CRANFIELD UNIVERSITY

Pascal Finkbeiner

UNDERSTANDING THE REMOVAL OF NATURAL ORGANIC MATTER USING ION EXCHANGE FOR DRINKING WATER TREATMENT

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Cranfield Water Science Institute

PhD Thesis
Academic Year: 2016 - 2019

Supervisor: Professor Peter Jarvis, Professor Bruce Jefferson
April 2019

CRANFIELD UNIVERSITY

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Cranfield Water Science Institute

PhD Thesis

Academic Year 2016 - 2018

Pascal Finkbeiner

UNDERSTANDING THE REMOVAL OF NATURAL ORGANIC MATTER USING ION EXCHANGE FOR DRINKING WATER TREATMENT

Supervisors: Professor Peter Jarvis and Professor Bruce Jefferson

April 2019

ABSTRACT

Drinking water processes that utilise surface water require the removal of natural organic matter (NOM), primarily to reduce the formation of harmful disinfection by-products. This is particularly important given that NOM concentrations in source waters have risen over the past decades in many parts of the world. An effective technology to remove NOM is ion exchange (IEX), which has reportedly offered high final water quality (low DOC, down to 0.25 mg L^{-1}) when used prior to coagulation. However, the performance of IEX varies depending on the water source characteristics and this is currently difficult to estimate. To better understand the relationship between physicochemical properties of NOM and their removal, the individual and combined characteristics charge, hydrophobicity and molecular weight were explored at pilot and bench scale. It was shown that charge plays a major role in the removal of NOM. Model compounds were increasingly removed with increasing charge density. While this emphasised the importance of charge, the results also showed that hydrophobicity became more important at low charge densities. Molecular weight distribution analysis revealed that medium sized organic compounds were dominant in the investigated waters and were well removed. However, high concentrations of this fraction were seen to limit removal. Size exclusion of high molecular weight compounds resulted in low removal of this NOM fraction. The most treatable water by IEX was identified to contain a high charge, a low concentration of high molecular weight compounds and a large proportion of hydrophobic organic matter. For these water types removal of 90% can be expected. Resin properties influenced the removal efficiency, not only by their state (virgin or used) but also by their properties. The use of three different resins showed that larger pore sizes improved the removal of NOM. Resin made of polystyrene was seen to provide higher removal of aromatic compounds due to the contribution of non-electrostatic interactions. The combination of IEX and coagulation showed consistently high treated water quality for varying source water through selective removal of NOM by IEX, which facilitated an improvement in the coagulation process, resulting in higher dissolved organic carbon and reactive disinfection by-product precursor removal.

Keywords:

Disinfection by-product formation potential, model compounds, LC-OCD analysis, resin fractionation, charge density.

ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisors Prof. Peter Jarvis and Prof. Bruce Jefferson for their enthusiasm, insightful feedback and constructive comments throughout my PhD and their efforts particularly during writing-up.

Many thanks to Graeme Moore from Scottish Water who supported me in every way during my placements into Scotland and made this period an enjoyable and exciting time. He enabled me to get an insight into Scottish Water and carry out experiments at their labs. Additionally, I would like to thank further people from Scottish Water: Walter Hill, who supported me through analytical and experimental discussions, and his curiosity and interest in the project, Joanna Redman and Viola Patriarca for their support and company during the pilot plant trials (without them this would have been a very lonely experience) and all the helpful people at Scottish Water, especially Magdalena Dudzic, Lisa Davies and Stuart Wilson. Also, thanks to Mitchell Sijm, Harry Scheerman, Jumeng Zheng and Holly Shorney-Darby from PWNT for their support and advice during the pilot trials. Nicky Campbell from TDC, who supported the operation of the pilot plant through repairs, maintenance and mechanical improvements.

Thanks to Tebogo Tseka who carried out important experiments during her placement at Cranfield, Pablo Campo-Moreno for his analytical advice, Monika Jodkowska for her analytical technical support and Ryan Pereira from Herriot Watt University for his cooperation and discussions.

Thanks to my fellow students and friends Dan, Sassi, Pablo, Alejandro, Sonia, Irene, Sabrina, Kanming, Joanna, Berta and Carlos for their company on this PhD journey.

Ein grosser Dank gilt auch meiner Familie, besonders meinen Eltern, die mich stets unterstützt und an mich geglaubt haben. Ihr seid spitze!

Hi Edwina, terima kasih. Kou turung aku di darum susah nga bresut sebab PhD ku nga turung aku abo PhD ku, tuu tanuk yun ku kga atin sanang mu. Terima kasih sebab turung aku nga pimanu ta duweh di Scotland, di UK so purug di PhD pimandai ku. Kou kana raru nga aku, nga kajun ata kanu buah dingeh.

“If we knew what it was we were doing,

it would not be called research, would it?”

Albert Einstein

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

BW	Backwash	
CCMF	Coagulation with ceramic membrane filtration	
CD	Charge density	meq g_{DOC}^{-1}
CDOC	Chromatographed dissolved organic carbon	mg L^{-1}
CIP	Cleaning in place	
CL	Charge load	µeq L^{-1}
DAD	Diode array detector	
DBP	Disinfection by-product	
DBP-FP	Disinfection by-product formation potential	
DCAA	Dichloroacetic acid	
DOC	Dissolved organic carbon	mg L^{-1}
EBW	Enhanced backwash	
GC-MS	Gas chromatography mass spectrometer	
HAA	Haloacetic acids	µg L^{-1}
HAA-FP	Haloacetic acid formation potential	
HMW	High molecular weight	
HPI	Hydrophilic	
HPLC	High performance liquid chromatography	
HPO	Hydrophobic	
IEX	Ion exchange	
ILCA	In-line coagulation	
LC-OCD	Liquid chromatography organic carbon detection	
LMH	Flux in litre per square metre per hour	L m^{-2} h^{-1}
LMW	Low molecular weight	
MCAA	Monochloroacetic acid	
MGG	Monogalloyl glucose	
MIEX	Magnetic ion exchange	
M_n	Number-average molecular weight	g mol^{-1}
M_w	Mass-average molecular weight	g mol^{-1}
MW	Molecular weight	
NOM	Natural organic matter	
PACl	Polyaluminium chloride	

PDADMAC	Polydiallyldimethylammonium chloride	
PGG	Pentagalloyl glucose	
PZC	Point of zero charge	
sHAA-FP	Specific haloacetic acids formation potential	mg g_{DOC}^{-1}
SIX	Suspended ion exchange	
sTHM-FP	Specific trihalomethane formation potential	mg g_{DOC}^{-1}
SUVA	Specific UV absorbance	L m^{-1} mg^{-1}
TCAA	Trichloroacetic acid	
THM	Trihalomethanes	µg L^{-1}
THM-FP	Trihalomethane formation potential	
TOC	Total organic carbon	mg L^{-1}
TPI	Transphilic	
UVT/UVA	Ultraviolet transmittance/absorption	
WTWs	Water treatment works	

1 INTRODUCTION

1.1 Background

As water passes through organic rich soils in the upland catchments of Scotland, some of this organic matter is dissolved into the water. As a result, this natural organic matter (NOM) is widely present in Scottish surface water sources used for drinking water supply. In recent decades, there have been increases in the NOM content of these water sources as a result of transformations in land use, decline in acidification (due to reduced sulphur dioxide emissions) and climate change (Frogbrook, 2017). The dissolved organic carbon (DOC) in these water sources has increased to an average of 6.6-7.7 mg L^{-1} with a reported range between 1.6 and 21.4 mg L^{-1} (Golea et al., 2017; Valdivia-Garcia et al., 2016). This has challenged water treatment works (WTWs) to be able to effectively remove enough organic matter from potable water prior to disinfection and distribution. NOM removal is important in order to ensure the aesthetic quality of the water is maintained and to limit the formation of disinfection by products (DBPs) upon chlorination. In many cases, surface water is treated by coagulation, which acts as the process for bulk removal of NOM. On occasion, water treated by coagulation exceeds the European Union regulatory limits of 100 µg L^{-1} for the trihalomethane (THM) DBPs (European Commission, 2018).

As a result, Scottish Water have explored different technologies to improve water quality and increase the resilience of drinking water treatment processes. Ion exchange (IEX) has been promoted as a suitable additional treatment step due to the high degree of charge contained on many of the compounds found in NOM (Bolto et al., 2004). Specifically, IEX as a pre-treatment to coagulation has been shown to be an effective way to reduce NOM and the reactive precursors of DBPs (Metcalfe et al., 2015). In these cases, NOM load has been shown to be considerably reduced by IEX, allowing for improved performance of the subsequent coagulation. The lower molecular weight fraction is amenable to IEX, whereas coagulation mainly targets the larger compounds, making the two processes complementary. The sludge volume has also been consequently reduced due to a decreased coagulant demand. However, there are only a small number of fluidised full-scale IEX systems being used for removal of NOM from drinking water. For example, there are different commercial fluidised IEX processes treating water in the Netherlands, Australia and the UK (Drikas et al., 2011; Koreman and Galjaard, 2016; Morgan and Balding, 2009). A number of factors influence whether IEX should be considered as a suitable treatment process for a given water source. These include the characteristics of the water source, brine disposal considerations, economic aspects and implementability (Drikas et al., 2011; Jarvis et al., 2013). The subject of this research was to determine the applicability of IEX for the treatment of water sources in Scotland that contained a high NOM concentration.

Here, the main focus was to explore the influence of different NOM characteristics on their removal by IEX. Previous research has shown that the important physicochemical parameters of NOM are the charge, molecular weight and hydrophobicity (Bazri and Mohseni, 2016; Bolto et al., 2004). However, in most cases these factors have been considered in isolation such that the combined influence of these key parameters is not currently understood. This research firstly considered treatment of a fluctuating water source over long-term operation using a pilot plant located at a Scottish Water WTWs to understand the selective removal of organics by IEX. Secondly, bench-scale experiments were undertaken treating different water sources, highlighting the additional treatability information obtained when water characteristics are considered together. Finally, model compound solutions were used to determine how NOM removal could be explained in greater detail through consideration of the molecular physicochemical properties.

1.2 Aims and objectives

The aim of this PhD thesis was to determine the role of physicochemical properties of organic compounds on their removal by IEX. This knowledge can then be used to inform and optimise the IEX process and ensure that DBPs are effectively controlled. It was hypothesised that the efficiency of IEX for NOM removal was a function of the organic matter charge, molecular weight and hydrophobicity. Further, the specific NOM removal by IEX facilitates improved performance in the removal of reactive DBP precursors in subsequent coagulation. Consequently, the following objectives were identified:

1. To understand the influence of the NOM composition on removal efficiency by IEX, coagulation and their combination for a fluctuating water source using a pilot-scale WTWs.
2. To determine the treatability of different water sources by IEX, coagulation and their combination.
3. To determine the individual and combined influence of charge, molecular weight and hydrophobicity of on the removal of selected model compounds.
4. To investigate the impact of IEX pre-treatment on downstream processes of coagulation and disinfection DBP formation.
5. To link the mechanisms of removal of model compounds with defined physicochemical properties to those seen for real waters.

1.3 Thesis structure

The thesis comprises a series of chapters written in the form of scientific publications. All papers were written by the first author, Pascal Finkbeiner, and have been edited by Prof. Peter Jarvis and Prof. Bruce Jefferson. Experimental work was undertaken by Pascal Finkbeiner, unless otherwise stated in subsequent section.

Chapter 2, *Understanding the potential for selective natural organic matter removal by ion exchange* by P. Finkbeiner, J. Redman, V. Patriarca, G. Moore, B. Jefferson and P. Jarvis has been published in *Water Research*. This chapter investigated the removal of NOM by IEX and subsequent coagulation using a suspended ion-exchange pilot plant (PWNT, Netherlands) over a period of 4.5 months. Evaluation of removal was based on charge, molecular weight and hydrophobicity at each treatment stage. Simultaneously, the removal of reactive DBP precursors was studied to determine the beneficial effects of the combined process. The results from Chapter 2 were obtained with the assistance of Joanna

Redman from Scottish Water who supported the operation of the pilot plant. Laboratory analysis (DOC, DBP formation potential, fractionation and anion determination) was carried out by Scottish Water laboratories (Juniper House, Edinburgh, UK). Liquid chromatography organic carbon detection (LC-OCD) analysis was carried out by Het Water Laboratorium (Haarlem, Netherlands).

Chapter 3, *The combined influence of hydrophobicity, charge and molecular weight on natural organic matter removal by ion exchange and coagulation* by P. Finkbeiner, G. Moore, R. Pereira, B. Jefferson and P. Jarvis has been submitted to *Chemosphere*. Different source waters from Scotland were investigated for their treatability by IEX and coagulation, as well as using the combined process. The collective consideration of physicochemical properties of NOM determined whether additional information on the removal process could be obtained. LC-OCD analysis was conducted by Ryan Pereira and Juliane Bischoff (The Lyell Centre, Heriot-Watt University, Edinburgh, UK). THM and haloacetic acid (HAA) analysis of the chlorinated and incubated samples was carried out by Scottish Water Labs (Juniper House, Edinburgh, UK).

In chapter 4, *Interactions between organic model compounds and ion exchange resins support understanding of NOM removal* by P. Finkbeiner, G. Moore, T. Tseka, T.T.I. Nkambule, B. Jefferson and P. Jarvis, the influence of individual physicochemical properties on the removal of model compounds was investigated. The results showed the benefit of using model compounds for evaluating the contribution of molecular structure on IEX removal processes. The experiments using MIEX resin were carried out by Tebogo Tseka from the University of South Africa, as part of an overseas placement. Size distribution analysis of the resin suspensions was conducted by an MSc student from Cranfield University. THM and HAA analysis of the chlorinated and incubated samples was carried out by Scottish Water laboratories (Juniper House, Edinburgh, UK).

Chapter 5, *Discussion: Ion Exchange - A way forward*, provides a guideline framework for the selection of IEX as a pre-treatment for different types of water sources, along with the potential benefits seen.

The final chapter 6, *Conclusions and Future Work* summarizes the key findings of this research and answers important research and operational questions that will enhance the understanding of NOM removal based on its physicochemical character.

1.4 References

Bazri, M.M., Mohseni, M., 2016. Impact of natural organic matter properties on the kinetics of suspended ion exchange process. Water Res. 91, 147–155.

Bolto, B., Dixon, D., Eldridge, R., 2004. Ion exchange for the removal of natural organic matter. React. Funct. Polym. 60, 171–182.

Drikas, M., Dixon, M., Morran, J., 2011. Long term case study of MIEX pre-treatment in drinking water; understanding NOM removal. Water Res. 45, 1539–1548.

European Commission, 2018. Proposal for a Directive on the quality of water intended for human consumption. http://ec.europa.eu/environment/water/water-drink/review_en.html (accessed 02 March 2018).

Frogbrook, Z., 2017. Natural Organic Matter in Drinking Water: Catchments. Edinburgh.

Golea, D.M., Upton, A., Jarvis, P., Moore, G., Sutherland, S., Parsons, S.A., Judd, S.J., 2017. THM and HAA formation from NOM in raw and treated surface waters. Water Res. 112, 226–235.

Jarvis, P., Sorre, M., Macadam, J., 2013. Report: Evaluation of Ion exchange technology for NOM removal in Scottish Water. Cranfield.

Koreman, E., Galjaard, G., 2016. NOM-removal at SWTP Andijk (Netherlands) with a New Anion Exchange, called SIX. Gewässerschutz - Wasser - Abwasser 239, 50.1-50.13.

Metcalfe, D., Rockey, C., Jefferson, B., Judd, S., Jarvis, P., 2015. Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process. Water Res. 87, 20–28.

Morgan, A., Balding, S., 2009. Ewden WTW & Graincliffe WTW - Raw Water Colour Reduction Schemes. UK Water Proj. Online - Water Treat. Supply 183–184.

Valdivia-Garcia, M., Weir, P., Frogbrook, Z., Graham, D.W., Werner, D., 2016. Climatic, Geographic and Operational Determinants of Trihalomethanes (THMs) in Drinking Water Systems. Nat. Sci. Reports 6, 1–12.

2 UNDERSTANDING THE POTENTIAL FOR SELECTIVE NATURAL ORGANIC MATTER REMOVAL BY ION EXCHANGE

P. Finkbeiner[a], J. Redman[b], V. Patriarca[b], G. Moore[b], B. Jefferson[a], P. Jarvis[a]*

[a]Cranfield Water Science Institute, Building 52a, Cranfield University, Cranfield, Bedford, MK43 0AL.
[b]Scottish Water, Castle House, 6 Castle Drive, Dunfermline, KY11 8GG.

2.1 Abstract

Dissolved organic carbon (DOC) removal from a river water source was investigated using ion exchange (IEX), coagulation and membrane filtration. The addition of IEX into the flowsheet, enabled enhanced reduction of DOC compared to coagulation and membrane processes alone. IEX removed compounds that detrimentally impacted on the coagulation step, improving overall removal and disinfection by-product formation potential (DBP-FP). The combined IEX and coagulation process reduced the specific DBP-FP (sDBP-FP) of the final water, with values as low as 18 mg g_{DOC}^{-1} for both haloacetic acids and trihalomethanes. The fractional composition of the removed DOC showed no significant difference between the combined process and coagulation alone. Similarly, no considerable change in the fractions was seen after IEX treatment occurred. Liquid chromatography-organic carbon detection analysis revealed that low molecular weight compounds (MW < 500 Da) were targeted more specifically by IEX compared to coagulation. The proportion of the removed chromatographed DOC was 22 and ≤7%, respectively. Charge analysis showed that high charge densities, associated with low molecular weight compounds, were closely linked to charge load reduction (r^2=0.67). Charge densities of raw water between 5.4 to 10.7 meq mg_{DOC}^{-1} resulted in charge load reductions of 12.6 to 22.7 µeq L^{-1} confirming the importance of natural organic matter (NOM) charge on the IEX process. The component of NOM removed by IEX that had a positive impact on coagulation was identified to be charged low molecular weight organic

compounds of all hydrophobicity levels, resulting in a reduced specific DBP-FP compared to coagulation alone.

2.2 Introduction

Natural organic matter (NOM) has increased in many surface waters across the world, due to climate change, land use transformation and declining sulphur emissions (Frogbrook, 2017). This has impacted on the effective operation of drinking water treatment systems (Matilainen et al., 2010). In many cases this has increased the organics loading onto the works above its treatment capacity, meaning that existing assets struggle to remove enough NOM. In addition to aesthetic impacts, process fouling, biofilm formation, and bacterial regrowth in the distribution network, residual NOM can cause the formation of disinfection by-products (DBPs) when disinfectants are added to the water (Leenheer and Croué, 2003; Matilainen et al., 2010). Some DBPs are potentially harmful to humans and have been linked to cancer (Richardson et al., 2007).

In previous literature, DBP focus is on the formation of trihalomethanes (THMs) and haloacetic acids (HAAs). These compounds are typically dominant by mass and are indicators of a wide range of other DBPs (Li and Mitch, 2018). Therefore, the concentration of these compounds in drinking water are regulated worldwide. In the US, THMs are limited to 80 µg L^{-1} and HAA5 at 60 µg L^{-1} while in the European Union THMs are regulated at 100 µg L^{-1}, and a recent proposal for HAA9 of 80 µg L^{-1} has been released (European Commission, 2018; UK Statutory Instruments, 2016; USEPA, 1998). The removal of organic precursors is the principal method to control DBPs. This can be achieved by many different processes, including coagulation, adsorption, ion exchange, advanced oxidation and filtration (Kastl et al., 2015; Matilainen et al., 2010; Watson et al., 2015; Zhang et al., 2015).

