CRANFIELD UNIVERSITY

Dan-Mihai Golea

Robust natural organic matter removal from Scottish water sources of variable DOC content

Cranfield Water Science Institute
STREAM Industrial Doctorate Centre

EngD
Academic Year: 2013- 2019

Supervisor: Professor Peter Jarvis
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This thesis is submitted in partial fulfilment of the requirements for the degree of Engineering Doctorate

(NB. This section can be removed if the award of the degree is based solely on examination of the thesis)

ABSTRACT

Natural organic matter (NOM) is found ubiquitously in raw water and is known to react with the chlorine used in water treatment to produce disinfection by-products (DBPs), some of which are potentially harmful to human health due to their links with cancers. Trihalomethanes (THMs) and haloacetic (HAAs) acids are the two types of carbonaceous DBPs widely regulated. The THMs and HAAs are widely regarded as being good indicators of the presence of the more than 500 other DBPs that have been found in treated drinking water. At large and medium sites in Scotland, the coagulation-flocculation process has long been the main control barrier for removal of the precursors for DBPs. At small sites, ultra and nano filtration membrane filtration processes have been considered a good solution due to their small footprint requirement and large volume of water output. In addition, granular activated carbon (GAC) filtration has long been employed for removal of organic matter. However, increases in the organic content of raw waters, stricter regulatory requirements and concerns over coagulant cost and availability have driven the reconsideration of how NOM laden water sources in Scotland are treated. This thesis investigated the approaches required to increase the robustness of drinking water supply to mitigate against these factors.

A stronger correlation was found between commonly measured water quality parameters and DBPs in raw water sources compared to treated water, which was as a result of the lower hydrophobic content of the latter. However, the DBP removal as a function of DOC reduction was calculated and revealed coagulation using ferric sulfate in the pH 4-5-5-5 range as the most feasible solution at large and medium sites. The use of GAC media with high pore uniformity would be appropriate at large or medium sited where up to 50% DOC reduction would be sufficient to control DBPs. At small sites, the tighter pore size membranes showed improved THM precursor removal, whilst most of these maintained a throughput of within 90% of the current membranes.

Keywords:

Natural organic matter, disinfection by-products, coagulation, spiral wound membranes, granular activated carbon

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Of course, I'd like to acknowledge my STREAM colleagues from Cohort V, especially the Scottish Water contingent Andy, Rob and Ryan for all their good humour and camaraderie.

Last, but certainly not least, I'd like to thank my fiancée, mother and brother for their patience and for putting up with my attempts to explain water treatment intricacies throughout this process.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AOC	Assimilable organic carbon
AQC	Assurance quality controls
BDOC	Biodegradable dissolved organic carbon
CA	Cellulose acetate
CD	Chlorine demand
CEPCI	Chemical engineering plant cost index
CP	Chloropicrin
CRI	Compliance risk index
Da	Dalton
DBP	Disinfection by-products
DBPFP	Disinfection by-products formation potential
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DWD	Drinking Water Directive
DWI	Drinking Water Inspectorate
DWQR	Drinking Water Quality Regulator
EC	European Commission
EEM-PARAFAC	Fluorescence excitation - emission matrices and parallel factor analysis
EU	European Union
FMAX	Maximum intensity of identified humic like fluorophore in the fluorescence spectrum
GAC	Granular activated carbon
GBP	Great British Pounds
HA	Haloaldehides
HAAFP	Haloacetic acids formation potential
HAN	Haloacetyl nitriles
HK	Haloketones
HMW	High molecular weight
HNM	Halonitromethanes

HNM	Halonitromethanes
HPI	Hidrophilic
HPO	Hydrophobic
i-HM	Iodo trihalomethanesI278/506 ratio of fluorescence absorption and emission
IN	Iodine number
LMH	Litre per meter hour
LoD	Limit of detection
MLD	Million litres per day
MWCO	Molecular weight cut-off
N-DBP	Nitrogenous disinfection by-products
NDMA	N-nitrosodimethylamine
NF	Nanofiltration
NOM	Natural organic matter
NPOC	Non purgeable organic carbon
OC	Organic carbon
Ofwat	Office for Water
PARAFAC	Parallel factor analysis
PPA	Polypiperazine thin-film
S_{BET}	Surface area determined using the Brunauer-Emmet-Teller formula
SD	Standard deviation
S-PS	Sulfonated polyethersulfone
SpW	Spiral wound (membrane)
SUVA	Specific ultraviolet absorbance
TCM	Trichloromethane
tHAAs	Total haloacetic acids
THMFP	Trihalomethanes formation potential
tTHM	Total Trihalomethanes
TOX	Total chlorinated organic carbon
TPI	Transphilic
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency

UV254	Ultraviolet absorbance at a 254 nm wavelength
WHO	World Health Organisation
WLC	Whole life cost
WQD	Water quality determinants
WTW	Water treatment work

1 1Chapter: Introduction

1.1 Background

Disinfection is applied at all water treatment works (WTWs) in the UK to reduce the pathogens in the drinking water to an acceptable level, usually this is achieved using a chlorine based disinfectant. One of the concerns associated with the use of chlorine disinfectants is the formation of disinfection by-products (DBPs). The link between carbonaceous chlorinated DBPs and natural organic matter (NOM) has been recognised and studied for over 40 years (Bond et al., 2011; Hua et al., 2007; Rook, 1977). DBPs are of particular concern in regions where source waters contain elevated levels of organic matter, such as are typical in Scotland. One of the main challenges of removing NOM from Scottish source water is the complex geography of the region and the seasonal variability in water quality (Sutherland et al., 2015; Valdivia-Garcia et al., 2016). This puts pressure on WTWs to be able to react to relatively quick changes in water quality. In order to effectively achieve this, NOM indicators are employed to monitor changes in the water composition and monitor treatment performance. Often, NOM surrogates such as dissolved organic carbon (DOC), UV_{254} absorbance and colour are used. More complex monitoring can also be carried out using, for example, fractionation of the NOM into components of differing hydrophobicity and molecular weight (Hu et al., 2015; Hua et al., 2015). Understanding the links between NOM indicators, treatability and regulated DBPs are considered important to ensure a quick reaction of the WTW operation to changes in the raw water quality and thus limiting the formation of DBPs.

The current approach for control of DBPs in drinking water is to regulate the concentration of trihalomethanes (THMs) to 100 µg/L. The underlying principle here is that by controlling THMs, other DBPs are also minimised. However, as more than 500 different DBPs have been identified, these relationships are not clearly defined for all DBPs (Richardson, 2002). There are plans to introduce a new regulatory limit of either 60 or 80 µg/L for either five or nine halo acetic acids (HAAs) to provide a more complete picture (European Commission, 2018).

From a total of ~245 sites around 90% of the drinking water produced in Scotland is through conventional coagulation with an aluminium salt followed by clarification and filtration processes. This has been the preferred NOM removal solution at large sites for the past 150 years. However, approximately 50% of the total numbers of WTWs are required to treat the remaining 10% of the drinking water. This is due to the sparse population density in the highlands and islands of Scotland. Of these, 45% employ membrane filtration, and some 15 are a spiral wound (SpW) membrane configuration. At these small and remote sites the frequent presence of an operator is not economically feasible. The SpW membranes are employed due to their low footprint and the high volumes of water treated.

A number of factors in relation to treatment of NOM laden water sources have challenged Scottish Water to re-evaluate how their treatment practice should be adapted to ensure robust treatment of high DOC water sources. These include:

a) changes in raw water quality that have caused increases in the concentrations of organic matter present in surface waters, an effect that has been seen more broadly in northern Europe and north America (Bhatnagar et al., 2017).

b) ongoing challenges in meeting current and proposed regulations associated with DBPs in final treated drinking water.

c) the remoteness and small size of many of the WTWs in Scotland. This factor influences treatment process selection and favours systems that require minimal maintenance and operator time.

d) the availability of new treatment products, particularly in relation to membranes and adsorbents, that may offer opportunities for enhanced removal of NOM from water.

This research considered how Scottish Water could change their operational practice to respond to these challenges and opportunities to improve NOM removal and reduce the level of DBPs seen in drinking water in Scotland.

1.2 Research development

The work presented herein was completed as part of the STREAM Industrial Doctorate Centre (IDC) in conjunction with the industrial partner, Scottish Water.

The first stage of this work was an assessment of the current situation within Scottish Water with respect to water quality and links to DBPs. The appropriateness of employing water quality parameters to determine THM and HAA regulatory breaches were investigated. Once the current position was assessed, a feasibility study was undertaken to determine how changing coagulant conditions might be a simple way by which water quality improvements could be made at coagulation sites in the Scottish Water region.

Adsorption of NOM onto GAC media was then considered as a means of improving overall levels of organic matter removal. As a relatively passive process, GAC presents opportunities for deployment at both small and remote WTW sites. In addition, given the broad range of GAC media available, understanding the features of GAC media that control NOM removal was considered an important aspect to research to determine the most appropriate position of GAC in the WTWs flowsheet.

Conventional coagulation and flocculation processes are often not practical at small and remote sites. To this end, spiral wound membrane filtration is often employed. At the time of the research, there was only one spiral wound membrane product that had been approved for use by the drinking water quality regulators (the Drinking Water Inspectorate in England and Wales and the Drinking Water Quality Regulator for Scotland). Therefore, there was a need to investigate the performance in terms of throughput and DBP precursor removal capability of alternative membrane products.

Subsequently, a risk based strategy to control THM and HAA formation for the next 20 years was proposed. The strategy encompassed the outputs of the current research in view of most reasonable low risk DBP control option when WTW remoteness and raw water quality were considered.

1.3 Aims and Objectives

The overall aim of the research was to understand and critically evaluate the current and alternative solutions for removing NOM as DBPs from waters with variable total organic carbon loads.

It was therefore hypothesised that:

- Faster and cheaper surrogates than measuring DBPs themselves could be used to predict DBP formation in Scottish Water sources.
- Lower disinfection by-product formation could be achieved through a change in coagulant and coagulation conditions at sites that use coagulation-flocculation as the main NOM removal mechanism.
- The removal of NOM is directly linked to the physical properties of granular activated carbon. With this information the position of GAC as either a “roughing” or “polishing” stage could be determined.
- Alternative membranes with smaller pores than those currently used would reduce the overall disinfection by-product formation.

The following objectives were set to test the four hypotheses and deliver against the overall aim (Figure 1-1):

Objective 1: To fully appraise the validity of using surrogates in the form of routinely measured water quality parameters (UV_{254}, DOC and colour) and the NOM hydrophobic content to determine THM and HAA formation.

Objective 2: To determine the water quality and economic benefits of employing optimised coagulation with alum or ferric sulfate compared to the current status quo with respect to improving NOM removal in view of ever increasing regulatory requirements and chemical costs.

Objective 3: To determine the physical features of GAC that control NOM removal when used at the beginning or the end of the WTWs to enable informed decisions to made on media selection.

Objective 4: To identify how membrane pore size and selectivity ratings influence NOM removal and THM formation based on treatment of a single water source in challenging conditions of NOM loading and high temperature.

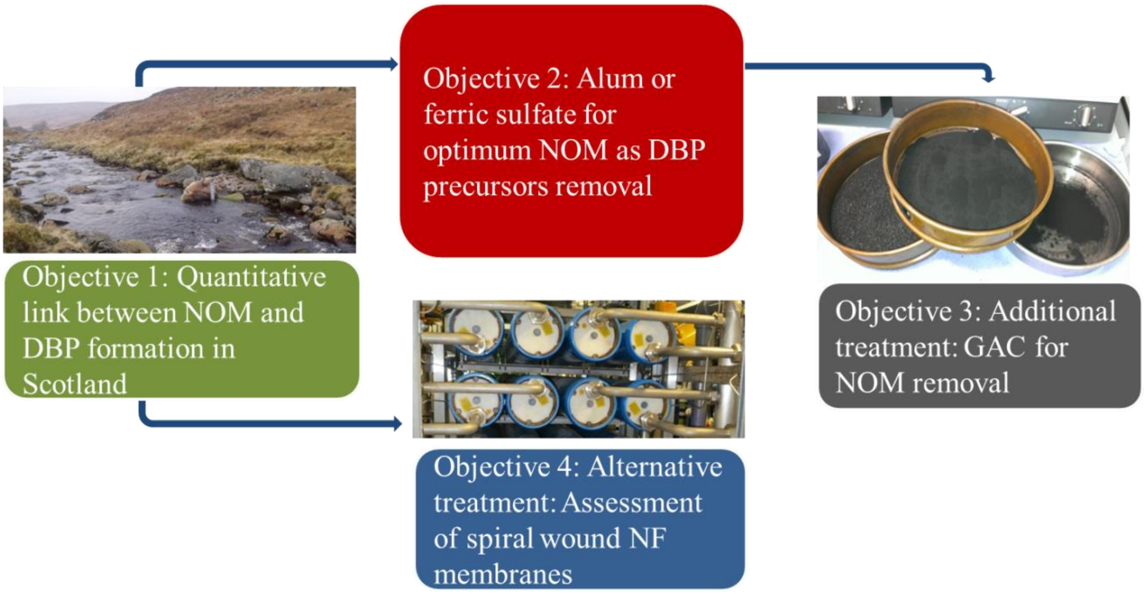

Figure 1-1 Graphical representation of the concepts behind the four objectives and how they link together.

1.4 Thesis Structure

The thesis was compiled as a series of chapters formatted as journal papers. For all the papers, Dan M. Golea was the primary author and editing was undertaken by the EngD supervisory team: Prof. Simon S. Judd, Prof. Bruce Jefferson and Prof. Peter Jarvis. All experimental work, with the exception of the historic data used in chapters 2 and 3 (Scottish Water archives), and the GAC physical characterisation (St Andrews University), was designed, coordinated and completed by Dan M. Golea at Cranfield University (UK) and Scottish Water Laboratories (UK), with contributions from Scottish Water laboratory technicians, and MSc students. The membrane pilot rig used to compare different membrane products was available courtesy of Scottish Water at the Scottish Water Gorthleck Development Centre.

Chapter 2 investigated the validity of correlating trihalomethanes (THMFP) and haloacetic acids formation potential (HAAFP) with routinely measured water quality parameters, in view of forecasting DBPFP. The analysis was undertaken on historic Scottish Water data, sourced from 30 WTWs over a 30 month period. In raw water, stronger correlations were observed between UV_{254}, DOC and HPO and THMFP and HAAFP. The correlations were much lower for treated waters due to the lower HPO (UV_{254} absorbent) content.

(Chapter 2, Paper 1 – published: Golea, D.M., Upton, A., Jarvis, P., Moore, G., Sutherland, S.T., Parsons, S.A. and Judd, S.J. (2017) 'THM and HAA formation from NOM in raw and treated surface waters', *Water Research*, 112, pp. 226–235.)

In Chapter 3, an economic feasibility study was undertaken to understand the potential financial implication of replacing alum sulfate with ferric sulfate to increase DBP precursor removal. Ferric sulfate was the most economically viable option.

Chapter 4 investigated the appropriateness of using GAC at two positions in the water treatment train. When treating water that had been marginally treated, the media was overloaded with NOM and was exhausted much sooner than the media that treated more extensively treated water. However, media with the most uniform pore size distribution was the best performer at both sites. In particular, the 5-10 nm mesopore volumes were identified as an important physicochemical media characteristic for NOM removal.

Alternative ultrafiltration/nanofiltration spiral wound membranes products were tested in view of reducing THM formation in Chapter 5. The THM generation in effluent correlated well with residual DOC as the proportion of highly reactive HPO fraction was found to decrease with the membrane pore size. The outcomes of this research helped obtain DWI approval for a new spiral wound membrane product in the UK. (Chapter 5, Paper 2 – published: Golea, D., Sutherland, S., Jarvis, P. and Judd, S. J. (2016) 'Pilot-scale spiral wound membrane assessment for THM precursor rejection from upland waters', *Separation Science and Technology*, 51(8), pp. 1380–1388.)

An overall discussion on treatment recommendations for treatment of NOM laden water sources for Scottish Water strategy was presented in Chapter 6. It was argued that a combination of optimised ferric sulfate coagulation at large and medium works and nanofiltration membranes at small works, respectively, could reduce the risk of THM regulatory breaches.

Finally, Chapter 7 presents a summary of key conclusions and potential further work that may be necessary to increase the robustness of WTWs treating raw waters with highly variable organic content. Alternative and novel coagulants, adsorbents and spiral wound membranes were recommended for further testing. A summary of the thesis structure and paper submission status is shown in Table 1-1.

Table 1-1 Thesis structure and paper submission status.

Chapter	**Objective**	**Title**	**Status**
1	--	Introduction	--
2	1	THM and HAA formation from NOM in raw and treated surface waters	*Water Research*, 112, pp. 226–235
3	2	Comparison between Al and Fe based coagulants for natural organic matter removal from upland surface waters	In preparation for submission to *Water Research*
4	3	The influence of GAC physicochemical properties on natural organic matter removal	In preparation for submission to *Water Research*
5	4	Pilot scale spiral wound membrane assessment for THM precursor rejection from upland waters	*Separation Science and Technology*, 51(8), pp. 1380–1388
6	--	Implications of the work: A strategy for DBP control in Scottish Water	--
7	--	Conclusion and Future Research	--

1.5 References

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2 Chapter: THM and HAA formation from NOM in raw and treated surface waters

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2.1 Abstract

The disinfection by-product (DBP) formation potential (FP) of natural organic matter (NOM) in surface water sources has been studied with reference to the key water quality determinants (WQDs) of UV absorption (UV_{254}), colour, and dissolved organic carbon (DOC) concentration. The data set used encompassed raw and treated water sampled over a 30-month period from 30 water treatment works (WTWs) across Scotland, all employing conventional clarification. Both trihalomethane (THM) and haloacetic acid (HAA) FP were considered. In addition to the standard bulk WQDs, the DOC content was fractionated and analysed for the hydrophobic (HPO) and hydrophilic (HPI) fractions. Results were quantified in terms of the yield (dDBPFP/dWQD) and the linear regression coefficient R^2 of the yield trend.

The NOM in the raw waters was found to comprise 30-84% (average 66%) of the more reactive HPO material, with this proportion falling to 18-63% (average 50%) in the treated water. Results suggested UV_{254} to be as good an indicator of DBPFP as DOC or HPO for the raw waters, with R^2 values ranging from 0.79 to 0.82 for THMs and from 0.71 to 0.73 for HAAs for these three determinants. For treated waters the corresponding values were significantly lower at 0.52-0.67 and 0.46-0.47 respectively, reflecting the lower HPO concentration and thus UV_{254} absorption and commensurately reduced precision due to the limit of detection of the analytical instrument.

It is concluded that fractionation offers little benefit in attempting to discern or predict chlorinated carbonaceous DBP yield for the waters across the geographical region studied. UV$_{254}$ offered an adequate estimate of DBPFP based on a mean yield of ~2600 and ~2900 µg cm^{-1} absorbance for THMFP for the raw and treated waters respectively and ~3800 and 3000 µg cm^{-1} for HAAFP, albeit with reduced precision for the treated waters. This is an amended version of the published paper.

Keywords: Trihalomethanes; haloacetic acids; UV$_{254}$; dissolved organic carbon; correlation coefficient.

2.2 Introduction

It has long been recognised that natural organic matter (NOM) is the precursor for the key chlorinated carbonaceous disinfection by-products (DPBs) of trihalomethanes (THMs) and haloacetic acids (HAAs) following chlorine disinfection (Bond et al., 2011; Hua et al., 2007; Rook, 1977). Experimental investigations in this field have been based either on chemical analogues of NOM (Bond et al., 2012, 2016; Gao et al., 2013), intended to assess the relative reactivities of key organic molecular functional groups, or empirical/heuristic studies of real waters. In the latter case DBP formation can be measured either in situ, i.e. in the treated water resulting from the site-based chlorination step (Sutherland et al., 2015), or more usually ex-situ using standard chlorination conditions to give the disinfection by-product formation potential (DBPFP). Normalising the DBPFP (THMFP and HAAFP for THM and HAA formation potential respectively) against the organic carbon (OC), or some other water quality determinant (WQD) provides the yield; if normalised against OC then this parameter is expressed in µg or µM DBP per mg or mM OC (or dissolved organic carbon, DOC).

Studies based on real waters (Table 2-1) have generally been limited to a small number (2-6) of water sources. Whilst other DBPs have been studied, and specifically nitrogenous species such as haloacetyl nitriles (HANs) and N-nitrosodimethylamine (NDMA), the focus has generally been on the carbonaceous species and on THMs in particular. However, nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HAN) and halonitromethanes (HNM) are increasingly of health concern. These compounds have been shown to be more toxic than the carbonaceous DBPs (Plewa et al., 2002) and with a greater impact on the overall toxicity from halogenated species in chlorinated waters

(Zeng et al., 2016) such that, once tested on animals, some have been incorporated in the WHO drinking water guidelines (World Health Organization (WHO), 2006).

A key aim of many reported studies has been to identify readily measurable water quality determinants (WQDs) which may provide a reliable indication of carbonaceous DBPFPs. As such, the linear correlation coefficient (R^2) is of key interest, since this indicates the legitimacy of employing the WQD as a surrogate for DBPFP. Reported DBPFP correlations have generally included either UV_{254} absorption or DOC as the benchmark. Some studies (Hua et al., 2015; Jung et al., 2008; Wei et al., 2008) have correlated yield with SUVA, the equivalent of DBP concentration or formation potential vs. UV_{254}, since both yield and SUVA (UV_{254} absorbance per unit DOC concentration) are normalized against DOC concentration. In recent years WQDs using fluorescence spectroscopy, based on the 2D contours of excitation-emission fluorescence spectra, have been employed to try and improve the correlation (Pifer et al., 2012, 2014b; Yang et al., 2015) Fluorescent components specific to molecular species recognised as DBP precursors are identified and quantified using PARAFAC analysis, employing methods originally proposed by Stedmon and co-workers (Stedmon et al., 2008).

Table 2-1 Summary of recent carbonaceous DBP formation correlation studies, 2008 onwards

DBP(s)	**Water source**	**WQD(s)**	**Fractionation**	**Strongest correlation (R^2)**	**Reference**
THMs	Raw/ultrafiltered surface water, Sd	UV_{254}, DOC	None	THMs vs DOC (0.76/0.58 raw/ ultrafiltered)	(Sutherland et al., 2015)
THMs, NDMA	Clarified surface waters, SC USA	UV_{254}, EEM–PARAFAC	None	THMs vs DOC (0.95)	(Yang et al., 2015)
THMs, HAAs, TOX, HAN, CP	Clarified surface waters, NA	SUVA	Chem + phys	THAAs yield vs SUVA[1] (0.80)	(Hua et al., 2015)
THMs, HAAs	Wastewater, Tu	UV_{272}, pH, Cl_2/DOC	None	THMs vs ΔUV_{272} (0.91-0.99, pH dep.)	(Uyak et al., 2014)
TCM	Surface water, WA USA	UV_{254}, DOC, EEM–PARAFAC	Chem	TCMFP vs $I_{278/506}$ (0.88)	(Pifer et al., 2014a)
THMs	Surface water, WA USA	UV_{254}, DOC, EEM–PARAFAC		TTHMFP vs UV_{254} (0.89)	(Pifer et al., 2014b)
THMs, HAAs	Surface water, Tu	UV_{254}, DOC, EEM–PARAFAC	Chem + phys	No significant correlation	(Karapinar et al., 2014)
THMs	Surface water, WA USA	CD, SUVA, EEM–PARAFAC	None	TCM vs F_{MAX} (0.84)	(Pifer et al., 2012)
THMs, HAAs, HAN, HKs,HAs, HNMs, i-THMs	Treated surface and borehole waters, England and Wales	NPOC, UV_{254}, SUVA,	None	Has vs UV_{254} (0.86)	(Bougeard et al., 2010)
THMs, HAAs	Raw/treated/surface waters, Italy, WA and DC,	UV_{272}, UV_{254}, TOC, DOC, SUVA	Chem	THM vs UV_{254} (0.99)	(Roccaro et al., 2009)

	USA				
THMs	Surface waters, Ch	SUVA	Chem + phys	THM yield vs SUVA[1] (0.39)	(Wei et al., 2008)
THMs	Clarified surface waters, SC USA	BDOC	None	TTHMFP vs BDOC (0.82)	(Teksoy et al., 2008)
THMs, HAAs and TOX	Surface waters, Ko	SUVA	Chem	TCM yield vs SUVA[1] (0.90)	(Jung et al., 2008)

BDOC Biodegradable DOC; NPOC non purgeable organic carbon; CD Chlorine demand; Ch China; CP Chloropicrin; DC District of Columbia; EEM–PARAFAC Fluorescence excitation–emission matrices and parallel factor analysis; FMAX Maximum intensity of identified humic-like fluorophore in the fluorescence spectrum; HAN Haloacetylnitrile; HA haloaldehydes, HK haloketones; HNM halonitromethanes; i-HMs iodo-THMs I278/506 Ratio of fluorescence absorption and emission; Ko Korea; nc No correlation; SC South Carolina; Sd Scotland; TCM Trichloromethane; TOX Total chlorinated organic carbon; Tu Turkey; WA Washington State; ΔUV272 Differential UV absorbance (Korshin et al, 1999).

[1] Yield vs SUVA is directly proportional to DBP concentration or FP vs. UV_{254}.

There has also been a substantial body of work analysing the influence of individual chemical and/or physical fractions of the organic material on the DBPFP and/or yield. In such studies chemical fractionation is applied on the basis of the degree of hydrophobicity of the organic material and physical fractionation based on molecular size. Fractionation studies have pointed to the hydrophobic (HPO) fraction and high molecular weight (HMW) components as having the highest THMFP (Hu et al., 2015; Hua et al., 2015). However, other organic fractions, and specifically the transphilic (TPI) fraction, of the NOM can contribute significantly to the overall DBPFP (Li et al., 2014). The HPO content alone thus cannot reasonably be used as the basis for either informing the appropriate chlorination process conditions or estimating the DBP levels in the treated chlorinated water. Moreover, fractionation methods do not lend themselves to on-line monitoring. Against this, since aromatic, humic compounds predominate in the HPO fraction (Bessiere et al., 2009; Weishaar et al., 2003), it may be expected for UV absorption (UV_{254}) to provide a reasonable indication of DBP formation potential (DBPFP) – as demonstrated in previous studies (Weishaar et al., 2003).

The current study assesses the validity of correlating THMFP and HAAFP against routinely-used water quality determinants of UV_{254}, colour and DOC, as well as the hydrophobic chemical fraction, based on a large data set (30 water treatment works, WTWs). The data set, encompassing a significant geographical region (Scotland) and time period (over two years) compares yield trends for raw and treated waters to assess the precision of the trends for both streams. The statistical significance of the yield correlations are quantified through classical linear correlation coefficient determination, allowing an appraisal of the actual practical viability of UV_{254} monitoring as a tool for predicting DBP formation.

2.3 Materials and methods

2.3.1 Sampling

The study was based on WTWs in Scotland employing conventional clarification with an alum coagulant. The 30 sites of interest (~15% of the total WTWs within Scotland) were selected based on high THMFP levels recorded for the treated waters (Valdivia-Garcia et al., 2016). All sites were fed with surface water, predominantly lowland (60%) or island (40%). 80% of the sites were located in the west of Scotland, the remaining 20% being evenly split between North and South (Figure 2-1).

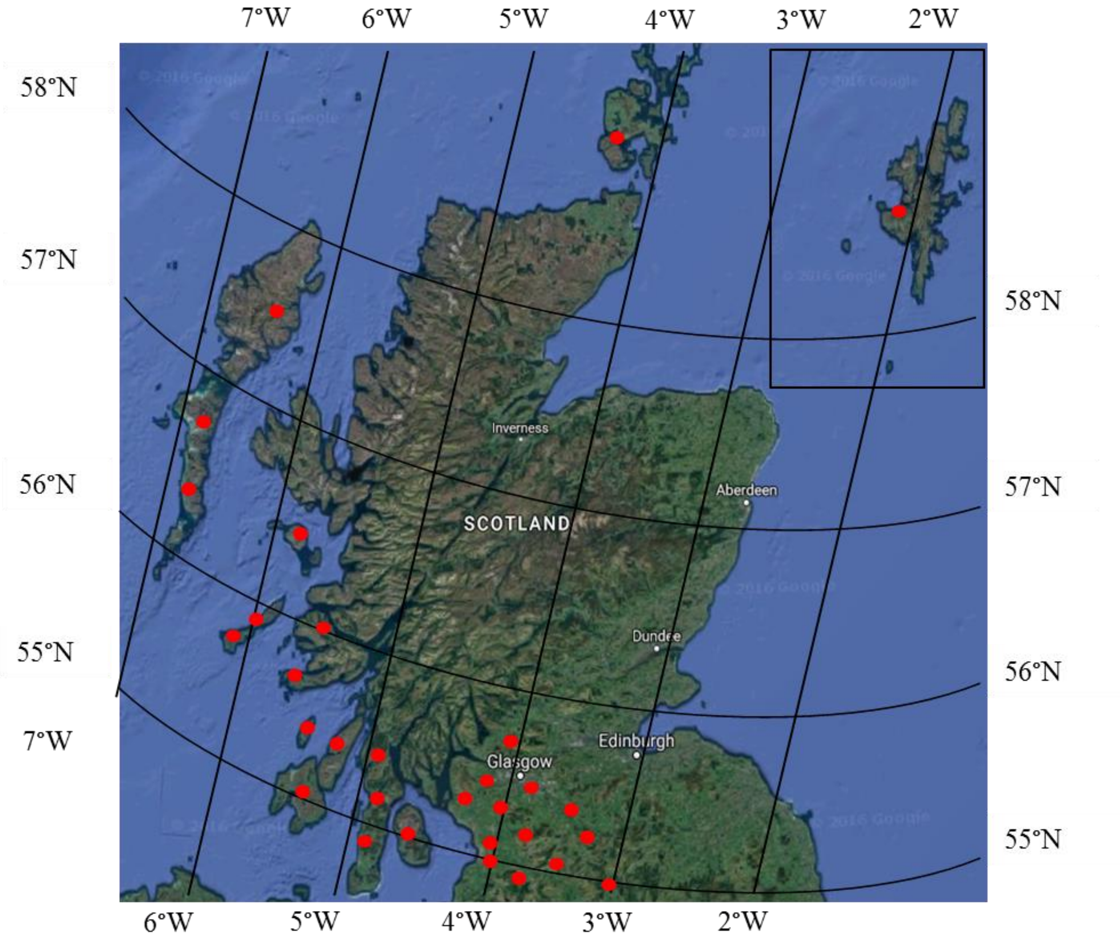


Figure 2-1 Map of Scotland highlighting the locations and coordinates of the WTWs investigated.

2.3.2 Sample analysis

Raw and treated water samples were collected over an 18-30 month period between January 2013 and June 2015 and analysed at the Scottish Water UCAS-accredited Edinburgh laboratories. Colour, pH, zeta potential, turbidity, UV_{254} absorbance and DOC concentration were determined according to published methods (APHA, 2012; Goslan et al., 2009). Assured quality controls (AQCs) were used so to account for data anomalies relating to equipment malfunction or technical error; data for an AQC reading with a difference of more than 15% were repeated or removed. The complete data set comprised of 330 and 205 data points for raw and treated water respectively, ranging from 10 to 25 samples per site depending on the time period.

Chemical fractionation into HPO, TPI and HPI (hydrophilic) organic matter was according to previously published methods (Bessiere et al., 2009), with the sample pH adjusted to 2.5 from the standard pH of 2 to counter precipitation of sparingly soluble organic solutes. Chlorination was undertaken on water sample diluted to a concentration of 1 mg C/L, buffered to pH 7 and added to 250 ml glass bottles with glass stoppers. Chlorine, as NaOCl, was added in excess, to ensure that the reaction was not chlorine limited, at a free Cl2:DOC ratio of 5:1; samples were stored in the dark at a controlled constant temperature of 25°C for 7 days. After 7 days, the chlorine in the samples was quenched with sodium thiosulphate crystals and the total trihalomethanes (THMs) and halo acetic acids (HAAs) were determined. THMs were measured using gas chromatography spectrometry with headspace injection using a modified method from USEPA 551 (USEPA, 1998). HAAs were measured using liquid-liquid separation and analysis by gas chromatography with mass spectrometric detection following USEPA method 552.3 (APHA, 2012; Goslan et al., 2009). Each measurement was determined after a minimum of 7 injections.

