions with DAF clarification the following was demonstrated:

- A 66% reduction in mixing cost (final two stages of flocculation turned off) could be achieved without any detrimental impact to floc characteristics or removal efficiencies
- A £51,000 pa saving (at 7p KWh), or an equivalent of 280t CO₂ reduction could be achieved on site by reducing mixing
- Tapered flocculation provides no benefit to floc structure or removal efficiencies

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6. Synthesis

Table 6-1 Project review

Chapter	Key Findings
Literature Review	Hydrophobic and hydrophilic acids are the two fractions which exert the greatest influence on treatment works in terms of coagulant dose and residual organics respectively. The DBP yield from both of these fractions varies temporally and spatially. Optimisation of an upland waters demonstrated the floc process, as well as organics removal is heavily influenced by zeta potential (-10mV and +8mV) and DOC:FE ratio (1:1).
Long Term Organics Monitoring	Seasonal trends in DOC and THMFP levels were measured under optimised and current operational conditions. Results indicated that UV ₂₅₄ could be used to predict coagulant dose and zeta potential could be used to indicate optimum coagulation conditions for DBP precursor removal for 16 sites. Results were utilised to analyse the cost of optimisation for organics removal, with sites then ranked in order of suitability for low pH coagulation.
Impact of different Source Waters on floc characteristics	Improved floc properties and organics removal can be achieved through optimisation of the zeta potential for all waters, however removals and floc properties can vary depending on the source water. Understanding of the fractional make up is thus important to assess the potential for optimisation of the coagulation process. Providing the electrostatic forces are minimised, increasing the NOM content of the floc matrix will lead to an increase in floc strength.
The scope for potential energy savings in the flocculation process	A site under optimised coagulation conditions with 3 stage flocculation and DAF clarification was demonstrated to have over 200% more energy than was required imparted in to the flocculation process. Turning off two of the three flocculators showed no detrimental impact to floc size distribution or removal efficiencies. As such a £51,000 pa saving (at 7p KWh), or an equivalent of 280t CO ₂ reduction could be achieved on site.

Findings have highlighted the temporal and spatial variability in organic material, both in total concentration as well as fractional make up (Wei *et al.*, 2008; Kenichi *et al.*, 2005). The operational implications of elevated periods of organics tend to be

detrimental to the process efficiency of clarification and filtration, leading to a reduction in filter run times and an increase in organic residuals (Eikebrokk *et al.*, 2004). In terms of fractional variations, increases in the charged hydrophobic material need to be met by increasing the coagulant demand in order to effectively reduce the negative charge and promote flocculation. If this demand is not met then organics residual and in turn DBP will rise. Increases in the uncharged hydrophilic material has causes a rise in organics residual, as since they have minimal charge they can not be removed via traditional coagulation methods. These increased organics levels are likely to contribute significantly towards DBP concentrations and breaches in THM regulations. To reduce the chance of failure, sites need to be optimised with regards to organics removal, however conditions need to be monitored due to changes in source water quality.

An optimised coagulant dose (1:1 ratio of DOC:Fe) can be achieved on site via the use of online monitoring of UV₂₅₄ absorption. Utilisation of a feed forward system within a control loop would ensure that an optimised dose could be provided even if water conditions vary. UV₂₅₄ absorption was found to have a strong relationship to DOC on a site by site basis. Using UV as a proxy for DOC, the 1:1 ratio of coagulant to DOC can thus be applied to site.

UV has the limitation of not providing any information on the colloidal charge within a system, so even if the correct amount of coagulant was being dosed, operating conditions could still be considered sub-optimum. Optimised charge conditions are deemed to be between $-8 < \zeta > +5 \text{mV}$ for organics removal and enhanced floc properties. As such, monitoring of the zeta potential for the dosed raw water could be utilised to monitor the acid dose to ensure enough positive charge was imparted in to system to allow charge neutralisation.

New dosing strategies show that optimisation improves clarified water quality for all water conditions both in removal efficiency and floc properties. As such, it was shown that the flocculation process is currently over engineered to a significant degree and that flocculated energy could thus be reduced on sites without any detrimental impact to flocs strength or size. Savings with regards to OPEX could thus be made through optimisation and re-evaluation of the flocculation process for a number of sites. This

information could also be used during the design stage of flocculation to reduce footprint and CAPEX.

The benefits of optimisation will differ depending on the site. This is related to the spatial differences observed in NOM fractions in addition to that of other parameters, such as alkalinity, which will determine the amount of NOM that can be removed and the acid dose, respectively. As such there is a trade off between the amount of NOM that can be removed and how much it would cost. Sites which respond well to optimisation (typically associated with high hydrophobic fraction content) and have low alkalinities are best suited for optimisation. Whilst high alkalinity water with a high hydrophilic content would be better off seeking alternative treatment if THMs were an issue.

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