Coagulation is the most widely used treatment for NOM removal (Metcalfe et al., 2015). Aluminium or iron based coagulants are used which form positively charged species and remove NOM in a reaction involving charge neutralisation and adsorption to flocs (Bond et al., 2011; Matilainen et al., 2010; Zhang et al., 2015). Coagulation preferentially removes charged species which tend to be of high molecular weight (HMW) and hydrophobic character, while substances of low molecular weight (LMW) are generally more recalcitrant to treatment (Drikas et al., 2003). Coagulation is therefore most effective in reducing DBP precursors for waters possessing a high proportion of hydrophobic compounds (Bond et al., 2011; Matilainen et al., 2010).

Ion exchange (IEX) is another increasingly applied process for the reduction of NOM. In this process, an anionic exchange resin is used to remove negatively charged organic compounds by the exchange of a counter ion, usually chloride, from the resin surface. A large proportion of NOM carries a negative charge, mostly attributed to acidic functional groups mainly present in an ionic form at pH >4 (Bolto et al., 2004; Galjaard, 2010; Gregor and Powell, 1987; Kam and Gregory, 2001).

IEX resins can be used in fixed columns or mixed in the water in suspended reactors in commercial systems such as suspended ion exchange (SIX) and magnetic ion-exchange (MIEX) processes (Cornelissen et al., 2009; Galjaard, 2010; Jarvis et al., 2008). For NOM removal applications, suspended systems have proven to be effective as a pre-treatment prior to coagulation. This configuration allows treatment of waters containing suspended solids and shorter contact times through increased rates of mass transfer (Bazri and Mohseni, 2016; Galjaard, 2010; Kishore and Verma, 2006). In the SIX process, the resin is suspended in the raw water and is separated after a defined contact time in a plug flow contactor. The used resin is regenerated before it is reinjected into the system (Shorney-Darby et al., 2014).

IEX targets removal of charged molecules, that may be of varying hydrophobicity, and is particularly effective for removal of LMW organics which can easily diffuse into the resin pores (Bazri and Mohseni, 2016; Drikas et al., 2003; Jarvis et al., 2008). A reduction in DBP formation potential (DBP-FP) in waters treated by IEX has been observed and some studies have found a similar or even superior reduction of DBP-FP compared to coagulation (Boyer and Singer, 2005; Metcalfe et al., 2015). However, reduction in both overall DBP concentration and the specific THM-FP (mg of DBP per g of dissolved organic carbon (DOC)) by IEX alone can be higher or lower than coagulation depending on the raw water composition (Metcalfe et al., 2015).

When IEX processes are used in combination with coagulation, higher removal of NOM and reduced DBP-FP compared to conventional coagulation has been consistently observed (Boyer and Singer, 2005; Metcalfe et al., 2015; Shorney-Darby et al., 2014). This is because different groups of organic compound are being targeted by the two processes to provide higher combined removal of NOM (Mergen et al., 2009). Several studies have also shown that IEX combined with coagulation reduces the specific DBP-FP, and some have found a further reduction than by optimised coagulation alone (Drikas et al., 2003; Jarvis et al., 2008), in certain cases even when there was no reduction in the specific DBP-FP after the IEX stage (Metcalfe et al., 2015).

Additionally, the amount of coagulant used has been shown to be considerably reduced in a combined IEX coagulation process (Crittenden et al., 2012; Jarvis et al., 2008) and an increase in floc strength was found by Jarvis *et al*. (2008). This suggests selective removal of organic compounds by IEX that improves coagulation performance. However, this may be occurring in a number of different ways and understanding these mechanisms is an important knowledge gap.

Investigations on DOC removal by IEX often look at MW and hydrophobicity to describe removal behaviour (Boyer and Singer, 2005; Grefte et al., 2013; Jarvis et al., 2008; Metcalfe et al., 2015). However, information linking NOM charge characteristics with removal is often overlooked. This is important given that NOM charge density is seasonally variable and can change rapidly (Sharp et al., 2006b). This is not always coincidental with a change in UV_{254} or DOC concentration, often the main way by which IEX dosing is controlled (Bolto et al., 2004; Mergen et al., 2009). In the current work the combined influence of NOM hydrophobicity, MW and charge were investigated to understand the selective removal of organics by IEX. The measurements enable opportunity to determine the importance of variable charge load and charge density on the IEX removal process.

2.3 Materials and Methods

An IEX pilot plant was used consisting of suspended ion exchange (SIX process from PWN Technology, Netherlands), in-line coagulation and ceramic membrane filtration (CCMF) with a nominal pore size of 0.1 μm and a surface area of 25 m^2 (Supplementary Information, Figure S 2.1). This was compared with a full scale water treatment works (WTW) comprising coagulation and membrane ultrafiltration (0.04 μm, 27.9 m^2 per unit). Water feeding both plants was from a holding reservoir containing water from the river Dee at Invercannie WTWs. This study was carried out between May and October 2017, following a commissioning and optimisation stage. Fresh resin was added to the SIX unit at the start of the study to enable understanding of the change in treatment performance as the resin was used multiple times. In this period, the pilot plant was operated with both units (SIX+CCMF). For a period of three weeks (14th August till 04th September) no SIX pre-treatment was used and raw water was directly coagulated and treated by the membrane (CCMF).

2.3.1 SIX and CCMF Pilot Plant

The process was run with and without the SIX process, enabling understanding of the influence of IEX on NOM removal by coagulation and membrane filtration. The IEX resin was a gel-type, strong base anion exchange resin with an acrylic backbone and quaternary ammonium groups in the chloride form (Lewatit S5128, Lanxess, Germany). The resin was selected based on a previous pre-screening process for the water source (Koreman and Galjaard, 2016). Raw water contacted with the resin under plug flow conditions at a flow rate of 7 $m^3\ h^{-1}$. A resin concentration of 25 $mL\ L^{-1}$ was applied at a contact time of 30 min based on data from a previous study (Zheng et al., 2018). The resin dose, contact time and flow was kept constant for the duration of the study. After the contactor, the resin was separated from the water by a lamella separator.The settled resin was collected and regenerated in batch mode with sodium chloride (25 $g\ L^{-1}$ Cl^-). Following IEX, water was adjusted to pH 6.4 using caustic soda and sulphuric acid. Polyaluminium chloride (PACl) was added as a coagulant at a dose based on the UV transmittance (UVT) of the water from an online solids-compensated

UVT unit (Spectro::lyser, S::CAN, Austria). The coagulant dose was calculated from algorithms developed from jar testing of the water (Supplementary Information, 2.8.2). The average coagulant dose for SIX+CCMF was 2.13 mg L^{-1} or 0.47 mg_{Al3+} mg_{DOC}^{-1} (range 0.19-6.04 mg L^{-1} or 0.07-0.82 mg_{Al3+} mg_{DOC}^{-1}) and for CCMF 3.73 mg L^{-1} or 0.75 mg_{Al3+} mg_{DOC}^{-1} (range 1.58-6.06 mg L^{-1} or 0.44–1.19 mg_{Al3+} mg_{DOC}^{-1}). After in-line coagulation (ILCA), the water was filtered through a ceramic membrane (pore size 0.1 µm, surface area 25 m^2) at a flux of 150 to 250 L m^{-2} h^{-1} (LMH). The membrane was backwashed (BW) after loading between 50 and 167 L m^{-2} and underwent an enhanced BW (EBW) after 500 to 1500 L m^{-2}. The EBW was carried out using NaOCl (100 mg L^{-1} free Cl_2) or H_2O_2 (100 mg L^{-1}, pH 2) (Supplementary Information, Table S 2.1). Samples were taken after treatment by IEX and then following membrane treatment.

2.3.2 Water treatment works

The WTWs operated at an average of 39 ML day^{-1}. Raw water was adjusted to pH 6.9 using lime. PACl was added as the coagulant. Dosing of PACl was automatically optimised based on raw water colour, approximately 1.2 mg L^{-1} Al^{3+} per 20 hazen, resulting in an average of 1.62 mg L^{-1} or 0.37 mg_{Al3+} mg_{DOC}^{-1} (range 0.35 to 3.34 mg L^{-1}; 0.22 to 0.70 mg_{Al3+} mg_{DOC}^{-1}). The coagulated water was filtered from out-to-in, using polyvinylidene difluoride S10V Evoqua membranes with a pore size of 0.04 µm. A total membrane surface area of 11,048 m^2 was available (6 cells, containing 396 elements each) allowing a flux of 21.4-30.2 LMH. Samples of raw water and permeate were taken for analyses.

2.3.3 Sample analysis

Samples for UVA_{254} measurement were pre-filtered with a 0.45 µm syringe filter and analysed using a Hach DR6000 spectrophotometer (Hach Lange, Germany, 5 cm quartz cuvette cell). DOC was measured using a non-purgable organic carbon method on a Shimadzu TOC-L analyser (EQS 24H) or a Skalar Formacs HT TOC analyser. All samples were passed through a 0.45 µm filter prior to analysis. A series of XAD7 and XAD4 resin were used to separate the DOC into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions using adapted methods described in Bond (2009). HAA- and THM-FP were determined from pre-filtered (0.45 µm) samples diluted to 1 mg L^{-1} DOC. Water was spiked with NaOCl to give 5 mg L^{-1} free chlorine and stored for 7 days in the dark at 25°C. After quenching with thiosulfate, the samples were analysed with Gas chromatography–mass spectrometry. Liquid chromatography-organic carbon detection (LC-OCD) was carried out to determine the relative molecular weight distribution of organic compounds in water as it passed through various treatment stages. Samples were analysed by Het Water Laboratorium (Haarlem, Netherlands) according to the methods described in Huber *et al*. (2011). In short, 1 mL of sample was injected onto a weak cation exchange chromatographic column (TSK HW 50S, Tosoh, Japan). A flow rate of 1.1 mL min^{-1} was applied and a UV and an organic carbon detector were used for quantification. The column by-pass (0.1 mL min^{-1}) was used as a reference for the total DOC of the sample. Software (ChromCALC) was used to identify the different peaks and integrate their area. A Poisson distribution defined the boundaries for the dominant peak and was used to determine the area of the remaining peaks. Further details can be found in the supplementary information of the referenced paper.

Zeta potential and charge density experiments of samples were determined using a zetasizer (Malvern Nano Series, Worcestershire, UK). For zeta potential measurements, samples were filled in a polystyrene latex folded capillary cell, equilibrated to 25°C and measured three times with a minimum of 10 and a maximum of 100 runs. Charge determinations were carried out for raw and IEX treated water, using an adapted method of Kam and Gregory (2001). Polydiallyldimethylammonium chloride (PDADMAC) was purchased from Sigma-Aldrich (Dorset, UK) and diluted to obtain a concentration of 416 mg L^{-1} for high DOC samples and 8.32 mg L^{-1} for low DOC samples. The solution was delivered stepwise to a stirred 15 mL sample adjusted to pH 7 by an autotitrator MPT-2 with a 3-ch degasser (Malvern), resulting in PDADMAC concentrations between 1.0 to 20.0 mg L^{-1} for raw water and 0.04 to 15.0 mg L^{-1} for SIX treated water. After each addition the solution was pumped into a folded capillary cell and zeta potential was measured. The point of zero charge (PZC) was determined by fitting a linear regression through the data points of at least three measurements and the PDADMAC concentration was converted into charge load (CL) using a charge density (CD) of 6.2 meq g^{-1} for PDADMAC (Mergen, 2008). CD was calculated by normalising the CL to the DOC of the sample to give meq per g DOC.

2.4 Results and discussion

2.4.1 DOC concentrations over time

The raw water was of low turbidity, 0.2-1.4 NTU, and low alkalinity, ranging between 10-29 mg_{HCO_3} L^{-1}, with nitrate and sulphate concentrations from 0.50-1.28 mg L^{-1} and 1.9-4.5 mg L^{-1}, respectively (Supplementary Information, Table S 2.2). The raw water entering the WTWs and the pilot plant fluctuated between 1.5 and 10.1 mg L^{-1} for DOC and 4.7 to 42.0 m^{-1} for UVA (Figure 2.1). The SIX process removed an average of 1.5 mg L^{-1} of DOC and 6.8 m^{-1} of UVA, with a maximum removal of 2.4 mg L^{-1} of DOC and 12.1 m^{-1} UVA. The DOC concentration after SIX removal generally tracked the pattern of the raw water, indicating a limitation of the resin for removal of DOC, possibly due to diffusion limitation.

The DOC concentration in the final water after SIX+CCMF had a mean of 0.7 mg L^{-1}, with values as low as 0.2 mg L^{-1} and a maximum of 1.4 mg L^{-1} (UVA 0.2 to 2.6 m^{-1}). This was considerably lower than the concentrations found in the final water for both the CCMF and the WTWs, which had a mean DOC concentration of 1.3 mg L^{-1} (range 0.5-2.2 mg L^{-1}) and 2.1 mg L^{-1} (range 1.4-2.8 mg L^{-1}), respectively.

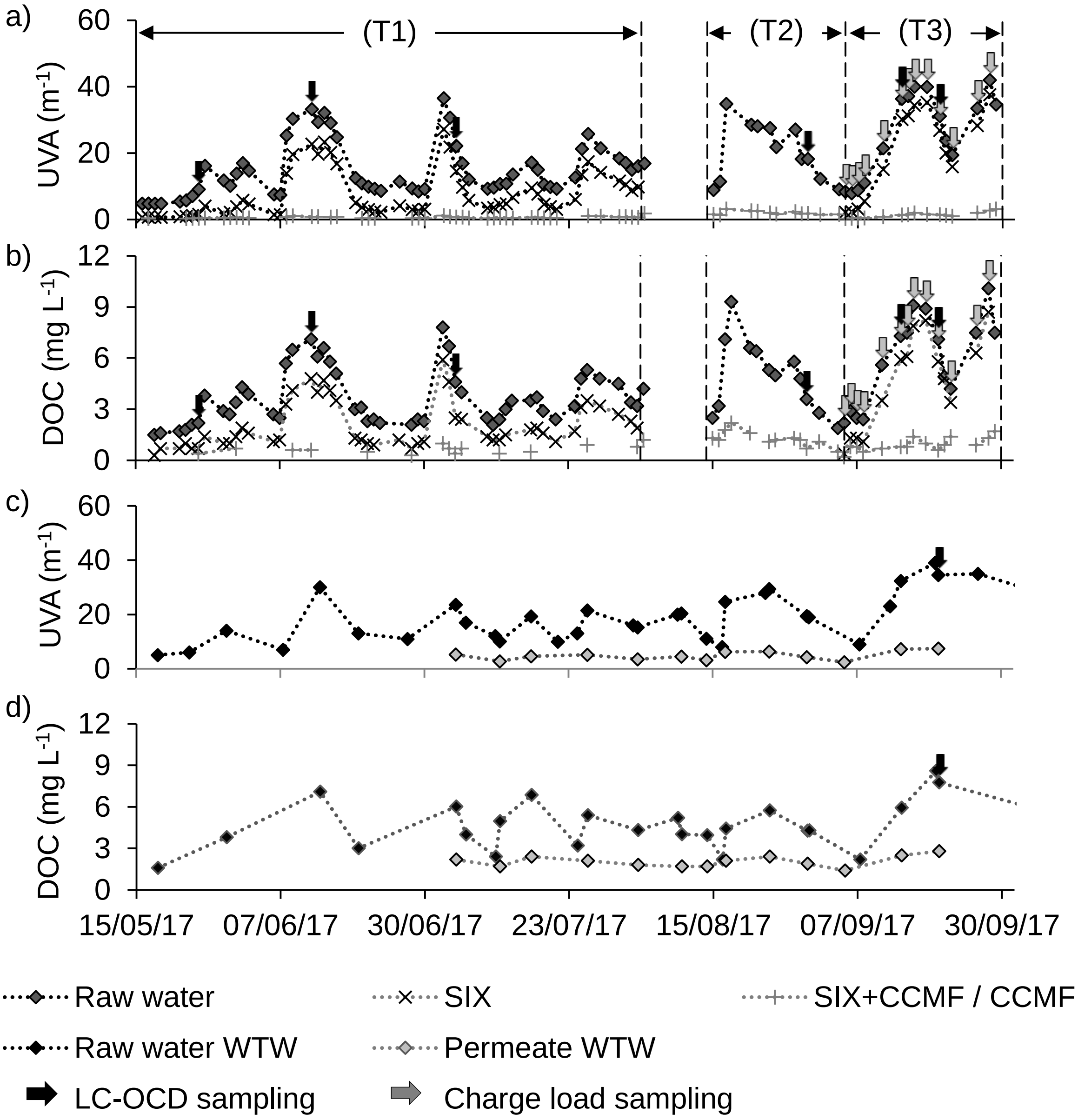


Figure 2.1: Time series data for DOC and UVA removal for the pilot plant in graph a) and b) before treatment (raw water), after SIX treatment (SIX effluent) and after coagulation with membrane filtration (final water). SIX operational parameters: resin concentration 25 mL L^{-1}, flow 7 m^3 h^{-1}; period (T1) operation with SIX and coagulation with membrane filtration (SIX+CCMF), period (T2) operation with CCMF only (no SIX pre-treatment), period (T3) operation with SIX+CCMF. Graph c) and d) UVA_{254} and DOC of samples taken from the WTW in Invercannie before treatment (screened raw water) and after coagulation with membrane filtration (permeate WTW), S10V membranes (27.9 m^2, 0.04 µm), 37 ML d^{-1}).

A cumulative probability plot showed that 82% of all DOC measurements were below 1 mg L^{-1} for SIX+CCMF while only 17% of the DOC measurements were below this value for CCMF and only 46% were below 2 mg L^{-1} for the WTW (Figure 2.2).

Robustness of DOC removal was evaluated using an adjusted method described by Jarvis *et al*. (2008). The steepness of the slope in the linear region of the cumulative probability curve between 15 and 85% was used to evaluate robustness, where a steeper slope indicates a more robust system (Figure 2.2). Comparison of the slopes identified that SIX+CCMF was 34% more robust than CCMF and 69% more robust than the WTW, showing that the SIX+CCMF process had a much narrower range around this lower mean value.

Additionally, the coagulant dose (Supplementary Information, Table S 2.1, coagulation control B) was 30% lower when SIX+CCMF was used compared to CCMF. This is in agreement with previous results where reductions of coagulant of up to 50-60% have been seen when IEX was used upstream of coagulation (Grefte et al., 2013; Jarvis et al., 2008; Metcalfe et al., 2015).