2.3.3 Statistical analysis

Data was analysed and correlations further investigated by simple linear regression using 95% confidence intervals. The strength and statistical significance of the correlations ($p<0.05$) were investigated further using the Pearson's correlation analysis using a method adapted from Valdivia et al, 2016. The results returned by box plots were confirmed statistically using Kruskal-Wallis analysis, appropriate for non-normally distributed data (Kruskal et al., 1952). Analyses were undertaken using the IBM SPSS Statistics version 22 software package and MS Excel.

2.4 Results and discussion

2.4.1 Water quality

The water quality range across all measured parameters (Table 2-2) indicate data for some parameters to be less scattered than others. Key parameters relating to NOM characterisation (% NOM recovery and %HPO) have standard deviation (SD) values below 15%. The SUVA SD value is similarly fairly consistent at 20% and the mean value of 4.72 and 2.09 L/(mgC.m) for raw and treated water respectively, comparable to those reported for other comparable surface waters (Bougeard et al., 2010; Hua et al., 2015; Pifer et al., 2014a, 2014b; Yang et al., 2015). Other parameters, in particular the colour and tHAA concentration, were more highly scattered due to seasonal impacts. Higher and more variable DOC mean values of 7.74 mg/L ± 43% SD were recorded than those reported for previous studies (Bougeard et al., 2010; Karapinar et al., 2014; Roccaro et al., 2009; Yang et al., 2015), but are characteristic of upland Scottish waters (Sutherland et al., 2015; Valdivia-Garcia et al., 2016). The %HPO fraction was also higher, at 69% in raw water than the figure of 35% reported by Karapinar et al (2014) (HPO=35%), but comparable to values of 72-73% reported for moorland and sub-tropical waters (Bessiere et al., 2009; Phetrak et al., 2016).

2.4.2 Strength of yield correlations

Overall, the strength of linear correlation (the R^2 values and Pearson's coefficient P) between DBPFP and the three WQDs studied for raw and treated water followed the following trends:

a) stronger and statistically significant correlations for THMFP (µg/L) (R^2 = 0.82 ($P = 0.91$, $p<0.05$) and 0.79, ($P = 0.89$, $p <0.05$) for UV_{254} and HPO respectively, Figure 2-2 a) than for HAAFP (µg/L) (R^2 = 0.77 ($P = 0.89$, $p <0.05$) and 0.74, ($P = 0.86$, $p <0.05$), Figure 2-2 c);

b) similar strength and significance of correlation of DBPFP with UV_{254}, HPO and DOC for raw water (R^2 = 0.82 - 0.79 (P = 0.91 - 0.89, $p <0.05$) for THMFP and 0.77 - 0.74 (P = 0.89 – 0.86, $p <0.05$)for HAAFP, Figure 2-2 and Figure 2-3 a ii, c ii)

c) slightly weaker correlations, but still statistically significant with colour (R^2 = 0.77 ($P = 0.88$, $p <0.05$) for THMFP, Figure 2-3 a i, and 0.75 ($P = 0.87$,$p <0.05$) for HAAFP, Figure 2-3 c i, raw water);

d) all correlations were statistically significant ($p<0.05$), although consistently stronger correlations for raw water (R^2 = 0.74-0.82, P = 0.86 – 0.91, $p <0.05$)) than for treated water (R^2 = 0.21-0.63, P = 0.79 – 0.45, $p <0.05$)) (Figure 2-2 and Figure 2-3, a vs. b, c vs. d)

Table 2-2 Average, standard deviation (SD), min and max for raw and treated water samples measured at 30 sites over a period of 18-30 month; the equipment measuring range and lower reporting limit are also provided.

Parameter	Measurement range	LRL[a]	Raw water sample					Treated water sample			
			Min	Max	Mean	%SD		Min	Max	Mean	SD
Calculated DOC(mgC/L)	0-20	<0.2	1.51	21.58	7.34	44%		0.85	3.45	1.80	29%
Measured DOC (mgC/L)	0-20	0-20	1.60	21.40	7.74	43%		0.80	3.70	1.92	31%
NOM fractionation recovery %	N/A	85-115	85	115	95	7%		85	115	95	8%
HPO (mgC/L)	0-20	<0.2	0.97	14.37	4.92	50%		0.40	1.68	0.89	29%
%HPO	N/A	N/A	30.21	83.23	65.90	14%		18.83	63.48	49.66	14%
TPI (mgC/L)	0-20	<0.2	0.24	4.42	1.26	48%		0.2	0.95	0.31	35%
%TPI	N/A	N/A	7.14	28.19	17.34	20%		7.10	34.30	17.48	18%
HPI (mgC/L)	0-20	<0.2	0.2	4.80	1.15	52%		0.22	2.40	0.60	43%
%HPI	N/A	N/A	3.13	48.83	16.76	46%		19.80	74.07	32.87	22%
THMFP yield (µg/mg C)	3.2-312.7**	<3.2	25.00	276.00	121.87	26%		24.00	169	77.80	21%
tTHM4 (µg/L) [b]	N/A	N/A	142.50	3723.6	972.10	58%		47.20	311	148.86	36%
HAAFP yield (µg/mg C)	5.3-200**	<5.3	27.00	336.00	154.27	36%		11.00	171	66.30	33%
tTHAA5 (µg/L) [c]	N/A	N/A	145.60	4729.4	1260.58	67%		21.60	410.4	128.86	49%
pH	N/A	N/A	4.63	9.20	6.86	11%		6.08	9.75	6.87	11%
Turbidity (NTU)	0-250	<0.2	0.20	91.25	2.66	254%		<LRL[a]	1.38	<LRL[a]	-

SUVA (L/mg/m C)	N/A	N/A	0.53	9.17	4.72	23%		0.95	3.64	2.09	20%
UV 254 abs (/cm)	N/A	<0.01	0.03	0.96	0.37	51%		0.01	0.08	0.04	25%
Zeta potential (mV) [d]	N/A	N/A	-31.60	-8.80	-17.66	-18%		-26.30	4.00	-8.53	-53%
Colour (mg/L Pt/Co)	0-60 [e, f]	<2	6.58	190.78	59.14	62%		0.04	5.36	2.16	53%

[a] Lower reporting limit

[b] The total THM is the sum of Chloroform, Dibromochloromethane, Bromodichloromethane and Bromoform

[c] The HAA5 Total is a total of monochloroacetic acetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid and dibromoacetic acid

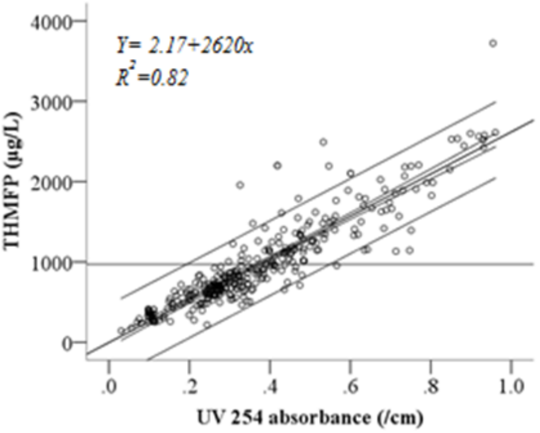
[d] A Zeta potential Standard (DTS1235) is run with every batch of analysis. The result should be 42 + 4.2 mV

[e] Highly turbid samples were filtered through 0.45 µm before measurement

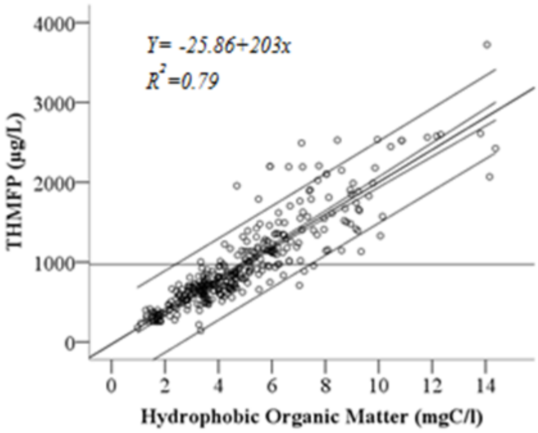
[f] Over the range samples were diluted to >10% of the range

*over the range samples were diluted to fit range

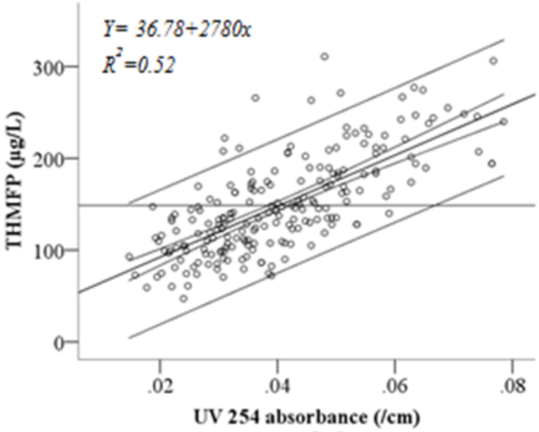
**According to Scottish Water UCAS approved methods the results for the drift standard are acceptable within 15 % of the expected values.



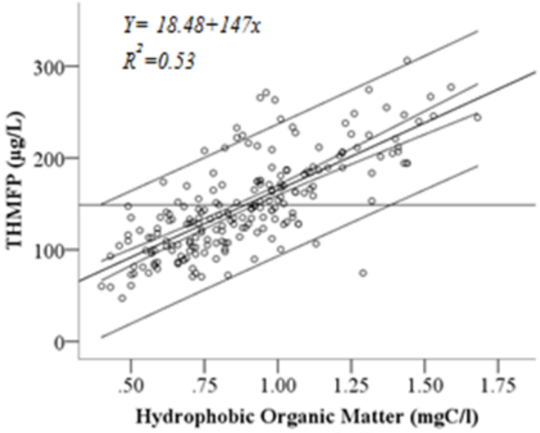
(a, i)



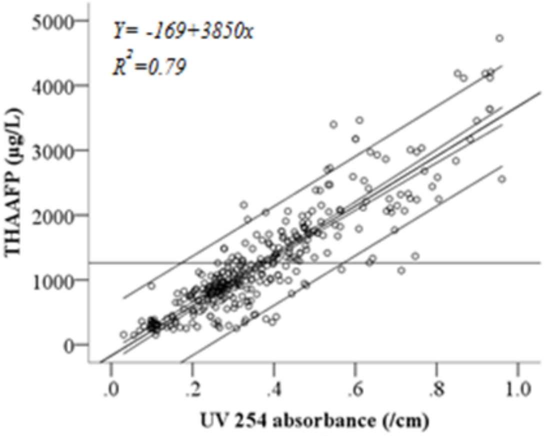
(a, ii)



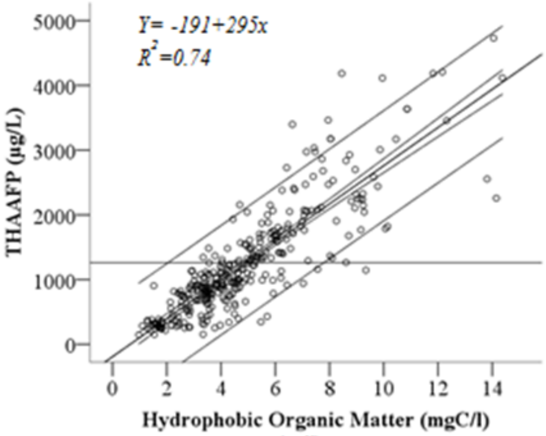
(b, i)



(b, ii)



(c, i)



(c, ii)

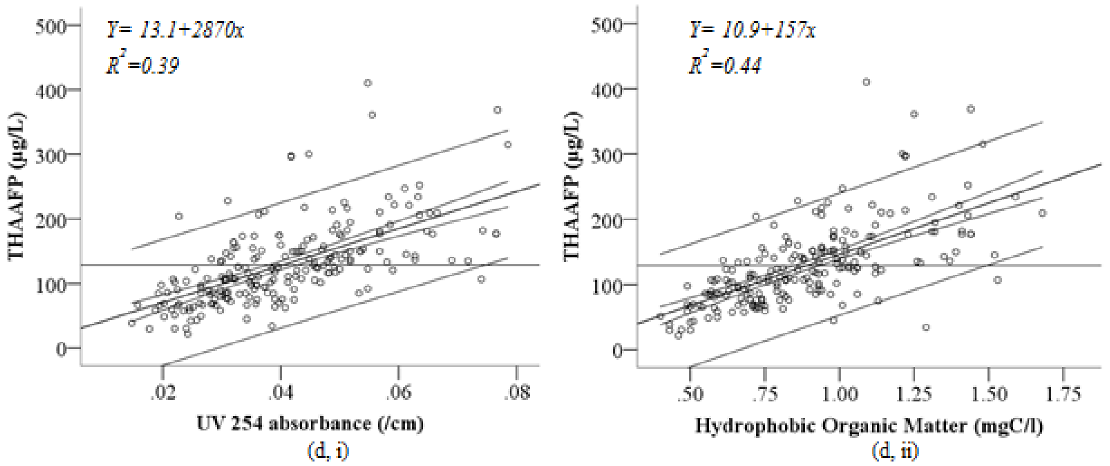
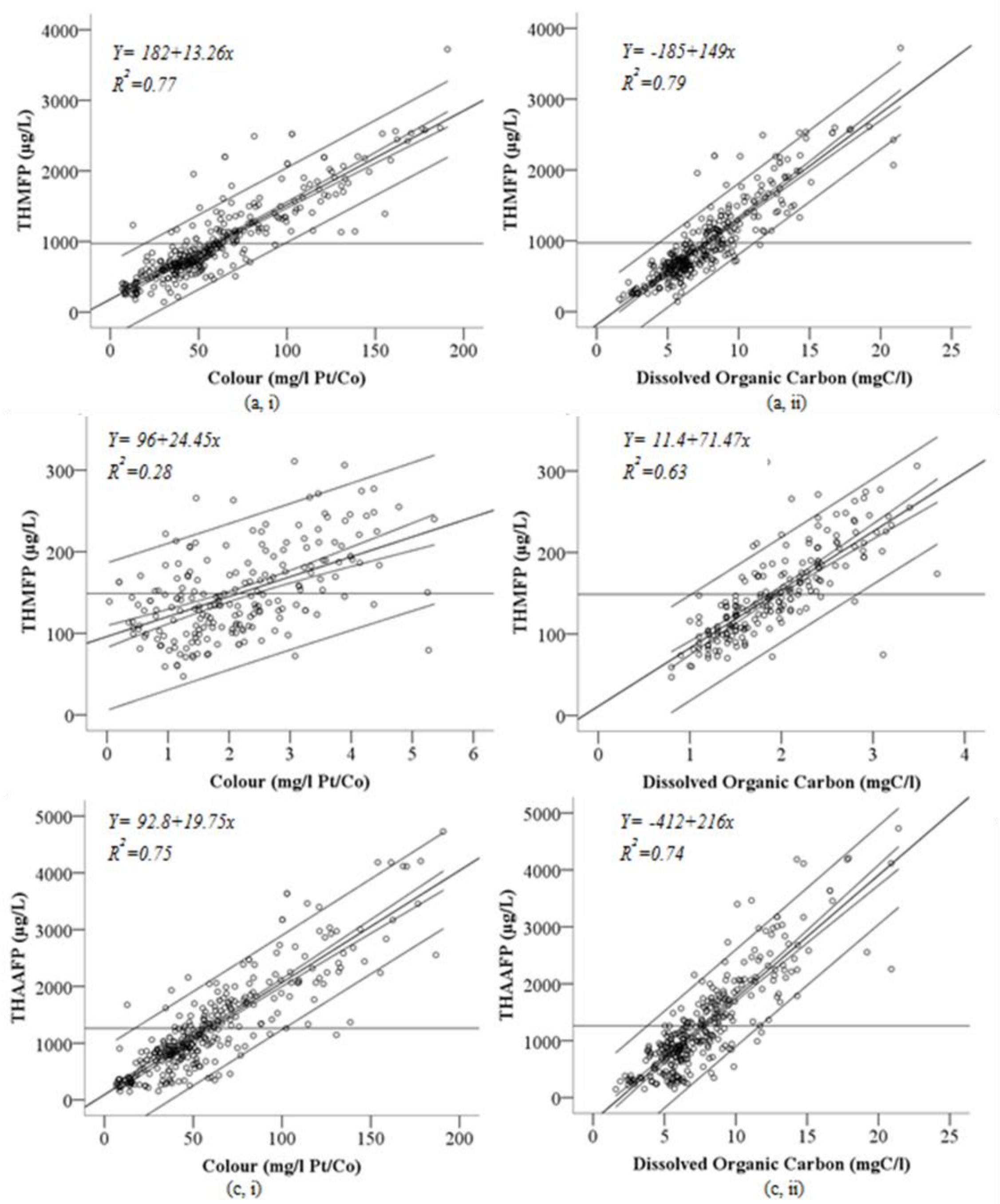


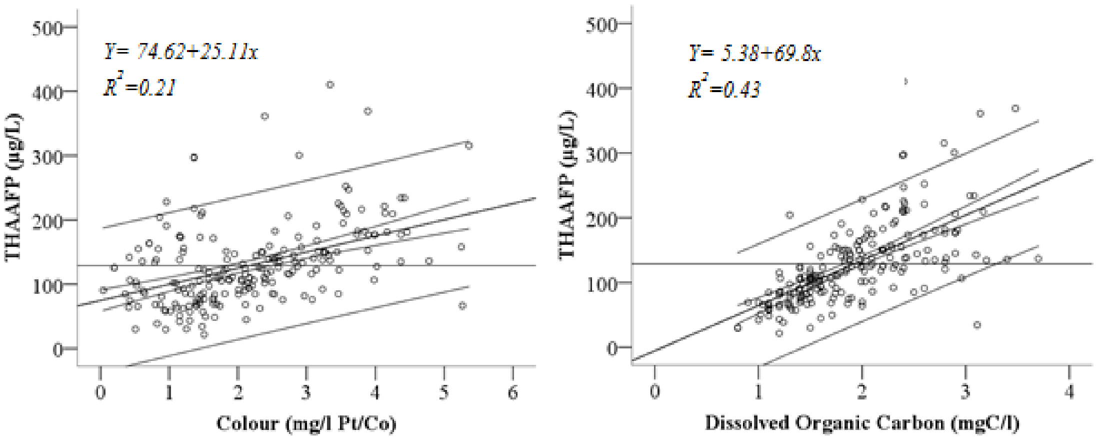
Figure 2-2 Examples of (a, c) raw and (b, d) treated water, for (a-b) THMFP and (c-d) HAAFP vs WQDs of (i) UV$_{254}$, and (ii) HPO, with 95% confidence intervals, confidence intervals to the mean, and mean DBP (µg/L) indicated.

The above observations reflect the higher conjugated molecular content of the raw water associated with aromatic compounds, which previous studies (Li et al., 2014; Weishaar et al., 2003) have associated with DBPFP. The almost identical trend in DBP yield when correlated with UV$_{254}$ and HPO for both THMs and HAAs reflects the expected close correlation of UV$_{254}$ with HPO (Figure 2-3). Colour, on the other hand, correlated more poorly with HPO, particularly for the filtered waters. The increased data scatter in the treated water measurements results from the reduced DOC levels in these samples. These low concentrations are closer to the limit of detection (LoD) of the instruments compared with the higher concentrations of the raw waters, resulting in lower precision. The HPO fraction and overall concentration in the raw water is considerably higher than in the treated waters, and is thus more precisely measured. The chemical characteristics of the HPO in the treated water are also affected by the WTW treatment train.


Y= 182+13.26x
R^2=0.77
THMFP (µg/L)
4000
3000
2000
1000
0
0
50
100
150
200
Colour (mg/l Pt/Co)
Y= -185+149x
R^2=0.79
THMFP (µg/L)
0
5
10
15
20
25
Dissolved Organic Carbon (mgC/l)
Y= 96+24.45x
R^2=0.28
THMFP (µg/L)
300
200
100
0
0
1
2
3
4
5
6
Colour (mg/l Pt/Co)
Y= 11.4+71.47x
R^2=0.63
THMFP (µg/L)
0
1
2
3
4
Dissolved Organic Carbon (mgC/l)
Y= 92.8+19.75x
R^2=0.75
THAAFP (µg/L)
5000
4000
3000
2000
1000
0
0
50
100
150
200
Colour (mg/l Pt/Co)
Y= -412+216x
R^2=0.74
THAAFP (µg/L)
0
5
10
15
20
25
Dissolved Organic Carbon (mgC/l)

(a, i) (a, ii)

(c, i) (c, ii)



(d, i)

(d, ii)

Figure 2-3 Examples of (a, c) raw and (b, d) treated water, for (a-b) THMFP and (c-d) HAAFP vs WQDs of (i) Colour and (ii) DOC, with 95% confidence intervals, confidence intervals to the mean, and mean DBP (µg/L) indicated.

2.4.3 Trends in yield

A comparison of the yield trends (d(DBPFP)/d(WQD)) for THM and HAA indicates them to be very similar. The ratio of the yields for the treated vs. raw water follows exactly the same pattern for both the THMs and HAAs (Figure 2-4). The yield with reference to UV_{254} changes insignificantly between the raw and treated water for either DBP, whereas against DOC the yield is 2-3 times lower for the treated water compared to the feed. This reflects the removal of the more reactive organic carbon components by the water treatment process, in keeping with expectations based on the efficacy of clarification (Parsons et al., 2004). Whilst some of the gradient values relate to correlations of very low R^2 values, particularly for the treated water trends for HAA (Figure 2-2 d and Figure 2-3 d), the data nonetheless strongly indicate similar behaviour for the two DBPs.

The correlation gradient for UV_{254} vs. HPO is reduced only by 40% from feed to treated water, compared with >60% for UV_{254} vs. DOC. Colour is reduced to levels in the treated water which are too low to allow it to be reliably used as a DBPFP surrogate for this stream (R^2 = 0.21-0.28, Figure 2-3 bi and Figure 2-3 di).

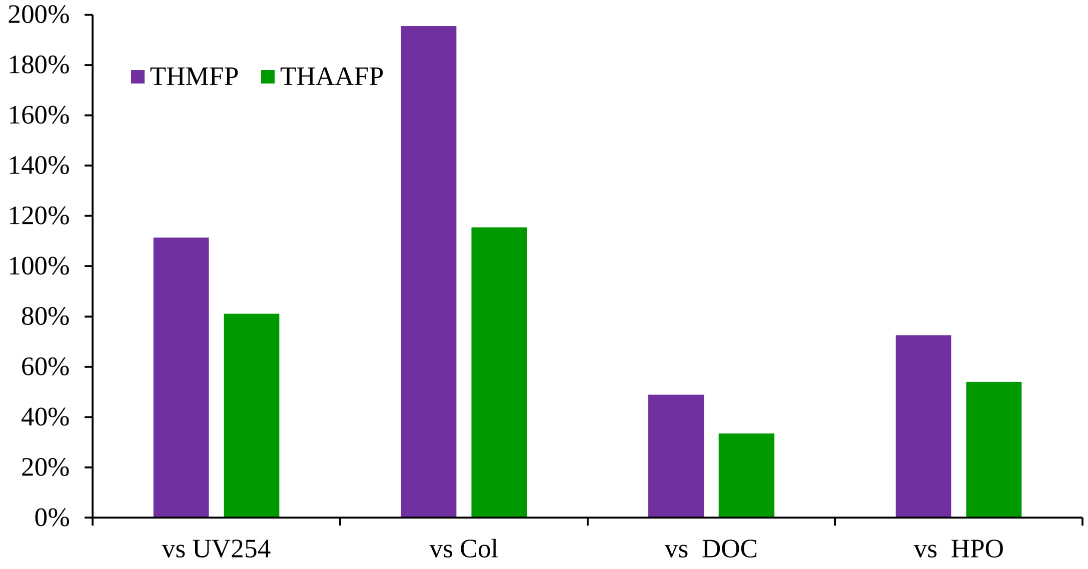


Figure 2-4 Ratio of gradient values, treated vs. raw, for the DBPFP correlations referred to in Figure 2-2 and Figure 2-3.

Comparison with published yield values (Table 2-3) reveals the mean yield values vs UV_{254} from the current study to be broadly similar to those previously reported for raw waters, though the range of reported values is extremely broad (from 1100 to 5300 µg per cm^{-1} for the THM data). The current study raw water THM yield R^2 values are also amongst the highest of those reported (Jung et al., 2008; Li et al., 2014; Pifer et al., 2014b), but lower for the treated waters. Yields are higher for the HAA species cf. THMs, as observed by previous authors (Delpla et al., 2016; Nguyen et al., 2013), with the absolute raw water yield values vs. mg DOC in the current study being somewhat higher than those reported previously (Delpla et al., 2016; Pifer et al., 2014b; Teksoy et al., 2008). The R^2 values for the raw water trends are not substantially lower than those reported for correlation with the fluorescence-based parameter of 0.88 (Table 2-1,(Pifer et al., 2014b)), suggesting that the value offered by more extensive EEM–PARAFAC analysis over that of UV_{254} monitoring is perhaps water quality-dependent.

Table 2-3 DBPFP yield values vs. DOC and UV_{254}, respectively.

DBP	**DOC (μg/mg)**		**UV_{254} (μg per cm^{-1})**		**Reference**
	Y	**R^2**	***Y***	**R^2**	
THM	124	0.90	-	-	(Yang et al., 2015)
THM	-	-	5278^1	0.5	(Hua et al., 2015)
THM	-	-	1220	0.91	(Li et al., 2014)
THM	91	0.75	$3602^{1,2}$	0.89	(Pifer et al., 2014b)
THM	-	-	2156	0.6	(Karapinar et al., 2014)
THM	-	-	1299	0.39	(Wei et al., 2008)
THM	61	0.81	-	-	(Teksoy et al., 2008)
THM	-	-	2405	0.88	(Jung et al., 2008)
THM	-	-	1102	0.65	(Jung et al., 2008)
THM	-	-	1630	0.51	(Weishaar et al., 2003)
THM	-	0.69	-	0.85	(White et al., 2003)
THM	-	0.72	-	0.79	(White et al., 2003)
THM	-	0.76	-	0.98	(White et al., 2003)
THM^3	-	0.90	-	0.99	(Roccaro et al., 2009)
THM^3	-	0.65	-	0.90	(Roccaro et al., 2009)
THM^3	-	0.45	-	0.87	(Roccaro et al., 2009)
THM	-	0.63	-	0.49	(Bougeard et al., 2010)
THM	149	0.79	2620	0.82	Current study, raw
THM	71	0.63	2780	0.52	Current study, treated
HAA	-	-	7743^1	0.80	(Hua et al., 2015)
HAA	-	-	1630	0.94	(Li et al., 2014)
HAA	-	-	2365	0.65	(Jung et al., 2008)
HAA	-	-	1991	0.69	(Jung et al., 2008)
HAA	-	0.53	-	0.35	(White et al., 2003)
HAA	-	0.69	-	0.76	(White et al., 2003)
HAA	-	0.74	-	0.98	(White et al., 2003)

HAA[3]	-	0.84	-	0.98	(Roccaro et al., 2009)
HAA[3]	-	0.84	-	0.98	(Roccaro et al., 2009)
HAA[3]	-	0.75	-	0.94	(Roccaro et al., 2009)
HAA	216	0.74	3850	0.79	Current study, raw
HAA	70	0.43	2870	0.39	Current study, treated

[1] Following a rainfall event.

[2] Converted from molar yields assuming fully chlorinated species to predominate.

[3] Average of 11 water sources

2.4.4 HPO trends

Figure 2-2 and Figure 2-3 indicate generally the same strength in the correlation of DBPFP with UV_{254}, DOC and HPO for both raw and filtered water. R^2 values are consistently lower for the treated water samples due to their generally lower yield values and imprecision associated with the previously-mentioned closeness of the DOC measurement to the LoD of the analytical instrument.

The distribution of the chemical fractions across the 556 water samples taken indicate higher proportions of HPO in the feed than treated waters, but with nonetheless a relatively high proportion of this fraction (50%±7.5) in the treated water (Figure 2-5). Since the HPO fraction is generally considered to be conducive to removal by conventional clarification (Parsons et al., 2004), this outcome suggests that some clarification performance improvement could be attained at many of the sites to reduce this fraction and the subsequent DBPFP.

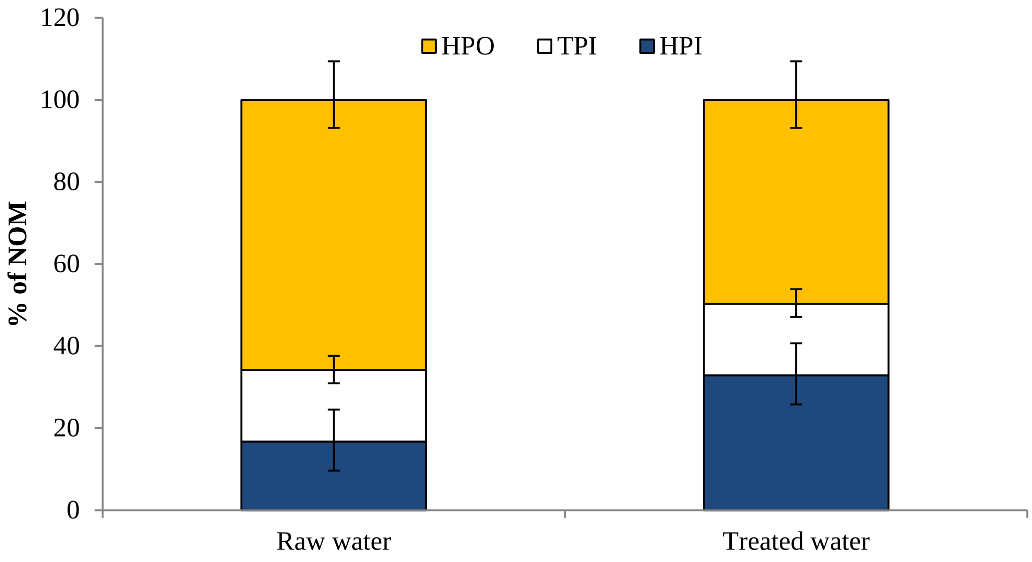


Figure 2-5 Distribution of organic fractions for raw and treated water, respectively.

Whilst there was reasonable consistency in the proportion TPI across all samples, making up approximately 15% of the total OC, the HPI and HPO fractions varied according to the site-based clarification efficacy. Since yield always decreased from feed to treated waters (Figure 2-4) and this can be associated with the change in HPO, a relationship can be discerned between the THM yield %HPO. Clustering of feed and treated water data is evident (Figure 2-6). For these two clusters there exists a threshold %HPO value (%$\mathrm{HPO}_{\mathrm{threshold}}$) at which the proportion of the treated water data points above threshold ($X_{treated}$) is the same as the proportion of raw water data below it (X_{raw}) as per (2-1):

$$X_{treated} = X_{raw} \text{ at } \%\mathrm{HPO} = \%\mathrm{HPO}_{\mathrm{threshold}} \qquad (2\text{-}1)$$

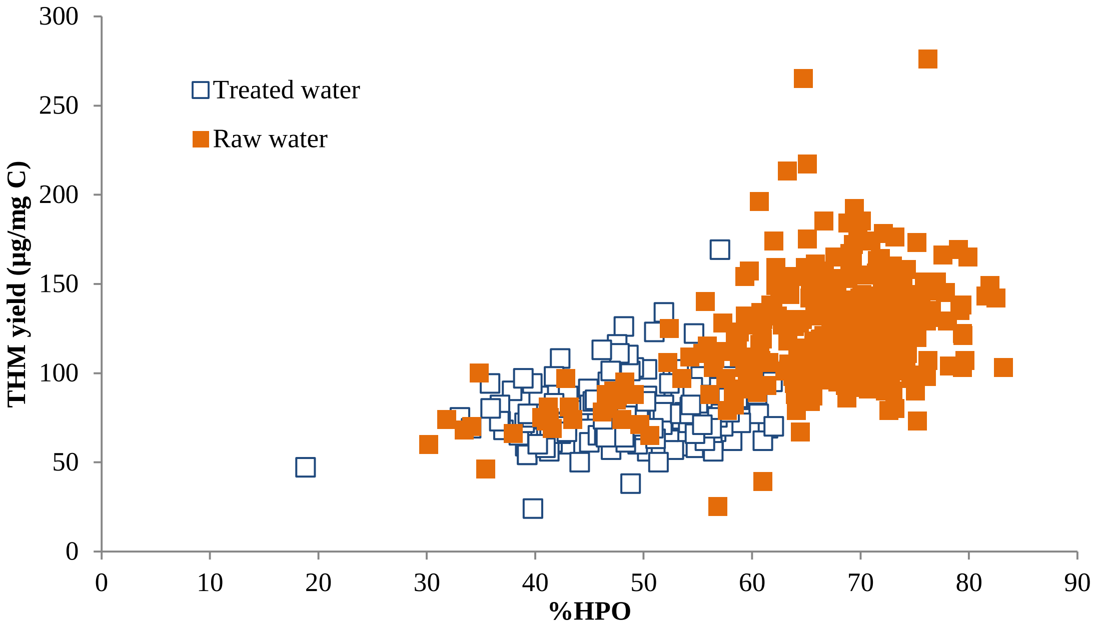
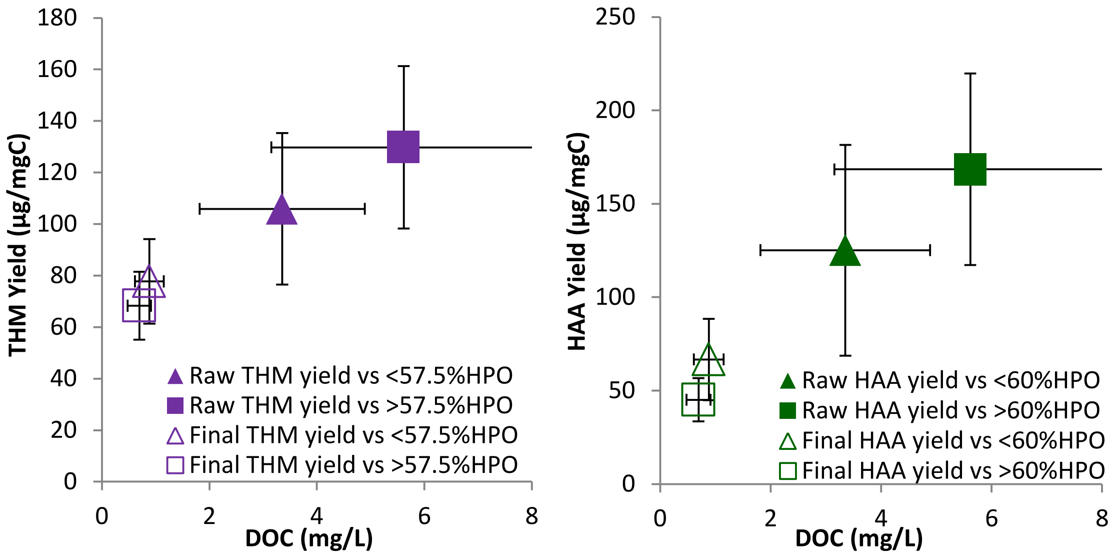


Figure 2-6 Correlations between yield THM vs %HPO, for raw and treated water samples.