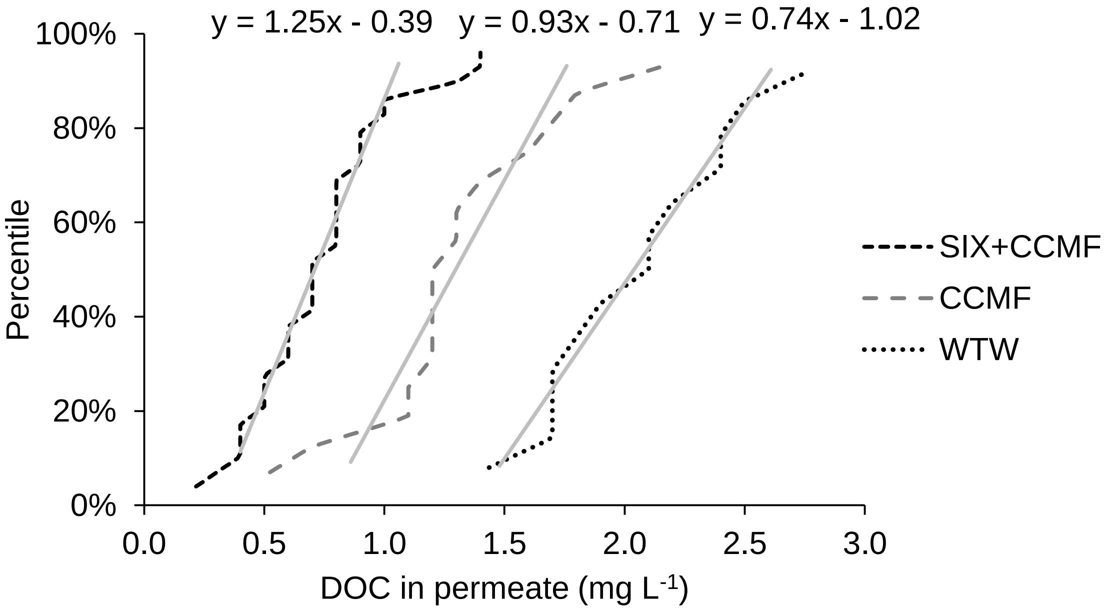


Figure 2.2: Robustness of the different treatment methods shown as linear regressions (between 15 and 85%iles) in the cumulative frequency plot of the DOC in final water of SIX+CCMF, CCMF and permeate from the WTW.

2.4.2 Formation potential of disinfection by-products

The reduction in DOC in the treated water was generally concurrent with a decrease in the DBP-FP. While the proportion of the SIX-removed NOM decreased with increasing NOM load due to limitations in the capacity of the resin for a consistent resin dose, the overall improvements in DOC and sDBP-FP were still observed following subsequent coagulation. An increased value in the raw water resulted in higher THM- and HAA-FP in the SIX treated water (Figure 2.3a, b). For example, raw water HAA- and THM-FP of 260 and 196 µg L^{-1} were reduced to 30 and 32 µg L^{-1} while a raw water DBP-FP of 2677 and 1525 µg L^{-1} for THMs and HAAs were reduced to 2210 and 1366 µg L^{-1}. This can be attributed to the lower relative NOM removal at higher initial concentrations, which were 2.4 and 8.6 mg L^{-1} DOC for the described cases. For the SIX+CCMF, a weaker but positive relationship was seen between the raw and treated water. However, overall the concentration of DBPs was lower than for all of the other treatment processes, regardless of the incoming DBP-FP. HAA- and THM-FP were measured as low as 9 and 7 µg L^{-1} with an average of 30 and 33 µg L^{-1}, respectively. Comparatively, the DBP-FPs obtained in the final water for CCMF and WTW as a function of the raw water DBP-FPs were consistently higher than for the final water of SIX-CCMF, demonstrating the benefit of the pre-treatment. This was particularly evident since the downstream coagulant dose to DOC ratio was much lower for the IEX treatment compared to CCMF: 0.47 and 0.75 mg_{Al3+} mg_{DOC}^{-1} respectively. The lowest HAA- and THM-FP values observed for CCMF were 52 and 57 µg L^{-1} and for the WTW 347 and 269 µg L^{-1}, respectively.

IEX treatment alone was not shown to reduce the specific DBP-FP (sDBP-FP) for variable incoming water quality with both the specific HAA-FP (sHAA-FP) and specific THM-FP (sTHM-FP) being similar to the incoming water quality (Figure 2.3c, d). However, the final water from the SIX+CCMF had much lower sHAA and sTHM-FP than all treatments. For example, the treated water from SIX+CCMF had sHAA and sTHM-FP of 18-68 mg g_{DOC}^{-1} (mean 39 mg g_{DOC}^{-1}) and 18-65 mg g_{DOC}^{-1} (42 mg g_{DOC}^{-1}) respectively. The mean sHAA-FP concentration was 41 and 79 % lower compared to CCMF and SIX while the average sTHM-FP was

35 and 65% lower, respectively. Comparatively, the average permeate sHAA-FP and sTHM-FPs from the WTWs were 107±16 mg g_{DOC}^{-1} and 80±7 mg g_{DOC}^{-1}.

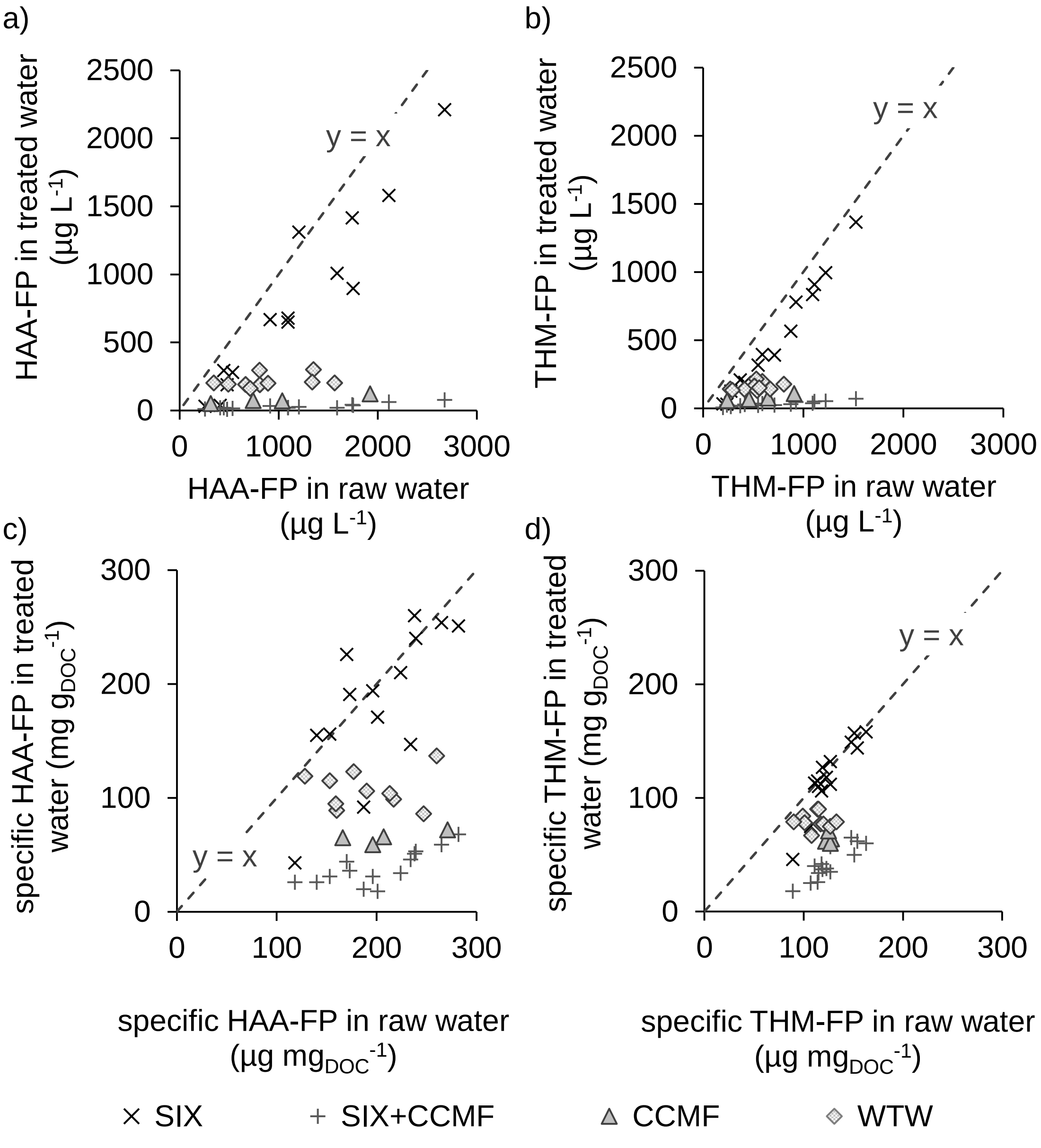


Figure 2.3: DBP-FP of the water treated by different steps/methods as a function of their raw water DBP-FP for HAAs (a) and THMs (b), and DBP reactivity expressed as specific formation potential of the water treated by different steps/methods as a function of their raw water sDBP-FP for HAAs (c) and THMs (d).

The results suggest that IEX plays a number of roles in improving NOM removal by eliminating a particular fraction of NOM that 1) enhances coagulation efficiency, providing increased removal of overall DOC; and 2) enables coagulation to subsequently remove higher levels of specific components of NOM that have a high DBP-FP. The following section investigates the key features of NOM that controls its removal and the DBP-FP dealing in turn with NOM hydrophobicity, MW and charge.

2.4.3 Hydrophobicity

With respect to hydrophobicity (Figure 2.4a), the hydrophobic compounds (HPO) represented the largest fraction in the raw water (62±6%), consistent with results reported in previous studies for similar types of NOM dominated water sources (Boyer and Singer, 2005; Sharp et al., 2006a). The transphilic (TPI) fraction accounted for 22±4% and the hydrophilic (HPI) fraction for 16±3% of the overall DOC. After SIX treatment, the proportions of NOM fractions did not change considerably. This was also found when other NOM specific suspended IEX resins have been investigated (Boyer and Singer, 2005; Jarvis et al., 2008), suggesting that no preferential removal of any of the fractions occurred. When the SIX effluent was coagulated and filtered (treated with CCMF), the proportion of the HPI fraction increased to 43±6%, while the HPO fraction was reduced to 35±4%. This was a result consistent with other studies that have shown preferential removal of hydrophobic NOM by coagulation (Jarvis et al., 2008; Sharp et al., 2006a).

To evaluate the influence of IEX on the final treated water, the removal of the fractions by the three treatment methods were compared. The removal was normalized to the total removed DOC to enable comparison of different overall NOM removals (Figure 2.4b). The average proportion of HPO in the removed DOC was 69±6%, 64±5% and 74±8% for SIX+CCMF, CCMF and WTW, respectively. TPI and HPI made up 21±5% and 10±2% of the removed DOC by SIX+CCMF, 26±4% and 10±3% for CCMF treatment and 22±8% and 4±3% for the WTW. To show whether the data sets were significantly different a Kruskal-Wallis test was applied (non-normally distributed data). The test showed the HPI fraction was significantly different, whereas HPO and TPI proportions were not, for the SIX+CCMF, CCMF and WTW ($p < 0.05$). Follow-up Mann-Whitney tests (Bonferroni correction: level of significance 0.0167) revealed that the proportional removal of HPI at the WTWs was the only fraction that showed a difference compared to SIX+CCMF (U_{HPI} = 1.0, r_{HPI} = -0.72) and CCMF (U_{HPI} = 0.0, r_{HPI} = -0.82). The low proportion of HPI removed at the WTWs (4±3%) was more than half of the removal seen for SIX+CCMF and CCMF (10±2 and 10±3%). This may be explained by the lower coagulant to DOC dose ratio used at the WTWs compared to the membrane used in the pilot plant (0.37 mg_{Al3+} mg_{DOC}^{-1} for the WTWs compared to 0.47 and 0.75 mg_{Al3+} mg_{DOC}^{-1} for SIX+CCMF and CCMF, respectively) due it using a tighter membrane (UF compared to MF). Although not amenable to coagulation, some removal of the HPI fraction occurs through adsorption onto precipitated coagulant solids (Jarvis et al., 2008). As a result, less precipitated coagulant surface area in the WTWs system was available, reducing opportunities for adsorption of this fraction.

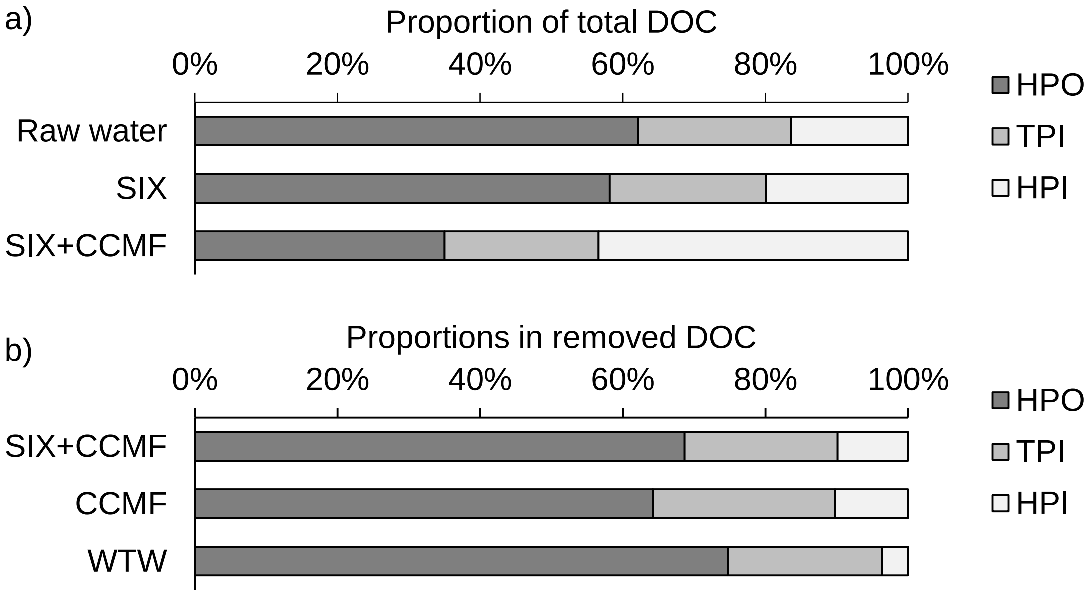


Figure 2.4: a) Percentage of DOC contributed by each of the fractions for water in the different steps of the SIX+CCMF process and b) Proportion of removed DOC attributed to each fraction for the different treatment methods.

Similar results to the overall DOC removal were seen for the DBPs, with no correlation between the removed DOC of the different fraction and the reduction in the sDBP-FP (Supplementary Information, Figure S 2.2). This is in line with researchers who have reported that all fractions contribute to the DBP-FP (Hua and Reckhow, 2007).

Removal of NOM by IEX is primarily driven by charge (Boyer et al., 2008), which is present to differing degrees in all of the hydrophobicity fractions (Boyer et al., 2008; Mergen et al., 2009; Sharp et al., 2006a). Removal of these organic compounds, or a fraction of, may be important in reducing significant DBP precursors. However, these results show that fractionation does not have sufficient sensitivity to show NOM which is selectively removed by IEX. In addition, other researchers have shown that hydrophobicity is not an essential characteristic for a compound to exchange onto an IEX resin (Jarvis et al., 2008; Mergen et al., 2009).

2.4.4 Molecular weight distribution

Molecular size is important in controlling removal by IEX due to size-exclusion effects (Bazri and Mohseni, 2016). The importance of the relative MWs of NOM on removal across the SIX and CCMF processes was investigated using LC-OCD. The LC-OCD chromatogram profiles for the different processes before and after treatment show 4 peaks (Figure 2.5). For all raw water samples, P2 was dominant, showing that the bulk of the DOC to be of medium molecular weight, around 1 kDa. The profile presented in Figure 2.5a shows a raw water with a DOC concentration of 6.5 mg L^{-1}, while the profiles in Figure 2.5b-d were from samples ranging between 2.3-7.4 mg L^{-1} DOC.

Integration of the peaks enabled a comparison of the removal of NOM by size to be made for the different treatment systems. When the raw water DOC concentration was low (2.3 mg L^{-1}), all peaks were substantially reduced (Figure 2.5b). In this case the area of P2 and P3 were reduced by 83% and 78% by SIX, respectively, while P1 showed a reduction of 19%. Removal of P2 and P3 was expected as these smaller molecules diffuse more easily into the pores of the resin and are not restricted to exchange sites on the outside, whereas larger molecules are rejected due to size exclusion (Bazri and Mohseni, 2016). Lower removal of organic compounds around P4 (40%) seems contradictory to this statement. However, as has been noted it is not only size that defines the removal, but also charge is of importance. Huber *et al*. (2011) reported elution of neutral LMW NOM around P4 (elution time of ≥60 min), suggesting these organic compounds carry little charge. P2 and P3 have been associated with charged organic compounds (Huber et al., 2011; Koreman and Galjaard, 2016; Shorney-Darby et al., 2014). For higher DOC concentrations (6.5 mg L^{-1}, Figure 2.5a), the removal for all peaks was much less pronounced. The removal obtained for P2, P3 and P4 were 13%, 20% and 17%, respectively. This can be explained by the limited capacity of the resin and possible blockage of the resin surface by large molecules at high DOC concentrations (Metcalfe et al., 2015).

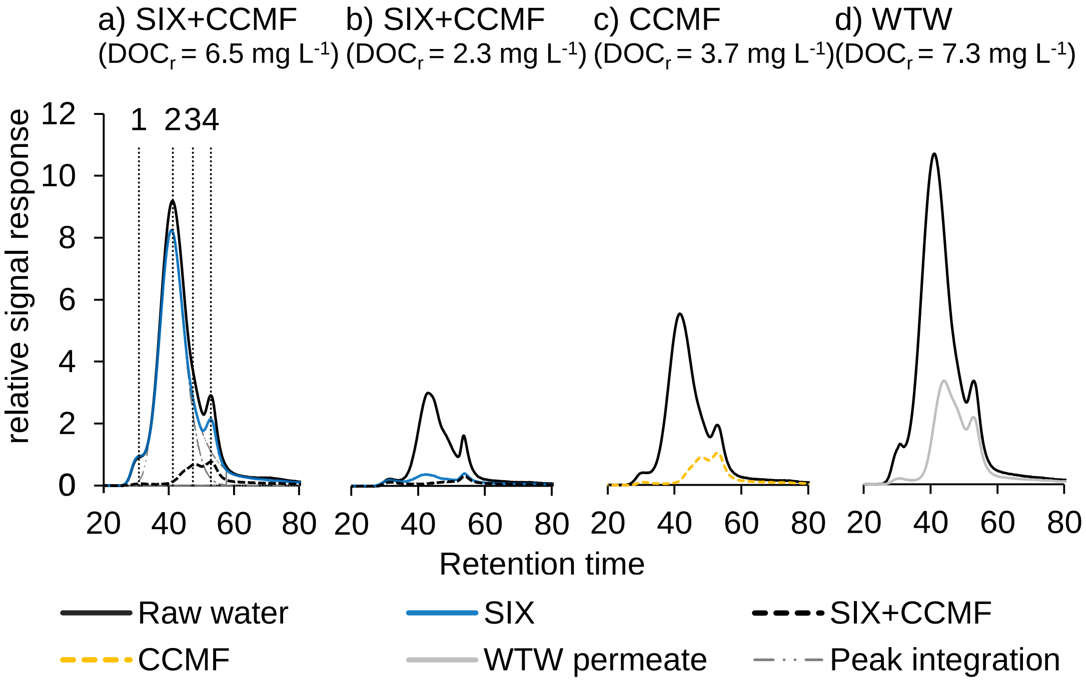


Figure 2.5: Selected LC-OCD chromatograms of the waters in the SIX+CCMF process for high (a) and low (b) raw water DOC concentrations; LC-OCD chromatogram of raw and final water for CCMF treatment (c); LC-OCD chromatogram for raw water and permeate of WTW (d); DOC_r = raw water DOC.

The water profile for SIX+CCMF showed a reduction of P1 and P2 by 88 and 100% compared to the SIX effluent showing the preferential removal of HMW fractions by coagulation (Figure 2.5a). These results are consistent with those seen in the literature (Bond et al., 2011; Boyer and Singer, 2005; Metcalfe et al., 2015). Likewise permeate of the WTW (Figure 2.5d), showed high removal of the HMW fraction shown in P1 (74%) and P2 (72%).

Overall, organic compounds represented in P3 and P4 were targeted more effectively by IEX, shown by their consistently lower combined DOC values in SIX+CCMF compared to CCMF treated water, across a broad range of water qualities (2.3 to 7.4 mg L^{-1}) (Supplementary Information, Figure S 2.3). This was further evidenced by determining the proportion of removed DOC for each of the different peaks from the chromatographed DOC (CDOC) (Figure 2.6). Organic compounds represented in P2 had the highest proportion of the removed CDOC for SIX (76%), while P3 and P4 accounted for 15% and 7%. For CCMF following SIX pre-treatment, 91% of the removed CDOC was from P2, while the values for P3 and P4 were both only 3%. This confirms that IEX has more specific removal of these LMW compounds compared to coagulation. The profiles for CCMF compared to the WTWs were very similar. This shows that although the combined process had higher overall removal, the compounds being targeted by the coagulation/membrane process was similar, a result consistent with the fractionation data. The relative MW analysis showed better removal of lower MW organic compounds compared to coagulation processes. However, IEX was effective in removing some organic compounds from all MW fractions apart from P1, the highest MW NOM as a result of size exclusion of these compounds (Metcalfe et al., 2015).

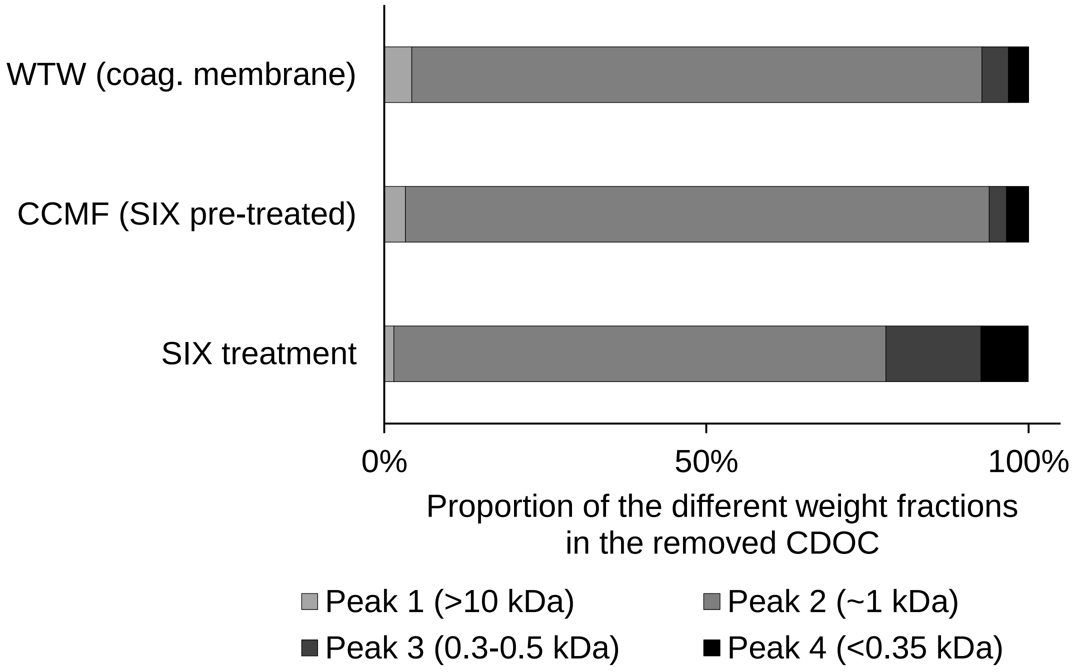


Figure 2.6: Comparison of the proportion of the size fractions of the removed CDOC (sum of peak 1 to 4) for the different treatment steps/methods.

2.4.5 Charge characteristics of NOM

The charge load (CL) of the raw water was between 15.6 and 82.7 µeq L^{-1} and the charge density (CD) ranged from 5.4 to 10.7 meq mg_{DOC}^{-1} showing variable charge composition of the raw water over the duration of the trial (Figure 2.7). These values are in line with CDs measured for other water sources and ranging from 0.3 to 10.2 meq mg_{DOC}^{-1} (Bazri and Mohseni, 2016; Mergen et al., 2008). As the CL in the raw water increased, the residual CL in the SIX increased in a linear fashion (Figure 2.7). This showed a limit to the amount of charge that could be removed by the resin, less than 0.1% of the theoretical resin capacity (1.25 meq mL^{-1}). Similarly low removal was reported by Mergen (2008), who investigated charge load removal from different waters using magnetic IEX resin (capacity 0.5 meq mL^{-1}) and found charge load removals of up to 31 µeq L^{-1}, utilising 0.6% of the resin capacity. This low utilisation was explained by organic compounds blocking the surface and internal pores of the resin. In addition, some compounds may be missed by the charge density method. For example, small compounds such as glutamic acid have been shown to be difficult to detected using the described titration method. Additionally, anions (sulphate, nitrate, hydrogen carbonate) compete with organic molecules (Boyer et al., 2008) and the required charge to remove these in the water source investigated here was calculated to be up to 2.9% of the capacity of the resin.

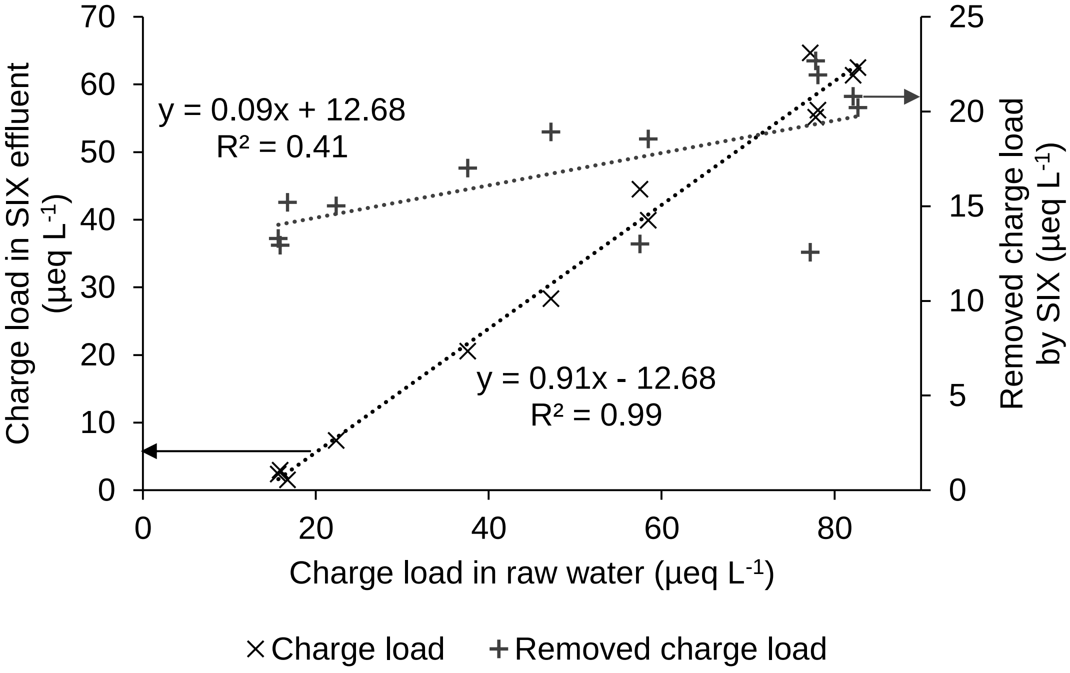


Figure 2.7: Relationship between the charge load in the raw water and in the SIX treated water, along with the charge load removed.

There was a weak positive correlation between raw water charge load and the removed charge load ($r^2 = 0.41$) (Figure 2.7). This showed that when there was more charge in the water, the SIX process was able to remove more of this charge load. As such, when a shift in the concentration of charged molecules and/or charged functional groups on individual molecules occurs in the raw water, this will influence the removal of NOM, even when the DOC concentration of the raw water does not change. It is therefore helpful to normalise the charge in the raw water to DOC and compare this with the amount of charge removed (Figure 2.8). There was a stronger relationship between these parameters (r^2=0.67) with higher charge density showing higher charge removal. For example when the CD in the raw water was 7.7 meq g_{DOC}^{-1} the charge load removal was 13.0 µeq L^{-1}, while for a CD of 10.4 meq g_{DOC}^{-1} the charge load removed was 21.9 µeq L^{-1}. In both cases the raw water DOC was 7.5 mg L^{-1}. This aligns with the fact that more highly charged molecules are preferentially removed due to the stronger affinity to the ion exchange resin (Bond et al., 2011).

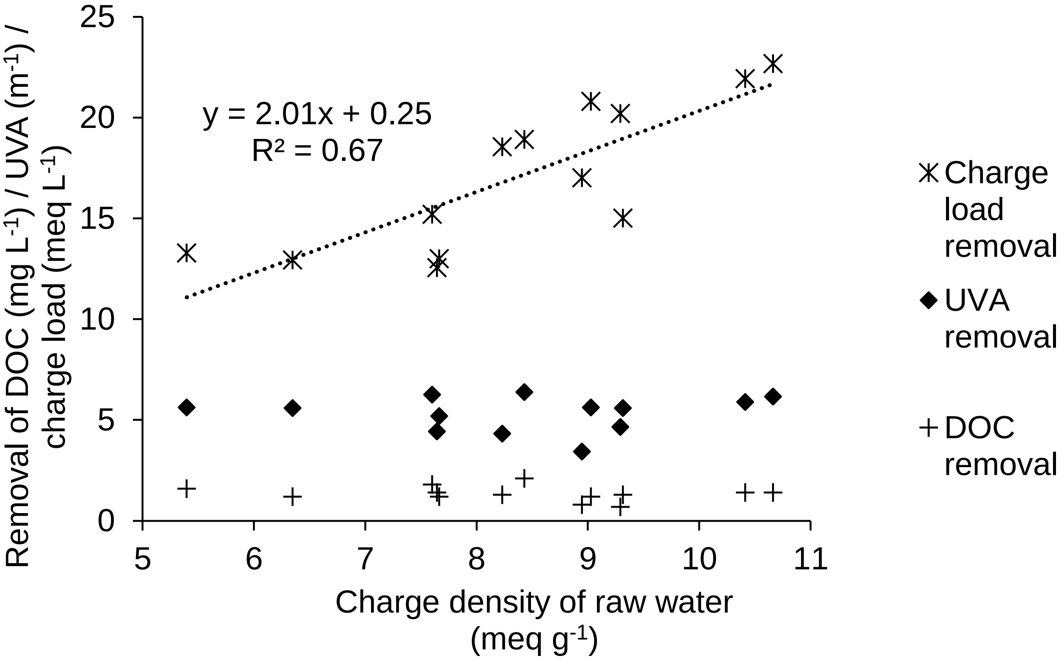


Figure 2.8: Relationship between the charge density in the raw water and removed charge load, UVA and DOC by SIX.

Studies investigating removal of model compounds by IEX have shown strong relationships between high removal and high charge density. For example, small organic acids such as citric and benzoic acids show high levels of removal (Finkbeiner et al., 2017). Given that LMW organic compounds were preferentially removed by IEX, it is plausible to consider that carboxylic acid compounds with high CD are well represented in the LMW fraction. The scatter around the relationship between CD and CL removal was attributed to the influence of the size of organic molecules. Large molecules with significant charge density will be less well removed due to size exclusion effects. This shows the importance of both NOM charge and molecular size when considering removal.

However, these results show that measuring charge density in the raw water is a more suitable parameter that can be used to determine removal by IEX compared to measurements such as DOC and UVA, where there was no correlation with removal (Figure 2.8). This is an important observation as many WTWs use online instruments that measure UV or DOC to control IEX resin dose. By using CD it would be possible to more effectively control the IEX dose in response to the change in charge load from the raw water, which as has been shown is not always commensurate with an increase in NOM concentration.

There was no obvious relationship between the DBP-FP and the charge density following the SIX process (Supplementary Information, Figure S 2.4). This further supports the view that IEX does not always directly reduce DBP reactivity, but facilitates better removal of the DBP precursors by coagulation. Previous work has shown that small organic acids inhibit the hydrolysis of aluminium coagulants by creating a stable complex between the metal salt and the ligands, particularly dicarboxylates such as citrate and oxalate (Violante and Violante, 1980). More recent work on the removal of humic acid by polyaluminium chloride has shown a detrimental effect when certain counter ions (including oxylate, citrate and malate) were present (Lin and Lee, 2013). Complexation of these anions with the coagulant was the mechanism proposed to explain a deterioration in the polyaluminium cluster structure, reducing the removal of the humic acid. Jarvis *et al*. (2015) showed that the presence of small acids such as aspartic and oxalic acid reduced coagulation efficiency, and some compounds (including aspartic acid) restricted floc growth. Organic compounds such as these would be effectively removed by IEX, allowing the coagulant to work more effectively on other compounds, such as larger humic acid compounds, which also tend to have higher DBP-FP.

Other investigations have reported that the use of IEX resulted in more stable flocs in subsequent coagulation compared to conventional treatment, attributed to the absence of organic compounds in the floc structure removed by IEX (Jarvis et al., 2008). Therefore, the reduction of specific compounds by IEX is believed to be responsible for improved coagulation by enhancing the interactions of the coagulant with the remaining organic compounds, improving floc formation and size, and increasing the available surface for adsorption of organic compounds. The present study has extended our understanding further by elucidating that these specific organics are charged compounds of LMW with hydrophilic, transphilic and hydrophobic character. For future investigation, analysis of the charge of the different size fractions could give a more detailed view on the interaction between molecular weight and charge density of organic compounds on their removal and the influence on the DBP-FP in the final water.

2.5 Conclusion

DOC and UVA of a fluctuating water source were successfully reduced using a novel suspended ion exchange technology upstream of coagulation and ceramic membrane filtration in pilot scale. The process gave improved performance compared to coagulation-filtration in both a pilot plant and at full-scale in terms of removal of sum parameters (DOC, UVA) as well as the (specific) formation potential of DBPs. Different characterisation techniques were applied to understand the selective removal of organics by SIX:

- Analysis of hydrophobic, transphilic and hydrophilic fractions revealed that there was no considerable change in the distribution of the fractions after SIX treatment compared to the raw water. The proportion of the removed DOC by SIX+CCMF compared to CCMF did not show a statistically significant difference. Therefore, hydrophobicity does not seem to be a contributor to suspended ion exchange in this case.
- Removal of compounds of a wide range of size was detected using LC-OCD and showed that IEX preferentially removes molecular weights of around 1 kDa.
- From charge measurements, it was discovered that higher charge densities improved the removal of charge load. The results showed that charge describes removal behaviour better than other more normally monitored parameters.
- The results of the combined analyses indicate that IEX removes specific charged organics of low molecular weight, regardless of their hydrophobicity and this improves the coagulation process resulting in a reduced sDBP-FP.

2.6 Acknowledgments

The authors would like to express their appreciation to Scottish Water for the financial support to carry out this research. The authors also thank the team at the Scottish Water labs for the analytical work conducted. Furthermore, they would like to acknowledge PWNT, Netherlands who designed the pilot plant and provided technical support during the project; HET Water Laboratorium, Haarlem, Netherlands for LC-OCD analysis and TDC, Aberdeen, Scotland for their mechanical and electrical engineering.

2.7 References

Bazri, M.M., Mohseni, M., 2016. Impact of natural organic matter properties on the kinetics of suspended ion exchange process. Water Res. 91, 147–155.

Bolto, B., Dixon, D., Eldridge, R., 2004. Ion exchange for the removal of natural organic matter. React. Funct. Polym. 60, 171–182.

Bond, T., 2009. Treatment of disinfection by-product precursors. PhD Thesis, Cranfield University.

Bond, T., Goslan, E.H., Parsons, S. A., Jefferson, B., 2011. Treatment of disinfection by-product precursors. Environ. Technol. 32, 1–25.

Boyer, T.H., Singer, P.C., 2005. Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors. Water Res. 39, 1265–76.

Boyer, T.H., Singer, P.C., Aiken, G.R., 2008. Removal of Dissolved Organic Matter by Anion Exchange : Effect of Dissolved Organic Matter Properties. Environ. Sci. Technol. 42, 7431–7437.

Cornelissen, E.R., Beerendonk, E.F., Nederlof, M.N., van der Hoek, J.P., Wessels, L.P., 2009. Fluidized ion exchange (FIX) to control NOM fouling in ultrafiltration. Desalination 236, 334–341.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., 2012. Ion Exchange, in: MWH's Water Treatment: Principles and Design. John Wiley & Sons, Inc., Hoboken, NJ, USA, pp. 1263–1334.

Drikas, M., Chow, C.W.K., Cook, D., 2003. The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth: An evaluation of magnetic ion exchange resin (MIEX) and alum coagulation. J. Water Supply Res. Technol. - Aqua 52, 475–487.

European Commission, 2018. Proposal for a Directive on the quality of water intended for human consumption. http://ec.europa.eu/environment/water/water-drink/review_en.html (accessed 02 March 2018).

Finkbeiner, P., Jarvis, P., Jefferson, B., Moore, G., 2017. New insight on the influence of physicochemical properties of natural organic matter on their removal by suspended ion exchange, in: Proceedings of the 14th IWA Leading Edge Conference on Water and Wastewater Technologies. Florianopolis.

Frogbrook, Z., 2017. Natural Organic Matter in Drinking Water: Catchments. Edinburgh.

Galjaard, G., 2010. SIX®: A New Resin Treatment Technology for Drinking Water. Water Pract. Technol. 4, 1–13.

Grefte, A., Dignum, M., Cornelissen, E.R., Rietveld, L.C., 2013. Natural organic matter removal by ion exchange at different positions in the drinking water treatment lane. Drink. Water Eng. Sci. 6, 1–10.

Gregor, J.E., Powell, H.K.J., 1987. Effects of extraction procedures on fulvic acid properties. Sci. Total Environ. 62, 3–12.

Hua, G., Reckhow, D.A., 2007. Characterization of Disinfection Byproduct Precursors Based on Hydrophobicity and Molecular Size. Environ. Sci. Technol. 41, 3309–3315.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). Water Res. 45, 879–885.

Jarvis, P., 2015. The impact of changing water quality on treatment of NOM laden water sources, in: Proceedings of the 6th IWA Specialist Conference on Natural Organic Matter in Drinking Water. Sweden.

Jarvis, P., Mergen, M., Banks, J., Mcintosh, B., Parsons, S.A., Jefferson, B., 2008. Pilot scale comparison of enhanced coagulation with magnetic resin plus coagulation systems. Environ. Sci. Technol. 42, 1276–1282.

Kam, S.K., Gregory, J., 2001. The interaction of humic substances with cationic polyelectrolytes. Water Res. 35, 3557–3566.

Kastl, G., Sathasivan, A., Fisher, I., 2015. A selection framework for NOM removal process for drinking water treatment. Desalin. Water Treat. 57(17), 7679–7689.

Kishore, K., Verma, N., 2006. Mass transfer study on counter current multi-stage fluidized bed ion exchanger. Chem. Eng. Process. 45, 31–45.

Koreman, E., Galjaard, G., 2016. NOM-removal at SWTP Andijk (Netherlands) with a New Anion Exchange, called SIX. Gewässerschutz - Wasser - Abwasser 239, 50.1-50.13.