Analysis of these data clusters indicates that $\%HPO_{threshold}$ = 57.5% at X = 12.5%. Correlation of mean DBP yield against mean DOC for samples having an HPO content above and below the 57.5% threshold, indicate the raw water samples have an 83% higher overall mean DOC level and generate a 37% higher yield of THMs (Figure 2-7 a). Applying the same process to the HAA data indicates a similar threshold value (60%), and a 64% higher yield of HAAs (Figure 2-7 b). Against this, for the treated waters the absolute different in both the DOC concentration and the yield between the high and low HPO waters is small, as indicated by the almost co-incident open data points at a DOC below 1 mg/L in Figure 2-7 a and Figure 2-7 b. However, such interpretation should be treated with caution, given the limitations of the NOM resin fractionation method (such as carry-over of material between fractions) and the closeness of the low DOC concentrations in the treated water fractions to the LoD of the analytical instrument.

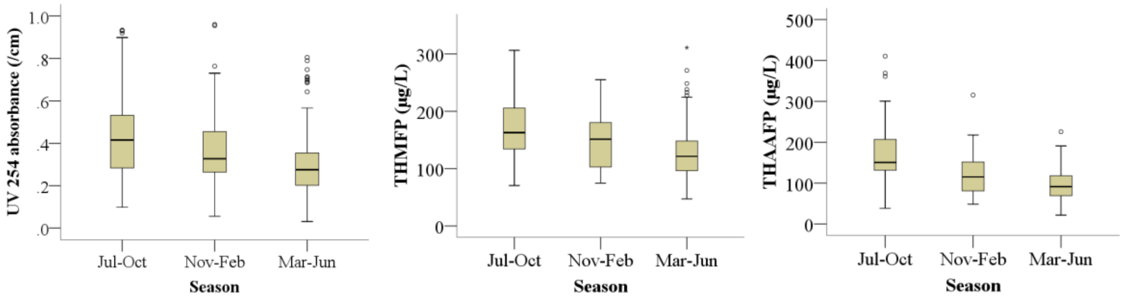


(a) **(b)**

Figure 2-7 DBP yield for (a) THMs and (b) HAAs vs DOC concentration for raw and treated waters, including standard error intervals: influence of HPO content.

2.4.5 Seasonal and geographical trends

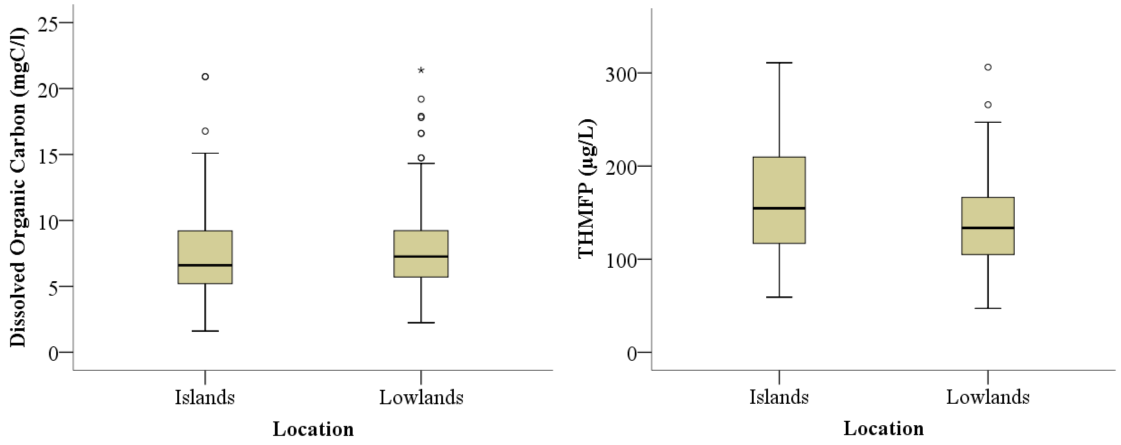
Seasonal and geographical data were analysed on a similar basis to a previous study (Sutherland et al., 2015) of regional THM trends The same three seasonal periods (defined as Jul-Oct; Nov-Feb; Mar-Jun) were identified largely based on anecdotal trends in DBPFP. The outcomes for concentrations of feed UV_{254} (Figure 2-8 a) and treated water THMFP (Figure 2-8 b) and THAAFP (Figure 2-8 c) over the three seasons illustrate a declining trend in both UV_{254} and treated water DBPFP from the Jul-Oct season to the Nov-Feb and Mar-Jun seasons. This result was confirmed as being statistically significant ($p < 0.05$) according to the Kruskal-Wallis (K-W) non-parametric test of differences (Kruskal et al., 1952). It also corroborates the outcomes of the Sutherland et al study based on membrane filtration WTWs as well as those of previous studies of the impact of seasonal temperatures on THMFP (Goslan et al., 2002; Karapinar et al., 2014; Wei et al., 2010). Accordingly, changes in DBP levels can be attributed to the concentration of reactive NOM, rather than changes in NOM reactivity.



(a) (b) (c)

Figure 2-8 Box plots-and-whiskers plots for a) raw water UV254 (/cm), b) treated water THMFP (μg/L), and (c) treated water THAAFP for the three seasons.

Analysis of locational trends, based on geographical region (“North”, “South”, “East” and “West”) revealed no clear trends. However, as with previous studies of the region (Sutherland et al., 2015; Valdivia-Garcia et al., 2016), a small but statistically significant (confirmed by the K-W analysis) increase in reactivity (i.e. increased DBPFP without a corresponding increase in the DOC level) was evident for the Scottish islands installations (Figure 2-9).



(a) (b)

Figure 2-9 Box plots-and-whiskers representing the a) DOC (mg/L) and THMP (μg/L) for the two locations in raw and treated water, respectively.

2.5 Conclusions

A study of trends in disinfection by-product (DBP) yield against the water quality determinants (WQDs) of UV_{254} absorption, dissolved organic carbon (DOC) concentration and the hydrophobic (HPO) fraction of the DOC has been conducted across the Scottish region. Raw and treated waters from 30 water treatment works (WTWs) were sampled over a 30 month period and trends in trihalomethanes and haloacetic acids (THMs and HAAs) determined.

Statistical analysis of the data trends has revealed:

- Linear regression correlation coefficient (R^2) values of DBP yield vs the various WQDs follow the same pattern for both THM and HAA, with slightly weaker correlations for HAAs.

- All WQDs are reasonable indicators of DBPFP in the raw waters sampled in the study, with only colour correlating slightly more weakly (R^2 = 0.77) with THMFP than the other surrogates UV_{254}, DOC and HPO (R^2 = 0.79-0.82); equivalent values for THAAFP were 0.63 for colour and 0.71-0.74 for the other three WQDs. Both UV_{254} and DOC thus appear to be as good an indicator of DBPFP as HPO for both THMs and HAAs, such that chemical fractionation offers little additional benefit in determining DBPFP for the waters studied;

- R^2 values for the corresponding correlations for treated waters were <0.56 for THMFP and <0.48 for THAAFP, apart from THMFP vs DOC (R^2 = 0.67), reflecting the reduced HPO content which represents the most reactive organic carbon component;

- Seasonal trends in DBPFP followed that of UV_{254}, with no apparent impact on yield, whereas as a slight increase in yield was evident with location specifically for island-based installations.

It is concluded that UV_{254} offers a reasonable surrogate for DBPFP across the geographical region studied, particularly with reference to THMs for which the measured correlation coefficient was 0.82 for the raw waters. Evidence suggests that this relates to the commensurately close correlation (R^2 = 0.91) between UV_{254} and the hydrophobic content of the DOC. However, the correlation is weaker for the treated waters due to the reduced HPO content and prevalence of other less reactive organics which nonetheless contribute to DBPFP.

2.6 Acknowledgments

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2.7 References

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3 Chapter: Comparison between Al and Fe based coagulants for natural organic matter removal from upland surface waters

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3.1 Abstract

The economic feasibility of changing coagulant using historic data from an alum and ferric sulfate jar testing campaign at 21 of the most challenging Scottish Water's WTWs was carried out. The status quo was compared to the best jar tests results, defined as maximum DOC removal with minimum coagulant dose. Ferric sulfate was better than alum sulfate at removing DBP precursors at two-thirds of the WTWs investigated. This was partly due to a lower ferric dose being required when the water pH was acidified to a 4-5-5.5 range. However, ferric performance was not dependent on the water alkalinity. A potential penalty for each Compliance Risk Index (CRI) point of up to £1.26 million for each index point over 1.5 was considered. Over a 20 year whole life cost (WLC), ferric emerged as the most viable economical solution, costing three times less than the current solution and 47% less than when using alum sulfate. The OPEX greatly outweighed CAPEX for all scenarios considered.

3.2 Introduction

Water quality in the UK is regulated by the Drinking Water Inspectorate (DWI) in England and Wales, and the Drinking Water Quality Regulator (DWQR) in Scotland, to ensure that water is wholesome and safe to drink (Drinking Water Inspectorate, 2016). Due to their potentially carcinogenic effect, chlorinated carbonaceous disinfection by-products (DBPs) are controlled in drinking water. Currently, the halogenated trihalomethanes (THMs) are regulated in the UK to 100 µg/L and are used as a surrogate for control of many organic DBPs (DWI, 2016). The European Union have recently announced plans to introduce a new regulatory limit for 9 or 5 haloacetic acids

(HAAs) to either a value of 80 µg/L and 60 µg/L, respectively (European Commission, 2018). In August 2018, the DWI introduced a new drinking water quality measure, the Compliance Risk Index (CRI) which replaces the existing Mean Zonal Compliance Index. The CRI is designed to highlight the risk arising from treated water compliance failures and account for the volume of water treated and the customers supplied (Drinking Water Inspectorate (DWI), 2018). The CRI for WTWs is calculated according to the equation (3-1):

$$\boldsymbol{CR}\mathbf{I} = \frac{\boldsymbol{Parameter\ Score\ x\ Assessment\ Score\ x\ Volume\ supplied}\ (\frac{\boldsymbol{m^3}}{\boldsymbol{day}})}{\boldsymbol{Total\ daily\ volume\ supplied\ by\ the\ company}\ (\frac{\boldsymbol{m^3}}{\boldsymbol{day}})} \quad \mathbf{(3\text{-}1)}$$

The DWI assessment score varies from as low as 1 for ‘Trivial’ or ’Unlikely to occur’ to as high as 5 for an ’Enforce’ notice, once the root cause of the failure has been considered (Drinking Water Inspectorate (DWI), 2018). Since THMs are currently considered a health risk, they are awarded a parameter score of 5. While the water supply regulations in Scotland have not yet adopted the CRI approach, it has been used here to demonstrate how changing water treatment might be financially impacted if a similar approach was used. For example, a THM compliance failure at a large site, supplying 100 ML/d that has been given an enforce order by the DWI Inspector, normalised by the 1.37 billion water a day treated by Scottish Water, would receive a CRI score of 1.83. An initial assessment of the 2019 price review plans for two English water companies suggested plans to include a penalty of £1.125 and £1.26 million for each index point over a CRI score of 1.5, respectively (Ofwat, 2019). Therefore, one failure as in the example above, when the maximum penalty is considered, would potentially incur a penalty of ~£416,000. The current plans include a CRI provision for THMs, however it is expected that the HAAs will also be considered under this framework once a regulatory limit is agreed.

It has long been established that DBPs form from the reaction between natural organic matter (NOM) and chlorine during the disinfection stage of the water treatment process

(Bond et al., 2011; Hua et al., 2007; Rook, 1977). Although the correlation relationships and strengths vary from water source to water source, it is generally agreed that a reduction in the organic carbon concentration minimises DBPs. Increasing and fluctuating concentrations of NOM in waters received by WTWs in northern Europe has placed significant pressure on treatment assets. Over 90% of the water volume treated by Scottish Water uses coagulation and flocculation followed by clarification. Coagulation is a physical-chemical process, usually involving the addition of a positively charged metal salt, typically aluminium (Al) or ferric (Fe) based, to reduce the repulsion potential between the negatively charged colloids (Bahadori et al., 2013; Sillanpää et al., 2018). The main reasons behind the use of Al and Fe coagulants (expressed as Al^{3+} and Fe^{3+}) are their relatively low cost and efficacy in removing turbidity and organic matter (Sillanpää et al., 2018). When directly compared, Fe based coagulants have been shown to obtain better NOM removal when compared with Al equivalents (Umar et al., 2016; Uyak et al., 2007). For example, ferric chloride ($FeCl_3$) was reported to remove NOM with a molecular mass >3000 g/mol better than aluminium sulfate ($Al_2(SO_4)_3$) (Matilainen et al., 2005). The higher charge density of Fe based coagulants has been attributed to the more efficient removal of NOM in the range 1000-4000 g/mol, when compared to Al based salts (Hahn et al., 2002). In addition, Fe coagulants have been reported to produce larger flocs than Al coagulants (Fitzpatrick et al., 2004; Jarvis et al., 2012; Xiao et al., 2010). The main controllable parameters that affect the efficiency of the coagulation/flocculation process are pH and the coagulant type and dose. High molecular mass colloidal species are generated when the reaction pH is higher than the minimum solubility of the coagulant, whilst medium and low MW polymers or monomers form when the opposite is true (Sillanpää et al., 2018). The pH for achieving optimum coagulation has been reported to be between 4.5-5.5 and 5-6 for Fe and Al based coagulants, respectively (Sharp et al., 2006).

The aim of this work was to demonstrate the water quality improvements that might be expected if Scottish Water coagulation sites were improved with respect to coagulant type and pH correction. The cost implications of changing coagulation conditions were then compared with the water quality penalties that may be seen if no changes are made, using the CRI approach.

3.3 Materials and methods

3.3.1 Water sampling

The coagulation efficacy study was undertaken on raw surface waters sourced ahead of conventional WTWs that used coagulation/flocculation and clarification treatment. Twenty of the WTWs were using alum as the main coagulant. The exception was WTW #10 which utilises ferric sulphate. The 21 sites have been identified as having an increased potential for high THM formation (Valdivia-Garcia et al., 2016).

3.3.2 Sample analysis

Retrospective analysis was undertaken on data obtained from jar tests on raw water samples collected from 21 WTWs for a period of 10 months from May to December 2013. These experiments were performed by Scottish Water personnel. Controlled jar tests with Al and Fe based coagulants were conducted on the same raw water samples at the UCAS accredited Scottish Water laboratories (Edinburgh). Subsequently, the pH, turbidity, conductivity, zeta potential, colour, UV_{254} absorbance and DOC were measured according to previously published methods (APHA, 2012; Golea et al., 2017). In addition, THMFP and HAAFP were determined for raw and treated water. Assured quality controls (AQCs) were used throughout the tests so as to limit user and equipment induced error; only a ±15% variance from standards was accepted, otherwise analysis was repeated or data removed

3.3.3 Coagulation design and parameters

The study was based on parameters currently in place at operational WTWs as well as alum and ferric controlled jar tests from 21 sites, mainly located in the Centre and West of Scotland (Figure 3-1). Scenario A investigated the current situation where alum (as Al) was dosed as a function of DOC on a 1:1 mass ratio. This was used as the basis for further calculations and the difference between the calculated values and results obtained at works was used to account for changes in raw water characteristics for further sludge production calculations. Scenario B considers the use of the DOC removal using the lowest alum dose during jar tests and Scenario C investigated the economic feasibility of replacing alum with ferric (Fe) coagulants (Figure 3-2). The potential issues relating to increased water acidity when using ferric were mitigated by introducing a secondary pre-filter lime dosing rig that increased the pH to Scenario A levels.

The 21 coagulation WTWs were split into three categories based on output volume: a) Large: >65 Ml/d; b) Medium: >10-65 Ml/d and c) Small: <10 Ml/d. Chemical and sludge disposal costs varied with respect to the location of the WTWs, hence the 21 WTWs were further split into ‘islands’ (WTWs #13, #15, #19, #20 and #21) and ‘mainland’ (the rest of the works).

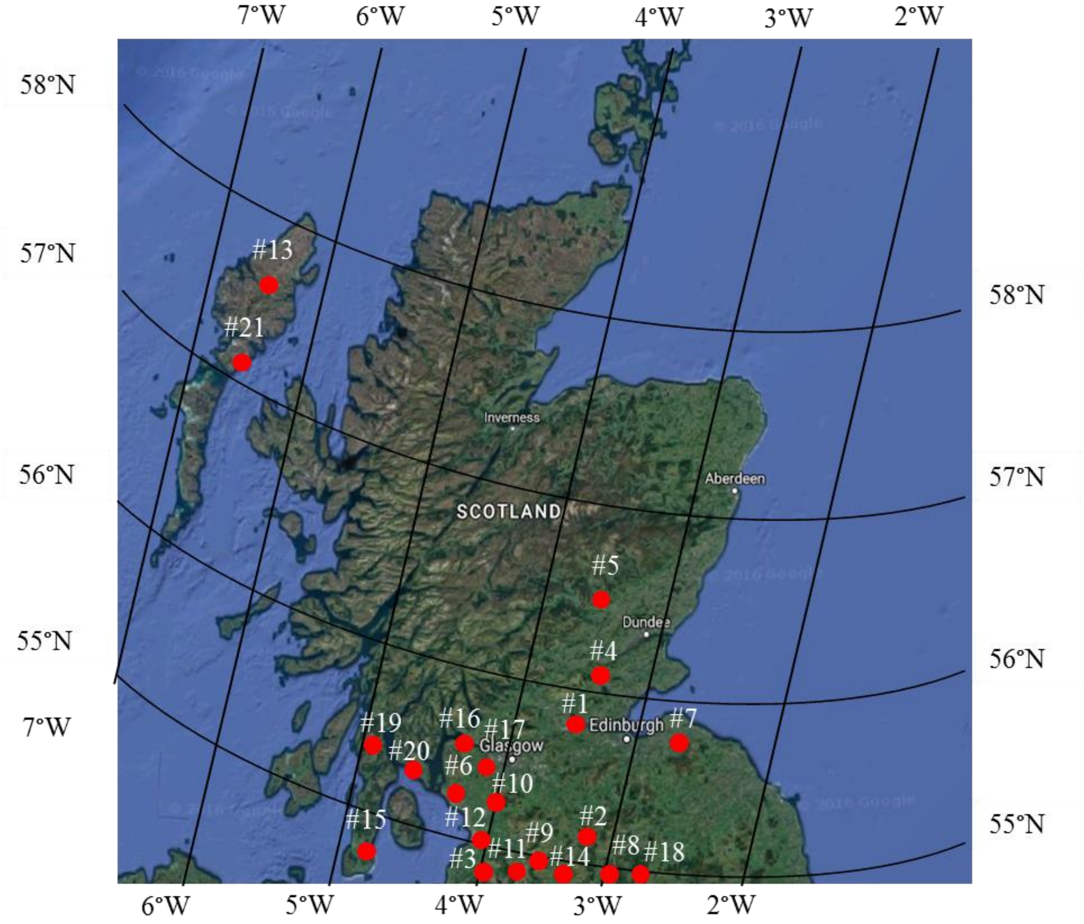


Figure 3-1 The 21 WTWs investigated in the current study.

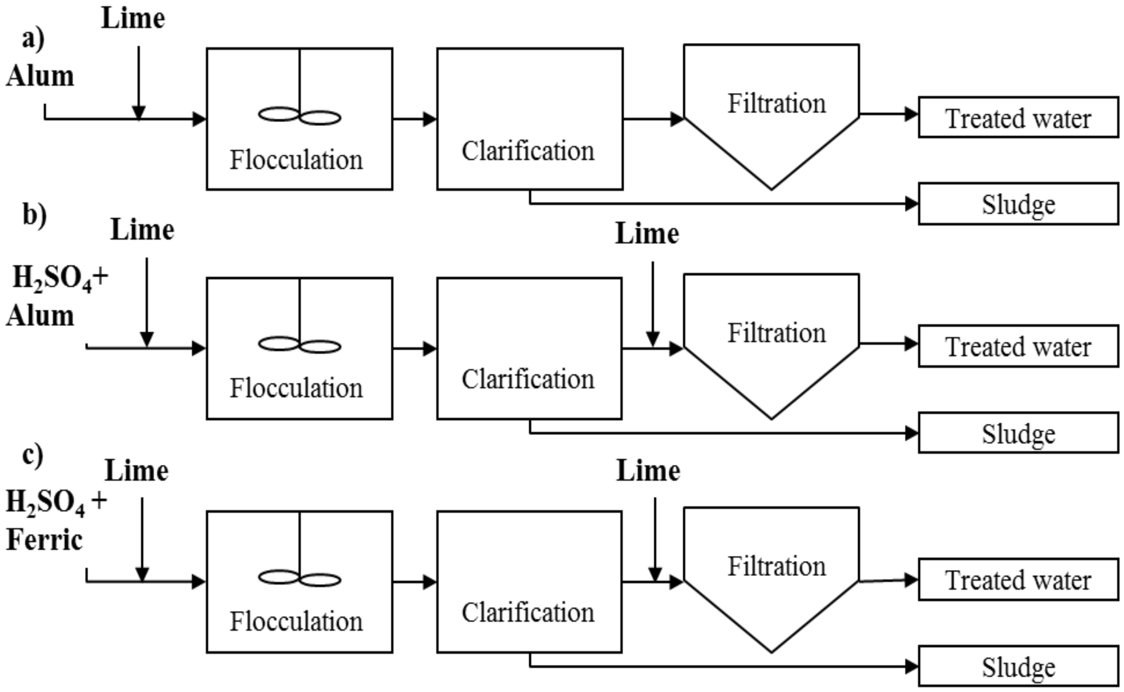


Figure 3-2 Simplified schematic of the 3 proposed scenarios: a) Scenario A-Current Alum with only 1 pH correction dosing point with lime, b) Scenario B- Jar tested Alum, c) Scenario C - Jar tested Ferric, when lime is used to raise the pH first to help optimise coagulation and with a second dosing point to raise the pH to the Scenario A, 6.1.

General and scenario specific design assumptions and omissions are listed in Table 3-1.The design parameters were validated using information available in the literature and data from the current thesis (Table 3-2). Further, the operational parameters of flow, coagulant dosing systems/pumps, mixing speed, hydraulic retention time, saturated air flotation and sand filters were assumed to remain constant. Therefore, the variables considered in the current study were a) coagulant type and dose, and b) acid pH correction requirement.

Table 3-1 Summary of assumptions and omissions for the economic evaluation.

Scenario	Design assumptions and omissions
General	Cost of chemicals assumed correct as of January 2019 Sludge disposal costs were calculated from 2019 forecasts in cost per tonne provided by Scottish Water Lime dosing rig assumed to be in place at all sites (used to correct pH during coagulation to ~6.1) Sand filter backwash undertaken once per day by fluidisation with air 100% of coagulant was assumed to be removed as sludge Coagulant was delivered as 8% as Al for alum and 12.5% as Fe for ferric sulphate A DBPFP to DBP 2:1 relationship was assumed, based on the measurements from one site where an online THM monitor was located. The DBP data from this instrument was compared to DBPFP data from the laboratory for a sample sourced on the same day.
A: the Status quo – alum coagulation	Asset replacement and refurbishment not included in the OPEX estimate Cost of 8% alum includes transport to site and are correct as of January 2019
B: Jar tested alum coagulation with acid dosing	The sludge disposal cost per tonne was assumed to remain constant A secondary lime dosing rig was required Acid dosing rig required
C: Jar tested ferric sulfate coagulation with sulfuric acid dosing	Costs correct for WTW #11, but include transport to site (considered equivalent to alum) A replacement ferric sulfate dosing rig was required due to ferric sulfate's increased corrosivity The sludge disposal cost per tonne was assumed to remain constant

	A secondary lime dosing rig was required Acid dosing rig required

3.3.4 Scenarios A, B and C design philosophy

Scenario A represents the current treatment process at the WTWs investigated. The current alum dose was calculated based on a 1:1 mass ratio of Al:DOC. Similarly, a 1:1 Fe:DOC ratio was used for the existing Fe WTWs. Literature average alkalinity and conductivity values for Scottish waters (Valdivia-Garcia et al., 2016) were used to account for the differences in raw water characteristics. Coagulated water was flocculated and clarified by dissolved air flotation or clarification (at WTWs #2, #6-9, #13) or membranes (WTWs #21), water was then sand filtered through rapid gravity filtration or pressure filter at WTWs #7 and #13). GAC media was employed at two WTWs (#12 and #14). Following filtration, the water was disinfected with chlorine (sodium hypochlorite) at most sites except at WTWs #3, #11 and #22, which used chloramination. The sludge produced was mostly used for land restoration, with only 4 “Island” sites disposing at landfills (WTWs #13, 15, #19 and #21). The raw and treated values measured at works as part of the tests were used as the basis for calculations and any error resulted was used as a multiplier in further cost calculation to account for variability in the raw water character. THMFP and HAAFP were not measured as part of the jar tests on raw and treated water, but were required in order to estimate the potential for improved compliance for DBP and so they were estimated from a model. Previous work, undertaken on 2.5 years data sourced at WTWs with water of similar characteristics, showed a relative relationship between DOC versus THM and HAA formation (Golea et al., 2017). A DBPFP to DBP 2:1 relationship was derived by measuring the THMFP (µg/L) on asample and compared to the THM (µg/L) measured at the works using an online THM monitor from the same day; it was then assumed that the relationship would apply for HAAHP and HAA, respectively. Once a DBPFP to DBP 2:1 ratio was applied the relationship became equations (3-2) and (3-3):

$$\boldsymbol{THM}\ (\mu \boldsymbol{g/L}) = \mathbf{5.7 + 35.73}\ \boldsymbol{DOC}\ (\boldsymbol{mg/L});\ \boldsymbol{R^2=0.63} \qquad \mathbf{(3\text{-}2)}$$

$$\boldsymbol{HAA}\ (\mu \boldsymbol{g/L}) = -\mathbf{2.69 + 34.9}\boldsymbol{x}\ \boldsymbol{DOC}\ (\boldsymbol{mg/L})\ ;\ \boldsymbol{R^2= 0.43} \qquad \mathbf{(3\text{-}3)}$$

Scenario B and C investigated jar tested coagulation with the addition of sulfuric acid and lime for pH correction for alum sulfate and ferric sulfate, respectively. A secondary pre-filtration lime dosage was considered to increase the pH to 6.1, as per Scenario A. The jar tests results were filtered by the maximum DOC removal with minimum coagulant dose. It was assumed that the coagulation rig would need to be replaced for Scenario C due to the ferric sulfate's increased corrosivity.

Design criteria and operational parameters were taken from literature, chemical technical data sheets and models commonly used in the water industry (RTW) (Table 3-2).

Table 3-2 Main design parameters and assumptions for Scenario A.

Design parameter	**Value and unit**	**Reference**
Flow	0.5-103 MLD	Current study
Average raw water pH	5.7-7.71	Current study
Average raw water conductivity	80.3 µS/cm at 20°C	(Valdivia-Garcia et al., 2016)
Raw water alkalinity	29.3 mg HCO_3/L	(Valdivia-Garcia et al., 2016)
DOC : coagulant	1:1	(Sharp et al., 2003)
Alum sulfate concentration	8%	Water company data
Alum sulfate specific gravity	1.3	Technical data sheet
Ferric sulfate concentration	12.5%	Water company data
Ferric sulfate specific gravity	1.55	Technical data sheet
Lime concentration	96%	Water company data
Lime slurry concentration during coagulation	5%	Water company data
Lime specific gravity	2.24	Technical data sheet
Pre-filtration pH	6.1	Water company data
Final water pH	< 8.5	Water company data

3.3.5 Economic evaluation

3.3.5.1 Capital cost estimates

Capital costs (CAPEX) were calculated in Great British Pounds (£) (McGivney et al., 2008), to 2018 prices using the Chemical Engineering Plant Cost Index (CEPCI) overall index for the period 2008 to 2018 using the following equation (3-4):

$$\frac{\boldsymbol{CEPCI\ in\ 2018}}{\boldsymbol{CEPCI\ in\ 2008}}\ \boldsymbol{x\ 2008\ GBP\ value = 2018\ GBP\ value} \qquad \textbf{(3-4)}$$

The calculation considered an average 7% interest rate over 10 years. Cost estimates for the main components were estimated from predesign construction cost curves in the literature (McGivney et al., 2008) (Table 3-3). No CAPEX investment was considered for Scenario A since this was a reflection of the status quo.

Table 3-3 Summary of capital costs estimates for main components calculated from predesign construction cost curves (McGivney et al., 2008).

Design parameter	WTW size (MLD)	Values (£'000)	Notes
Scenario B: Lime dosing CAPEX	Large	718±517	The cost estimates include the lime silo with bin activator and dust collector, a slacker to prepare the lime slurry, piping, valves, gravimetric dry chemical feeder and meters.
	Medium	223±154	
	Small	77±70	
Scenario C: Lime dosing CAPEX	Large	880±298	
	Medium	431±122	
	Small	132±61	
Scenario B: Sulfuric acid dosing	Large	~19	Sulfuric acid delivered liquid with a concentration >93% implies a more hazardous storage and feed. The cost estimates includes secondary containment to protect from other reactive chemicals
	Medium	~19	
	Small	18.8±32	
Scenario C: Sulfuric acid dosing	Large	~23	
	Medium	~20	
	Small	19±49	
Scenario B: Carbon steel tank	/m^3	1.237	Additional storage required for increase 8% alum for jar tested coagulation (Sinnott, 2005)
Scenario C: ferric sulfate dosing rig	Large	353±52	The cost estimate was based on a 47% ferric chloride solution. The cost include storage tanks, metering and transfer pumps, valves and piping and the enclosures.
	Medium	232±26	
	Small	115±28	

3.3.5.2 Operational costs estimates

The operational costs (OPEX) were calculated in Great British Pounds (£) and converted to 2018 prices using the CEPCI as described above. The costs were sourced from a combination of literature and data available from water companies in the UK (n.

Table 3-4). Sludge disposal costs were estimated based on the current Scottish Water costs multiplied by the proportion increase resulting from calculating chemical dose and DOC removal used at the time the tests were undertaken.

Table 3-4 Summary of operational cost estimates based on recent data sourced from water companies in the UK.

Parameter	**Value (/tonne)**	**Notes**
8% Alum sulfate	£137±79	Costs vary widely depending on location (islands versus mainland). The costs include transport and are predicted for after April 2019.
12.5% Ferric sulafate	£168±85	Estimates based on the current cost of ferric sulfate at WTW #10; delivery included.
96% Sulfuric acid	£213	Estimated cost used in predesign calculations at water companies across the UK
Lime	£97	Estimated cost used in predesign calculations at water companies across the UK

3.3.5.3 Whole life cost estimate

Whole life cost (WLC), defined as a period of 20 years, was calculated using the design parameters in Table 3-2 and equation (3-5) below:

$$\boldsymbol{WLC = CAPEX + (OPEX\ x\ 10.59)} \qquad \textbf{(3-5)}$$

The 10.59 factor was derived using a calculation of the present day WLC includes the CAPEX and OPEX required for operational and maintenance, and does not include asset replacement and refurbishment costs until mothballed. A 7% interest rate was considered.

3.4 Results and discussion

3.4.1 Raw water characteristics

Around half of the WTWs investigated were small (52%), with medium and large making up the rest, 29% and 19%, respectively. The average WTW flow ranged from the largest #1 at 103.5 Ml/d to the smallest # 21 at 0.5 Ml/d. On average, the WTWs were operated within 70% of their respective design capacity with #17 operated at only 34.5 % whilst #11 was operated at 87.8% of capacity.

The water pH was relatively stable in the acidic to neutral range. The lowest average pH of 5.7 was measured at WTW #13, and the highest was at WTW #15 (7.7), with the largest variance observed at WTWs #1 (7.3±0.4).

DOC concentration varied widely both geographically and seasonally. The lowest average raw water DOC of 3.1±0.5 mg/L was observed at WTW #4 and the highest was seen at WTWs #10 with a value of 13.7 mg/L. The highest variance in DOC was observed at WTW #16, where the average DOC was 13.4 mg/L, with a range between 5.6-28.8 mg/L). Likewise, turbidity varied from an overall average of 1.8 NTU to a minimum of 0.6 NTU at WTW #9 to a maximum of 4.7 NTU at WTW #16.

Table 3-5 Raw water characteristics and volume outputs.

Site number	Average DI (Ml/d)	Design Capacity (Ml/d)	Average raw water pH	Average raw water DOC (mg/L)	Average turbidity (NTU)
#1	103.5	125	7.28	6.7	1.59
#2	100.2	129	7.34	4.9	0.60
#3	77.8	120	6.53	7.6	1.28
#4	65.2	91	7.64	3.1	2.31
#5	28.4	42	7.08	4.3	0.35
#6	24.2	46	6.94	8.9	0.94
#7	19.3	32	7.70	5.5	0.60
#8	18.9	22	7.39	7.9	4.46
#9	16.1	25	6.68	8.7	1.20
#10	10.3	20	6.69	13.7	2.26
#11	5.7	6.5	7.27	7.7	1.31
#12	4.3	8.0	7.35	9.4	1.18
#13	3.5	6.5	5.70	5.0	2.10
#14	3.3	4.9	7.13	6.4	0.56
#15	2.7	3.8	7.71	8.0	4.82
#16	2.7	6.0	7.18	13.4	2.37
#17	2.5	6.0	7.29	8.5	1.13
#18	2.4	3.4	7.26	8.0	2.78
#19	2.1	3.5	6.49	10.2	0.84
#20	1.2	2.6	7.11	7.7	3.30
#21	0.5	0.6	5.98	7.8	0.69

3.4.2 DOC removal comparison between Scenarios A, B and C

Overall, 14 out of the 21 sites investigated showed improved removal when using ferric sulfate. Three sites (WTWs # 13, #20 and #21) did not show an improved DOC removal when coagulation was jar tested using either Fe or Al compared to the performance of the WTWs. Most WTWs saw an improvement for both Fe and Al, however WTW #3 showed an improved DOC removal only with alum, whilst WTWs #7, #12, and #10, conversely showed an improved DOC removal with ferric only (Figure 3-3).

For the large sites, the highest improvement was observed at WTW #4 with jar tested alum which returned a decrease in residual DOC of 2.1 mg/L, which translated to a removal efficiency of 73%, compared to only 4% obtained at the WTWs from a raw water DOC of 2.8 mg/L. The lowest overall improvement for jar tested coagulants was noted at WTW #3, where the removal efficiency at the WTWs was 72.3% and was only bettered by 6% using jar tested alum. Here jar tested ferric only achieved a removal efficiency of 69.4%. Residual DOC was lower when using jar tested ferric when compared to the WTWs and jar tested alum at the two largest sites (WTWs #1 and #2). Residual DOC was lower by up to 0.6 mg/L when compared to both the jar tested Al and WTWs alum dosing, respectively.

At medium sized WTWs, the average DOC removal was around 74.5% generating a residual DOC of 1.9 mg/L DOC. The highest reduction in residual DOC of 2 mg/L was noted at WTW #8 when using the jar tested alum dose. This was 0.7 mg/L DOC less than the residual DOC obtained with jar tested Fe and equated to a 99.2% DOC removal.The lowest overall improvement using jar tested coagulants was noted at WTW #10. A 0.8 mg/L higher residual DOC was observed when using jar tested Fe compared to the WTWs Fe dosing. This was 1.3 mg/L DOC lower than the residual DOC obtained using jar tested ferric, which outperformed the works ferric by 0.5 mg/L DOC.

A wider performance range was noted at small WTWs. Three out of the eleven small WTWs investigated (#13, #20 and #21) showed no improvement in the residual DOC when using either of the jar tested coagulant doses. This may be indicative of an optimised treatment downstream of the coagulation stage treatment train which obtained between 70-98% removals in conditions of low-medium alkalinity. The high overall

DOC removal at WTW #21 may be due to the filtration stage being an ultra-filtration membrane. On the other hand, at WTWs #17, jar tested ferric marginally outperformed jar tested alum (by ~ 0.3 mg/L DOC) and reduced the residual DOC by an average of 2.8 mg/L when compared to the works alum dose (driven by a max of 7.2 mg/L DOC from a raw water source of max 9.5 mg/L DOC).

In general, most of the WTWs showed improved DOC removal when using ferric rather than alum (86% of the WTWs). Only at three WTWs was jar tested alum shown to outperform jar tested ferric (Figure 3-4).

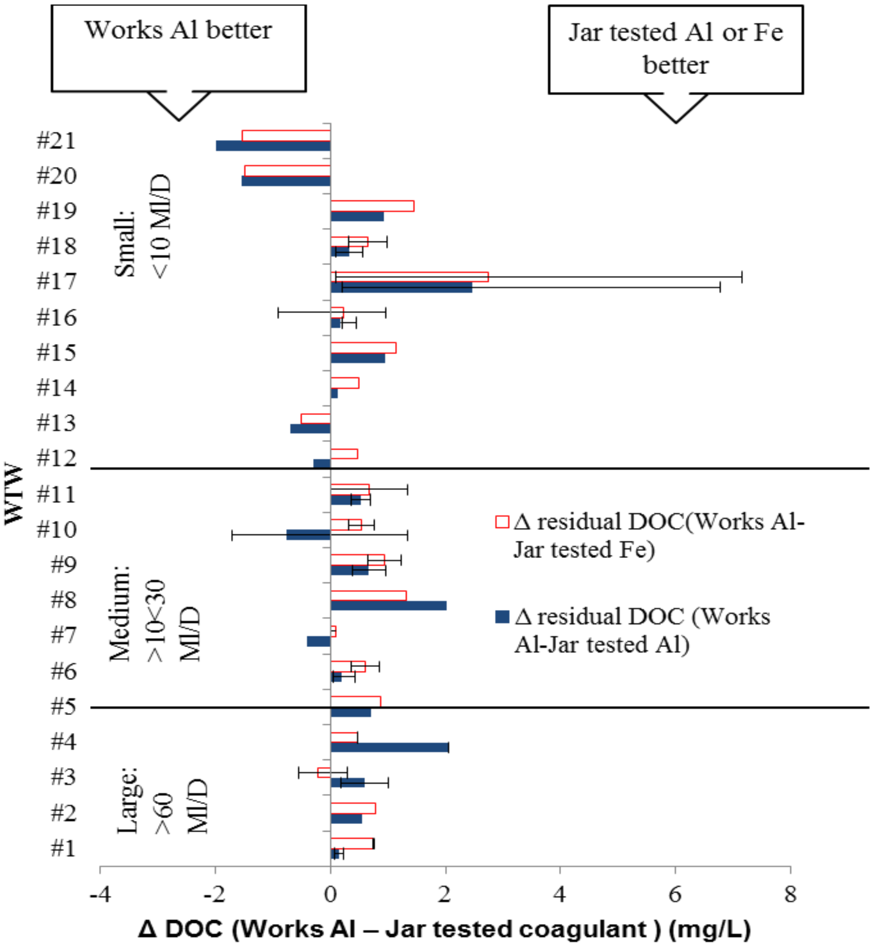


Figure 3-3 Differences in residual DOC obtained at works and with jar tested coagulants (error bars show minimum and maximum values and were applied where data was available).

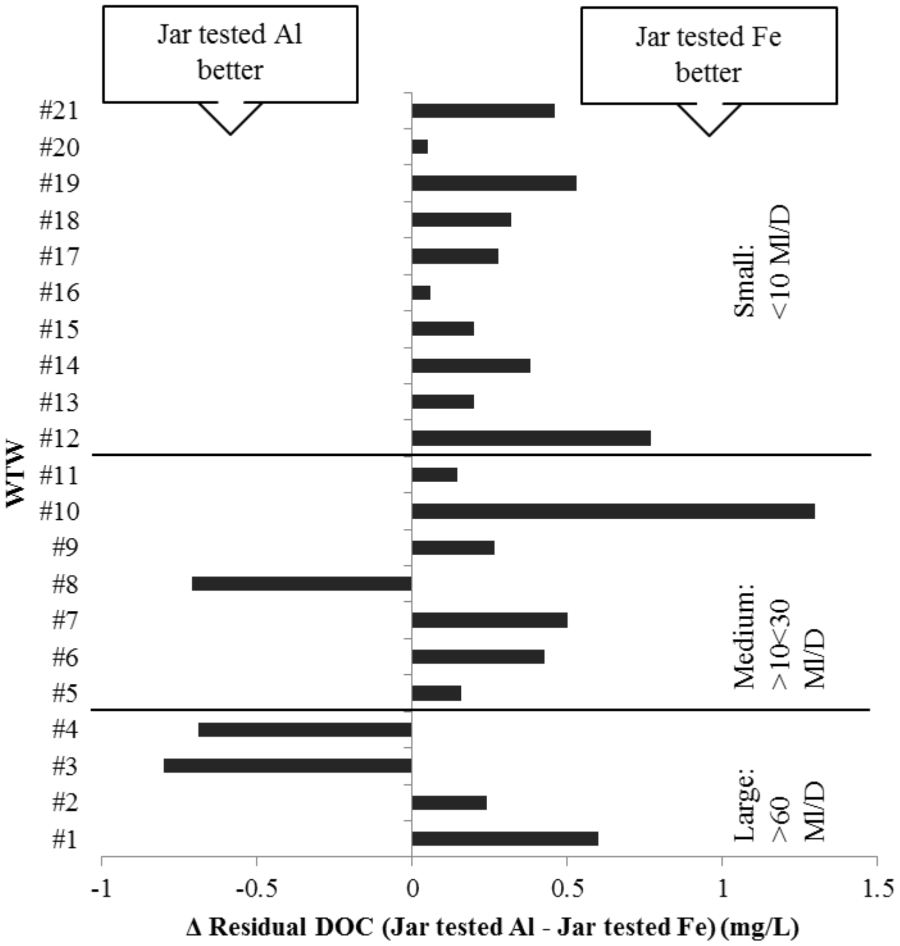


Figure 3-4 Comparison of the jar tested coagulants removal efficiency for DOC.

3.4.3 Link between DOC and DBP formation reduction

The works and calculated THM values correlated together relatively well (R^2=0.78) while the corresponding HAA values correlated to a lesser degree (R^2=0.49) (Figure 3-5). This enabled THMs and HAAs to be estimated for the status quo and for the jar tested coagulation systems with some degree of accuracy. However, as the aforementioned figures were predictions based on calculations from trend lines that had some significant scatter, the results obtained were used in a comparative fashion rather than in an absolute way.

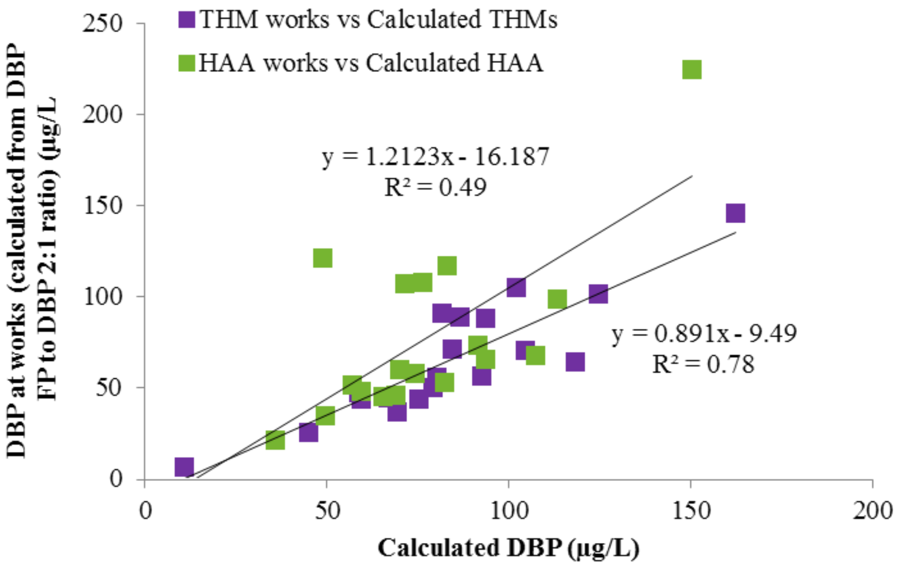


Figure 3-5 Correlations between DBPs at works (calculated as a 2:1 ratio DBP FP vs DBPs) versus Calculated DBPs using the equations from (Golea et al., 2017).

While only a snapshot, sites #4, #11, #15, #17, #18 and #19 would be at risk of failing both the 100 µg/L THM and a potential 80 µg/L HAA regulatory limit, whilst site #9 and #12 would only fail the latter. However, more sites produced DBPs close to the regulatory limit and only #7 and #21 produced THMs below the Scottish Water prescribed concentration value (PCV) of 50 µg/L (0.45µg/L and 10.7 µg/L, respectively). Both jar tested coagulation scenarios would be expected to reduce the predicted failure rates (Table 3-6).

The DBP improvement performance when using ferric compared to alum was consistent with the DOC findings. All WTWs, with the exception of #3, #4 and #8, showed reductions in THMs when using ferric, although wide ranges were noted at #3 and #4. This ranged from improvements as low as 7.5 µg/L at WTW #20 to as high as 52.2 µg/L at #10. For HAA, ferric outperformed alum in a similar fashion, albeit to a lesser degree at all WTWs except #3, #4, #8, #16 and #20. The minimum improvement achieved using ferric was 2.4 µg/L HAA at #11, whilst the maximum was 42.7 µg/L HAA at #10 (Figure 3-6). Conversely, at the sites where alum outperformed ferric, a maximum 22.9 µg/L THM was obtained for WTW #3, and a minimum of 19 µg/L THMs at #4, respectively. For HAAs, the values ranged from as high as 31 µg/L, to as low as 0.6 µg/L, at WTWs #3 and #19 (Figure 3-6).

Table 3-6 Comparison between current and jar tested calculated DBP formation

Nr	Average DI (Ml/d)	Calculated THM (µg/L) at works	Calculated HAA (µg/L) at works	Calculated THMs (µg/L) after alum tests	Calculated HAAs (µg/L) after alum tests	Calculated THMs (µg/L) after ferric tests	Calculated HAAs (µg/L) after ferric tests
#1	103.5	78.9	68.9	73.8	63.8	52.3	42.9
#2	100.2	66.8	57.0	47.1	37.8	38.6	29.4
#3	77.8	81.4	71.3	60.5	50.9	89.1	78.8
#4	65.2	108.6	97.8	34.8	25.8	59.5	49.8
#5	28.4	58.6	49.0	33.2	24.2	27.5	18.6
#6	24.2	75.2	65.2	68.6	58.7	53.4	43.9
#7	19.3	45.0	35.7	59.3	49.7	41.4	32.2
#8	18.9	80.0	69.9	7.8	-0.6	33.2	24.2
#9	16.1	93.4	83.0	69.7	59.8	60.2	50.5
#10	10.3	86.4	76.2	113.8	102.9	67.3	57.5
#11	5.7	102.0	91.4	83.1	72.9	77.9	67.8
#12	4.3	92.5	82.1	103.2	92.6	75.7	65.7
#13	3.5	59.3	49.7	84.3	74.1	77.2	67.1
#14	3.3	61.4	51.8	57.2	47.6	43.6	34.3
#15	2.7	104.3	93.6	70.4	60.5	63.2	53.5
#16	2.7	69.3	59.4	63.2	53.5	61.1	51.4
#17	2.5	162.2	150.2	73.9	64.0	63.9	54.2
#18	2.4	118.1	107.1	106.3	95.6	94.8	84.4
#19	2.1	124.3	113.2	91.5	81.1	72.5	62.6
#20	1.2	84.3	74.1	139.3	127.8	137.5	126.1
#21	0.5	10.7	2.2	81.8	71.6	65.4	55.6

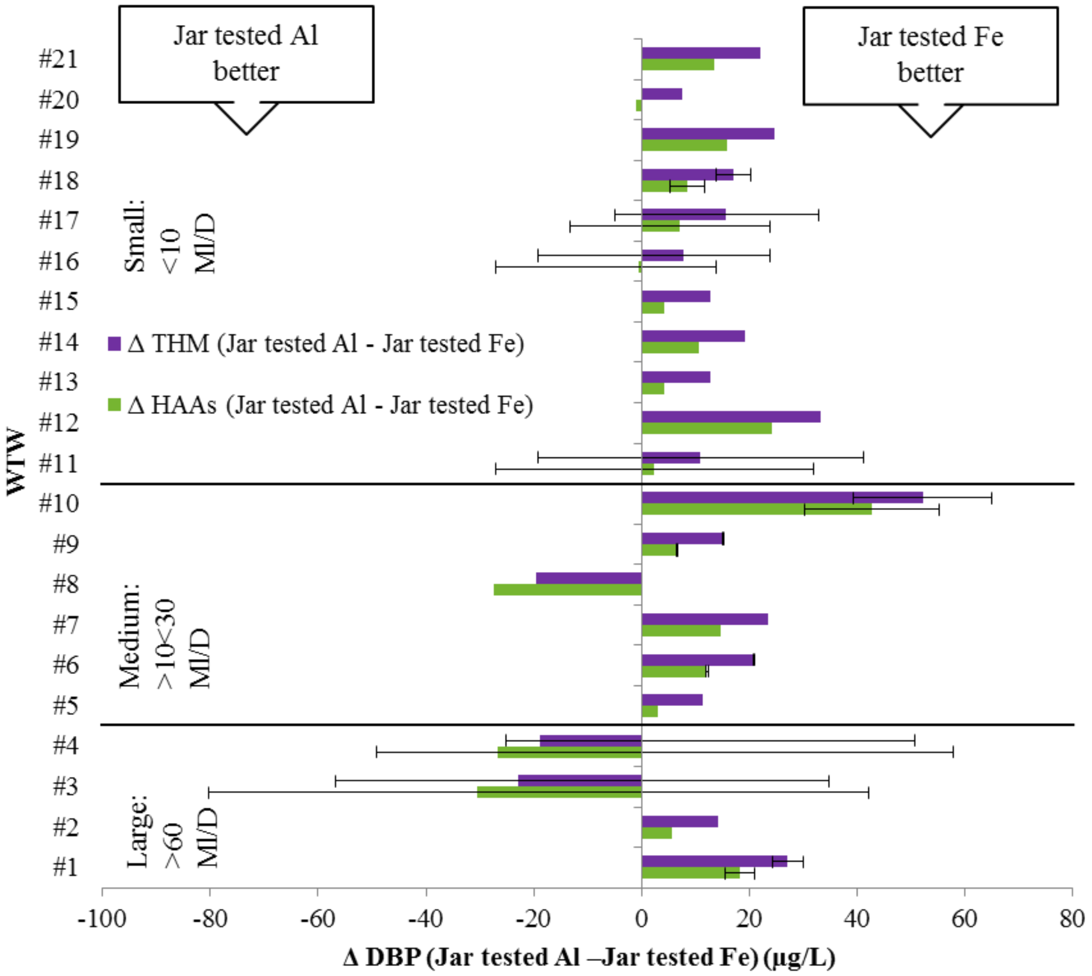


Figure 3-6 Comparison between the DBP values achieved with jar tested alum and ferric, respectively (error bars show minimum and maximum values and were applied where data was available).

3.4.4 Changes in chemical dosage

While improved DOC removal was expected under improved conditions, this may require both a change in the pH of coagulation and the applied coagulant dose. When comparing the pH of coagulation at WTWs, jar tested alum required a higher pH, whilst ferric required more acidic conditions (Figure 3-7). An average pH of 6.2±0.2 and 4.8±0.2 was required for alum and ferric, respectively. These pH ranges were in agreement with previously reported figures for both Fe and Al (Sharp et al., 2006). The jar tested alum pH average of 6.2±0.2 was marginally higher than the value of 6.1 used at the WTWs.

At large WTWs, jar tested alum coagulation required a marginally more acidic pH of 6.1 and 6.0 for WTWs #1 and #3, respectively, whilst a less acidic pH was required for WTWs #2 and #4 (6.2 and 6.5). In contrast, ferric required a larger acid dose to achieve the most acidic pH of 4.8 at WTW #4 and the least acidic pH 5.1 at WTW #3.

Similarly, for medium sized WTWs a more acidic pH was required for ferric, and ranged from as low as 4.4 at #10 to as high as 5.1 at WTWs #6. For alum, jar tested coagulation required a decrease in pH for WTW #10 and #9, by 0.3 and 0.01, respectively, and a less acidic environment for the rest of the works.

The trend continued at small WTWs; alum required less acidic conditions at WTWs #11, #12, #15, #16, #20 and #21. The values ranged from a minimum decrease in acidity of 0.07 at #11 and#21 and a maximum of 0.29 at #16. Conversely, WTWs #13, #14, #17, #18, and #19, required more acidic water, with pH ranging from as low as 5.8 to as high as 6.07 at WTWs #13 and #17, respectively.

As expected, a more acidic pH was required for all small WTWs. The required decrease in pH ranged from as much as 1.9 at #13 to as little as 1.35 at #14.

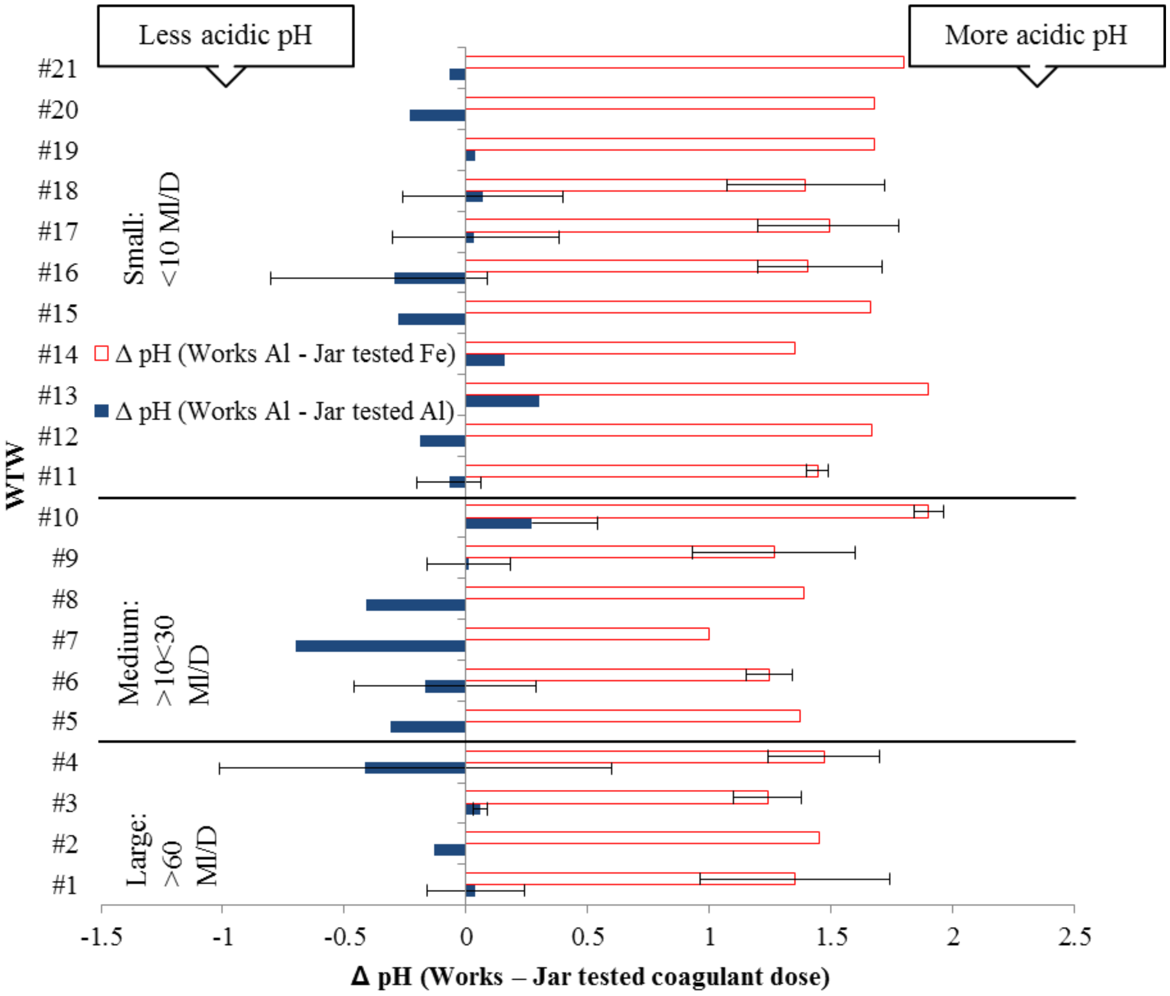


Figure 3-7 pH conditions at WTWs compared to jar tested coagulation (error bars show minimum and maximum values and were applied where data was available).

In general, the pH correction led to a saving in coagulant dose at most works. The highest saving was noted at medium and small sites (Figure 3-8). However, most notable exceptions were seen at WTWs #1, #10, and #4, where the current coagulant dose was lower by 16.8 mg/L, 24.4mg/L and 75.7mg/L for alum . Similarly, the current coagulant dose was lower by 14.6 mg/L, 24.3mg/L and 47.5 mg/L, at WTWs #1, #4 and #10, respectively.

It was further observed that the current coagulant dose was lower than the equivalent weight of jar tested alum coagulant at WTW #16, by 34 mg/L. Similarly, a larger dose of ferric sulfate than the status quo for alum was required at WTWs #7 and #15, at 12 and 28 mg/L respectively (Figure 3-8).

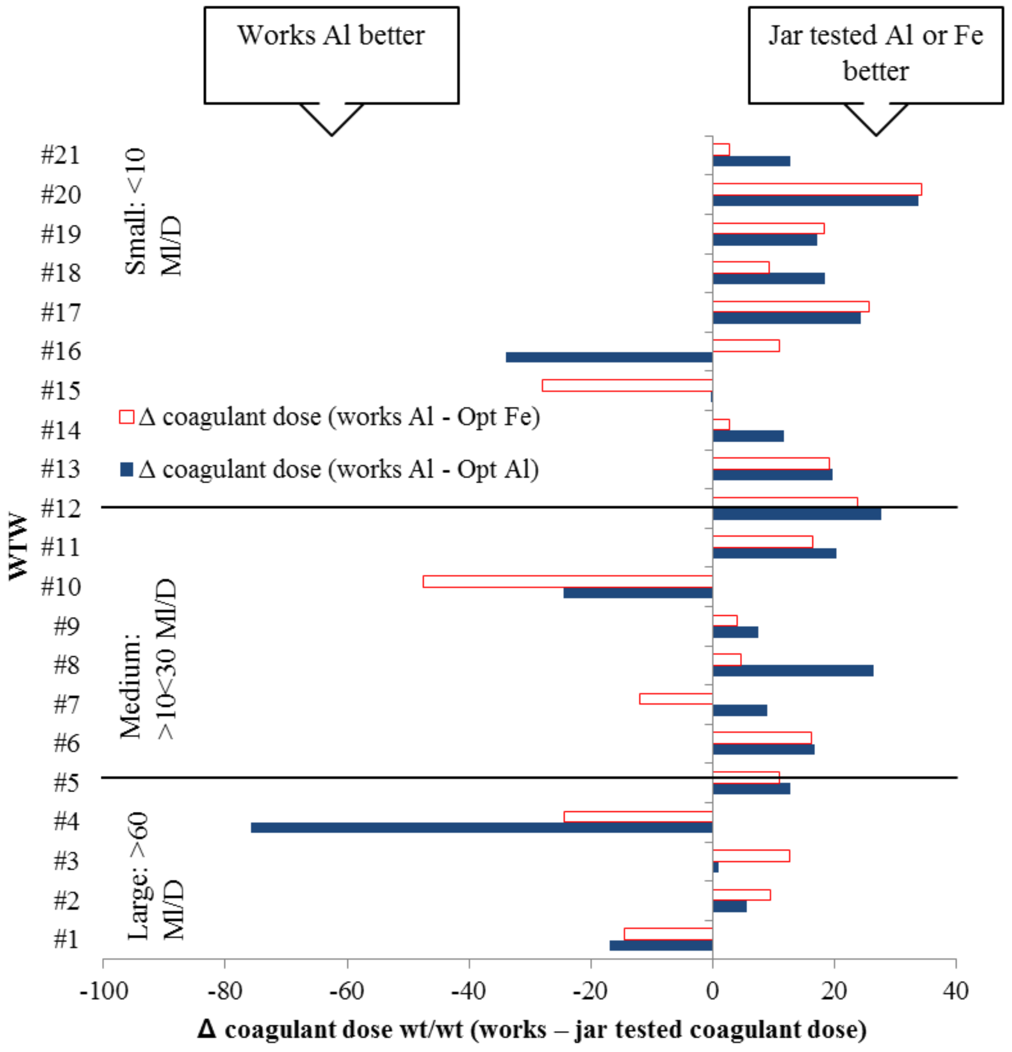


Figure 3-8 Coagulant dose at WTWs compared to the doses used during jar tested coagulation on a wt/wt basis.

3.4.5 Capital cost estimate

The following cost calculations were based on increased capacity required for lime and alum as well as a complete replacement of the coagulant dosing rig, due to ferric's higher corrosivity. Total initial CAPEX calculations for the 21 WTWs, based on the parameters identified in the current study, required an investment of ~£3.35 million to upgrade the alum dosing compared to ~£7.5 million to switch to ferric coagulant. This represents a potential 2.24 fold increase in CAPEX for the ferric compared to alum dosing systems.

The CAPEX for large WTWs was around 1.7 times higher when using jar tested ferric compared to jar tested alum. However, at medium and small WTWs, ferric CAPEX was estimated to be 2.6 and 3.7 times higher than the jar tested alum CAPEX, respectively (Figure 3-9).

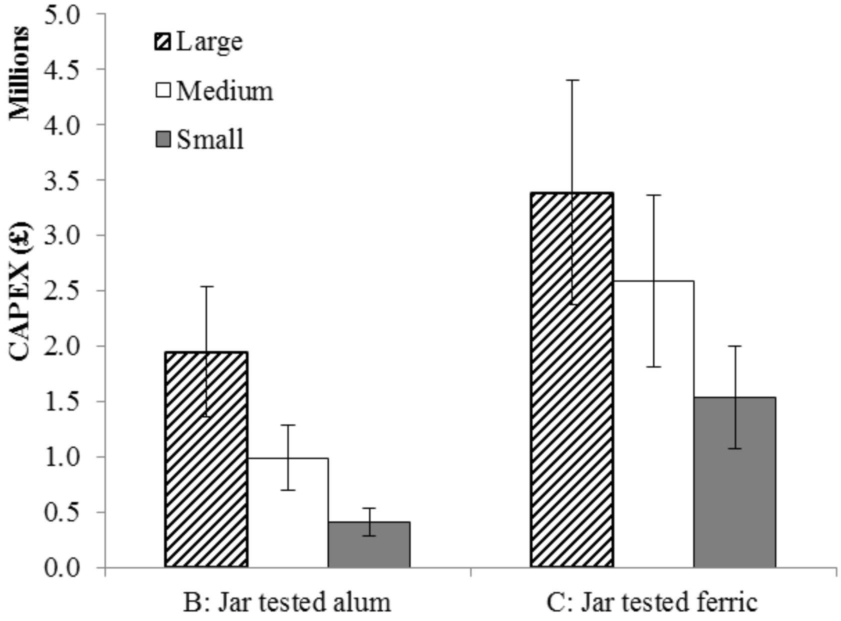


Figure 3-9 CAPEX estimates for Scenarios B and C with ±30% variation.