Leenheer, J.A., Croué, J.-P., 2003. Characterizing Aquatic Dissolved Organic Matter. Environ. Sci. Technol. 37, 18A–26A.

Li, X., Mitch, W.A., 2018. Drinking Water Disinfection Byproducts (DBPs) and Human Health Effects: Multidisciplinary Challenges and Opportunities. Environ. Sci. Technol. 52, 1681–1689.

Lin, Y., Lee, D.-J., 2013. Coagulation of Natural Organic Matters Using Aluminum Tridecamer (Al13) with Counter Ions. J. Water Sustain. 3, 239–249.

Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment : A review. Adv. Colloid Interface Sci. 159, 189–197.

Mergen, M.R.D., 2008. Impact of magnetic resin on DOC removal and downstream water treatment processes. PhD Thesis, Cranfield University.

Mergen, M.R.D., Adams, B.J., Vero, G.M., Price, T.A., Parsons, S.A., Jefferson, B., Jarvis, P., 2009. Characterisation of natural organic matter (NOM) removed by magnetic ion exchange resin (MIEX ® Resin). Water Sci. Technol. Water Supply 9, 199.

Mergen, M.R.D., Jefferson, B., Parsons, S.A., Jarvis, P., 2008. Magnetic ion-exchange resin treatment: Impact of water type and resin use. Water Res. 42, 1977–1988.

Metcalfe, D., Rockey, C., Jefferson, B., Judd, S., Jarvis, P., 2015. Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process. Water Res. 87, 20–28.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., Demarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water : A review and roadmap for research. Mutat. Res. 636, 178–242.

Sharp, E.L., Jarvis, P., Parsons, S.A., Jefferson, B., 2006a. Impact of fractional character on the coagulation of NOM. Colloids Surfaces A Physicochem. Eng. Asp. 286, 104–111.

Sharp, E.L., Parsons, S.A., Jefferson, B., 2006b. Seasonal variations in natural organic matter and its impact on coagulation in water treatment. Sci. Total Environ. 363, 183–194.

Shorney-Darby, H.L., Galjaard, G., Metcalfe, D., Rockey, C., 2014. Ceramic membrane filtration of a surface water treated with ion exchange, in: Proceedings of the American Membrane Technology Association Conference, Las Vegas, NV. pp. 1–10.

UK Statutory Instruments, 2016. The Water Supply (Water Quality) Regulations 614.

USEPA, 1998. National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts. Fed. Regist. 63, 69390–69476.

Violante, A., Violante, P., 1980. Influence of pH, concentration, and chelating power of organic anions on the synthesis of aluminum hydroxides and oxyhydroxides. Clays and Clay Miner. 28, 425–434.

Watson, K., Farré, M.J., Knight, N., 2015. Enhanced coagulation with powdered activated carbon or MIEX secondary treatment: a comparison of disinfection by-product formation and precursor removal. Water Res. 68, 454–66.

Zhang, Y., Zhao, X., Zhang, X., Peng, S., 2015. A review of different drinking water treatments for natural organic matter removal. Water Sci. Technol. Water Supply 15, 442–455.

Zheng, J., Sijm, M., Koremann, E., 2018. Final Report – January 2018, Combined SIX ® , ILCA ® and CeraMac ® Pilot Testing at Invercannie Water Treatment Works, Scottish Water. Andijk.

2.8 Supplementary Information

2.8.1 Pilot plant details

The SIX pilot plant consisted of ion exchange (Unit I) and in-line coagulation with ceramic membrane filtration (Unit II) (Figure S 2.1). For comparison, details of the main treatment works sourcing the same water is shown.

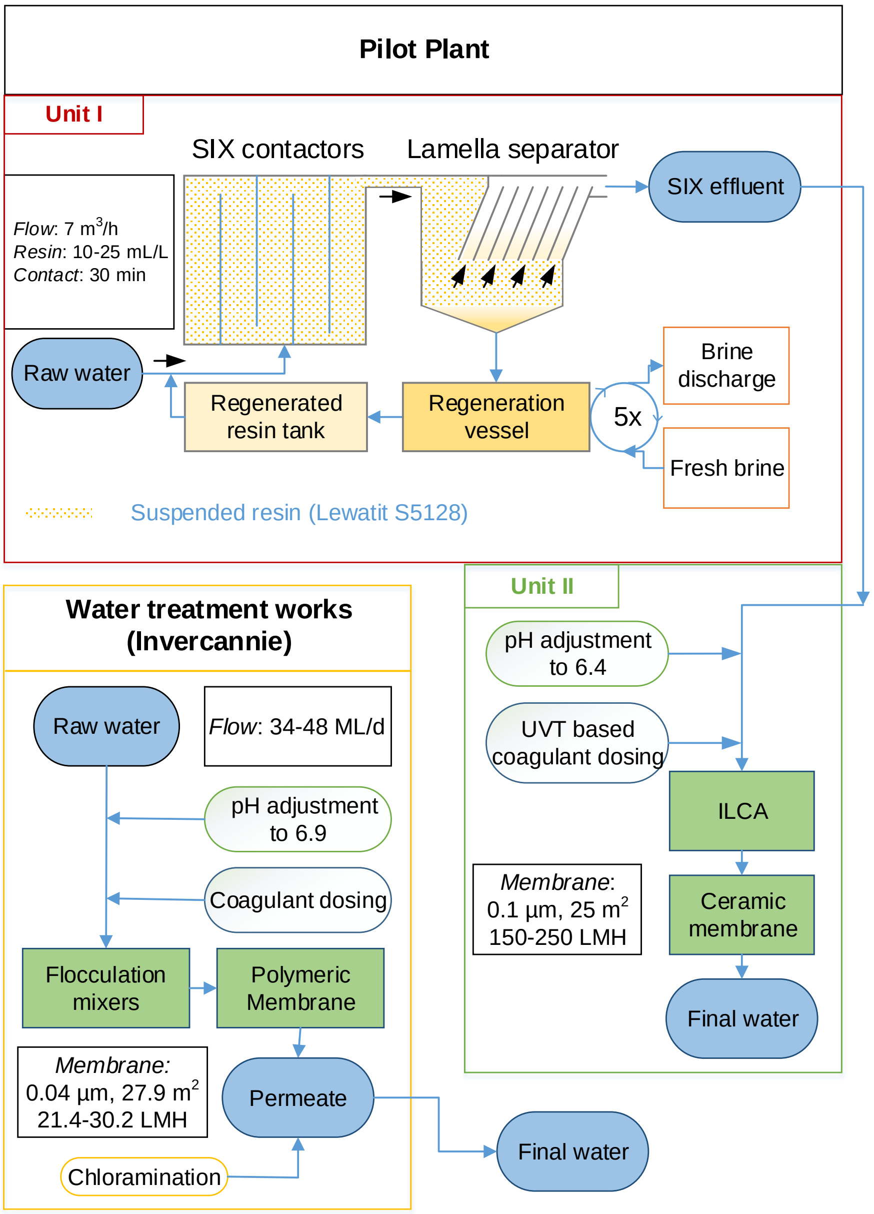


Figure S 2.1: Schematic of pilot plant, red: Unit I, suspended ion exchange, Lewatit S5128 resin; green: Unit II, coagulation (poly aluminium chloride) and membrane; yellow: water treatment works in Invercannie, Scotland, coagulation (poly aluminium chloride) and membrane.

2.8.2 Coagulation control in pilot plant

In Unit 2 of the pilot plant (Figure S 2.1) polyaluminium chloride was added for coagulation based on UVT values of water entering Unit II. UVT measurement were obtained using an online solids-compensated UVT Spectro::lyser (S::CAN, Austria). UVT values are then transferred into coagulant dose using the following equation (S2.1):

$$coagulant\ dose\ (ppm\ Al^{3+}) = S * UVT\ feed\ (\%) - T \qquad \text{(S2.1)}$$

where S and T are variables determined by jar tests. The algorithms used during the pilot trial can be found in Table S 2.1

Unit 2 was operated under varying conditions to determine critical flux and optimise backwash (BW) regimes. The 10 different runs, partially with sub-runs, are listed in Table S 2.1, giving start and end date, flux, coagulation control algorithm and BW settings. Cleaning in place (CIP) was carried out between different runs either by (a) conventional cleaning or (b) with ozone. The CIP procedures for (a) used NaOCl (500-750 mg L^{-1}), recirculating 2-3 h a volume of up to 100 L at 1.5 $m^3\ h^{-1}$ followed by acidic H_2O_2 (100 mg/L, pH 2), recirculating 2-3 h a volume of up to 100 L at 1.5 $m^3\ h^{-1}$ or (b) ozone (5.7, 8.3 mg/L) with a circulation of 2-3 h.

2.8.3 Figures and Tables

Table S 2.1: Operational details of Unit II (CCMF)

Run	Start date*	End date*	Flux L m^{-2} h^{-1}	Coagu-lation control	BW loading L m^{-2}	EBW loading L m^{-2}	EBW regime
1	23/05	03/06	150	A, M1, M2	50	500	4X, 1Z
2	08/06	13/06	175	A, M*	50	500	4X, 1Z
3	15/06	16/06	200	A	50	500	4X, 1Z
3b	20/06	30/06	200	A	50	500	4X, 1Z
4a	04/07	10/07	250	A	50	500	4X, 1Z
4b	10/07	13/07	250	B	50	500	4X, 1Z
4c	13/07	25/07	250	B	100	1000	4X, 1Z
5	26/07	03/08	200	B	100	500	4X, 1Z
6a**	04/08 ***	22/08	200	B	100	500	4X, 1Z
6b**	22/08	29/08	200	C	100	500	4X, 1Z
6c**	29/08	30/08	200	C	100	1000	4X, 1Z
6d**	30/08	04/09	200	B	100	1000	4X, 1Z
7	04/09	11/09	200	B	166.67	1000	4X, 1Z
8	11/09	19/09	200	B	166.67	1500	4X, 1Z
9	19/09	28/09	200	B	166.67	1500	1X, 1Z
10*	29/09	02/10	200	B	166.67	1500	1X, 1Z

*all dates refer to 2017, **run without SIX treatment (CMF), started without CIP (cleaning in place), *** pilot plant off between 04 and 14 August; M1 (Manual control = 0.39 ppm Al^{3+} (23-25 May, 30-31 May and 08 June), M2 (Manual control = 0.19 ppm Al^{3+} (29 May)); Coagulation control based on algorithm in Eq.2 with A (S =-0.1326, T = 13.0003), B (S =-0.0752, T = 7.6324), C (S = -0.0657, T = 9.1588); power cut on 25 September, (S= -0.0602, T= 6.1059); Enhanced Backwash (EBW) regime: X used NaOCl (100 mg/L free Cl_2), Y used H_2O_2 (100 mg/L, pH 2).

Table S 2.2: Raw water physicochemical characteristics

Parameter	Unit	Minimum	Maximum	Average
DOC	(mg L^{-1})	1.5	10.1	4.4
UVA	(m^{-1})	4.7	42	18.1
Turbidity	(NTU)	0.2	1.4	0.6
Conductivity	(µS cm^{-1})	33	74	51
pH	Hydrogen ion	6.8	7.9	7.3
Alkalinity	(mg_{HCO3-} L^{-1})	10	29	20
Chloride	(mg_{Cl-} L^{-1})	4	8	6
Nitrate	(mg_{NO3-} L^{-1})	<0.5	1.28	0.74
Sulphate	(mg_{SO4-} L^{-1})	1.9	4.5	3.1

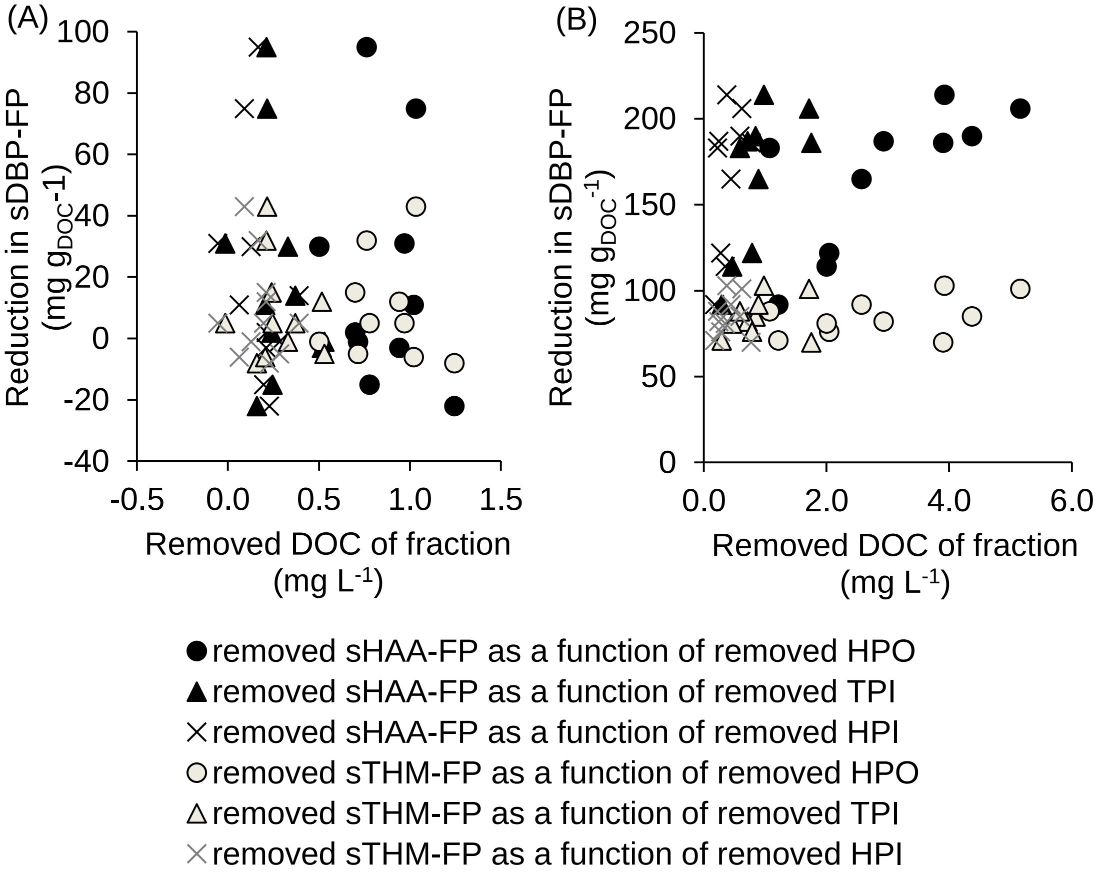


Figure S 2.2: Removal of the specific HAA- and THM-FP as a function of DOC removal of the different fractions for SIX+CCMF treated water.

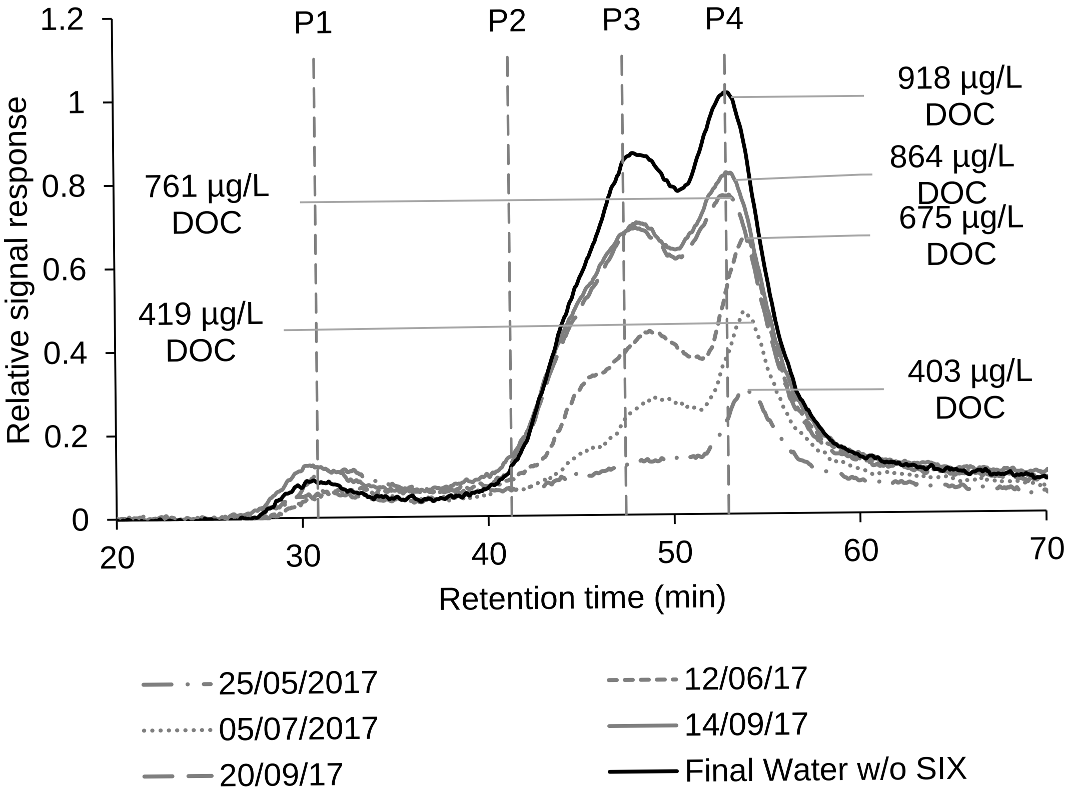


Figure S 2.3: Profile of final water of SIX+CCMF compared to CCMF for different sample dates.

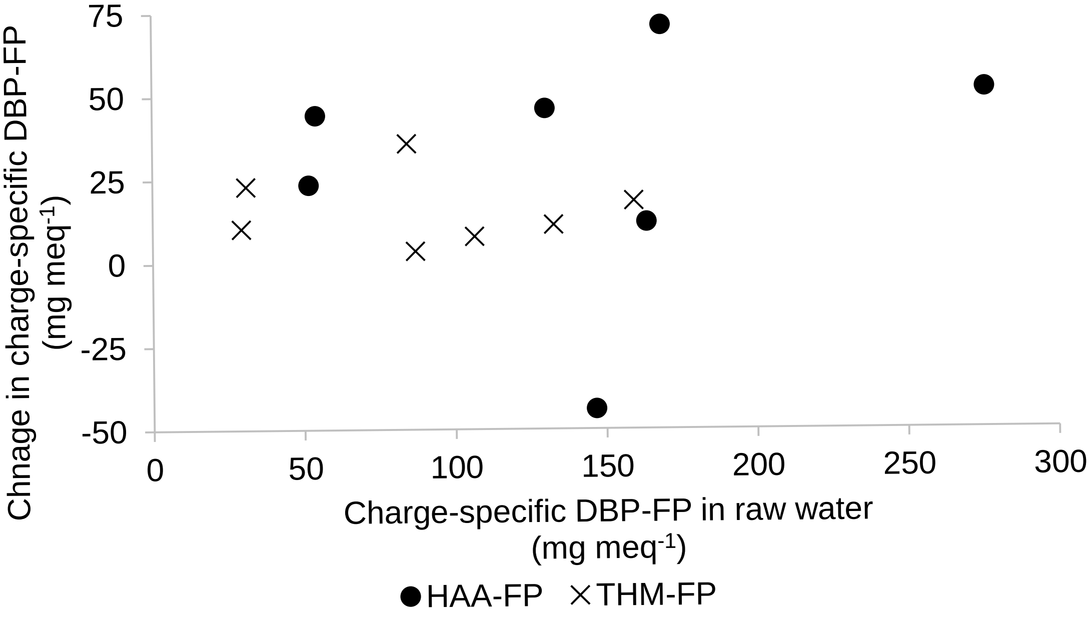


Figure S 2.4: Change in charge specific DBP-FP as a function of the raw water values.