Proportionally, the additional lime rigs needed for pH correction had the highest impact on CAPEX for both jar tested alum and ferric scenarios, with 59% and 55% of CAPEX, respectively. The need for additional 8% alum sulfate storage had an impact of 39% (Figure 3-10a) whilst replacing the alum dosing rigs for ferric impacted CAPEX by 44% (Figure 3-10b). The sulfuric acid feed rigs had the lowest impact on CAPEX for both options B and C, with 2% and 1% impact on total estimated CAPEX, respectively (Figure 3-10).

It is worth noting that the pH correction required for jar tested coagulation with both alum and ferric (Figure 3-7) resulted in an increase in lime storage for WTWs #1, #4, #7, #10, #15, and #16 for Scenario B and for all but WTWs #11, #12, #17 and #20 for Scenario C, respectively. Similarly, pH correction with sulfuric acid was required for both scenarios at WTW #2, #5, #14 and #17, and #18 for Scenario B and #19 for Scenario C.

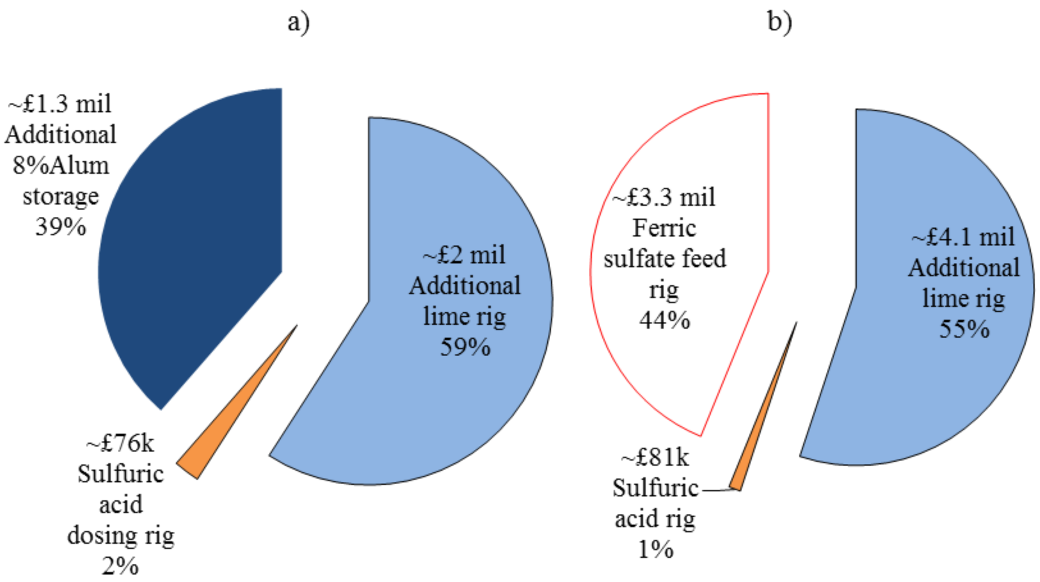


Figure 3-10 Major component contributions to CAPEX for a) Scenario B (jar tested alum) and b) Scenario C (jar tested ferric).

3.4.6 Operational cost estimate

The OPEX cost estimate showed that Scenario C using jar tested ferric was the most economical overall. Jar tested ferric cost 16%, 31% and 47% less than the current OPEX at works when alum was employed for large, medium and small WTWs, respectively. The yearly costs were 22% higher for jar tested than works alum at large WTWs, but 21% and 28% lower at medium and small WTWs, respectively. When jar tested alum and ferric OPEX were compared, the latter was 49%, 8% and 15% less costly than the former, for large, medium and small works, respectively (Figure 3-11).

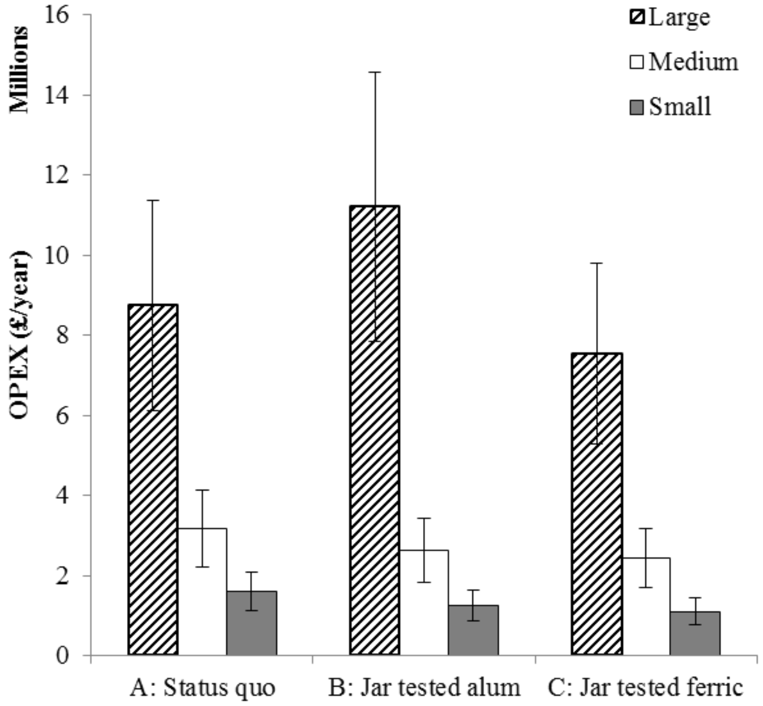
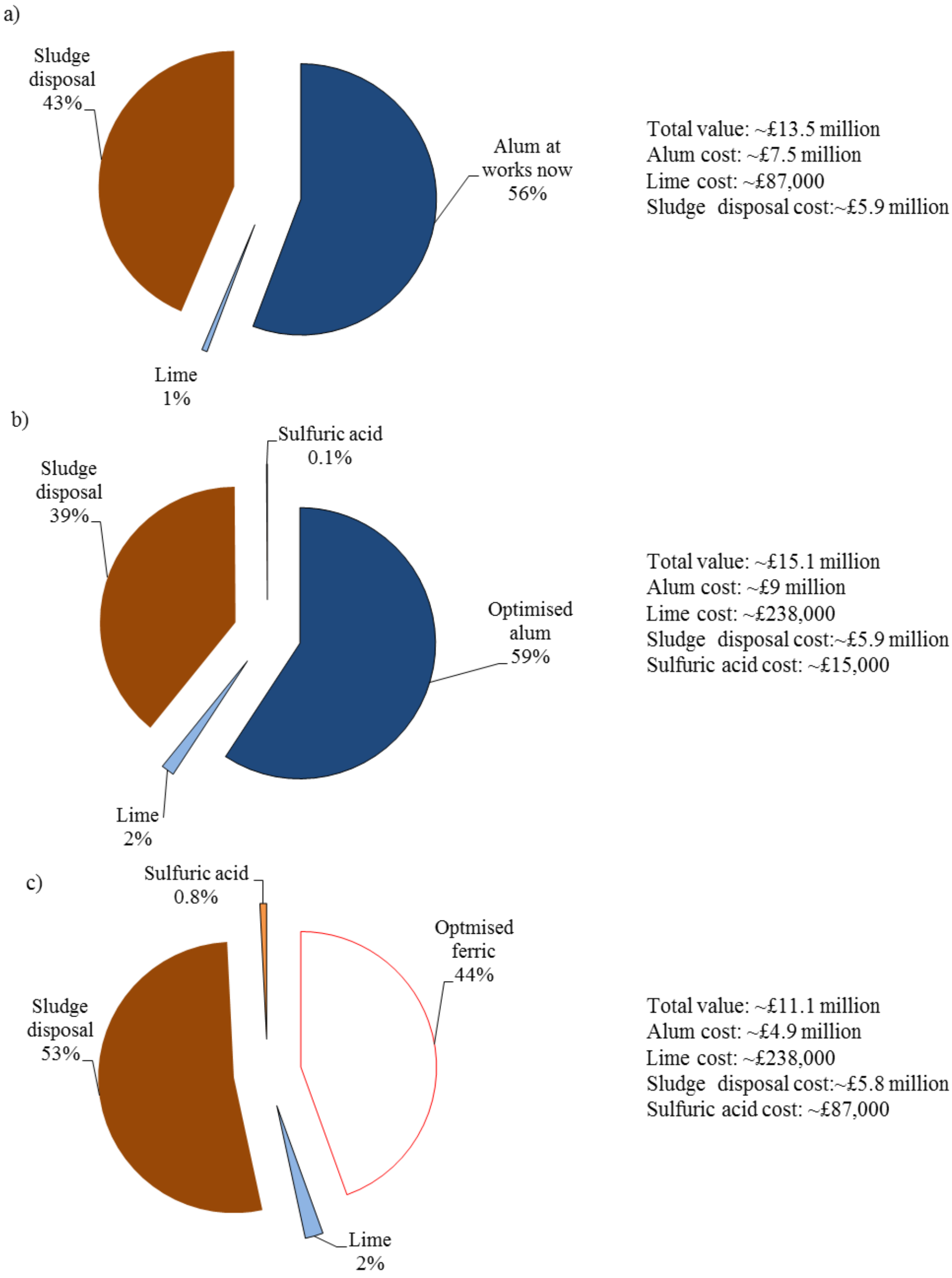


Figure 3-11 OPEX estimates for Scenarios A-C considering current cost estimates for both coagulants (± 30% variation).

The estimated annual OPEX costs were highest for jar tested alum (option B), followed by the current solution (option A) and jar tested ferric (option C) with values of ~£15.1 million, ~£13.5 million and ~£11.1 million, respectively (Figure 3-12). A trade-off between a decrease in the cost of coagulant and an increase in the cost of sulfuric acid that was required to reduce the pH to the recommended range of 4.5-5.5 was observed for ferric (Figure 3-12 c). The major contributing cost for the current and jar tested alum solution was alum (56% 59%) followed by sludge disposal (43%, 39%) and pH correction with lime (1%, 2%) (Figure 3-12a,b). Ferric represented 44% of the overall yearly OPEX for Scenario C, whilst sludge disposal was the highest contributor at 53%. The pH correction with lime was a similar cost to the increase in alum required (2% of OPEX). Sulfuric acid, used to drop the pH for jar tested alum and ferric, represented the smallest proportion of the yearly OPEX at between 0.1-0.8% (Figure 3-12). The increase in sulfuric acid for Scenario C was as a result of the lower pH required to achieve improved coagulation with ferric (Figure 3-7). However, this led to a lower wt/wt ferric than alum dose required which led to an overall reduction in cost.



Total value: ~£13.5 million
Alum cost: ~£7.5 million
Lime cost: ~£87,000
Sludge disposal cost:~£5.9 million

Total value: ~£15.1 million
Alum cost: ~£9 million
Lime cost: ~£238,000
Sludge disposal cost:~£5.9 million
Sulfuric acid cost: ~£15,000

Total value: ~£11.1 million
Alum cost: ~£4.9 million
Lime cost: ~£238,000
Sludge disposal cost:~£5.8 million
Sulfuric acid cost: ~£87,000

Figure 3-12 Contribution of major components to the OPEX for a) Scenario A, b) Scenario B and c) Scenario C.

3.5 Whole life cost estimates

The potential cost avoidance of using dose obtained from coagulation versus the status quo in view of potential CRI penalties was investigated. A WLC of 20 years was estimated using present day CAPEX and OPEX estimates that did not include repairs and maintenance.

A maximum potential CRI score of 3.28 was calculated when the DWI algorithm was applied to the potential regulatory breaches at sites #4, #9, #11, #12, #15, #17, #18, and #19 calculated above (Table 3-6). The estimated penalty assumed that the HAA regulatory requirement was in force and Scottish Water would be given an Inspector's Assessment score of 5 for each potential breach. It was further assumed that the other Scottish Water breaches would amount to at least the minimum threshold score of 1.5, and that the sites would only fail once a year. Thus, the potential CRI penalty for breaching potential DBP regulatory requirements for one year would amount to ~£4.13 million pounds.

A notable difference in overall costs was noticed even when ±30 variation in data was considered, used to account for changes in costs and water quality. Employing jar tested ferric appears to be the most economically feasible 20 year strategy for water treatment when a potential CRI penalty/cost avoidance of ~£43.8 million was considered (calculated as the potential CRI score of 3.28 over the threshold of 1.5 times the £1.26 million per index point and includes a 7% interest) (Figure 3-13). The average ~£22 million WLC for jar tested ferric, assuming no DBP breaches for the 8 sites, was around 34% of the £64 million status quo and 45% less than the ~£40 million, if using jar tested alum.

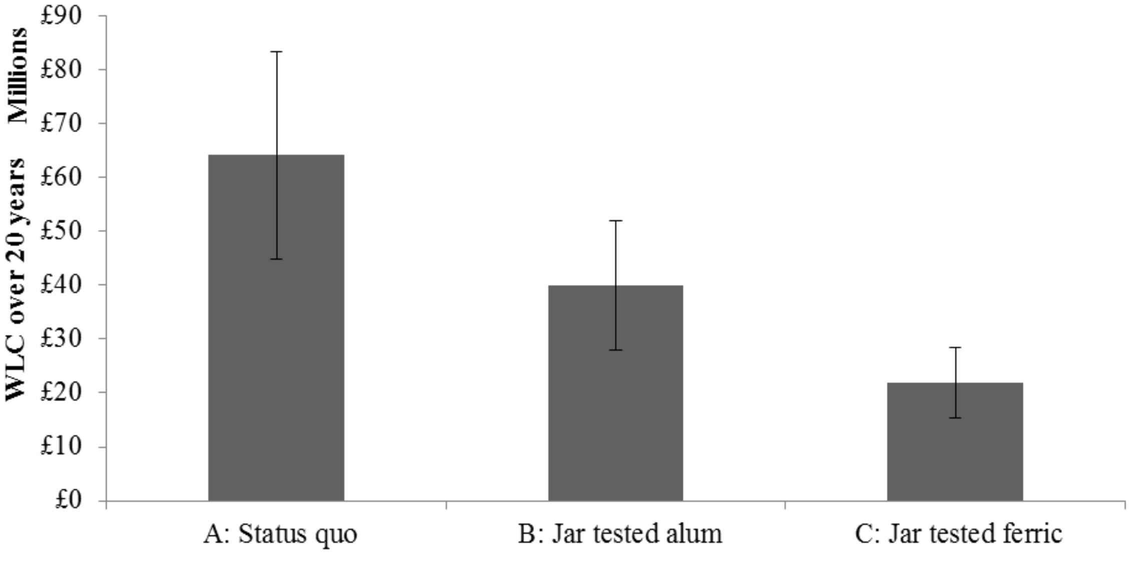


Figure 3-13 WLC estimates using present costs and potential CRI penalty/avoidance, for the three scenarios (with fixed ±30% variance).

3.6 Conclusions

- Ferric sulfate outperformed alum sulfate at two-thirds of the works investigated
- A lower overall ferric sulfate dose was required when compared to jar tested and works alum due to the pH reduction by using sulfuric acid
- Jar tested ferric sulfate was the most cost effective option when a 20 year WLC strategy was considered, despite CAPEX being over two times higher than the jar tested alum solution
- OPEX costs vastly outweighed CAPEX costs when a 20 year time frame was considered
- Jar tests with alum and ferric sulfate did not always return a lower DOC residual value than at three out of the five “Island” works (e.g. #13, #20 and #21), suggesting a better downstream treatment, membrane in #21’s case
- Ferric sulfate did not necessarily outperform alum only in waters with medium alkalinity

3.7 Acknowledgements

The Scottish Water help with sourcing the historic data and financial support from the Engineering and Physical Sciences Research Council (EPSRC) through funding of the STREAM IDC is gratefully acknowledged.

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4 Chapter: The influence of GAC physicochemical properties on natural organic matter removal

4.1 Abstract

Due to operational and economic feasibility constraints, natural organic matter (NOM) removal can be difficult to achieve at remote/small sites. Granular activated carbon (GAC) is a widely used treatment option, due to its relatively low maintenance and efficiency. The appropriateness of GAC for removal of NOM and disinfection by-product (DBP) precursors was investigated. Batch adsorption tests were a good tool for ranking media performance prior to pilot testing. All GAC media showed a low selectivity for specific removal of precursors of regulated DBPs and their control was a function of organic carbon removal. The 5-10 nm range of mesopores was an important GAC characteristic since it correlated well with DOC removal and DBP reduction. The uniformity of pore size distribution was also a common characteristic for the best media performance. In column tests, the media produced from bovine bones (Brimac) performed in the top three media for NOM removal. The best media, XC 30, outperformed the more commonly employed GAC (208 EA and F400) by 43-48%, for two different water types. The throughput at BV_{80} for UV_{254} appeared to be a good indicator of DBP precursor breakthrough for a water source with a high DOC. However, due to much lower concentrations of DBP precursors in the water source, the correlations were notably lower for the water source that was pre-treated with a conventional coagulationflocculation solution prior to GAC filtration.

4.2 Introduction

Granular activated carbon (GAC) has been used extensively in drinking water treatment for a variety of roles, including removal of pesticides, heavy metals and other micro pollutants, and more recently in wastewater reuse (Hoslett et al., 2018; Sun et al., 2018). However, GAC filtration following conventional coagulation/clarification processes is also frequently applied for additional removal of natural organic matter (NOM) and to improve the bio-stability of the water, through removal of assimilable organic carbon (Bhatnagar et al., 2017; Graf et al., 2014; Velten et al., 2011). GAC may also be employed at the beginning of the water treatment works (WTWs) as a “roughing” filter to aid with NOM and pesticide removal (Ratnayaka et al., 2008; Reckhow et al., 2010).

NOM has the potential to form many different disinfection by-product (DBP) compounds, with over 500 having been identified to date and some are considered potentially hazardous to human health (Richardson, 2002). From a regulatory perspective, the trihalomethanes (THMs) and haloacetic acids (HAAs) are the ones that have gained the most attention. Often, these DBP groups have the highest concentration by mass and their control has been assumed to control other DBPs (Gibert et al., 2013; Golea et al., 2017). In the UK, the only regulated halogenated DBPs are the THMs with a prescribed value of 100 µg/L (Golea et al., 2016). Recent proposals from the European Union are for a HAA regulatory value of 80 µg/L or 60 µg/L (European Commission, 2018) for 9 and 5 HAAs, respectively, which would align with similar regulations in the USA.

The selection of the most appropriate technology for removal of NOM is dependent on a number of factors. This includes the remoteness of the site, the size of the water treatment plant, the footprint available and the availability of operators to control the processes. For example, in Scotland, 90% of the total drinking water volume produced is through conventional coagulation and clarification at a small number of large WTWs. However, the remaining 10% of the potable water is produced from a large number of small WTWs, accounting for more than 50% of the total number of WTWs in Scotland. As these sites tend to be remote and serve a small population, WTWs often consist of membrane filtration due to their robust operation and reliable performance. GAC is also widely used as it is a passive process that needs limited operator input. In these cases, much is expected from the GAC as the NOM loadings can be very high while the adsorption rates for organic compounds onto the adsorbent can be slow (Cheng et al., 2005; Hoslett et al., 2018). However, GAC is still considered one of the best solutions for NOM removal due to its cost efficiency and versatile use at WTWs of various sizes (Bhatnagar et al., 2017; Iriarte-Velasco et al., 2008).

It is known that the high molecular weight (HMW) hydrophobic (HPO) NOM is readily removed by conventional coagulation-based treatment. Therefore, the influent to GAC processes in a secondary treatment stages are usually dominated by low molecular weight (LMW) and hydrophilic (HPI) NOM (Matilainen et al., 2006). The HPO fraction is generally more reactive with chlorine, usually resulting in the formation of high concentrations of THMs (Golea et al., 2017). When GAC is used as a roughing filter, the main loading of NOM is from hydrophobic and high MW organic compounds. Thus, the character of the NOM and the characteristics of the GAC media are important and influences the position of adsorption processes in the WTWs flowsheet (Valdivia-Garcia et al., 2016).

The precursor and activation process has an impact on the GAC physicochemical properties, creating a wide range of products suitable for the removal of various pollutants. GAC has a large surface area onto which NOM and other micro pollutants can adsorb. It is generally agreed that larger, hydrophobic, non-polar and less soluble molecules are more readily removed by GAC than smaller, non-polar, highly soluble ones (Chae et al., 2013). Therefore, a compatible pore size distribution (PSD) is required for NOM removal (Dastgheib et al., 2004). Relative to the types of NOM likely to adsorb on to GAC, pores are typically defined as being micro- (1-2 nm), meso- (2-50 nm) and macro-pore (Dastgheib et al., 2004). Typically, large molecules such as biopolymers and humic substances (molecular diameter >2nm width and MW 1-10 kDa) are adsorbed in mesopores and thus the proportion of available adsorption sites in the mesopore range becomes a limiting factor in their removal. However, the MW and hydrated diameter of the NOM molecule alone is not considered sufficient to assess NOM adsorption onto GAC. Other factors such as hydrophobicity should also be considered as low MW (LMW) hydrophilic compounds are poorly removed by GAC.

Given the ever-increasing regulatory requirements around DBP formation it is of interest to determine a) the best GAC media for DBP precursor removal from different water sources and b) the most effective GAC media position in the treatment train. Therefore, the aim of this work was to understand how different GAC properties influenced removal of NOM from different types of water source and to correlate the NOM characteristics with the media pore characteristics using batch adsorption tests and continuous rapid small scale column tests. This will enable more informed decisions to be made on GAC media selection for enhanced NOM removal.

4.3 Methods and materials

4.3.1 Sampling

Source water was taken from two different WTW locations in Scotland to enable comparison of treatment of water with different levels of pre-treatment (Figure 4-1). WTW A treated an average of 0.1 million litres per day (MLD) and employs direct filtration through a pressure sand filter (PSF); followed by three 11 metric tonnes GAC pressure filters. WTW B, treated ~0.27 MLD and consisted of conventional coagulation (Coag) flocculation (Floc), dissolved air flotation (DAF), rapid gravity filtration (RGF) solution followed by three 11 metric tonnes GAC pressure-filtration contactors. The water used in the current study was taken after PSF at WTWs A (referred to as water A) while at WTWs B, water was taken after RGF (water B).

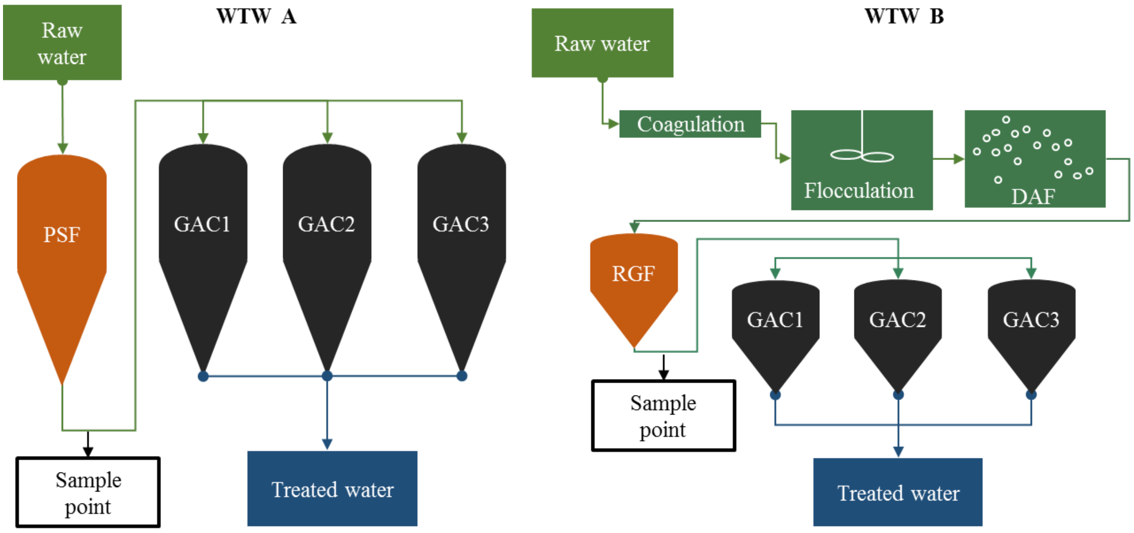

Figure 4-1 Water treatment flow sheet at the 2 WTWs GAC based and Coagulation/Flocculation, dissolved air flotation, rapid gravity filtration and GAC for WTWs A and B, respectively

4.3.2 GAC media

GAC media sourced from four different precursor materials were used in this study:

- Bituminous coal (COL-L900 (Carbon-Activated LTD), Filtrasorb F400 and Carbosorb 30 (Chemviron))
- Coal (208 EA (Chemviron), HYDRODARCO (HD) 4000 (Norit Inc), Hydraffin XC30 (Donau Carbon)),

- Coconut shell (DEO, HT5 (Eurocarb), FY5 (CPL Carbon Link)) and
- Bovine bones (Brimac).

The media were selected to cover a wide range of PSD and available surface area. They were used to investigate the effectiveness of narrow (0.7-1.7 nm) -, micro (1-2nm) -, and meso (2-50nm) -pore volumes and size ratios on the effectiveness of NOM, as DBP precursor, removal.

4.3.3 GAC preparation

For the batch adsorption isotherm tests, the GAC media was crushed and sieved to between 38-90 µm, to ensure pseudo-equilibrium was reached after 24 hours. Media was washed thoroughly in ultrapure water, dried overnight at 105 °C and kept in a desiccator until use. GAC doses of between 0-20 mg were added into 100 mL of water samples and stirred continuously in an orbital shaker (New Brunswick Scientific) at 200 rpm for 24 hours at 20 ° C. The water samples were filtered (0.45 µm, Fisher Scientific, Loughborough, UK) prior to analysis. For the rapid small scale column tests (RSSCTs), the GAC was crushed using a hammer mill, and then subsequently sieved to between 212 and 300 µm, so that a column diameter to particle size ratio of >30:1 could be maintained to avoid channelling effects. GAC was then rinsed and dried overnight (Philippe et al., 2010). GAC media was wetted by boiling in DI water for 10 minutes prior to use. Media preparation in this way has been shown to have no significant impact on the internal structural pore features of the GAC (Ando et al., 2010).

4.3.4 GAC characterisation using N_2 pore size distribution

The GAC pore size distribution was established using N_2 and was undertaken at St Andrews University. The total pore volume of GAC media that was dried overnight at 110°C was obtained using the adsorbed volume of N_2 gas near the saturation volume (P/P0=0.98) (Iriarte-Velasco et al., 2008). Surface area was calculated from the S_{BET} method. The pore size distribution (PSD) was determined using density functional theory (DFT) for narrow and micropores <2nm and mesopores 2-36 nm (maximum limit for the DFT model) (Velten et al., 2011). The DFT model was employed to help provide a more accurate interpretation of the isotherm data for non-homogenous liquids on microporous materials (Lastoskie et al., 1993) and was calculated assuming a graphite model with slit shape geometry using a Micrometrics ASAP 2010 machine (Iriarte-Velasco et al., 2008; Moore et al., 2001)

4.3.5 Adsorption capacity batch tests

Preliminary adsorption tests were undertaken and 24 hours were found sufficient to achieve a point close to equilibrium (pseudo-equilibrium). The adsorption capacity after 24 hours (q_e in mg DOC/g adsorbent) was calculated from equation (4-1)

$$\boldsymbol{q_e = \frac{C_i - C_e}{D_o}} \qquad \textbf{(4-1)}$$

Where D_o was the adsorbent concentration (g/L) and C_i and C_e were the initial and equilibrium concentrations (mg DOC/L).

The D_o for water A and B was obtained from preliminary experiments as 150 and 50 mg/L, respectively. These concentrations were selected so as to remove sufficient DOC over 24 hours, whilst also ensuring that at least 1mg/L DOC remained in solution after adsorption and to enable subsequent THMFP and HAAFP analysis to be undertaken. All tests were carried out in duplicate.

4.3.6 Rapid small scale column tests

1000 L of post sand filter water from WTW A and WTW B were collected and passed through rapid small scale columns tests (RSSCTs) for eight GAC media over two weeks. RSSCTs were designed and built using the parameters in equation (4-2 and (4-3) (Crittenden et al., 2012). This translated to a constant empty bed contact time ($EBCT_{SC}$) of 4.24 minutes with a constant GAC bed volume of 24.7 mL. A proportional intra-particle diffusivity (PD) model (x=1) was used after considering the type and size of the NOM compounds in the source waters.

$$\boldsymbol{\frac{EBCT_{SC}}{EBCT_{LC}} = [\frac{d_{p,SC}}{d_{p,LC}}]^x = \frac{t_{SC}}{t_{LC}}} \qquad \textbf{(4-2)}$$

$$\boldsymbol{M_{SC} = EBCT_{LC} x \frac{d_{p,SC}}{d_{p,LC}} x\, Q_{SC}\, x\, \rho_{p,LC}} \qquad \textbf{(4-3)}$$

$EBCT_{LC}$ and $EBCT_{SC}$, $d_{p,LC}$ and $d_{p,SC}$, t_{LC} and t_{SC} are the empty bed contact time (min), particle diameter and operation time for the large and small column respectively. M_{SC} and Q_{SC} are defined as the mass of the media (mg) and flow (mL/min) in the small column, respectively, whilst the ρ_{pLC} is defined as the density of the GAC particle (mg/mL) in the large column. Equation (4-3) was used to ensure that the different GAC media densities were accounted for.

4.3.7 Sample chlorination and DBP formation potential determination

Water samples were diluted to a concentration of 1 mg C/L, buffered to pH 7 and added to 250 ml glass bottles with glass stoppers. Chlorine as NaOCl was added to the solution at a free Cl_2:DOC ratio of 5:1 and samples were stored in the dark at a controlled temperature of 25°C for 7 days. After 7 days, the chlorine in the samples was quenched using sodium thiosulphate crystals and the total of four trihalomethanes (THMs) and five halo acetic acids (HAAs) were determined. THMs were measured using gas chromatography mass spectrometry with headspace injection using a modified method from USEPA 551 (USEPA, 1998). HAAs were measured using liquid-liquid separation and analysis by gas chromatography with mass spectrometric detection following USEPA method 552.3 (APHA, 2012; Goslan et al., 2009). A minimum of 7 injections were undertaken for each measurement.

4.4 Results and Discussion

4.4.1 Source water characterisation

The source waters under investigation had very different quality composition due to the differences in the pre-treatment each had received. For water A, water has passed through pressure sand filtration for removal of particulates, while water B had been more comprehensively treated by coagulation and clarification processes. The pH and conductivity were lower for water A than for water B, with values of 6.8 and 8.1, and 166 and 569 µS/cm, respectively. The DOC for water A was double that of water B, while the UV_{254} was 3.75 times higher. This, together with the high HPI value for water B, shows that it has a more hydrophilic NOM composition. Moreover, the higher DOC and HPO concentration and specific THM FP values for water A resulted in total DBP concentrations that were 2.4 and 8 times higher than for water B for the worst case formation of tTHMs and tHAAs, respectively (Table 4-1). Therefore, the GAC at WTW A was subjected to much higher loadings of hydrophobic NOM. The specific THMFP was 20% higher in water A compared to water B, while the HAAFP was 4.2 times higher. Specifically, THMFP was measured as 113.1 µg THM/mg DOC for water A, composed of 87% chloroform, 11% bromodichloromethane, 2% dibromochloromethane and <1% bromoform. Equivalent figures for water B were 90.4 µg THM/mg DOC, with a similar proportional make up of THM species. Similarly, the HAAFP was 134.6 and 42,6 µg HAAs/mg DOC for water A and B, respectively. The dominant HAA species were dichloroacetic and trichloroacetic acids.

Table 4-1 Physicochemical characteristics of the two different water sources.

Parameter	Water A	Water B
pH	6.8	8.1
DOC (mg/L)	5.98	3.12
UV254 (/cm)	0.254	0.068
SUVA (mg/L/m)	4.25	2.18
tTHM (µg/L)	676.3	282
THM FP (µg /L per mg DOC)	113.1	90.4
tHAA (µg /L)	1006.4	126
HAA5 FP (µg/L per mg DOC)	168.3	40.4
Colour (mg/L Pt/Co)	33	4.47
Turbidity (NTU)	0.37	0.1
Conductivity (µS/cm)	166	569
HPO (mg/L)	3.44	1
TPI (mg/L)	1.25	0.71
HPI (mg/L)	0.37	1.05

4.4.2 Physical characteristics of media

The GACs under investigation had a range of physical characteristics (Table 4-2). The mesopore volumes ranged from as low as 0.004 cm^3/g up to 0.324 cm^3/g for FY5 and HD4000 media respectively. The DFT areas of pores >2nm ranged from between 3 and 110 m^2/g for FY5 and HD4000 respectively. In these extreme cases this was despite HD4000 having only a 22% higher total pore volume compared to FY5, while FY5 had only a 40% larger surface area (S_{BET}). Most of the media pores were found to be in the narrow and micropore range. The exception was HD4000 which had a mesopore volume more than double that of the volume of the next media (XC30) at 0.324 cm^3/g and 0.156 cm^3/g respectively. None of the media had pores with a width >27.3 nm. The highest total volume was observed for HT5 (0.581 cm^3/g) with most of the volume available in the 1-2 nm pore size range (0.401 cm^3/g). The media with the most even PSD was seen for XC30 with 0.212, 0.205 and 0.156 cm^3/g distributed between narrow, micro and mesopores, respectively out of a total of 0.511 cm^3/g. The media granulation ranged from values between 1.4-3.35 mm for FY5 to 0.42-1.7 mm for Carbosorb 30.

There was good agreement between the S_{BET} values measured in the current study and those reported by the supplier and other researchers (Table 4-2). The exceptions were the S_{BET} for Brimac (bone char) and the total pore volume for F400. For Brimac, S_{BET} was previously reported by to be between 130-283 m^2/g, whilst total pore volume was reported to be 0.287 cm^3/g (Moreno et al., 2010; Nili-Ahmadabadi, 2011). However, here measurements were much higher; between 705-841 m^2/g. The total pore volume was measured to be 0.430-0.403 cm^3/g. For F400, the total pore volume was measured to be 20% lower than previously reported in other studies. The measured micropore volume of 0.271 cm^3/g compares with literature values of between 0.309-0.340 cm^3/g (Summers et al., 2010) and 0.404-0.410 cm^3/g (Dastgheib et al., 2004; Gibert et al., 2013) (Table 4-2). It was not obvious why these differences were observed given the close agreement in measurements for the other media. However the differences are likely to reflect the media's sample heterogeneity, a point noted by other researchers (Ando et al., 2010). Regardless, the surface area for Brimac was still the lowest measured for all of the GACs investigated here.

Table 4-2 The physicochemical properties of the media used for removal of NOM from two different water sources.

GAC media	V_{total} (cm³/g) DFT determined to <30nm	Pore width (nm)	$V_{narrow\ pores}$ (cm³/g) width 0.7-1.7 nm	$V_{micropores}$ (cm³/g) width 1-2nm	$V_{mesopores}$ (cm³/g) width 2-50 nm	DFT area (m²/g)			Granulation (mm)*	S_{BET} from supplier* (m²/g)	S_{BET} I (m²/g)	S_{BET} II (m²/g)	IN* (mg/g)	Precursor*
						0.7-1.7nm	1-2nm	>2nm						
COL-L900	0.460	≤26.1	0.289	0.347	0.112	444	506	72	0.425-1.70*	900-1000*	977±5	998±7	900*	Bituminous Coal*
F400	0.442	≤26.1	0.258	0.271	0.073	431	416	49	0.425-1.70*	1050*	1032±5	904	1050*	Bituminous Coal*
Carbosorb 30	0.410	≤26.1	0.239	0.210	0.055	385	384	29	0.42-1.70*	900*	928±6	966±3	900*	Bituminous Coal*
208EA	0.517	≤16.1	0.262	0.301	0.120	424	465	67	0.6-1.7*	1000*	1078±6	1001±5	1000*	Coal*
HD4000	0.513	≤25	0.127	0.144	0.324	190	209	110	0.6-2*	725*	614±4	603±4	650*	Coal*
XC 30	0.511	≤26.1	0.212	0.205	0.156	325	340	66	0.6-2.36*	1000*	986±6	1004±5	950*	Coal*
DEO	0.331	≤27.3	0.163	0.174	0.013	274	285	8	0.6-1.70*	800*	809±11	837±3	825*	Coconut shell*
HT5	0.581	≤27.3	0.372	0.401	0.029	621	652	14	0.42-1.70*	1400*	1419±12	1423±6	1300*	Coconut shell*
FY5	0.400	≤16.1	0.270	0.288	0.004	452	471	3	1.40-3.35*	1150*	1043±11	988±5	1100*	Coconut shell*
Brimac	0.430	≤25	0.209	0.246	0.131	334	373	62	0.7-2.38*	200*	841±3	705±4	700 *	Bovine bones*
*Data sourced from supplier technical sheets														

On closer investigation of the PSD, differences were noted between the media in terms of the available pore volumes relative to the pore width (Figure 4-2). Whilst most media had pore volumes in the narrow and micropore ranges (0.7-1.7 and 1-2 nm), the HD4000 had the most uniform PSD with a substantive proportion of 2-50 nm (69.2%), 1-2 nm (30.8%) and 0.7-1.7 nm (27.1%) pores. The lowest uniformity of PSD was seen for GAC media sourced from coconut shell, with 98.8%, 92.9%, and 93.1% of the pore volumes in the 1-2nm range, for FY5, DEO and HT5 respectively. Carbosorb 30 and F400 had the lowest uniformity of the coal based GACs, with 75.7 and 66.7% of pore volumes in the 0.7-1.7nm range, and 17.4 and 19% in the 2-50 nm range, respectively.

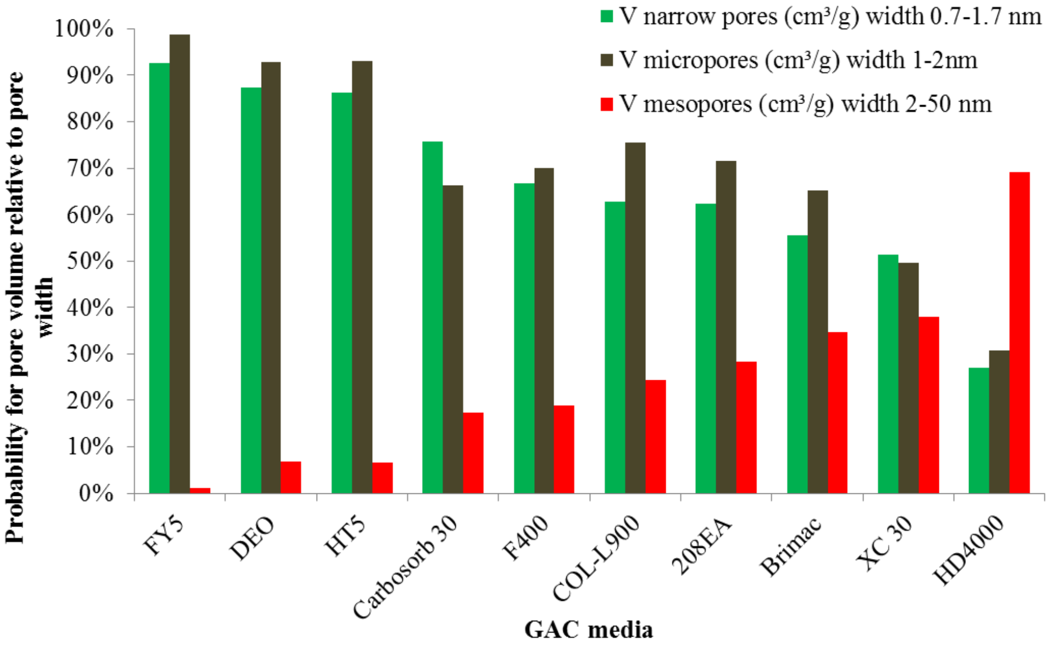

Figure 4-2 GAC pore volumes relative to their respective pore width.

4.4.3 Batch adsorption isotherms

Batch adsorption isotherms were undertaken on waters A and B to determine the effectiveness of the various media in terms of overall NOM and THM precursor removal for the different water types. There were some big differences in the DOC adsorption observed for the different media, with DEO being the poorest and XC30 the best for both water types. DEO removed 1.19 and 1.76 mg/g for water A and B while XC30 removed 20.68 and 27.13mg/g respectively (Figure 4-3a, and Figure 4-4a).

None of the GAC media had a particular selectivity for removal of THM precursors, where THMFP values remained between 112.5 and 100.3 µg THM/mg DOC for water A and 75.2 and 82.7 3 µg THM/mg DOC for water B (Figure 4-3b, and Figure 4-4b). The total THMFP removal was proportional to the adsorption capacity of the GAC (and hence overall DOC removal) for both water sources (Figure 4-3c, and Figure 4-4c). No other GAC indicators such as the IN or S_{BET} values correlated with the NOM adsorption capacity (Table A - 1).

A higher adsorption capacity for DOC was observed for water B compared to water A. For example, XC30 removed 25 mg DOC/g from water B compared to 20 mg DOC/g for water A. Similarly, the tTHM formation was lower at WTW B compared to that at WTW A. This was due to the fact that water B had been conventionally treated by coagulation and clarification processes resulting in removal of HMW hydrophobic organic compounds. Such NOM is known to cause pore blockage, reducing the overall NOM removal, an effect that was observed for water A (Karanfil et al., 1999).

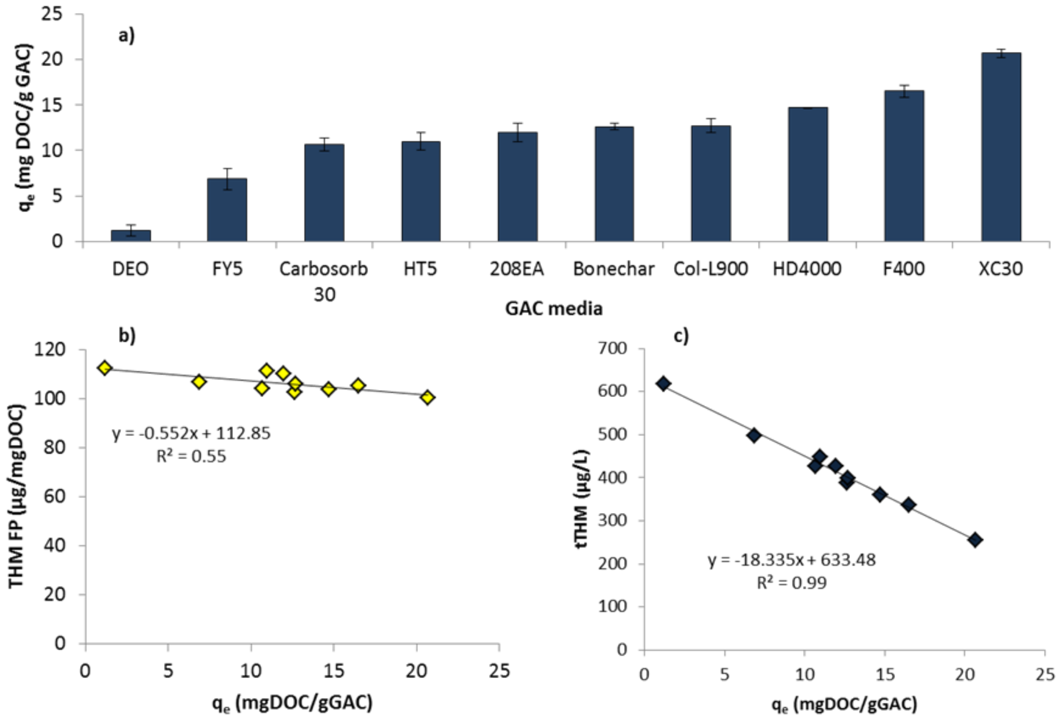

Figure 4-3 Adsorption capacity (q_e) of the different GAC considering DOC (a) and the relationship between q_e and THM FP (b) and tTHMs (c) for water A.

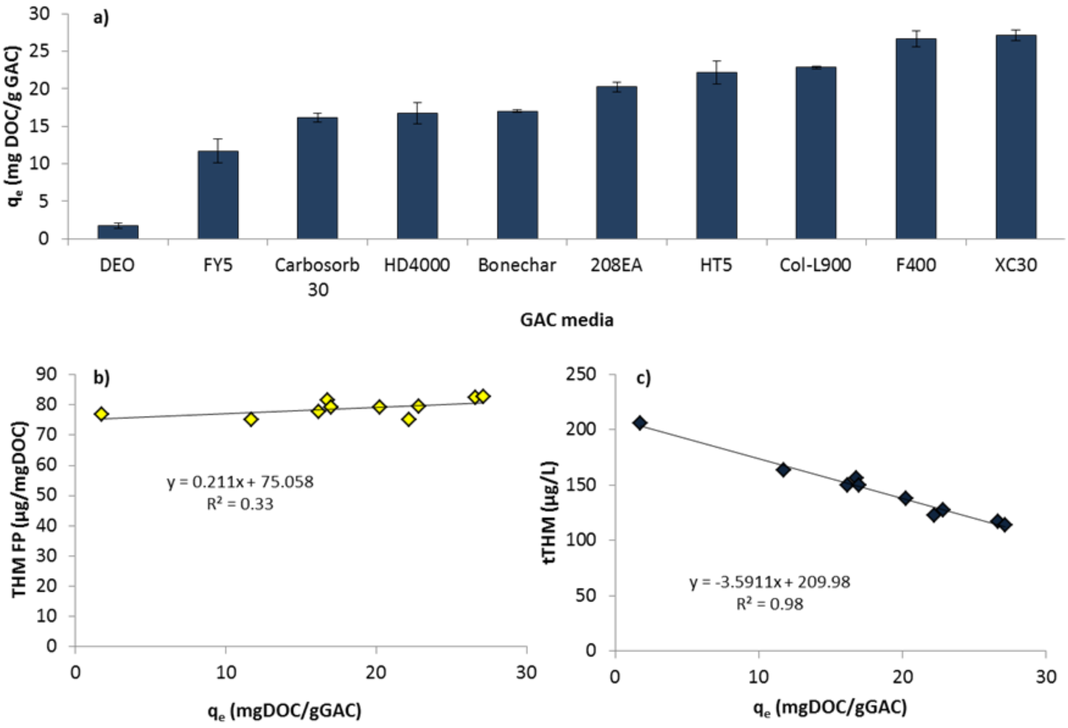

Figure 4-4 Adsorption capacity (q_e) of the different GAC considering DOC (a) and the relationship between q_e and THM FP (b) and tTHMs (c) for water B.

4.4.4 Rapid small scale column tests

To understand whether the DOC removal was consistent during continuous treatment compared to the batch experiments, RSSCTs were undertaken. The performance of the different GAC followed similar profiles, with general agreement with the batch tests with respect to the best and worst performing media (Figure 4-5a, b). The breakthrough curves were much steeper for water A compared to water B, due to the higher organic loading in the higher DOC water (Table 4-1) and the presence of larger NOM molecules that exhausted the GAC surface area more rapidly.

Overall, the coal based media performed better than the other GAC for both water sources. In the case of water A, the DOC removal efficiency decreased progressively over time from a high of 93.6% to a low of 26.2% for XC30 after 22,000 BVs. For F400, equivalent removal reduced from 92.6% to 14.8%. While F400 had a high initial DOC removal compared to the other coal based media, the removal dropped below that of XC30 and 208 EA after 500 BVs. F400 had the lowest volume of mesopores (0.073 cm^3/g) compared to the other coal media: XC30 – 0.156 cm^3/g; 208EA - 0.120; and

COL-L900 - 0.112 cm^3/g. The hydrated diameter of dissolved organic matter has previously been reported to be in the size range between 0.5-5 nm, meaning that mesopores (2-50 nm) provide larger accessible adsorption sites for NOM macromolecules (Dastgheib et al., 2004; Karanfil et al., 1999; Moore et al., 2001; Velten et al., 2011). For water B, XC30 was again the best performer, removing 91.9% DOC initially and resulting in 50.6% removal after 24,000 BVs. The other coal based GAC also performed well, removing 90-91% DOC initially and progressively declining to between 28-37%, for F400, 208EA and COL-L900 after 24,000 BVs. F400 had a marginally worse performance than 208EA, but not as low as COL-L900, suggesting that for water B, high mesopore volume may not be the only limiting factor for NOM adsorption by GAC. For water B, many of the larger MW organic compounds had been removed as a result of the upstream coagulation process, resulting in a higher proportion of smaller MW organic compounds being present in the water, molecules that can access the smaller pores in the GAC (Graf et al., 2014; Iriarte-Velasco et al., 2008).

The Brimac media performed comparatively well for both water sources considering its lower surface area compared to the other GAC tested. Brimac removed 91.3% and 89.9% DOC initially and progressively decreased to 20.4% and 33.3% after 22,000 and 24,000 BVs for water A and B, respectively. GAC media produced from coconut shell were least effective at DOC removal. The HT5, FY5 and DEO DOC removal started at between 18.2-88% and progressively decreased to between 2-31%. The HT5, FY5, and DEO media mesopore volumes were the lowest of the media tested (0.029, 0.004 and 0.013 cm^3/g). These results are in agreement with the fact that coconut shell based media were predominantly microporous and preferentially adsorb low molecular weight hydrophilic organic matter due to the large available surface area and corresponding PSD (Graf et al., 2014). Similar trends as for the DOC were noted for total THMs and total HAAs for the two water types, where the reduction in DBPs tracked the DOC removal (Figure 4-5b,c, e, and f).

Other limiting factors such as temperature (as a factor influencing the type of organic compounds found in the water) and pH point zero charge (pH_{PZC}) may have influenced the results, however these factors were not measured as part of this study.

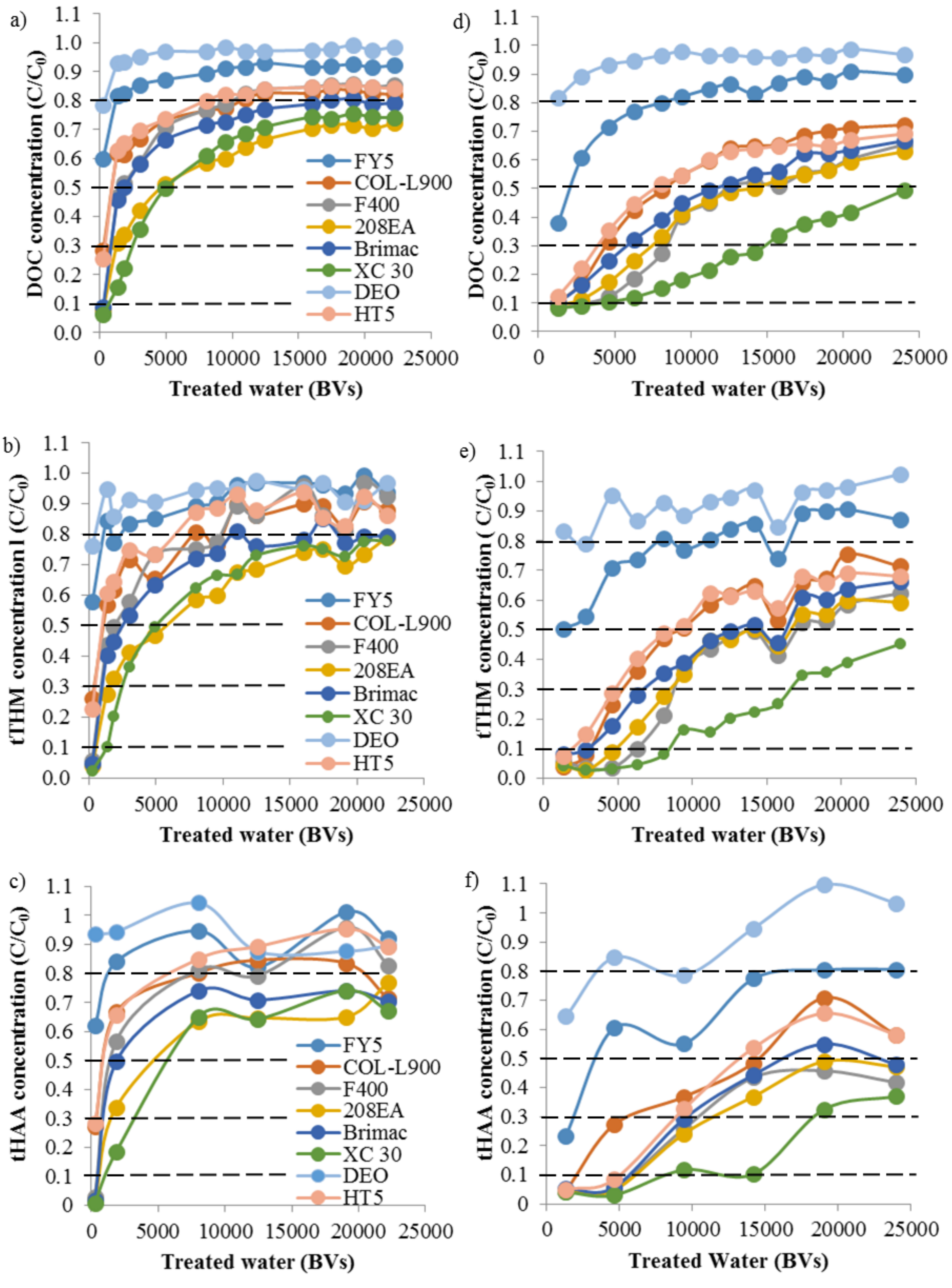

Figure 4-5 Reduced DOC, tTHM and tHAA versus treated water, in bed volumes (precursor breakthrough at BV_{10}, BV_{30}, BV_{50}, and BV_{80}, highlighted by the dotted lines) for water A (a, b, c) and water B (d, e, f).

The throughput to 10% (BV_{10}) for DOC was not reached by FY5 and DEO for either water source and by COL-L900 and HT5 for source A, showing the rapid exhaustion of the media and a high quantity of non-adsorbable NOM. The throughput to 30%, 50% and 80% breakthrough (BV_{30}, BV_{50} and BV_{80}) were determined from DOC breakthrough data and investigated further for each media to show the differences in media performance for DOC removal (Table 4-3).

The initial throughput to BV_{30} confirmed XC30 as the better media for DOC adsorption for both waters. For source A, XC30 treated almost double the amount of water (2514 BVs) than the next best GAC (208EA), and three and seven times more water than Brimac and the best coconut shell based media, HT5. The Brimac GAC performed at a similar level to the F400 benchmark media. Both FY5 and DEO failed to achieve a quantifiable BV_{30} due to rapid exhaustion (<<1242 and <<503 BVs, respectively). The same order of removal was seen when the BV_{50} was considered although the differences were less pronounced. The XC30 was the best performer (5059 BVs of water treated) closely followed by 208EA, while the HT5 treated only 19% of this volume. The difference between the BV_{80} for the best and worst GAC was significant. For example the BV_{80} was not achieved after 24,000 BVs for XC 30 and 208EA, while the worst performing media only achieved a BV_{80} of 503. For the other GAC, Brimac treated 40% more water than F400, while COL-L900 treated the same BVs of water as HT5 (946).

For water B, the media performance was different. While XC 30 was the best performing GAC with a BV_{30} of 14,911, F400 had the next highest BV_{30}, although this was 44% less water than that treated by XC30. The same trends were observed for the BV_{50}, where DEO and FY5 treated the lowest volume of water. DEO did not record a BV_{50} as this had been achieved before the first sample was taken (<<1183 BVs). FY5 treated less than 10% of the BVs treated by XC 30. Only FY5 and DEO obtained a measurable BV_{80}, with all of the other media continuing to remove more than 20% of the DOC after BVs >24,000.

These results compare well with previous work on NOM removal by GAC, with relatively low BVs of water treated before breakthrough had been observed (Li et al., 2007; Velten et al., 2011). However, most media were able to remove between 20-30% of DOC after extended run times for both water sources, indicating a limited potential for continuous removal. In comparison, for removal of micropollutants using GAC continually higher levels of removal are typically observed following much longer operation. For example, 80% removal of the antibiotic sulfamethoxazole was still observed after more than double the number of BVs (~68,000 BVs) (Greiner et al., 2018).

Table 4-3. Throughput to DOC for an EBCT$_{LC}$ of 20 minutes at 30%, 50% and 80%, BV$_{30}$, BV$_{50}$ and BV$_{80}$, respectively for the GAC media investigated via RSSCT at WTWs A and B.

GAC media	WTW A			WTW B		
	BV$_{30}$	**BV$_{50}$**	**BV$_{80}$**	**BV$_{30}$**	**BV$_{50}$**	**BV$_{80}$**
FY5	<<1242	<<1242	1242	<<2041	2041	8284
COL-L900	355	946	10710	4467	8284	>>8284
F400	858	1775	10030	8402	12308	>>12308
208EA	1301	4704	NR	7455	13728	>>13728
Brimac	858	1775	17101	5798	11657	>>11657
XC 30	2514	5059	>>5059	14911	23964	>>23964
DEO	<<503	<<503	503	<<1183	<<1183	1183
HT5	355	946	8047	3875	7633	>>7633

Depending on the raw water characteristics, a trigger for regeneration before threshold DOC, tTHM and tHAA breakthroughs are reached can be estimated from water determinants that are easier to measure online. For example, UV$_{254}$ monitors are often present to monitor inlet and inter-stage water quality. The breakthrough to UV$_{254}$ was therefore matched to the DBP breakthrough curves, for both water sources A and B. For water A, breakthrough of UV$_{254}$ at BV$_{30}$ and BV$_{80}$ correlated well with the BV$_{50}$ for tTHM and the BV$_{50}$ for tHAA. For water B, however, the correlations were much weaker. This can be explained by the higher concentration of UV$_{254}$ absorbing and hydrophobic organic compounds typically dominant in water A, while water B contained more hydrophilic and lower MW NOM. Hydrophobic NOM typically forms more DBPs than hydrophilic material and therefore the DBP breakthrough was more closely linked to the UV$_{254}$ in the source water where this organic fraction was more prevalent (Bougeard et al., 2010; Karapinar et al., 2014).

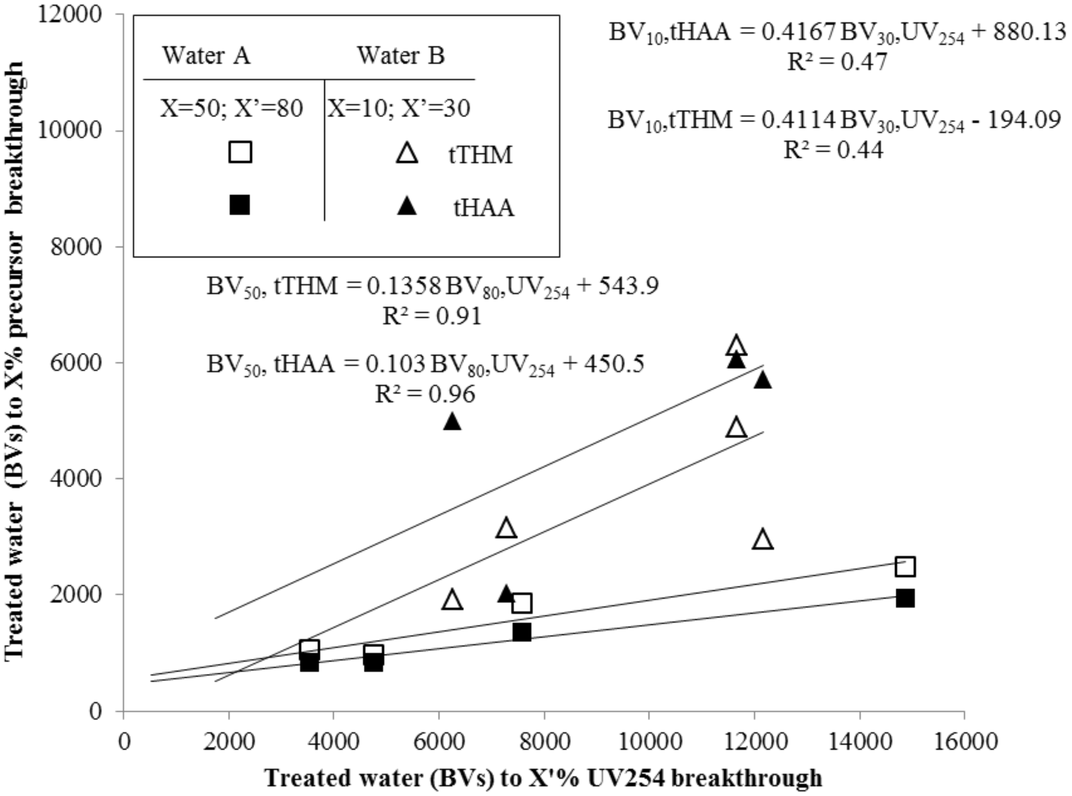

Figure 4-6 UVA$_{254}$ breakthrough to 80% and 30% correlated to DBPs' breakthrough for GAC media.

4.4.5 Correlations between RSSCTs and GAC characteristics

For water A good correlations were noted for both DOC and tTHM removal at the start of the run (BV$_{30}$) with the absolute pore volumes with diameters between 5-10 nm (Figure 4-7a). For other pore sizes, much weaker correlations were observed. As the run progressed, the pores in the media became blocked and so the availability of large pores becomes limiting hence stronger correlations were seen at the BV$_{80}$, with R^2 values of 0.86 and 0.80 for DOC and tTHMs, respectively (Figure 4-7 a). For water B, the beginning of the run at BV$_{30}$ saw a weak correlation between DOC and tTHMs with the PSD, potentially due to the nature of NOM in the feed water and the larger adsorption space available in the media. As the run progressed, and the mesopore availability became limiting, the BV$_{50}$ DOC correlated well with the PSD (R^2=0.83) (Figure 4-7b). These data suggest that GAC with a pore volume greater than 0.025 cm^3/g GAC in the 5-10 nm range offer higher DOC and tTHM precursor removal, with the best gains made from the treatment of the water with the lower initial DOC loading (water B).

These results were in line with other findings regarding the importance of small mesopores for DOC adsorption by GAC media (Greiner et al., 2018).

Therefore, the important characteristics of GAC media that were important for the removal of NOM, particularly at high loadings, were the availability of mesopore volumes in the 5-10 nm width range. However, the best performing GAC also had a more uniform pore size distribution, thus allowing for a wider range of NOM to adsorb. This was thought to explain the high levels of adsorption seen by the bonechar Brimac media, which had a more even distribution of pores than many of the other GAC. Other factors not explored in this study such as the surface charge and functionality are also expected to influence removal of NOM from water.

The relatively fast breakthrough to 50% DOC and tTHM for the higher DOC water source shows a limited capacity for long term removal of these compounds. This demonstrates that GAC media is not the most effective solution for bulk NOM removal. However its role as an effective polishing process was shown for water B, where longer term reduction in DOC and DBP precursors were seen.

For example, for WTW A, if an average flow of 0.1 MLD and 33 metric tonnes GAC vessels were considered and there were no changes to the influent raw water characteristics, then the BV_{30} for THMs and HAAs would be reached after ~2.2 and ~2.9 years, respectively. However, the next best media, 208EA, would be able to treat water to BV_{30} for THMs and HAA for only ~1.36 and ~1.31 years, respectively.

In comparison, for WTW B, with a higher average flow of 0.27 MLD and the same sized vessels, XC30 would be able to remove THMs and HAAs precursors by 30% for ~5.6 and ~6.12 years, respectively. The next best media, F400 and 208 EA, would remove DBP precursors by up to 30% for ~2.9 and 3.5-3.8 years, respectively.