3 THE COMBINED INFLUENCE OF HYDROPHOBICITY, CHARGE AND MOLECULAR WEIGHT ON NATURAL ORGANIC MATTER REMOVAL BY ION EXCHANGE AND COAGULATION

P. Finkbeiner[a], G. Moore[b], R. Pereira[c], B. Jefferson[a], P. Jarvis[a]*

[a]Cranfield University, Cranfield, Bedford, MK43 0AL.

[b]Scottish Water, Castle House, 6 Castle Drive, Dunfermline, KY11 8GG.

[c]The Lyell Centre, Heriot-Watt University, Research Avenue South, Edinburgh, EH14 4AP.

3.1 Abstract

The character of source waters and the state of resin (virgin or regenerated) are important factors influencing the treatability of surface waters for natural organic matter (NOM) removal by ion exchange (IEX). Three different source waters were investigated using virgin and pre-used anion exchange resins, coagulation (Coag.), and ion exchange combined with coagulation (IEX&Coag). In this research hydrophobicity, size distribution and charge were used to evaluate the removal of NOM. Dissolved organic carbon (DOC) removal by pre-used IEX resin was 67-79%. A consistent ratio of different hydrophobicity fractions was found in the removed DOC, while the proportion and quantity of the molecular weight fraction around 1 kDa was important in understanding the treatability of water. High NOM loading was associated with an increased concentration of this size fraction. For pre-used resin, where the number of exchange sites were reduced due to resin deterioration over time, this resulted in a limited removal as the organic compounds were restricted to easily accessible exchange sites. Comparatively, virgin resin achieved higher DOC removals (86-89%) as resin fouling was absent. Higher initial charge density in the water resulted in higher charge load removal. Charge density and the proportion of the hydrophobic fraction were found to be important indicators for the specific disinfection by-

product formation potential (sDBP-FP). The reduction of sDBP-FP depended on the raw water composition and the resin state. Treatment of raw water with pre-used resin decreased the sDBP-FP by between 2-43%, while the use of virgin resin resulted in a reduction of between 31-63%. The highest water quality was achieved when the combination of IEX and coagulation was used, reducing DOC and the sDBP-FP well below that seen for either process alone.

3.2 Introduction

Treatment of surface water to remove natural organic matter (NOM) is important for aesthetic reasons (Brezinski and Gorczyca, 2019), the reduction of both disinfection by-product (DBP) precursors and the associated chlorine demand of the water (Jeong et al., 2015), as well as minimisation of biofilm formation (EPA, 1994). NOM is derived from different sources and is distinguished between that of an allochthonous and autochthonous origin. The latter is produced in the aquatic environment as a result of microbial activity. For example, extracellular and intracellular matter is released from algae and bacteria into water (Pivokonsky et al., 2016). This organic matter is composed of aliphatic biomolecules that are usually of low colour. Allochthonous NOM originates from terrestrial sources and is mainly formed of breakdown products from plants (Sillanpää et al., 2018). The released allochthonous NOM, which is transported to receiving surface waters by percolation through the soil or surface run-off, is a diverse mixture of organic compounds usually high in colour, due to aromatic moieties present in humic substances (Ailkenhead-Peterson et al., 2003; Croué et al., 2000).

NOM removal from surface waters has been successfully demonstrated by ion exchange (IEX), which has proven to be particularly efficient when used in combination with coagulation (Finkbeiner et al., 2018; Jeong et al., 2015; Kitis et al., 2007; Metcalfe et al., 2015). In the IEX process, anionic NOM is adsorbed onto a polymer resin for the exchange of a counter ion.

The charge profile of the organic matter has been shown to be one of the dominant influences on its removal by IEX (Boyer and Singer, 2008a). While IEX can remove organic compounds of all size ranges, a preference towards low molecular weight (LMW) compounds has been seen due to size exclusion of large molecules. However, the highest removal did not correspond with the water sources that contained NOM with the lowest MW profile (Bazri and Mohseni, 2016; Metcalfe et al., 2015). Other researchers have evaluated the influence of aromaticity, found that IEX favoured the removal of UV absorbing compounds (Boyer and Singer, 2005; Grefte et al., 2013; Kitis et al., 2007). Preferential removal of hydrophobic compounds has been linked to physical attraction forces involving hydrophobic and van der Waals interactions between the lipophilic moieties and the resin, and hence an increase in entropy once removed (Rahmani and Mohseni, 2017; Tan and Kilduff, 2007). However, as high charge density resides predominantly in the hydrophobic fraction of the NOM (Sharp et al., 2006b), this charge could have been a more important factor in the removal of NOM than its hydrophobicity. This clearly suggests that investigating one or two of the physicochemical parameters gives only a limited understanding of NOM treatability by IEX. Therefore, it is important to consider hydrophobicity, molecular weight and charge together to understand the removal of NOM and understand in what way source water composition influences how organic compounds access exchange sites on the resin.

Treatability also needs to be linked to the state of the resin. Mergen *et al.* (2008) reported that when using virgin (fresh/unused) resin, higher NOM removal was seen with an increase in the hydrophobicity of the organic matter. Conversely, after resin had been used in multiple cycles, a decrease in water treatability was observed as the hydrophobicity increased. This was explained by blockage of the resin pores by high molecular weight (HMW) organic matter with consecutive use, inferring that the hydrophobic fraction was rich in HMW organics. It has also been reported that in the presence of humic acid a loss of capacity was observed even after the resin had been regenerated, as a result of resin fouling (Gönder et al., 2006). Resin fouling takes place when macromolecular organic compounds are irreversibly bound to the resin due to entrapment as well as hydrophobic and coulombic interactions. In addition, chemical and physical degradation of IEX resin leads to the reduction in the number of functional exchange groups (Harland, 1994; SenGupta, 2017).

To date, there has not been a comprehensive comparison of NOM removal by IEX that takes into account the combined effects of molecular size, the hydrophobicity and charge of organic matter for a range of different source waters, using virgin and pre-used resin. The aim of this work was therefore to determine the additional treatability information that can be obtained when these water characteristics are considered together. Additionally, the role of the resin state on removal of NOM was investigated.

3.3 Materials and Methods

3.3.1 Source water

Three waters were collected from reservoirs fed by different catchment areas in Scotland. Water A was from a catchment composed of a mix of soils with more organic rich soils compared to mineral soils. Additionally, the reservoir that collected water from the catchment has historically experienced algal blooms and hence contained some autochthonous NOM. Water B was from a reservoir fed by a small catchment that contained both mineral and organic rich soils. Water C was from a catchment of organic rich soils, composed equally of moorland and forestry (Zoe Frogbrook, Scottish Water, personal communication, 22/03/2018).

Table 3.1: Water composition and catchment details

Water	Catchment area	DOC (mg L^{-1})	SUVA (L mg^{-1} m^{-1})	pH	NO_3^-	SO_4^{2-}	HCO_3^-
A	Mix of soils (organic > mineral soils)	11.4	5.0	8.0	3.6	<0.2	38.5
B	Mix of soils (organic rich and mineral soils)	7.6	4.3	7.1	1.4	2.5	15.0
C	100% organic rich soils (1:1 moorland: forestry)	8.4	5.6*	6.5	<0.5	3.4	10.0

DOC = dissolved organic carbon, SUVA = specific ultraviolet absorption.

3.3.2 Jar tests – Ion exchange and coagulation

The different raw waters were collected and stored at 4°C (to minimise compositional changes) until jar tests were performed. The water was treated in four different ways, using: i) virgin resin (fresh, unused resin), ii) pre-used resin from a full scale IEX plant that had been used in operation for more than 3 years and had undergone multiple loading and regeneration cycles, iii) coagulation of the ion exchange treated water and iv) coagulation of the raw water.

Ion exchange experiments: For all IEX experiments a strong base anion exchange resin (Lewatit S5128) was used. The resin had a gel-type nature and had an acrylic backbone functionalised with quaternary ammonium groups with a total capacity of 1.25 eq L^{-1} and a bead size ranging between 0.4 and 1.6 mm (for >90 vol%) according to the manufacturers information. This resin has been successfully tested in pilot and full-scale operation (Finkbeiner et al., 2018; Koreman and Galjaard, 2016; Metcalfe et al., 2015). A resin dose of 25 mL with a 30 min contact time was selected as it was representative of the conditions used in the full scale process (Finkbeiner et al., 2018). Jar tests were carried out using both virgin and pre-used IEX resin. Virgin or pre-used resin was rinsed with DI water (10-20x resin volume (RV)) and then stirred in 20 RV of DI water (150 rpm, 10 min). Subsequently the resin was converted fully to the chloride form by stirring (150 rpm, 30 min) in 20 RV sodium chloride solution with a concentration of 40 g L^{-1} as was used in the pilot trials, which is typical to that used in full scale applications of the process (Finkbeiner et al., 2018)). The supernatant was removed and the resin was rinsed with 20 RV DI water and cleaned by a washing step using 20 RV DI water, stirred for 30 min (150 rpm).

The regenerated resin was filled in a measuring cylinder and the volume was adjusted to 50 mL after the resin had settled. The resin was transferred into a beaker and excess water was removed by decanting or using a syringe. A raw water volume of 2 L was added to the resin and the suspension stirred for 30 min (150 rpm). The resin was then settled, and treated water was decanted and collected for subsequent coagulation testing and analysis. This protocol was repeated 14 times to generate a total volume of 28 L of IEX treated water in order to produce sufficient volume for analysis and subsequent experiments (coagulation).

Coagulation experiments: In coagulation jar tests, 1 L of raw or IEX treated water was used. A predetermined volume of acid (HCl, 0.1 N) or base (NaOH 0.1 N) and polyaluminium chloride (1.06 g L^{-1} Al^{3+}) were added during the rapid mixing stage (250 rpm, 60 s). The slow mixing period was 20 min (40 rpm), and flocs were allowed to settle for 30 min.

The optimum coagulant dose and pH (5.8) were determined by ultraviolet absorbance (UVA) and zeta potential measurements after the slow mixing stage. For IEX treated water the same coagulation pH set point was used as for the raw water. The volume of three jar tests were combined for analysis. Experiments were carried out in duplicate.

3.3.3 Analysis

Samples were filtered (0.45 µm) and analysed for dissolved organic carbon (DOC), UVA_{254}, fractionation, molecular weight distribution and DBP formation potential (DBP-FP). Charge measurements were carried out on unfiltered water to ensure that a zeta potential measurement could be made.

A spectrophotometer (DR6000, Hach Lange, Germany) was utilised to measure UVA_{254}. The DOC concentration was determined on TOC analyser using the non-purgable organic carbon method (Shimadzu TOC-L). Tap water spiked with 8 mg L^{-1} potassium hydrogen phthalate and 5 mg L^{-1} calcium carbonate was used as quality control with a precision target of 5%.

To fractionate the DOC, the samples were acidified and passed sequentially through XAD7 and XAD4 resin columns, which retain the hydrophobic (HPO) and transphilic (TPI) fraction, respectively. The effluent from the second column was collected as the hydrophilic (HPI) fraction. Both columns were eluted with a sodium hydroxide solution (0.1 N) and analysed for DOC after acidification.

Charge measurements were carried out in triplicate on a Zetasizer equipped with an autotitrator (Malvern Nano Series, Worcestershire, UK). A sample volume of

15 mL was adjusted to pH 7 and polydiallyldimethylammonium chloride (PDADMAC) (Sigma-Aldrich, Dorset, UK) was added incrementally to obtain concentrations between 0 and 30 mg L^{-1}. The sample was circulated to a connected folded capillary cell in the Zetasizer where zeta potential was measured after each addition and pH was automatically corrected to 7. The required concentration of PDADMAC to reach the point of zero charge was used to calculate the charge load of the sample based on the charge density of 6.2 meq/L for PDADMAC. Charge density of the sample was determined by normalising the charge load by the DOC concentration.

The molecular weight profile of NOM compounds were investigated using the next-generation Model 9 liquid chromatography organic-carbon detection (LC-OCD) system (Huber et al., 2011). Samples were filtered through 0.45 µm polyethersulfone (PES) syringe filters and stored chilled (0-4°C) in pre-combusted glass "TOC" vials until analysis, which occurred within 2 days of sample collection. 1 mL was injected onto a size exclusion column (SEC; 2 mL min^{-1}; HW50S, Tosoh, Japan) with a phosphate buffer (potassium dihydrogen phosphate 1.2 g L^{-1} and 2 g L^{-1} di-sodium hydrogen phosphate x 2 H_2O, pH 6.58) and separated into five NOM fractions: P1-P5. All peaks were identified and quantified with bespoke software (Labview, 2013) normalized to International Humic Substances Society humic and fulvic acid standards. The samples were analysed in duplicate. The reported peak area for each fraction and the LC-OCD profiles were obtained from average values of duplicates and replicates.

For determination of the formation potential of haloacetic acids (HAA) and trihalomethanes (THM), samples were diluted to 1 mg L^{-1} DOC and chlorinated with NaOCl to result in approximately 5 mg L^{-1} of free chlorine. The samples were incubated for 7 days at 25°C, before they were quenched with thiosulfate. HAAs were extracted with MTBE and methylated at 50°C with acidic methanol. The neutralised MTBE extract was reduced to 0.5 mL and the concentration of monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) were determined with gas chromatography mass spectrometry (GC-MS). A headspace method was used to quantify the four THMs (chloroform, bromoform, bromodichloromethane and dibromochoromethane) on a GC-MS.

The total resin capacity was measured according to a modified procedure described by Harland (1994). Resin was converted to the chloride form using NaCl (100 g L^{-1}), following the regeneration steps for resin preparation. A volume of 10 mL resin was stirred in 500 mL of a sodium nitrate solution (1%) for 15 min (150 rpm). The displaced chloride was determined using argentometric titration with potassium chromate indicator to provide the total capacity of the resin.

3.4 Results and discussion

The average DOC concentration of water A, B and C were 11.4, 7.6 mg L^{-1} and 8.4 mg L^{-1} (Table 3.2). This range was relatively high compared to the average concentration of 6.6 mg L^{-1} reported for raw waters across Scotland (Valdivia-Garcia et al., 2016). The high specific UVA (SUVA) values (4.3 - 5.6 L mg^{-1} m^{-1}) for all waters was indicative of the presence of aromatic compounds derived from humic substances of allochthonous origin, which was a reflection of the high proportion of organic rich soils present in the catchments (Fabris et al., 2008).

DOC concentrations in the investigated waters were reduced by between 67 and 79%, equating to absolute removal ranging from 5.9 to 7.7 mg L^{-1}, using pre-used resin at a concentration of 25 mL L^{-1} (Table 3.2). This was higher than the removal seen for other waters treated by the same IEX resin at comparable initial DOC concentrations. For example, from a low land river source 8 to 32% (up to 2.3 mg L^{-1}) was removed for raw water DOC concentrations of between 7 and 10 mg L^{-1} using 25 mL L^{-1} resin (Chapter 2). Metcalfe *et al.* (2015) observed a DOC reduction of 38 and 65% (2.3 and 2.6 mg L^{-1}) from an upland and lowland river with initial DOC concentrations of 6 and 4 mg L^{-1}, respectively, at a resin concentration of 18 mL L^{-1}. Overall, this indicates that the waters selected for this study were particularly amenable to IEX pre-treatment.

Table 3.2: Concentrations of DOC after different treatment and SUVA values for raw water for the three water sources.

	Treatment	Water A	Water B	Water C
DOC ($mg\ L^{-1}$)	Raw	11.4	7.6	8.4
	IEX	3.7	1.7	1.8
	IEX (virgin)	1.3	1.1	1.2
	Coag	1.5	1.8	2.3
	IEX+Coag	0.6	0.7	0.7
SUVA ($L\ mg^{-1}\ m^{-1}$)	Raw	5.0	4.3	5.6

The use of virgin resin increased the DOC removal to between 86 and 89%. For water A, B and C the removed DOC was 2.4, 0.6 and 0.6 mg L^{-1} higher than for the pre-used IEX. This showed a difference in deterioration of the resin that was dependent on the water source.

The water matrix can have an effect on IEX treatment, such as complexation of organic carboxylate groups by divalent cations and competition between inorganic anions for exchange sites (Li and Elimelech, 2004; Tan and Kilduff, 2007). However, the nitrate and sulphate concentrations were low (Table 3.1) and the charge capacity required for the exchange of these anions similar between the waters; 58-74 µeq/L. Hence, it is not expected that these anions are of importance when explaining the findings. The alkalinity of the waters were considered low (Spellman, 2010) and a competition between bicarbonate and organic molecules for exchange sites has previously been described as negligible (Boyer and Singer, 2008a). Therefore, the difference in alkalinity between the waters was also seen as unimportant for the interpretation of the results.

Coagulation removed less DOC than IEX treatment with pre-used or virgin media for water B and C. For example, the residual DOC after treatment using pre-used resin, virgin resin and coagulation was 1.8, 1.2 and 2.3 mg L^{-1} in water C. Water A, however had a residual of 3.7 and 1.5 mg L^{-1} for IEX and coagulation treatment, respectively, whereas virgin resin achieved a higher removal resulting in a DOC concentration of 1.3 mg L^{-1}. IEX combined with coagulation delivered the lowest DOC concentration for all waters with values between 0.6 and 0.7 mg L^{-1} equating to a total DOC removal of 91 to 94%. This was in agreement with previous studies in which the synergistic effect of the combination of the two treatments was demonstrated (Drikas et al., 2011; Humbert et al., 2007; Metcalfe et al., 2015). Additionally, IEX pre-treated water required a lower coagulant dose, with a reduction of 39, 42 and 24% Al^{3+} mg_{DOC}^{-1} for water A, B and C, respectively, consistent with other research (Grefte et al., 2013; Kitis et al., 2007).

3.4.1 The removal of fractions of differing hydrophobicity

Resin fractionation was used to distinguish hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) character of the organic compounds. In the raw water, the proportion of the HPO, TPI and HPI fraction were 62, 25 and 13% in water A, respectively (Figure 3.1). Although the HPO was the dominant fraction, water B and C contained proportionally more transphilic and hydrophilic NOM, with 51, 28, 21% and 52, 30, 18% for HPO, TPI and HPI respectively. The prevalence of the HPO fraction can be expected for waters from these catchment areas, which all contain a degree of organic rich soil (Sharp et al., 2006b).

In each water, the concentration of all fractions were reduced following treatment by pre-used IEX. The proportions of the fractions after IEX in water A did not change substantially in comparison to the raw water, with values of 64, 20 and 16% for the HPO, TPI and HPI, respectively. This was in accordance with observations seen in previous research (Chapter 2). However, for water B and C, IEX treatment changed the ratio considerably, with a shift towards more hydrophilic NOM; the proportion of the HPI fraction was 50 and 45% in treated water B and C, respectively. To explain this behaviour, the proportion of each fraction in the removed NOM was evaluated (Supplementary Information, Figure S 3.1). This showed that the fractions of the DOC removed by IEX were similar for all of the waters, regardless of the initial water composition: ranging from 57-61% for HPO; 27-31% for TPI; and 12-14% for HPI. The consistently high proportion of the HPO fraction in the removed DOC suggests that the resin had a higher ratio of exchange sites that allowed hydrophobic interactions and therefore showed a selectivity towards compounds from the HPO fraction.