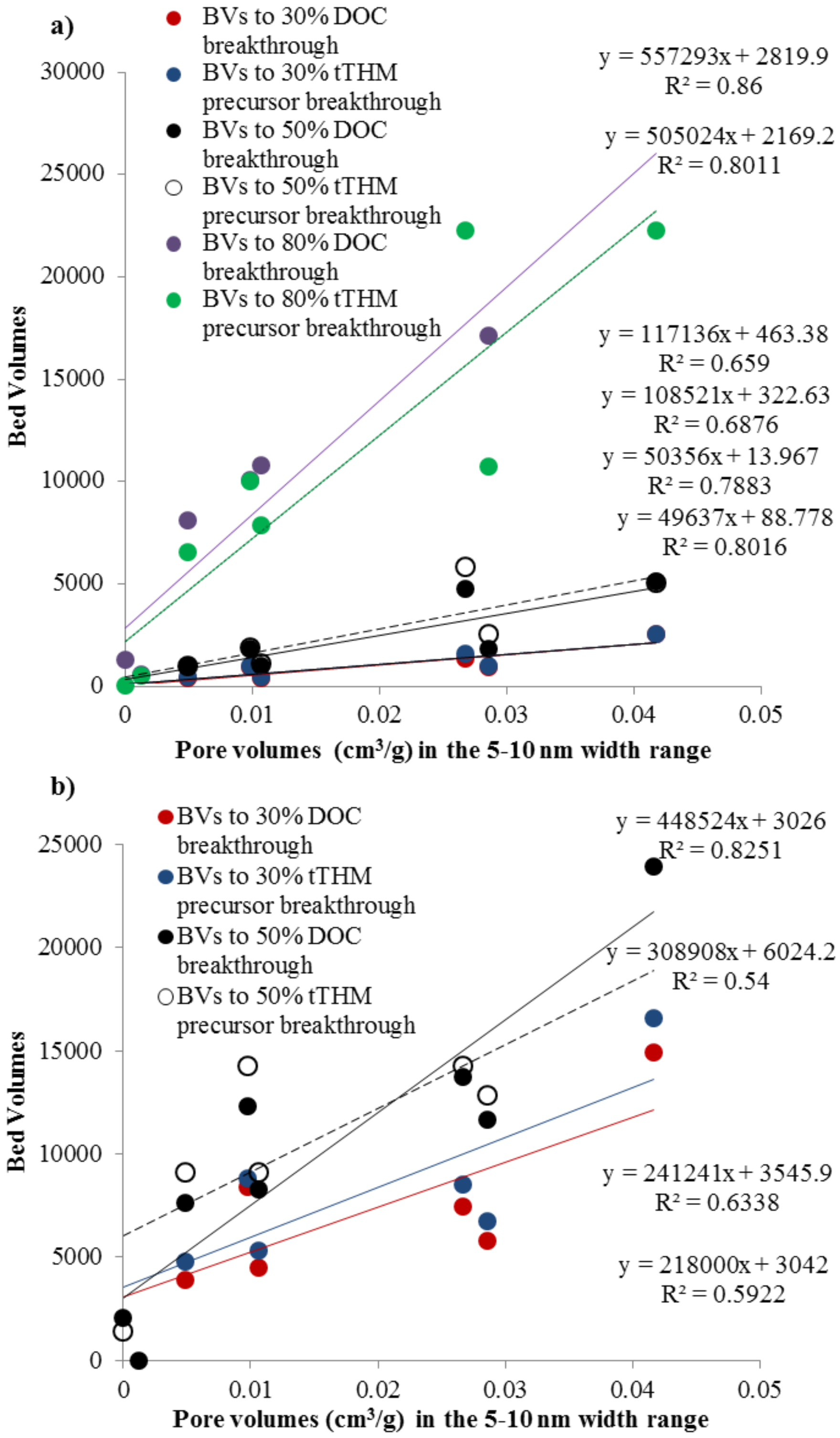

Figure 4-7 Pore volumes (cm^3/g) in the 5-10 nm width range correlated to DOC, tTHM and tHAA breakthrough for water A (a) and B (b) respectively.

4.5 Conclusions:

A link between NOM characteristics and GAC media physicochemical properties was sought. After testing two different water sources the following conclusions were drawn:

- Batch adsorption tests were a good indicator of initial NOM removal and were an effective tool to rank media ahead of pilot testing.
- All media investigated showed a low selectivity for THM and HAA precursors. As a result, the tTHMs and tHAAs removal was primarily subject to the reduction of DOC to a sufficiently low level.
- The volume of mesopores in the range of 5-10 nm size range correlated well with DOC, tTHM and tHAA showing that this parameter was important for selection of GAC for NOM removal.
- Brimac media performed well for both water sources despite lower S_{BET} values. This suggests that the media adsorption capacity for NOM may be due to other factors such as surface charge and its basicity.
- The best performing media at both waters was identified: XC 30 was able to treat 48% and 43% more water than the next best performing GAC from source A and B, respectively.
- The BV_{80} for UV_{254} could be used to predict tTHM and tHAA breakthrough for water A, since it correlated well with $BV_{50,}$ tTHM and $BV_{50,}$ tHAA, For water B, however, the correlations were much weaker as a result of lower concentrations of DBP precursors being present in the water source.

4.6 Acknowledgments

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5 Chapter: Pilot scale spiral wound membrane assessment for THM precursor rejection from upland waters

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5.1 Abstract

The outcomes of a pilot-scale study of the rejection of trihalomethanes (THMs) precursors by commercial ultrafiltration/nanofiltration (UF/NF) spiral-wound membrane elements are presented based on a single surface water source in Scotland. The study revealed the expected trend of increased flux and permeability with increasing pore size for the UF membranes; the NF membranes provided similar fluxes despite the lower nominal pore size. The dissolved organic carbon (DOC) passage decreased with decreasing molecular weight cut-off, with a less than one-third the passage recorded for the NF membranes than for the UF ones.

The yield (weight % total THMs per DOC) varied between 2.5% and 8% across all membranes tested, in reasonable agreement with the literature, with the aromatic polyamide membrane providing both the lowest yield and lowest DOC passage. The proportion of the hydrophobic (HPO) fraction removed was found to increase with decreasing membrane selectivity (increasing pore size), and THM generation correlated closely ($R^2 = 0.98$) with the permeate HPO fractional concentration.

5.2 Introduction

It has been recognised for more than 40 years that the reaction of natural organic matter (NOM) with chlorine generates chlorinated disinfection by-products (DPBs) generally and trihalomethanes (THMs) specifically (Bond et al., 2012). In the UK the prescribed concentration value (PCV) of THMs in potable water is currently 100 µg L^{-1} (DWI, 2012). An established option for addressing this issue is the removal of the NOM using membranes. A large amount of research has been conducted to ascertain the precise characteristics and chemical functional groups within the NOM dissolved organic carbon (DOC) responsible for THM generation, both upstream and downstream of a membrane separation process (Bond et al., 2010; Hua et al., 2007; Hyung Kim et al., 2005). A review of the recent available literature suggests that the yield of total THMs (tTHMs), defined as weight % total THMs per DOC, in treated water tends to be in the range of 2-8 % THMs per DOC (Sutherland et al., 2015). Thus, whilst the residual DOC level provides an indication of THM formation propensity (THMFP in µg L^{-1}), such that DOC passage through the membrane is a useful performance indicator, the yield is subject to significant variation.

Membranes of appropriate selectivity - generally in the tight ultrafiltration (UF)/loose nanofiltration (NF) region - have been shown to be reasonably effective for removing DOC, and thus THM precursors (Cortés-Francisco et al., 2014; Sutherland et al., 2015). However, an examination of available data for NF/UF membranes (Table 5-1) reveals widely varying trends in DOC passage and yield with membrane selectivity. In many cases (Hu et al., 2014; Hua et al., 2007; Özdemır, 2014) there is no recognisable trend in either DOC or yield with perm-selectivity as represented by the molecular weight cut-off, or MWCO (Figure 5-1b and Figure 5-1d). Data are very highly scattered, with relative standard deviation (SD) values of between 5 and 41% and 17-67 %, for DOC passage and yield respectively - as reflected in the error bars in Figure 5-1d. Dissolved organic nitrogen (DON) passage similarly does not correlate with MWCO (Figure 5-1a, (Xu et al., 2011). It is only in one case (Figure 5-1e, (de la Rubia et al., 2008),) that there appears to be the expected relationship of increasing DOC passage with increasing membrane MWCO. This report, based on 10 different feed waters predominantly from the Murcia region of Spain, also suggests an increase in yield with increasing MWCO, albeit with anomalously high yield values for one particular membrane (at 260 Da MWCO). Against this, three of the other papers (Hu et al., 2014; Hua et al., 2007; Özdemır, 2014) indicate that the highest yield is obtained at the lowest MWCO (Figure 5-1). Outcomes are significantly affected by the acknowledged seasonal variations in NOM characteristics (Wei et al., 2010).

Table 5-1 Literature data, yield and DOC passage.

Water source(s)	**Membrane(s)**	**%DOC passage vs. MWCO**		**%DOC passage vs. yield**		**References**
		Gradient	**R^2**	**Gradient**	**R^2**	
Crevillente	*Millipore YM1*	0.036	0.85	-0.015	0.0001	(de la Rubia et al., 2008)
Guadalest	*Millipore YC05*	0.058	0.97	0.38	0.37	
La Pedera	*DOW NF270*	0.049	0.94	0.0044	0.0002	
Tibi	*DOW NF90*	0.066	0.80	0.45	0.094	
Villajoyosa	*Alfa Laval NFT50*	0.013	0.04	0.079	0.048	
Mayayo		0.04	0.96	0.91	0.79	
Regueron		0.067	0.98	0.79	0.54	
Reina		0.036	0.87	0.49	0.058	
Segura River		0.038	0.98	0.38	0.49	
Taibilla		0.059	0.85	-0.053	0.025	
Yellow River	*Millipore*	-6.01	0.58	-0.032	0.046	(Hu et al., 2014)
Danjiaongkou Reservoir	*Millipore YM10*	-4.7	0.25	0.2	0.44	
Repentigmy	*Millipore YM10*	-2.4	0.58	-0.48	0.97	(Hua et al., 2007)
Waco	*Millipore YM3*	2.3	0.04	1.9	0.85	
Winnipeg	*Millipore YC 05*	3.67	0.11	1.16	0.057	
Terkos raw	*Millipore YM*	-31	0.7	5.4	0.97*	(Özdemır, 2014)
- post ozonation		-35	0.73	8.5	0.91*	
- post coag/flocc		-41	0.74	30	0.90*	
- post filtration		-38	0.74	6.2	0.44*	
*24 hr THM FP method, others 7 days THM FP method						

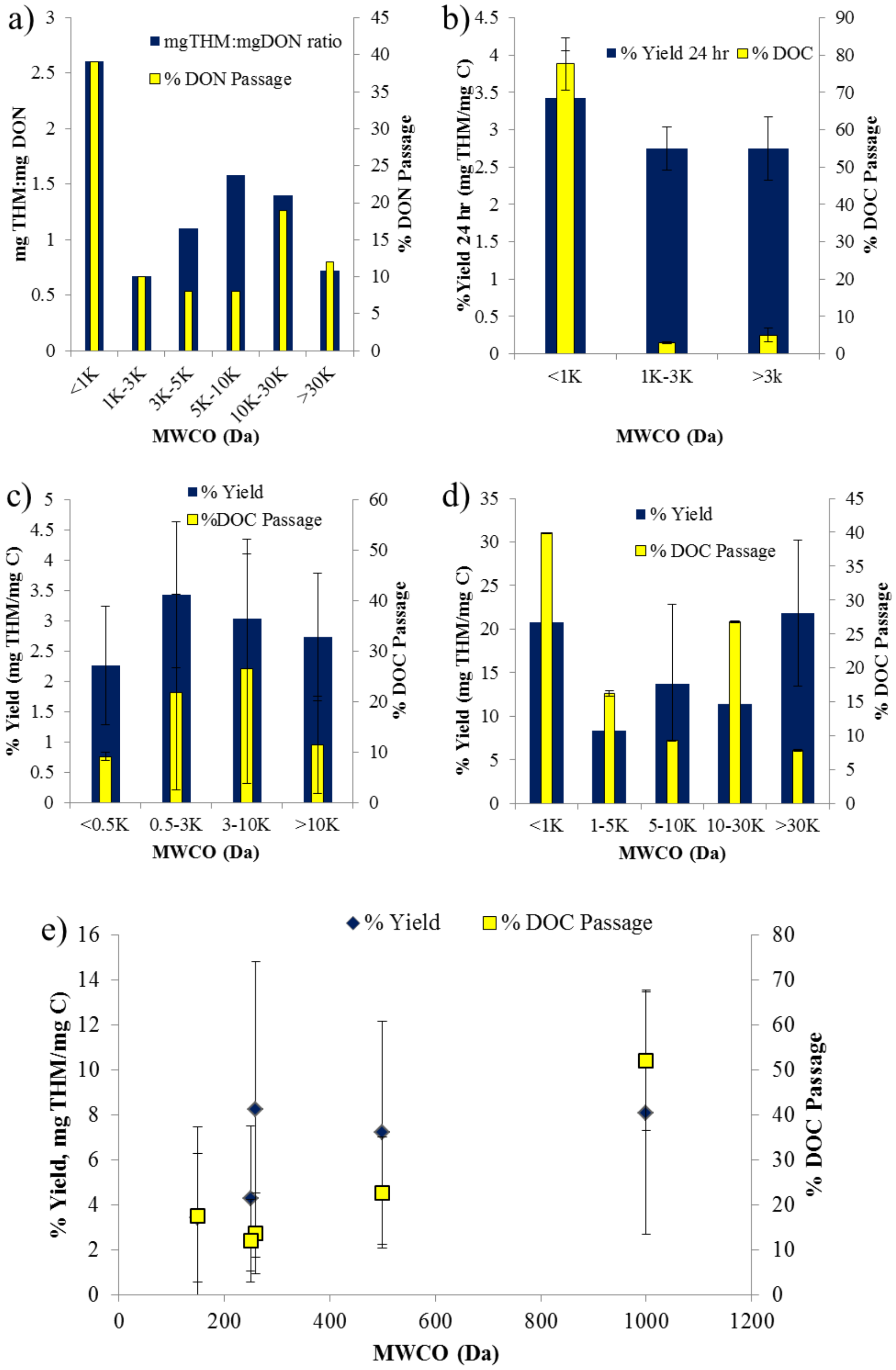

Figure 5-1 % Yield and % DOC passage determined from reported literature data a (Xu et al., 2011), b (Özdemır, 2014), c (Hua and Reckhow, 2007), d (Hu et al., 2014), e (de la Rubia et al., 2008).

THMFP and yield studies in this area have often encompassed chemical fractionation (Bond et al., 2009; Goslan et al., 2004; Kucukcongar et al., 2013; Phetrak et al., 2016; Zhao et al., 2013). It is generally considered that the hydrophobic (HPO) fraction of the NOM, associated with humic acids, generates higher yields than the hydrophilic fraction (Goslan et al., 2004; Hu et al., 2014; Hua et al., 2007), though exceptions to this observation have been reported (Marhaba et al., 2000). Whilst it is well known that the hydrophobic (HPO) fraction is preferentially removed by conventional clarification, the remaining hydrophilic (HPI) fraction is nonetheless capable of generating THMs (Hua et al., 2007; Marhaba et al., 2000). There is no evidence of significant differences in yield from HPI and transphilic (TPI) fractions (Hua et al., 2007).

Available reported data indicate unpredictable and sometimes contradictory trends in DOC passage and yield. DOC molecular size appears to be a poor indicator of yield across different waters, and trends are only likely to be discernible for single water sources. The HPO fraction is generally recognised as representing the most reactive component of the NOM generating THMs (Goslan et al., 2004; Hu et al., 2014; Hua et al., 2007), but there is again little consistency across different studies regarding the actual yield. The aim of this work is to assess (a) the DOC removal capability of membranes of different MWCO and/or selectivity ratings, and (b) trends in THM yield with membrane characteristics, based on a single feedwater. It is of further interest to establish whether the classical hydrophobicity/hydrophilicity chemical fractionation of the organic matter is of significance regarding yield.

5.3 Materials and methods

5.3.1 Materials

The pilot plant (Figure 5-2) was based at a water treatment works in the Scottish Highlands, fed with surface water of low dissolved solids and relatively high DOC (Table 5-2). It comprised four streams, each fitted with a standard commercial 1 m long, 100 mm diameter spiral-wound membrane element housed in a glass-reinforced plastic (GRP) pressure vessel. A single pump (30 m^3/h flow, 5.9-6.2 bar feed pressure depending on temperature) was used to feed all four streams, with flows to each stream metered by individual control valves, and the conversion set at ~10% per stream. The feed water was fed to a blend tank where it was mixed with the retentate stream from the four individual streams, providing a means to increase the feed organics concentration by a factor of ~3 (Table 5-2) to replicate the maximum challenge to the membranes when operating at a total conversion of 80% at full scale. On reaching the target concentration factor of 3 the plant was operated as a closed loop, i.e. recirculating both feed and permeate, so as to sustain the target feed organic carbon concentration, for a period of 48 hours. Two consecutive 9-day campaigns were conducted.

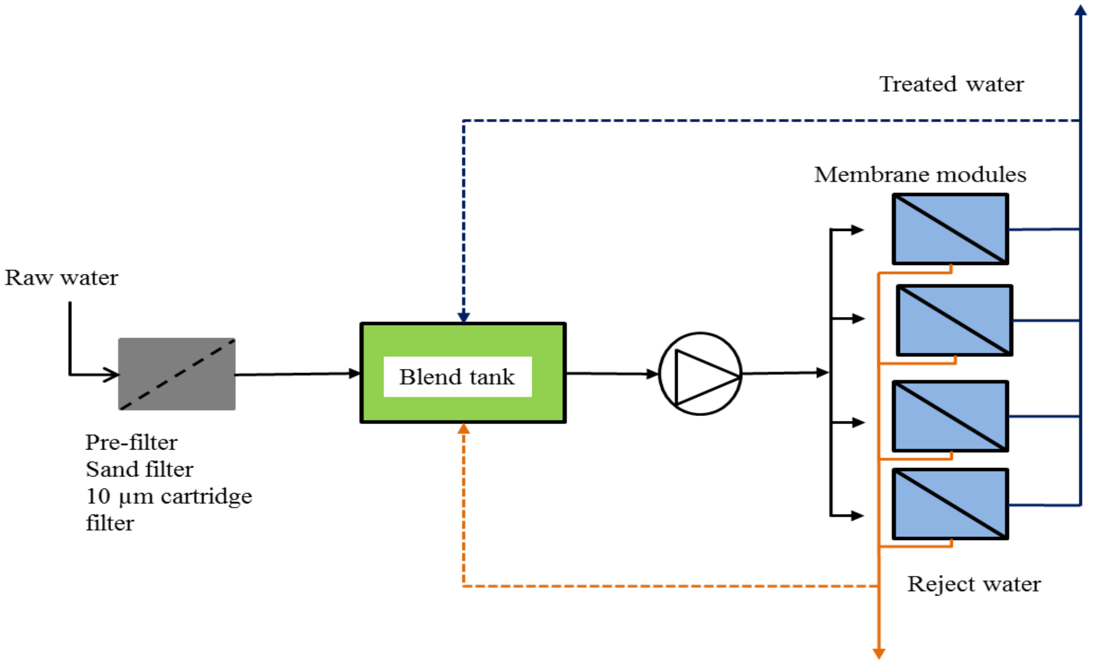

Figure 5-2 Pilot test rig configuration.

Table 5-2 Feed and blend water characteristics.

Parameter	Campaign 1				Campaign 2			
	Raw		Blend		Raw		Blend	
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
Colour (mg/L Pt/Co)	43	19	102	35	57	8	144	25
DOC (mg/L)	4.2	0.5	17	5.1	7.4	1.8	18	3.2
UV_{254} (m^{-1})	27	10	68	20	42	12	88	14
SUVA (L/(mgC.m))	6.5	2.9	3.8	0.77	5.9	1.9	5	0.11
Conductivity (mS/cm,20°C)	29	1.2	62	10	24	1.8	40	6.2
pH	6.4	0.07	7.5	0.07	6.3	0.1	6.8	0.2
Calcium (mgCa/L)	1.5	0.1	4.8	1.2	1.2	0.05	2.8	0.5
Manganese (µgMn/L)	23	16	38	6	16	0.7	31	4.4
Iron (µgFe/L)	350	7.9	53	9	370	12	250	25
Temperature (°C)	9.7	1.3	23	12	9.2	0.7	21	14
Turbidity (NTU)	0.6	0.23	0.2	0	0.58	0.3	0.27	0.06

The specifications of the membrane material investigated varied from a UF of 8000 Da MWCO to an NF of 260 Da (Table 5-3). Membranes #1 and #6 were used in both campaigns as controls (Table 5-3), and the remaining membranes as test products. Membranes classified as NF were assumed to have an element of charge rejection, as opposed to purely physical rejection based on molecular size for the UF membranes. Membrane materials included cellulose acetate and sulphonated polyethersulphone, these being less widely studied than the classical polyamide/polypiperazine NF membranes.

Table 5-3 Spiral wound membrane MWCO and material characteristics.

Membrane ID	Campaign	Membrane MWCO (Da)	Membrane material	Membrane type
#1	1st ,2nd	260	Polypiperazine thin-film (PPA)	NF
#2	1st	700	Cellulose acetate (CA)	NF
#3	1st	1000	Sulfonated polyethersulfone (S-PS)	UF
#4	2nd	2000	Cellulose acetate (CA)	UF
#5	2nd	3000	Sulfonated polyethersulfone (S-PS)	UF
#6	1st, 2nd	8000	Cellulose acetate (CA)	UF

5.3.2 Pilot plant operation

Two campaigns, each of nine days each, were undertaken consecutively. Samples of raw, filtered, blend and permeate water were collected at 48 hours intervals and delivered on the same day to the Scottish Water laboratories. Analysis was undertaken for colour, turbidity, UV_{254} transmittance, dissolved organic carbon (DOC), and natural organic matter (NOM) fractionation by adsorption, the latter based on a method adapted from Bessiere et al (2009) (Bessiere et al., 2009) and applied to single samples. The seven day THM yield was determined by chlorinating all samples and using a modified form of the USEPA Method 551.1 (USEPA, 1998). All laboratory analyses followed methods routinely employed by Scottish Water Laboratories (APHA, 2012). Laboratory analyses were supplemented by on-site tests for colour (mg/L Pt) using a Hach Lange DR 3900 (UV_{410} absorption set programme measured in a 4 cm cuvette), turbidity (NTU) using a Hach 2100P portable turbidimeter, and temperature (°C) and pH using a Hach HQ30d flexy portable pH and temperature meter.

The recirculation of the retentate and permeate in a closed loop caused an increase in the feed water temperature increased to up to 34°C due to frictional forces. Membrane flux and permeability were normalised to 20°C using the viscosity correction equation (5-1):

$$\boldsymbol{\mu_T = 5.167 \times 10^{-7} T^2 - 4.657 \times 10^{-5} T + 1.727\, x\, 10^{-3}} \qquad \textbf{(5-1)}$$

where μ_T in kg m^{-1} s^{-1} is the viscosity at temperature T and μ_{20} the value at 20°C (1.009 kg m^{-1} s^{-1}). The normalised flux for 20°C (J_{20}) for a measured flux of J_T at temperature T is then given by **(5-2**)

$$\boldsymbol{J_{20} = J_T \times \frac{\mu_T}{\mu_{20}}} \qquad \textbf{(5-2)}$$

The normalised permeability (K_{20}) was determined from the normalised flux and recorded trans-membrane pressure (TMP) in bar **(5-3**).

$$\boldsymbol{K_{20} = \frac{J_{20}}{TMP}} \qquad \textbf{(5-3)}$$

5.4 Results and discussion

5.4.1 Reproducibility

The assigned flux and measured permeability of the two control membranes were similar, despite the differences in selectivity, but the flux and permeability values for the second campaign somewhat lower than the first. For the first campaign the flux values of the two controls (Membranes #1 and #6) were 57±7 and 57±3 litres per meter per hour (LMH) respectively, compared with 46±9 and 49±3 LMH for the second campaign. The corresponding permeability values were 10±1.6 and 10±0.8 LMH/bar for Campaign 1 and 7.8±2.1 and 8.2±1.0 LMH/bar for Campaign 2. The lower values recorded for the second campaign presumably reflected the more highly fouling nature of the feedwater. Fouling is normally associated with the colour, UV_{254} and/or turbidity levels – all of which were 29-41% higher on average in the blend water for Campaign 2 than that for Campaign 1.

Reproducibility of the %yield across the two campaigns was good, with the Membrane #1 values being 2.5±2% and 2.4±0.3% for the first and second campaigns and the corresponding Membrane #6 values being 7.0±2% and 8.2±2%. Conversely, the %DOC passage values were more unpredictable, with Membrane #1 values of 7.0±4% and 3.9±1% and Membrane #6 values of 24±9% and 14±2% for the two campaigns, respectively, giving an overall relative standard deviation of 40-41%. This trend of reduced DOC passage is consistent with that of the higher fouling propensity, reflected in the flux and permeability trends.

5.4.2 Flux and permeability

Fluxes varied widely according to the membrane selectivity (expressed as MWCO) and material characteristics (Table 5-3). The only polypiperazine membrane tested, and the most selective in terms of the stated MWCO (260 Daltons), provided a normalised flux (52 LMH) and permeability (9.1 LMH/bar) comparable with the least selective 8000 Da MWCO membrane. The significant decrease in selectivity between the 2000 and 8000 Da MWCO cellulose acetate (CA) membranes was not reflected in a commensurate increase in permeability (7.4 and 9.1 LMH/bar respectively) (Figure 5-3). The recorded permeabilities are higher than values of 3.3-4 LMH/bar previously reported for various pilot and full scale NF plants (Hu et al., 2014; Özdemır, 2014; Xu et al., 2011), probably due to the near-virgin state of the membranes used in the current study.

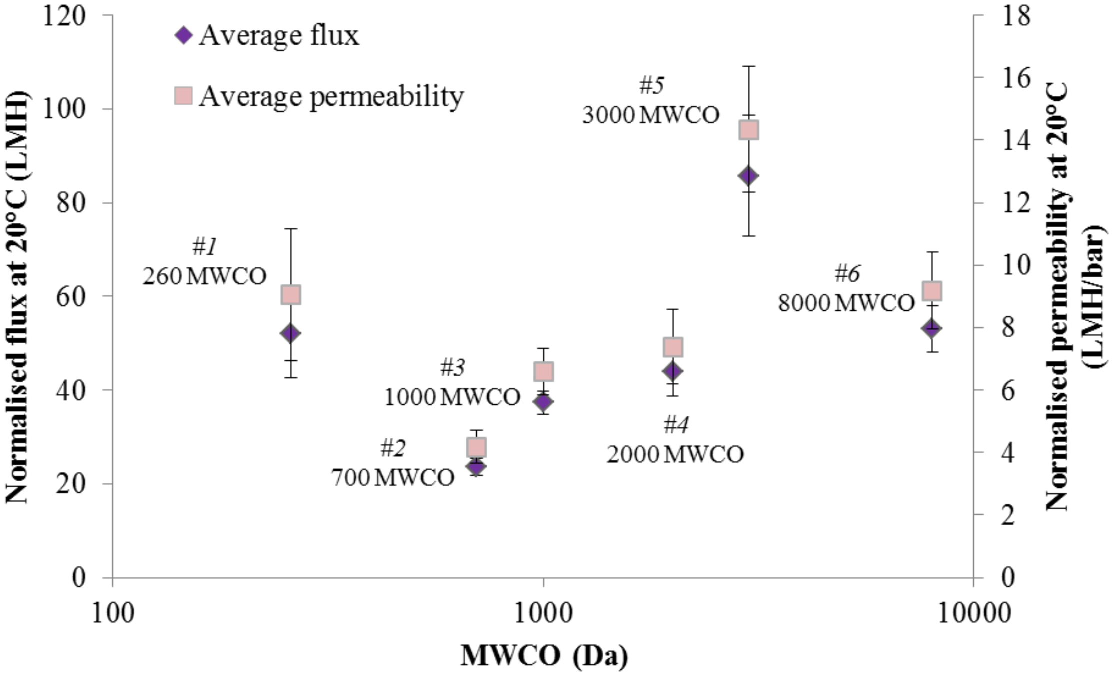

Figure 5-3 Normalised flux and permeability at 20°C for the six membrane products.

5.4.3 Yield and DOC passage

The %yield for the permeate samples across all the membranes tested ranged from 2.4 to 8.2, roughly according to selectivity expressed as MWCO (Figure 5-4). Results were in good agreement with the range of yield previously recorded for Scottish surface waters across 35 full-scale membrane installations (Sutherland et al., 2015), despite the elevated temperatures of the current study. For the two NF membranes (denoted 260 and 700 Da MWCO) the permeate tTHM level was notably low, in accordance with the low recorded DOC passage (Figure 5-6).The yield was found to increase with decreasing selectivity for both campaigns, corroborating previously reported trends (de la Rubia et al., 2008). The correlation between yield and the specific UV_{254} absorbance (SUVA) was poor (R^2= 0.69) (Table 5-4), supporting previous observations (Ates et al., 2007; Fukasaku, 2014; Hua et al., 2015) and suggesting that the permeate organic matter present is predominantly non-aromatic. Whereas UV_{254} and SUVA are often considered to be good THMFP indicators in waters having a DOC concentration and SUVA values above ~3 mg/L and ~4 L/(mgC.m) respectively (Goslan et al., 2004; USEPA, 1998; Weishaar et al., 2003), for low SUVA values (< 2 L/(mgC.m)) the correlation is less valid. Measured SUVA values revealed the permeate from the most porous UF membranes (Membranes #5 and #6) to have the highest SUVA values (3.8-4.5 L/(mgC.m)) on average), compared with 1.4 or less on average for all other membranes (Table 5-4).

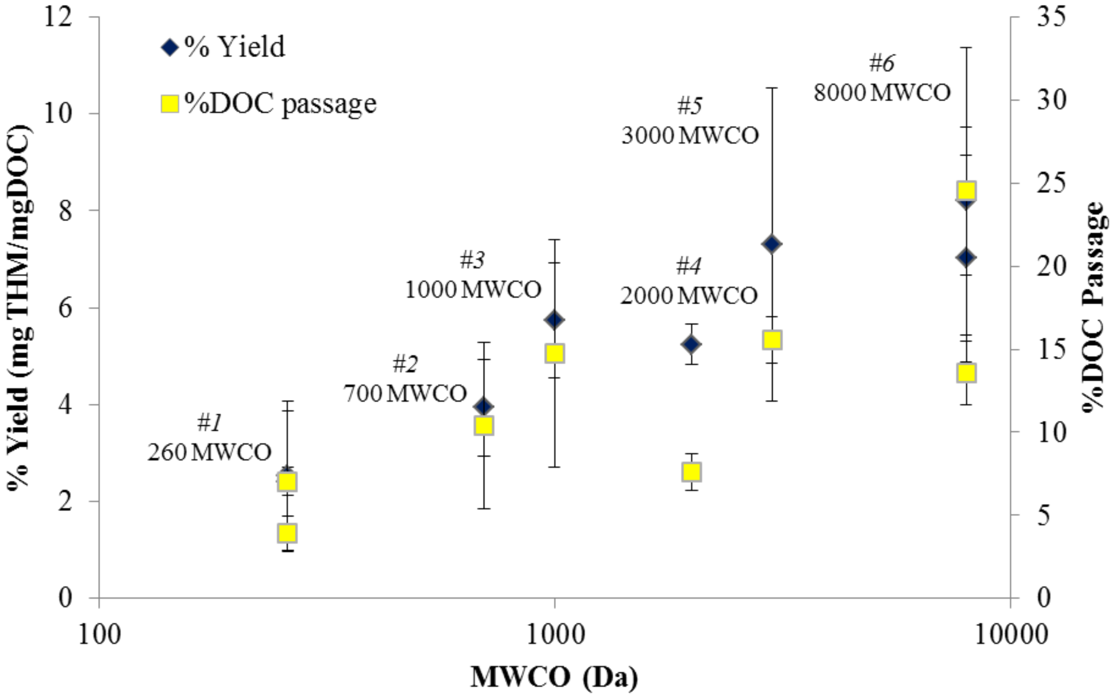

Figure 5-4 Yield and % DOC passage across the two campaigns, with two sets of data for the control membranes.

Table 5-4 Specific UV_{254} absorbance of measured permeate and blend water samples.

Sample	**Campaign 1**		**Campaign 2**	
	SUVA L/(mgC.m)	**Stdev**	**SUVA L/(mgC.m)**	**Stdev**
Raw	6.5	2.9	5.9	1.9
Filtered	6.2	2.5	5.7	1.9
Blend	3.8	0.77	5.0	0.11
Membrane #1	1.4	1.2	1.0	0.44
Membrane #2	0.83	0.45	-	-
Membrane #3	1.0	0.49	-	-
Membrane #4	-	-	1.7	0.5
Membrane #5	-	-	4.5	3.5
Membrane #6	3.8	0.59	3.8	3.2

5.4.4 NOM fractions

Measured concentrations of individual organic chemical fractions revealed the selectivity for the HPO fraction to increase with decreasing MWCO, with the NF membrane providing the greatest removal of this fraction (Figure 5-5). As a result of this perm-selectivity the proportion of HPI organics permeating the membrane increased from 9-12% in the feed to a decreasing trend of between 29 and 57% in the permeate, the percentage increasing with increasing membrane selectivity. The yield of 2.4-2.5% THM/DOC for the most selective membrane, and thus the greatest permeate HPI proportion, is in good agreement with previously reported values (Hua et al., 2007) based on Millipore membranes of 0.5, 3 and 10 kDa MWCO (Table 5-1). The HPI removal was highest for the most selective membranes, the 260 and 700 Da for Membranes #1 and #2 respectively, providing 71 and 76% removal respectively, and lowest for the least selective 8,000 Da MWCO membrane (57% removal). Similar removals of 71% of HPI-acids have been reported for conventional clarification (Weishaar et al., 2003). The transphilic (TPI) NOM fraction is characterised by lower aromatic content than HPO (Goslan et al., 2009) and correspondingly lower SUVA values: it is comparable to HPI as a THM precursor in waters with low humic content (Hua et al., 2007).

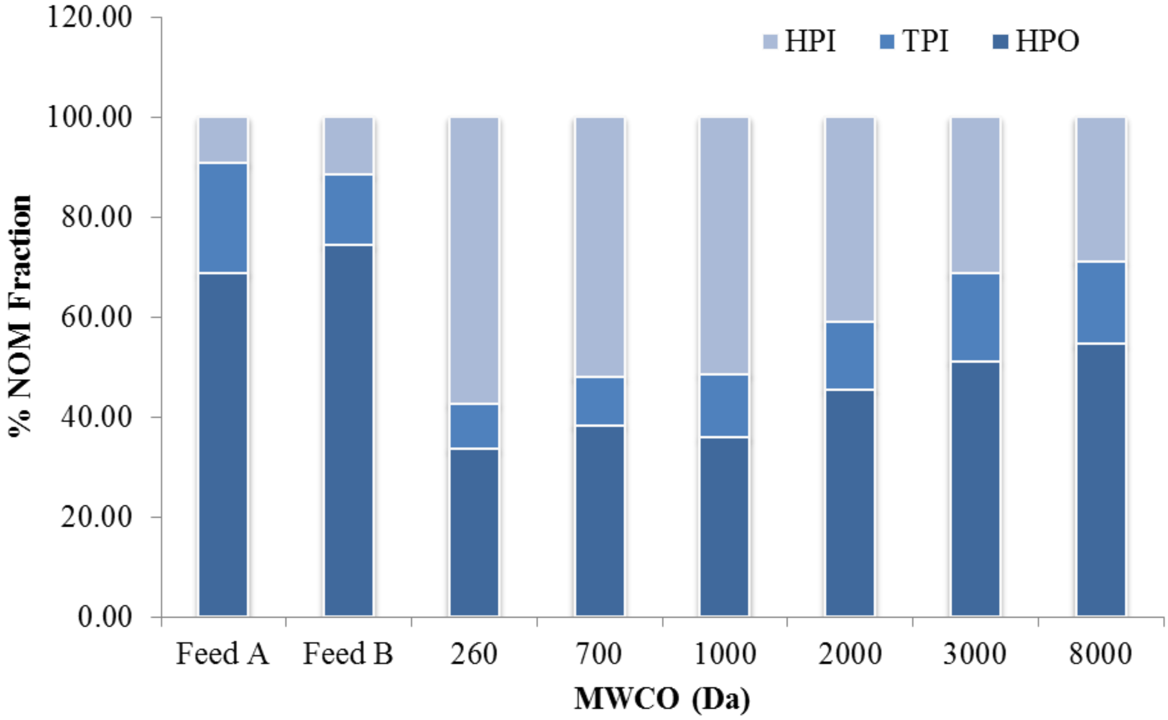

Figure 5-5 Total THMs vs. a) recovered DOC, b) hydrophobic (HPO) NOM fraction, and c) hydrophilic (HPI) NOM fraction.

A good correlation (R^2 = 0.97-0.98) between the measured permeate tTHM and the DOC and the HPO fraction concentrations was observed across the six membranes tested (Figure 5-6a and b). The corresponding correlation with the HPI fraction (Figure 5-6c) was markedly weaker (R^2 = 0.73). Whilst these trends appear to corroborate those previously reported (Parsons et al., 2004), the current data set is based on single rather than replicated measurements and relatively low carbon recovery (50-75%) by the extraction method. Notwithstanding this, there is apparently a closer correlation of tTHM with the HPO fraction than the HPI one.

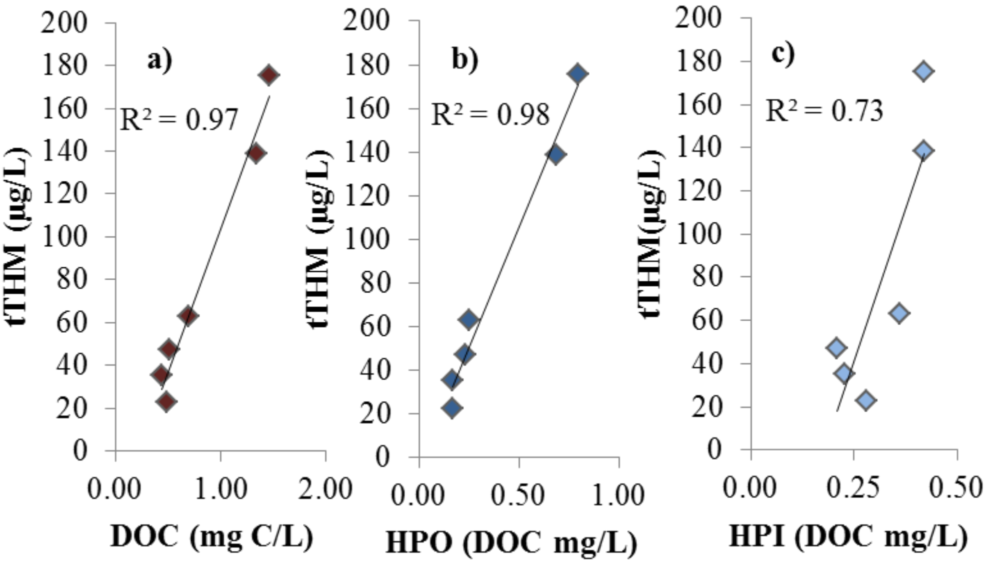

Figure 5-6 Total THMs vs. a) recovered DOC, b) hydrophobic (HPO) NOM fraction, and c) hydrophilic (HPI) NOM fraction.

5.5 Conclusions

A pilot-scale study of the performance of candidate membranes for the removal of natural organic matter (NOM) for ameliorating trihalomethane (THM) formation in potable water treatment has revealed that:

- Flux and permeability trends vs. molecular weight cut-off (MWCO) for the ultrafiltration (UF) membranes followed the expected trend of decreasing flux with MWCO, the exception being the second most porous product Membrane #5. The nanofiltration (NF) membranes provided similar fluxes despite differences in the rated MWCO.

- Recorded flux values were markedly higher than those previously reported in the literature for full and pilot plants.

- Dissolved organic carbon (DOC) passage decreased with decreasing MWCO, an intuitive outcome which nonetheless conflicts with more unpredictable trends previously reported for NOM removal by membranes. The mean DOC passage of the two NF membranes tested was significantly lower – 4-8% compared to 11-25% – than the UF membranes.

- The yield of THM also decreased with decreasing MWCO, varying between 2.5 and 8% in reasonable agreement with the range of values reported in the literature. Membrane #1 – the only aromatic polyamide tested – provided both the lowest yield as well the lowest DOC passage.
- The membrane selectivity for hydrophobic (HPO) increased with decreasing MWCO; the most highly-selective NF membrane provided the largest proportional removal of the HPO fraction. The residual HPI fraction made up 29-57% of the total DOC, the proportion increasing with decreasing MWCO.
- The total THM concentration correlated well (R^2>0.97) with both the DOC and HPO fraction, with a much poorer correlation (R^2 = 0.73) with the HPI fraction.

5.6 Acknowledgments

The financial and practical support of EPSRC (under the STREAM programme) and Scottish Water are gratefully acknowledged.

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6 Implications of the work: A strategy for DBP control in Scottish Water

The overall aim of the research was to *understand and critically evaluate the current and potential applicable solutions for removing natural organic matter (NOM) from waters with variable total organic carbon loads*. The context for this work is related to the minimisation of the resultant DBPs that form during and after chlorination. Specifically, this was understanding and assessing options that minimise the risk of exceeding the current THM and future HAA regulatory limits. In line with global practice, Scottish Water's current strategy to deliver this is to minimise DBPs by reducing the concentration of precursor organics to an appropriate level. This is achieved by either (a) coagulation with alum followed by clarification, filtration and potentially GAC or (b) nanofiltration.

Assessment of the status quo, *coagulation with alum,* indicated a number of sites where the residual DOC, post coagulation, remained rich in organics characterised as hydrophobic (Chapter 2). The corresponding organic molecules have been previously shown to be relatively amenable to removal by coagulation (Sharp et al., 2006) and hence indicate that the currents sites may not be operating at their optimised potential. Further, comparison to other water companies that treat similar raw waters (high DOC, low alkalinity) indicates a preference for the use of ferric based coagulants as they are reported to remove more DOC than alum under optimised conditions (Umar et al., 2016; Uyak et al., 2007); Chapter 3). The alternative is to use a sorption process either before or after coagulation. Whilst it is becoming increasingly common to consider ion exchange for pre-treatment (Finkbeiner et al., 2018), GAC offers additional flexibility as it can be used either side of the coagulation stage. In addition, the technology is already established and can be used with infrequent regeneration as long as reduced DOC removal is acceptable. Upgrading the current GAC was assessed in terms of alternative media on the market that offer enhanced DOC (Chapter 4) providing an easy and low maintenance option. Equivalent requirements of low maintenance for remote rural sites, coupled with a need to minimise chemical use, also leads to the use of nanofiltration (NF) membranes (Chapter 5). The current membrane product has undergone a reformulation providing an opportunity to assess the potential for enhanced removal with alternative NF products (Chapter 5).

Accordingly, the findings from the current work can be used to consider four possible future strategies:

1. Maintain the status quo
2. Optimise current coagulation or switch to the use of ferric
3. Include pre or post treatment with GAC
4. For membrane sites, switch to new membrane products that provide enhanced removal.

The effectiveness of the different strategies was considered in relation to the same common assessment parameters: dissolved organic carbon (DOC), UV_{254} absorbance and hydrophobic (HPO) natural organic matter (NOM) content (Figure 6-1). To provide a context of the risk-reward balance of the different options, the potential costs associated with non-compliance was estimated through the Compliance Risk Index approach being used in England and Wales (Chapter 3). In addition, the membrane sites remain at risk as the current configuration allows for 11-25% DOC passage which can have a relatively high HPO fraction of up to 47% which has a relatively high THM reactivity formation potential.

6.1 Maintaining the status quo?

Analysis of full scale data across Scottish Water (Chapter 2) identified some trends between surrogate measurement parameters and the resultant DBP formation levels, most significantly with the UV_{254} absorbable content of the water (Chapter 2). Analysis of the global data set revealed substantial scatter such that an overall global correlation is not of practical value. However, the overall trends confirmed that the waters followed previous learning concerning optimisation of coagulation for NOM rich waters (Parsons et al, 2004). Further, the analysis of the treated waters indicated that DOC values of over 1 mg/L corresponded to sites with an elevated risk of high DBP levels (Chapter 2). Importantly, it should be noted treated water levels as low as ~0.4 mg/L may be required in the July to October season (Sutherland et al., 2015; Valdivia-Garcia et al., 2016). This reflects the variation in reactivity that is known to exist within each organic fraction classified with similar surrogate parameters such as the TPI or HPI concentration (Hu et al., 2015; Hua et al., 2015) as well as potential bleed of specific organic compounds within different fractions depending on the other constituents present (Bond et al., 2012).

The observation that some waters contained relatively high proportions of HPO in treated water suggests that the performance of the coagulation-flocculation processes has the potential for improvement (Chapter 3). Optimisation of the coagulation process has been previously shown to commonly occur at, or near, the dose ratio of 1:1 Al: DOC (Sharp et al., 2003). Analysis of the current sites revealed that the DOC removal at 15 of the 21 sites investigated may be improved. Adjustment to ensure that all sites dosed at the improved ratio indicated that ~1.68 million tonnes of alum per year would be required over the next 20 years. When a potential CRI penalty of £44 million was applied for the sites that would breach regulatory limits for THM and HAAs at 8 sites for the same period, a whole life cost (WLC) of £64.2 million was estimated for the status quo, in comparison to £22 million for the best optimised scenario. These figures are likely to be higher, considering the increases in raw water DOC expected over the next 20 years (Bhatnagar et al., 2017) as well as the expected increase in the cost of coagulant (Keeley et al., 2014). However, even under improved coagulant conditions, the use of alum may still lead to elevated DBP levels due to its known lower efficacy towards DOC removal compared to ferric sulfate (Chapter 3)

6.2 Switch to Ferric sulfate

For large and medium WTWs, changing the coagulant to ferric sulfate may be an option. Improved DOC removals, ranging from between 4 and 73% were seen for 18 out of the 21 WTWs investigated when jar tests coagulation conditions were compared to the current WTW dosing (Chapter 3). From these tests ferric outperformed alum at 86% of the sites. Whilst only a snapshot, the lower residual DOC equated to a reduction of calculated DBPs below regulatory limits for all but one site for THMs (#20) and all but two sites (#18 and #20) for HAAs, when the higher (80µg/L) limit was applied and hence can be suggested as a viable option (Section 3.4).

Implementation of the use of ferric requires some modification to the infrastructure on the sites due to the difference in chemical properties, and an increase in lime dosing would be required to avoid discoloration in the network. Moreover, an increase in coagulant dose and DOC removal results in additional sludge production that requires disposal. Estimates of the total costs associated with this switch revealed a WLC over 20 years of £22 million, £44.2 million lower when compared to the status quo.

6.3 Add GAC

Assessment of potential media for use in GAC adsorption of residual NOM revealed that in general, a 20-30% DOC removal by GAC was expected (Chapter 4). However, one specific media, XC30, offered elevated removal levels of up to 50% indicating that different media could be used on a site specific basis to tailor to the required need for DOC removal. Importantly, this means that sites currently employing alum coagulation could be enhanced through post GAC treatment avoiding the need to change coagulant, and reducing total chemical usage which can be important in relation to the logistics of chemical supplies. The solution provides benefits in relation to the ease of retrofit at various sizes of works, and its long term robustness and the low operator input requirements (Bhatnagar et al., 2017; Iriarte-Velasco et al., 2008). This is balanced with the costs related to replacement and regeneration once the media becomes saturated. The replacement costs for Water B, with an average flow of 0.27 MLD and design capacity of 1.05 MLD, were estimated to be approximately £5000 per tonne when using F400 media for the three 11 tonnes contactors, with a once a year frequency in regeneration (personal communication). This equates to £165,000 per year in media replacement costs. This would then further convert to £1.75 million over the next 20 years. The cost of replacing the GAC media with this frequency would be notably higher than switching to ferric at a WTW of this size. Although each site has individual challenges and therefore specific design parameters, a rough cost comparison can be made with WTW#15 (Chapter 3). The cost of switching to ferric sulfate at this WTWs that treating raw water of similar quality, but a supply that was 10 times greater than for WTW A, amounted to a CAPEX of ~£260,000 and a yearly OPEX of ~£174,000, which would convert to ~£2.1 million over the next 20 years.

The XC30 media was provisionally quoted to be 12% higher in cost than F400. However, during laboratory tests, the XC30's removal capacity for DOC, total THMs and total HAAs, calculated from THM and HAA formation potential, was found to be nearly ~33%, ~25% and 8% higher than F400 (Chapter 4).

The total THM and HAA formation potential in pre-GAC treated water at WTW B was measured to be ~260 µg/L and ~130 µg/L, respectively. Here, a 2:1 ratio of THMFP to THM concentration can be applied to estimate the THMs at works (Chapter 3). Therefore, the 55% THM precursor removal shown by XC30 would be sufficient to reduce the risk of breaching the regulation for THMs, whilst the HAAs in the pre-GAC treated water would not breach the higher 80 µg/L proposed limit (Chapter 4). It is worth noting that 8-10% of the DOC was not removed during the initial stages of operating the GAC columns, potentially due to a portion of the NOM being non-adsorbable in character. Therefore, as the upstream process becomes more efficient at removing adsorbable NOM, the overall percentage DOC removal, and subsequent reduction in DBP formation may be lower than that reported in the current study. The respective values will therefore need to be determined on a case by case basis.

6.4 Change the spiral wound membrane product at small sites

The comparison of the new membrane products revealed that they outperformed the current product for DOC and THM removal. At the same time, all membranes matched the current membrane for water throughput to within 90% (Section 5.4).

Two specific spiral wound (SpW) membranes were identified as viable candidates. The best overall product was membrane #1, which restricted DOC passage to less than 5% whilst enabling equivalent flux to that of the current membrane even though the membrane was classified as having the lowest molecular weight cut off (MWCO). The drawback of using membrane #1 was its low tolerance to chlorine, used for membrane cleaning. The other viable product was membrane #4 which delivered a similar DOC passage as membrane #1 but had a similar chlorine tolerance to the current product. In this case the disadvantage was a reduction in achievable flux which was 90% of membrane #1 and of the currently used membrane.

Overall, the enhanced DOC removal achieved by the new membranes (max 95 %) translated into the ability to reduce the THMs to below regulatory requirements. This was despite the elevated conditions of DOC (17±5.1 mg/L) and temperature (23±12 °C). Membranes #1 and #4 reduced the total THM formation from ~370 µg/L measured in the feed to 23 µg/L and 47 µg/L, respectively, well below the regulatory requirement of 100 µg/L. The cost of employing the new membranes will have to be determined on a site specific basis after more full scale tests are undertaken. The tests are necessary to inform on the overall adequacy of supplying only 90% of the flow which may not be sufficient to satisfy demand at smaller sites. Moreover, as a result of more membrane fouling, the cleaning regime may need to be altered due to the new products' smaller pores.

6.5 Proposed strategy for NOM removal

A proposed strategy for mitigating the risk of regulatory breaches due to DBP failures by reducing the NOM measured as DOC is presented in Figure 6-1. The effectiveness of the treatment solutions investigated in the current researched was assessed in terms of their ability to reduce the magnitude of DBP failures.

At large and medium WTWs, where the use of conventional coagulation-flocculation with alum was prevalent, breaches with a magnitude that can be reduced by a DOC reduction of <30 % may be mitigated by employing GAC filtration. The 30% DOC limit was selected to conservatively account for the use of the best performing media, XC30, and an increase in the proportion of non-adsorbable NOM in the feed water. However, if the mitigation required involves a reduction >30% or if the cost of retrofitting GAC media becomes unfeasible, then a switch to ferric sulfate may be considered. Subsequently, should a change in coagulant not mitigate the risk of breaching regulatory limits for DBPs and a further 30% DOC reduction is required, than GAC media filtration should be considered. If that is still not sufficient, than alternative treatment options not investigated in this study may be more appropriate.

A similar approach can be considered for small WTWs, where the current SpW membrane product represents the main treatment and therefore the status quo. The new products showed an up to 95% reduction in DOC, however further reduction may be required and GAC media could be subsequently employed. Although not covered in the current study, anecdotal evidence from SpW membrane sites where GAC filtration is currently employed suggests that care must be taken when operating the GAC filers intermittently (seasonally) as the media becomes fouled relatively quickly and requires replacement/regeneration after every July-October season, on a yearly basis.

Therefore, the risk of failure to meet DBP regulatory requirements becomes a cost versus benefit balance between maintaining the status quo and incurring CRI penalties and either: a) maintaining the status quo and adding GAC filtration; b) switching to ferric and new membrane products at large, medium and small sites, respectively or; c) switching to ferric and new products with the addition of GAC filtration, if required, to remove the risk long term and potentially future proof the WTWs in view of increases in DOC.

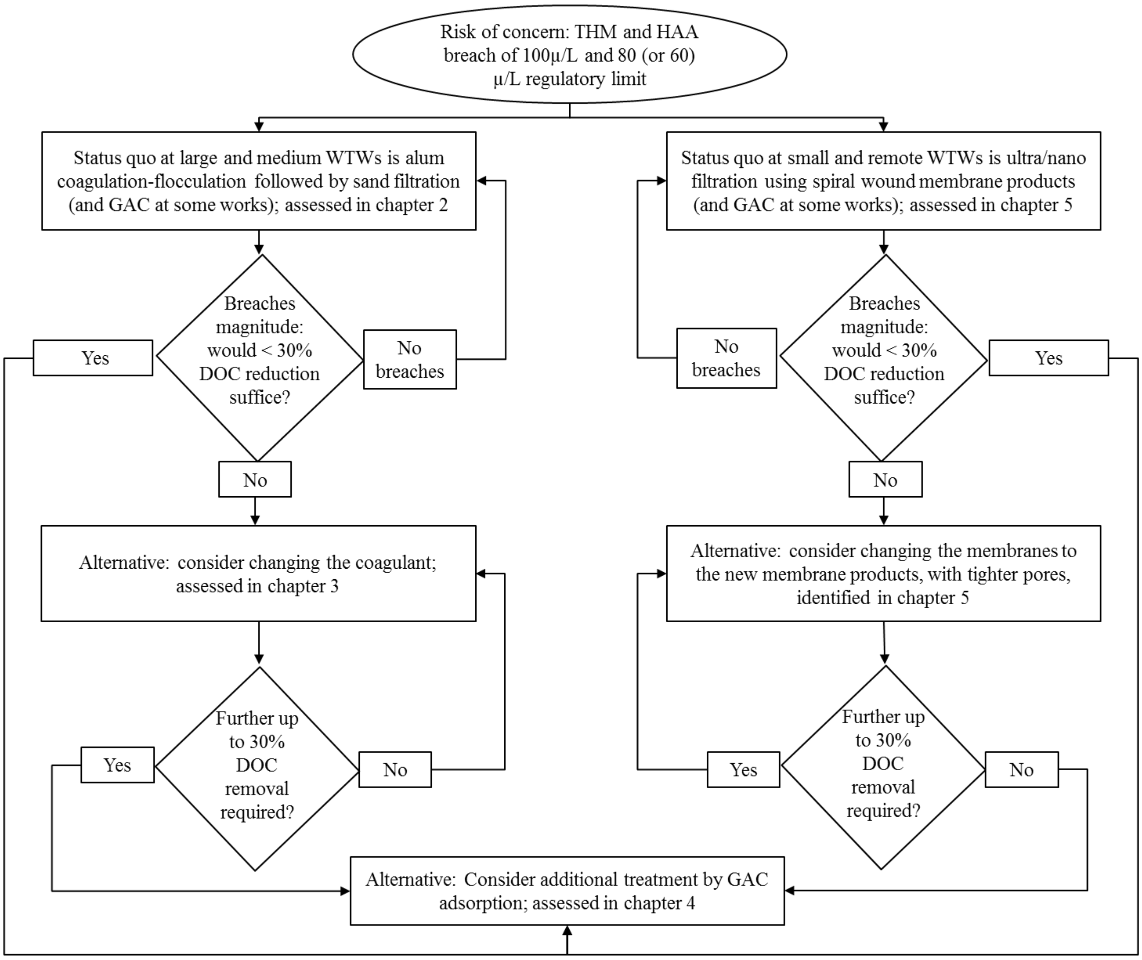

Figure 6-1 Current and alternative NOM control solutions to mitigate the risk of regulatory DBP breaches.

6.6 References

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7 Conclusions and Further Research

7.1 Conclusions

The findings of the current study demonstrate that: a) frequently measured water quality determinants were reasonable indicators for disinfection by-product formation; b) ferric coagulation was the most effective solution when coagulation was used as the main treatment for DBP precursor control in the Scottish Water region; c) GAC filtration was an appropriate control for DBPs when a 20-30% reduction in organics was sufficient; and d) nanofiltration membrane products with smaller pores reduce the THM formation whilst maintaining the throughput flow at 90% of the current water production.

The specific conclusions pertaining to the objectives are listed below:

Objective 1: To fully appraise the validity of using surrogates in the form of routinely measured water quality parameters (UV_{254}, DOC and colour) and the NOM hydrophobic content to determine THM and HAA formation.

- All water quality determinants were noted to be reasonably good indicators of DBPFP in the raw waters sampled in the study, with only colour correlating slightly more weakly with THMFP than the other surrogates (UV_{254}, DOC and HPO). Both UV_{254} and DOC thus appear to be as good an indicator of DBPFP as HPO for both THMs and HAAs, such that chemical fractionation offers little additional benefit in determining DBPFP for the waters studied (Chapter 2).
- For treated waters, the correlations were much weaker between water quality parameters and THMFP and HAAFP, although the understanding of these links and ability to determine DBP formation faster is markedly more important since no further treatment is applied (Chapter 2).
- The same patterns were observed for THMFP and HAAFP correlated with the various commonly measured water quality determinants, although the relationships were slightly weaker for HAA when linear regression correlation coefficient (R^2) values were compared (Chapter 2).
- Seasonal trends in DBPFP followed that of UV_{254}, and no apparent impact on yield was noted; although a slight increase in yield was evident geographically, for island-based WTWs, particularly (Chapter 2).

Objective 2: To determine the water quality and economic benefits of employing optimised coagulation with alum or ferric sulfate compared to the current status quo with respect to improving NOM removal in view of ever increasing regulatory requirements and chemical costs.

- Ferric sulfate outperformed alum sulfate at two-thirds of the WTWs investigated (Chapter 3).
- Jar tested ferric sulfate was the most cost effective option when a 20 year whole life cost (WLC) strategy was considered, despite CAPEX being three times higher than the jar tested alum solution (Chapter 3).
- OPEX costs vastly outweighed CAPEX costs when a 20 year time frame was considered (Chapter 3).
- Jar tests with alum and ferric sulfate did not always return a lower DOC residual value than at three out of the five "Island" WTWs (WTWs #13, #20 and #21), indicating that the additional downstream treatment to coagulation at these sites may be more effective than at others. For example, improvements were seen at WTW #21 where a membrane process followed the coagulation stage, rather than the conventional clarification by sedimentation or dissolved air flotation (Chapter 3).

Objective 3: To determine the physical features of GAC that control NOM removal when used at the beginning or the end of the WTWs to enable informed decisions to made on media selection.

- Adsorption isotherms were a good indicator of initial NOM removal and were an effective tool to rank media ahead of pilot testing, although they only offered a snap shot of NOM removal by GAC (Chapter 4).
- None of the investigated media showed a high selectivity for THM and HAA precursors. Therefore, the removal of tTHMs and tHAAs was primarily a function of DOC reduction to a sufficiently low level (Chapter 4).
- The volume of mesopores in the range of 5-10 nm size range were observed to be an important parameter for GAC selection for NOM removal. The volume of

mesopores in this range correlated well with DOC, tTHM and tHAA (Chapter 4).

- The best performing GAC had a more uniform pore size distribution, thus allowing for a wider range of NOM to adsorb. This was XC 30 which treated 48% and 43% more water than the next best performing GAC from source A and B, respectively (Chapter 4).

Objective 4: To identify how membrane pore size and selectivity ratings influence NOM removal and THM formation based on treatment of a single water source in challenging conditions of NOM loading and high temperature.

- The flux and permeability trends versus the membrane tightness represented as molecular weight cut-off (MWCO) for the ultrafiltration (UF) membranes showed a decrease in flux with MWCO, as expected. The exception was the second most porous product Membrane #5. The nanofiltration (NF) membranes provided similar fluxes despite differences in the rated MWCO (Chapter 5).

- Recorded flux values were notably higher than those previously reported in the literature for full and pilot plants (Chapter 5).

- Dissolved organic carbon (DOC) passage decreased with decreasing MWCO, an intuitive outcome which nonetheless conflicts with more unpredictable trends previously reported for NOM removal by membranes. The mean DOC passage of the two NF membranes tested was notably lower – 4-8% compared to 11-25% – than the UF membranes (Chapter 5).

- The yield of THM also decreased with decreasing MWCO, varying between 2.5 and 8% in reasonable agreement with the range of values reported in the literature. Membrane #1, the only aromatic polyamide tested, provided both the lowest yield as well the lowest DOC passage (Chapter 5).

- The membrane selectivity for hydrophobic (HPO) increased with decreasing MWCO; the most highly-selective NF membrane provided the largest proportional removal of the HPO fraction. The residual HPI fraction made up

29-57% of the total DOC, the proportion increasing with decreasing MWCO (Chapter 5).

- A weaker, albeit relatively high correlation ($R^2 = 0.73$) was observed between the HPI fraction versus total THM concentration, whilst, as expected, the latter correlated well ($R^2>0.97$) with both the DOC and HPO fraction, with (Chapter 5).

7.2 Further Research

The further areas of research identified during the course of the project are listed below:

- From chapter 3: Coagulation
    - Investigate alternative coagulants that could be used for more efficient removal of The DBP precursors, although their commercial application may not be immediate. For example other metal salts, such as titanium (Ti) and zirconium (Zr) have shown improved removal of low and medium molecular weight 100-2000 g/mol compounds (Hussain et al., 2014; Okour et al., 2009). Inorganic synthetic polymeric coagulants, obtained from pre-hydrolysed metal-ion coagulants such as polyaluminium chloride (PAC), polyferric chloride (PFC), polyferric sulfate (PES) as well as other composite inorganic compounds (Sillanpää et al., 2018) have also been explored for elevated levels of NOM removal. Ion exchanged doped hybrid aluminium coagulants have been developed specifically and showed an improved removal of low molecular NOM over conventional and synthetic polymer coagulants (PAC) (Zhao et al., 2016).
- Chapter 4: GAC media.
    - The 5-10 nm width mesopores appeared to correlate best with DBP precursor removal. It would be of interest to understand other physicochemical properties of the media that control removal of organics, for example the surface charge properties and the chemical groups on the surface of the activated carbon.
    - More extensive trials at pilot and full scale are needed to understand the lifespan of the media and to identify a method to accurately schedule

    - media replacement based on the carbon usage rate and influent water characteristics.
- Chapter 5: Ultra/nano filtration spiral wound membranes
    - The current study investigated the performance of the current and alternative spiral wound membrane products for removing THM precursors using a pilot scale rig. The next stage of work needed would be to understand the HAA precursor removal as well to determine the removal performance under normal operational conditions (temperature and flow).
    - The most effective spiral wound membrane was not considered an appropriate retrofit solution due to its sensitivity to chlorine which would create operational complications. It would be of interest to assess alternative non-chlorine based cleaning options and disinfection regimes and the feasibility of replacing the current product with the best performing membrane at full scale WTWs.

7.3 References

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APPENDICES

Table A-1 Correlations between measured reduction in DOC, THMs and HAAs and commonly measured adsorption capacity parameters

Parameter	**WTW A R^2 values for Parameter vs**						**WTW B R^2 values for Parameter vs**					
	DOC		**THM**		**HAA**		**DOC**		**THM**		**HAA**	
	C/C_0 initial	**C/C_0 at breakthrough**	**C/C_0 initial**	**C/C_0 at breakthrough**	**C/C_0 initial**	**C/C_0 at breakthrough**	**C/C_0 initial**	**C/C_0 at breakthrough**	**C/C_0 initial**	**C/C_0 at breakthrough**	**C/C_0 initial**	**C/C_0 at breakthrough**
V_{total} (cm³/g)	0.46	0.48	0.46	0.42	0.43	0.07	0.57	0.54	0.61	0.55	0.58	0.47
$V_{narrow\ pores}$ (cm³/g)	0.05	0.02	0.05	0.00	0.05	0.06	0.25	0.03	0.23	0.05	0.30	0.07
$V_{micropores}$ (cm³/g)	0.06	0.03	0.05	0.01	0.05	0.03	0.26	0.02	0.25	0.03	0.31	0.06
$V_{mesopores}$ (cm³/g)	0.64	0.79	0.66	0.71	0.65	0.95	0.46	0.70	0.52	0.65	0.39	0.62
DFT area 0.7-1.7 nm	0.03	0.00	0.25	0.00	0.03	0.14	0.18	0.01	0.16	0.02	0.23	0.04
DFT area 1-2 nm	0.03	0.02	0.03	0.00	0.03	0.07	0.21	0.01	0.19	0.02	0.25	0.04
DFT area >2nm	0.63	0.72	0.63	0.52	0.64	0.87	0.49	0.59	0.57	0.56	0.43	0.60
Granulation	0.13	0.07	0.12	0.03	0.08	0.06	0.03	0.11	0.12	0.06	0.02	0.07
SBET	0.05	0.03	0.05	0.01	0.04	0.12	0.17	0.06	0.16	0.08	0.20	0.06
IN	0.0003	0.0035	0.0001	0.027	0.0001	0.044	0.003	0.004	0.028	0.015	0.066	0.0058