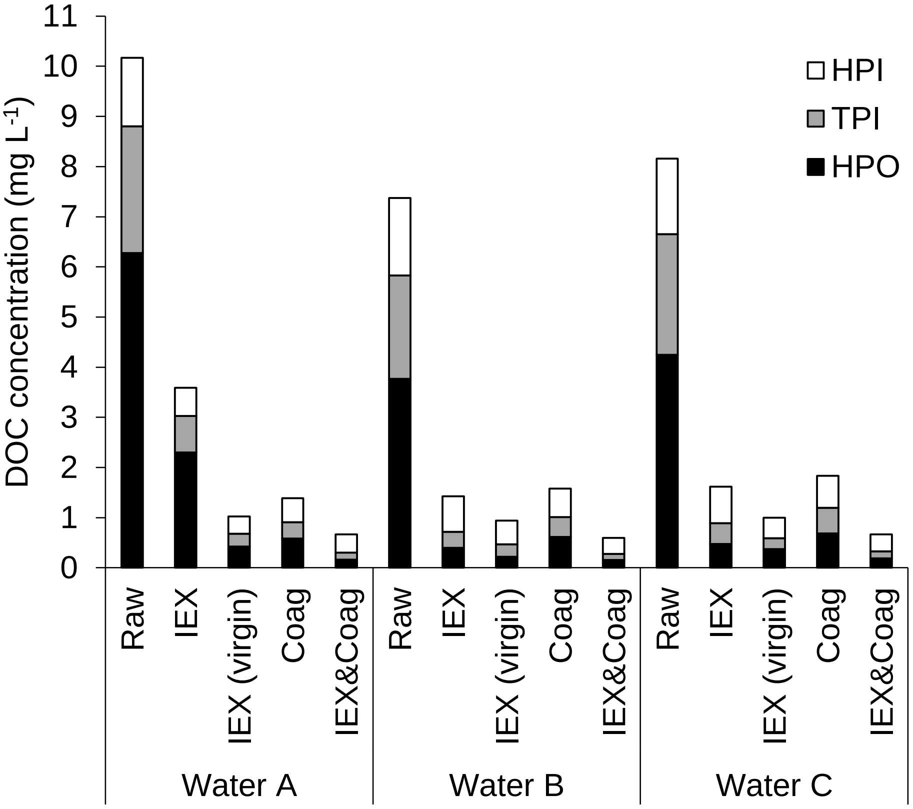


Figure 3.1: Proportions of the different hydrophobicity fractions of the DOC following the different treatment steps (Raw = raw water; IEX = after ion exchange treatment (pre-used resin); IEX (virgin) = after ion exchange treatment (virgin resin); Coag = after coagulation; IEX&Coag = after IEX (pre-used resin) and subsequent coagulation.

When virgin resin was used, higher overall removal was observed for each fraction in the three test waters. The HPO, TPI and HPI fraction of water A were reduced by 93, 90 and 75% (Figure 3.1), compared to 63, 71 and 59% for the pre-used resin. Similar trends were seen for water B and C, although the differences between virgin and pre-used resin were not as prominent as seen for the more hydrophobic NOM present in water A. This suggests that the lower relative removal of the DOC in water A was caused by the high HPO fraction (6.28 mg L^{-1}), which was 1.5-1.7 times as high as in the other waters.

After coagulation the proportion of fractions in the waters were 38-41% HPO, 24-28% TPI and 34-36% HPI, indicating a preferential removal of the HPO fraction. However, when IEX treated water underwent coagulation, a further reduction of the DOC in the HPO, TPI and HPI fraction compared to the individual stages was detected, resulting in residual values of 0.2, 0.1 and 0.3-0.4 mg L^{-1}, respectively, in all treated waters. Evaluation of the removed DOC by coagulation of IEX pre-treated water A, showed favourable removal of the HPO fraction, while the HPI fraction was removed by only 35%. On the other hand, the relative reduction of the DOC in water B and C, was similar for all three fractions (HPO 60-61%; TPI 63-66%; HPI 53-55%). In these cases, the HPI represented the highest proportion of the DOC in the removed organic matter. This contradicts previous research which shows that the HPO fraction is usually preferentially removed by coagulation for most types of water (Matilainen et al., 2010; Wang et al., 2013). The high ratio of the HPI in the removed DOC was explained by the low concentration of the HPO fraction after IEX treatment; 0.4 to 0.5 mg L^{-1} in water B and C, respectively. This enabled the coagulant to target other organic compounds that would normally be less well removed, a phenomena seen before in IEX treated water prior to coagulation (Metcalfe et al., 2015).

3.4.2 Influence of the size of organic compounds on their removal

In the LC-OCD analysis, the proportion of chromatographed DOC (CDOC) vs total sample DOC is quantified via a column bypass. Organic compounds were primarily separated by their molecular size, with large molecules eluting first. The traces of all three raw waters (Figure 3.2) follow the same pattern with a dominant second peak (P2) at a retention time of 19 min, which has been described to contain aromatic compounds in the region of 1 kDa (Huber et al., 2011). The proportion of CDOC in this peak increased with higher DOC values. For example, the peak was 77% of the CDOC for water A (total DOC = 11.4 mg L^{-1}), while for water B and C which had DOC concentrations of 7.6 and 8.4 mg L^{-1}, this peak was 68 and 69% of the CDOC.

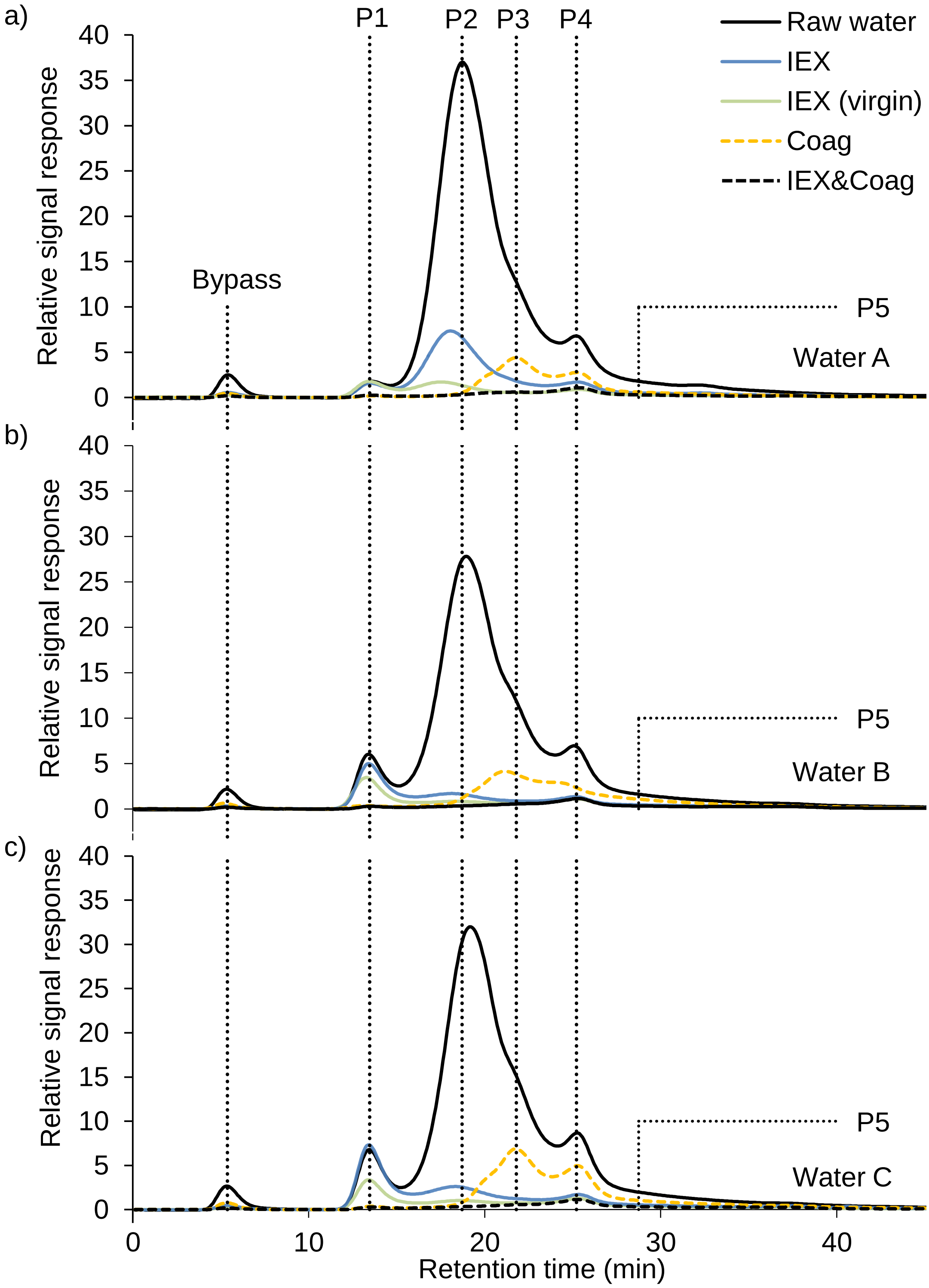


Figure 3.2: LC-OCD traces for different waters and treatment stages; retention time of peak 1 (P1): 13 min, peak 2 (P2): 19 min, peak 3 (P3): 22 min, peak 4 (P4): 25 min, final fraction (P5): from 29 min; by-pass: detection of DOC from restricted flow that bypassed the column.

The first peak (P1) at 13 min, containing the largest MW compounds, had a low CDOC proportion (3.4%) for water A compared to proportions of 9.5% for water B and 8.6% for water C, with measured CDOC values of 0.29, 0.74 and 0.78 mg L^{-1}, respectively. The traces of the UV detector (254 nm) showed a strong signal in P1 for water C with a SUVA of 13.6 L mg^{-1} m^{-1} compared to the other waters with values of 5.6 to 6.4 L mg^{-1} m^{-1} (Supplementary Information, Figure S 3.2). These values reflect the high aromatic content associated with the allochthonous origins of the organic matter in these waters, which is in contrast to the very low UV signal for P1 reported by Huber at al. (2011) who assigned this peak to biomolecules such as polysaccharides.

For the three waters, the third (P3) peak eluting at 22 min had similar CDOC ranging from 0.83 to 0.94 mg L^{-1} equating to 9.7 to 10.9% of the CDOC. The fourth peak (P4) at 25 min represented the smallest fraction, and was 1.9 to 3.2% of the CDOC. Compounds eluting after 29 min constituted the final fraction (P5), for which the proportions were between 8.2 and 8.9%. The differences of the NOM in terms of the molecular sizes between the waters was therefore predominantly due to the change in P1 and P2.

The lowest reduction by IEX was found for P1 due to size exclusion of the high MW compounds in this fraction. The removal for water A, B and C was 39, 34 and 9%, respectively. This fraction made up the majority of the residual CDOC in water B and C after IEX, which was 0.49 and 0.71 mg L^{-1} (equating to 36 and 38% of the CDOC). On the other hand, the highest reduction of all size fractions by IEX was seen for P2. For example, in water B, the CDOC of this fraction was reduced by 4.9 mg L^{-1} to a residual of 0.37 mg L^{-1}. The removal was dependent on the initial concentration of this peak and was greater for water B (93%) and C (91%), while in water A the reduction was 82%. However, when using virgin resin removal of P2 increased to 94-96% for all waters. These observations indicated that there was a limitation in the treatability of this size fraction. This can be linked to the type of organics found in this peak and how they occupy IEX exchange sites. P2 contains substances such as humic (HA) and fulvic acids (FA) (Huber et al., 2011). While such compounds are attracted to the exchange sites of the resin, the size of these molecules can be limiting. The hydrodynamic radii of these molecules have been determined to be >1.1 nm, with aggregated molecules having diameters in the micro meter range (Kawahigashi et al., 2011; Klučáková, 2018). Size exclusion phenomena can therefore occur as the microporous gel-type resins, with pore sizes typically < 2-4 nm (Bhandari et al., 2016; Harland, 1994), can restrict compounds such as HA and FA to the exterior regions of the resin. Therefore, in the case of pre-used resin, where a degree of fouling has occurred, the more limited available exchange sites on the surface of the resin cannot satisfy the removal of these compounds, particularly for water sources that contain high loadings of NOM, such as in water A. Support for this hypothesis comes from the results observed for the virgin resin, where much higher removal was seen due to the absence of irreversibly bound NOM on easy to access exchange sites.

Within the polydisperse P2 fraction, generally a preference towards removal of smaller molecules was seen for IEX. This was demonstrated by an increase in the number-average molecular weight (M_n) of the P2 peak by up to 67% (Supplementary Information, Table S 3.1). For example, water A showed a M_n of 630 g mol^{-1} for raw water which increased to 903 and 837 g mol^{-1} for treated water by pre-used and virgin resin, respectively. This indicated a shift in the composition of P2 towards molecules of higher MW remaining in the water for treatment following IEX. This was consistent with previous reports showing greater removal of lower MW organics, due to increased diffusion (Bazri and Mohseni, 2016; Cornelissen et al., 2008).

The lower MW compounds (P3-P5) were well removed by IEX (59-73%), however, to a lesser extent than P2. Water A showed the lowest removal between the waters for P3 and P4 explained by the greater concentration of high MW organics in the P2 size fraction. Gönder *et al.* (2006) showed that HA reduced resin capacity by pore blocking, which in turn hinders diffusion of LMW compounds into the pores. Removal of P5 was similar for all waters with a reduction around 66%.

Coagulation proved to be efficient in removing size fraction P1 (83-88%) and P2 (86-94%) for all three waters. The lower MW fractions, P3 and P4, had a lower removal, especially for water C (Figure 3.2c). These results were consistent with results showing the amenability of higher MW fractions and limitations in the removal of LMW compounds by coagulation widely reported in the literature (Boyer and Singer, 2005; Drikas et al., 2003; Humbert et al., 2007).

As previously seen, IEX combined with coagulation was efficient in reducing DOC (Metcalfe et al., 2015). For example, the removal of P1 and P2 in water B was 94 and 98%, respectively, representing a slight improvement by IEX&Coag compared to coagulation alone. For the LMW fractions P3-P5, there was a generally higher increase in the removal than for P1 and P2 when the combined treatment was used. The P3 size fraction, for example, was reduced by 42, 62 and 15% by coagulation and 88, 88 and 72% by IEX&Coag for water A, B and C, respectively. After the combined treatment the residual CDOC in P3 was between 0.10 and 0.26 mg L^{-1}. The traces for the combined treatment of IEX and coagulation followed the same pattern for all of the investigated waters and the residual DOC concentration was around 0.6 mg L^{-1} (Supplementary Information, Figure S 3.3). The molecular weight distribution of the organic matter in the treated water was not correlated to that seen in the raw water when the treatment combination was used, showing the synergistic effect achieved by the dual process.

3.4.3 The importance of charge load and density

In the IEX process, the charge of the organic compounds is important, as the exchange of anions has been seen to be enhanced for molecules with a higher charge density (Bazri and Mohseni, 2016; Boyer and Singer, 2008a). The raw waters exhibited charge loads (CL) ranging from 53 µeq L^{-1} for water C, 73 µeq L^{-1} for water B, to 120 µeq L^{-1} for water A (Figure 3.3). Normalising these values with the DOC concentrations provides the charge density (CD) of the NOM in the water. Water A and B had a high CD of 10.5 and 9.7 meq g_{DOC}^{-1}, respectively. For these high CD waters, elevated absolute CL removal by IEX of 93 and 70 µeq L^{-1} was observed. However, the residual CL was quite different in water A (26 µeq L^{-1}) compared to water B (3 µeq L^{-1}), equating to a CD of 7.1 and 1.9 meq g_{DOC}^{-1}, respectively. The high residual CD in water A indicates a limitation in the treatability of this water. Looking at the CD of the removed fraction for water A and B, values of 12.1 and 11.9 meq g_{DOC}^{-1} were observed, respectively, suggesting a similar amenability of charged compounds and supports the view of a limitation of exchange sites on the resin when treating this water type.

The lowest CD was seen for the NOM in raw water C at 6.2 meq g_{DOC}^{-1}, which reduced to a CD of 3.3 meq g_{DOC}^{-1} after IEX treatment. This indicates either the presence of organics of overall lower valency or a higher proportion of un- or low charged molecules in water C. For this water the CL removal was 47 µeq L^{-1} with a residual of 6 µeq L^{-1}. It is important to note that the removal of charge was not consistent with the relative DOC removal from the water, which was lowest for water A and similar for water B and C (Table 3.2).

When virgin resin was applied, only small or negligible increases in CL removal was observed for water B and C, for which CL was reduced by 71 and 49 µeq L^{-1}, resulting in CD of 2.1 and 2.9 meq g_{DOC}^{-1}, respectively. The CL in water B was very well removed by IEX. Both pre-used and virgin IEX reduced the CL by 96 and 97%, respectively. Water C, which had the lowest CD before treatment, experienced a CL removal of 94% by virgin resin compared to 89% by pre-used resin. A much larger difference, however, was observed for water A. The CL of this water was lowered by 117 µeq L^{-1} or 98%, giving a CD of 1.9 meq g_{DOC}^{-1} by the virgin resin, compared to a reduction of 93 µeq L^{-1} or 78% by pre-used IEX. The relative removal of CD and CL followed the order of A>B>C while the relative DOC removal for virgin resin was A>B≈C.

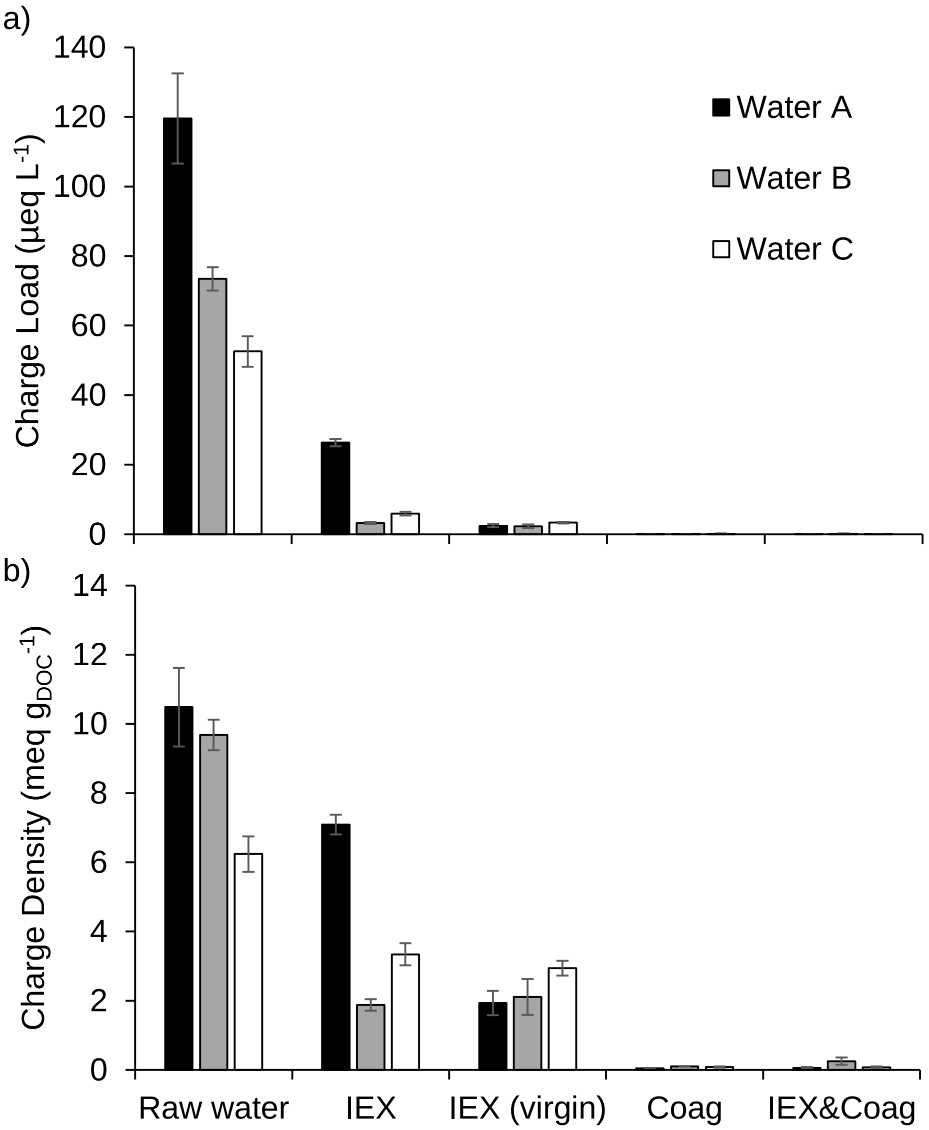


Figure 3.3: Charge load (a) and density (b) of raw water and after the different treatment stages.

The ratio of the removed CL for pre-used and virgin resin was 0.80 in water A, compared to water B and C that had charge removal ratios close to unity (0.99 and 0.95, respectively). This implies some limitations in the removal of organic compounds from water A. However, in all cases the exchange capacity of the resin was not reached in the treated waters. Even in the case of the highest overall removal of charge for water A, only a small proportion of the exchange capacity of the resin was utilised. The total capacity of the resin, estimated by titration of the resin against silver nitrate, was 0.76 meq mL^{-1} for regenerated resin, 0.27 meq mL^{-1} for unregenerated resin and 1.15 meq mL^{-1} for virgin resin, equating to 6.25 to 28.75 meq at the resin concentration of 25 mL L^{-1}. These results were consistent with the view that much of the removal of organic matter was limited to the surface (or near to) of the resin, on easily accessible exchange sites. For water with lower NOM loads (such as water B and C), this was less important as the near-surface exchange sites could meet the demand of the water (hence the small or little differences in the removal between virgin and pre-used resin). As a result, resin fouling or degradation did not significantly impact on the removal of charge. For waters with high loads of charged NOM, reduction in removal was likely to occur as a result of reduction in available exchange sites near the resin surface.

The CL and CD were near zero when coagulation was applied to water with and without IEX treatment. This was expected as the coagulant dose was adjusted to get close to charge neutralisation.

3.4.4 Treatability evaluation of the different waters by IEX

Considering individual NOM properties provided only a partial answer to fully understand organic matter removal by IEX, as interactions with the resin was influenced by all parameters. Hence evaluating the water treatability based on one of the characteristics can be misleading, illustrated by a comparison to interpretations at the availability of results from each analysis (Table 3.3).

The HPO was the fraction that was best removed, although the ratio of the fractions removed was equal for the different waters (Chapter 3.4.1). While this was thought to be a result of selectivity that favoured exchange of HPO over HPI compounds, consideration of the charge provides more complete understanding. A similar distribution of charge across the fractions between the waters was thought to explain the results. This was supported by the previously reported high CD in the HPO fraction, whereas the HPI fraction was of a low CD in different waters (Sharp et al., 2006b). A positive correlation between CD and the proportion of the HPO fraction for raw and treated water (Supplementary Information, Table S 3.2, r = 0.39), supported the view that a high proportion of charged compounds reside in this fraction.

Table 3.3: Summary of results for the individually considered parameters and their combination

	Individual results		Combined results	
	IEX	Controlling factors	IEX	Controlling factors
Hydro-phobicity	Higher proportion of selective sites for hydrophobic compounds	Limitation due to HPO fraction	Distribution of charge different hydrophobicity fractions	Limitation due to high concentration of compounds around 1 kDa
Size	Lower removal of high MW compounds due to size exclusion	Limitation due to P2	Lower removal of P3 to P5 due to lower CD	Limitation of size linked to limited reduction of CD and HPO fraction
Charge	Higher CL removal at higher CD Virgin: Larger CD reduction for higher initial CD	Limitation at high CL	Removal of low/un-charged compounds reflected in LC-OCD measurement	Limitation due to surface blockage

Without the knowledge of the charge composition of the water, the large difference between the virgin and pre-used resin for the removal of the HPO fraction in water A could be interpreted as an oversaturation by hydrophobic compounds or insufficient resin capacity. However, as the measurements of the total capacity and the charge load of the water showed, this was not the case. The results of the LC-OCD measurements provided further information, suggesting that the high concentration of P2 led to a limitation of the exchange sites through blocking of pores and blinding of surface sites by large molecules (Chapter 3.4.2). This was thought to limit the removal ability of the resin for high DOC waters, which in turn had a lower treatability. This was consistent with research that reported a decline in removal efficiency when resins are used in multiple cycles and has been attributed to surface blocking by aromatic high molecular weight (HMW) compounds (Bazri and Mohseni, 2016; Kitis et al., 2007;

Mergen et al., 2008). Furthermore, irreversible resin blinding through entrapment of large aromatic organic compounds, such as humic acid, has been reported to cause removal deterioration (Gönder et al., 2006; Harland, 1994). The high SUVA and high proportion of the HPO fraction in the investigated waters, particularly water source A, indicates that the presence of this type of compounds can lead to loss of capacity and removal efficiency.

If removal was explained solely by size exclusion of HMW compounds, a higher removal for molecules of decreasing MW would be expected. However, the results showed that P3 to P5 were removed to a lesser extent than P2 even though these had a lower MW and should be less affected by size exclusion. A higher CD of the organic compounds in the P2 size fraction was thought to explain the results and was supported by a positive correlation between CD and the proportion of P2 (Supplementary Information, Table S 3.2, r = 0.43). Furthermore, the lowest relative removal and the highest residual in this size fraction (water A) coincided with the highest residual CD (water A).

Charge measurements considered in isolation, showed a higher CL removal when the CD was higher and a higher CD reduction when virgin resin was used (Chapter 3.4.3). However, the limited removal observed for a high CD water could not be explained. To understand the controlling factors, the knowledge of the high concentration of the P2 size fraction was required. All individual analyses showed that there was a limitation in the treatability of water A by IEX. However, the explanation differs for each characterisation method. When considering all three parameters the results suggest that the removal was limited due to surface blockage by a fraction of hydrophobic and molecular weight compounds around 1 kDa (P2) of high charge.

These results show that it is paramount to characterise the charge, hydrophobicity and molecular weight distribution of NOM simultaneously. Furthermore, charge measurements of the hydrophobicity and size fractions will provide further insight into the removal mechanism, as well as analysis of the MW distribution of the hydrophobicity fractions.

3.4.5 Disinfection by-product formation potential (DBP-FP)

The specific DBP formation potential (sDBP-FP) was measured to evaluate the impact of IEX on precursor removal. For water A, which had a particularly high sHAA-FP, no selective precursor removal by IEX was observed with sHAA-FP of 230 and 221 mg g_{DOC}^{-1} for untreated and treated water, respectively (Figure 3.4). Similar figures for the sTHM-FP were 139 mg g_{DOC}^{-1}, both before and after treatment. However, for water B and C, a reduction of 46 and 49 mg g_{DOC}^{-1} was seen for sTHM-FP for raw water values of 103 and 124 mg g_{DOC}^{-1}, respectively. A decrease in sHAA-FP by IEX was only seen in water B, where a reduction of 54 mg g_{DOC}^{-1} was observed. These results were consistent with the literature, where some water sources have shown a decrease in DBP-FP by IEX, while others have seen no change (Drikas et al., 2003; Finkbeiner et al., 2018; Metcalfe et al., 2015). This reflects the inherent complexity and differences observed between water sources. Aligned with the greater selectivity towards aromatic compounds, the use of virgin resin resulted in lower sDBP-FP, compared to pre-used IEX. Coagulation reduced the sHAA- and sTHM-FP to values ranging from 63 to 75 mg g_{DOC}^{-1} and 76 to 80 mg g_{DOC}^{-1}, respectively, equating to a reduction in reactivity of between 48 and 67% in respect of sHAA-FP and 22 and 45% for sTHM-FP. Treatment with IEX&Coag resulted in the largest reduction of sDBP-FP attributed to the removal of charged, LMW compounds by IEX and hence improved precursor removal by subsequent coagulation (Chapter 2). Water A, B and C had sHAA-FP of 44, 34 and 30 mg g_{DOC}^{-1} equating to a reduction between 75 and 81%, while the sTHM-FP was 52, 52 and 46 mg g_{DOC}^{-1} corresponding to a reduction of 49 to 63% after the combined treatment.

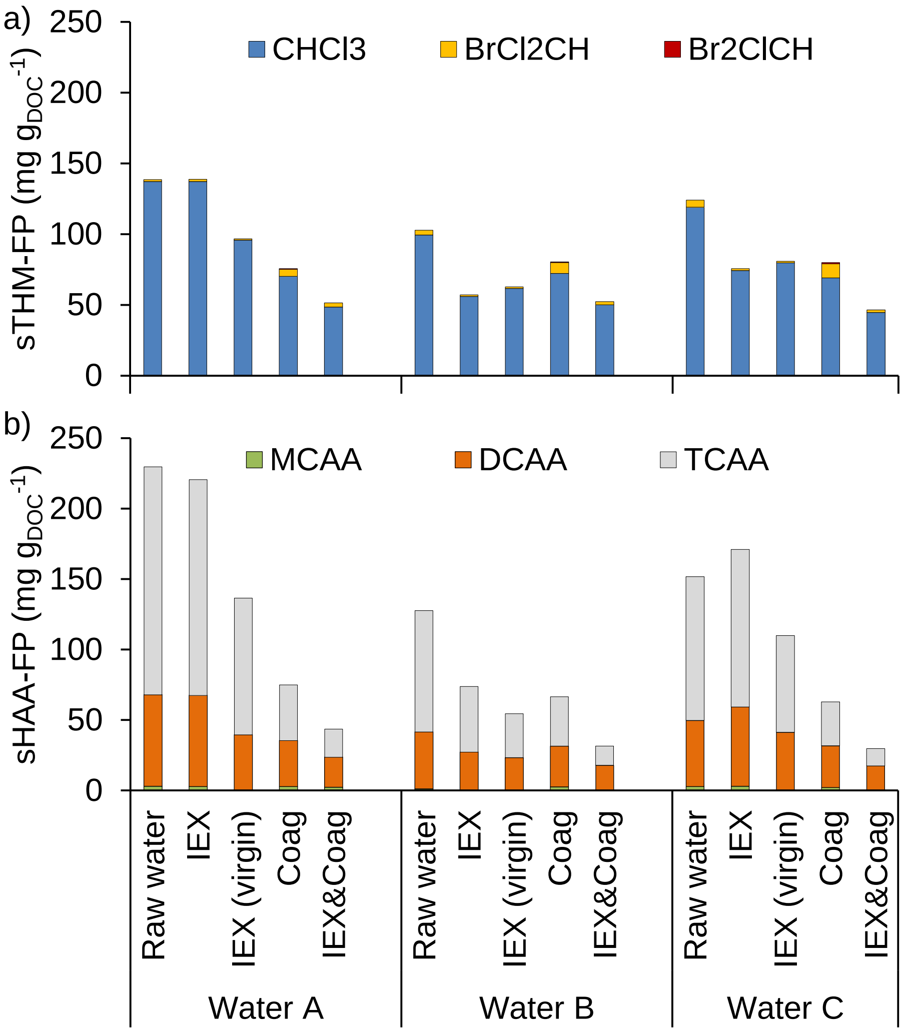


Figure 3.4: Specific THM-FP (a) and sHAA-FP (b) for raw waters and treatment methods of different source waters.

Generally, IEX decreased the brominated sDBP-FP, associated with the removal of bromide by IEX (Boyer and Singer, 2005). For example, in water C a reduction from 5.1 mg g_{DOC}^{-1} to 1.4 and 1.2 mg g_{DOC}^{-1} by pre-used and virgin was observed. Treatment of the three waters by coagulation, which had little impact on the bromide concentration, resulted in a 2-4 times increase of the brominated sDBP-FP compared to raw water. The increased bromide to DOC ratio after the treatment, led to a shift towards the formation of brominated DBP (Boyer and Singer, 2005). Water treated by IEX&Coag had a higher brominated sDBP-FP than IEX alone: for water A, B and C, the brominated sDBP-FP after the combined treatment was 3.0, 2.3 and 1.8 mg g_{DOC}^{-1}, respectively. This was also explained by the increased bromide to DOC ratio after coagulation, however this was to a lesser extent than in coagulated water due to the bromide removed by the IEX component. The formation of brominated DBPs is important as they are regarded to be of higher toxicity than their chlorinated counterparts (Richardson et al., 2007). However, the values reported here are only indicative as they were obtained from formation potential test, which are conducted with an excess of chlorine, disfavouring the incorporation of bromine into the structure and hence underestimate brominated DBPs (Bond et al., 2012).

The sDBP-FP is related to the molecular structure of organic compounds, but readily measurable physicochemical properties can be used to correlate with the formation potential when comparing similar source waters (Golea et al., 2017). In order to understand the relationship between the water quality, IEX treatment and DBPs of the investigated waters, the CD, P2 and HPO fraction of the different treatment steps were plotted against the sum of sTHM- and sHAA-FP (Figure 3.5). These have been shown to represent approximately 50% of the total organic halide concentration in chlorinated water and upto 80% of the species that can be measured (Boyer and Singer, 2005; Losty et al., 2018). The HPO fraction in water correlated positively with the sDBP-FP in a linear manner when values of all waters and treatment stages were considered ($r^2 = 0.78$, Figure 3.5a). Water A showed the largest reduction of the HPO fraction from 62 to 25% and for the sDBP-FP from 368 to 64 mg g_{DOC}^{-1} in raw water and after IEX&Coag treatment, respectively.

It is interesting to note, that the data points where coagulation was involved (δ and ε) were clustered together. After the treatment by coagulation alone the HPO fraction was between 37 and 40% with corresponding sDBP-FPs ranging from 143 to 151 mg g_{DOC}^{-1}. In contrast, when water was treated by IEX using pre-used or virgin resin (β and γ) a larger variation was seen. For example, a HPO fraction of 28 and 30% for IEX treated water resulted in sDBP-FPs of 131 and 247 meq g_{DOC}^{-1}, in water B and C, respectively. This implies that the molecules that were removed by IEX vary in terms of reactivity with chlorine for each water, while for treatment involving coagulation precursor removal was more consistent.

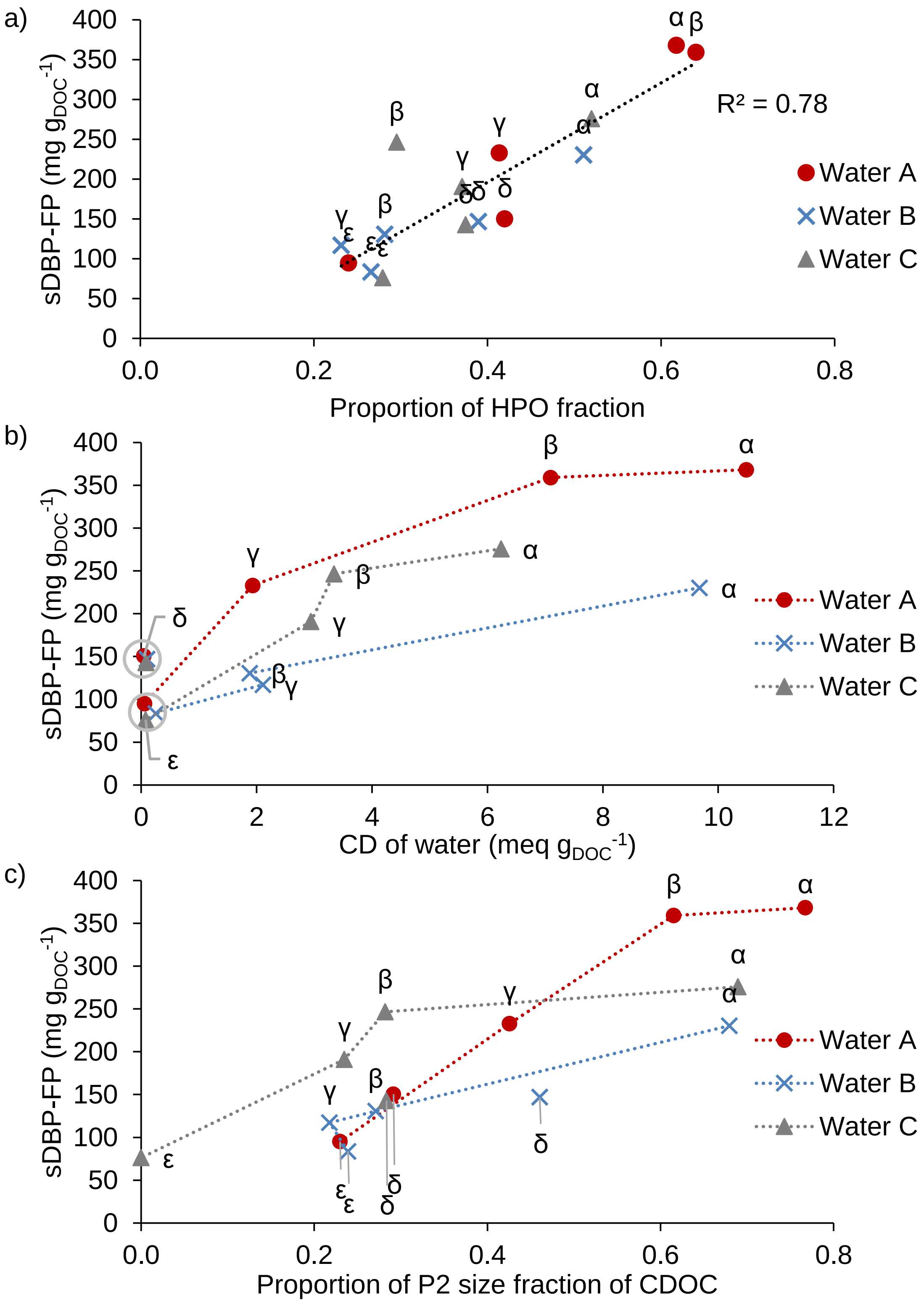


Figure 3.5: Relationship between the sDBP-FP and the water parameter a) HPO proportion (r^2 was calculated incorporating values of all waters), b) CD (separated for the three waters) and c) P2 size fraction; the different treatment stages are indicated by α = raw water, β = IEX, γ = IEX (virgin), δ = coagulation, ε = IEX&Coag.

As the CD increased, there was an increase in the total sDBP-FP, however, the relationship was not linear and was different for each water source (Figure 3.5b). Even though raw waters generally had a higher sDBP-FP before treatment, it is important to recognise that initially high CD waters did not necessarily correlate to high sDBP-FP. For example, water A with a CD of 10.5 meq g_{DOC}^{-1} had a sDBP-FP of 368 mg g_{DOC}^{-1}, whereas water B with a similar CD had a considerable lower sDBP-FP of 230 mg g_{DOC}^{-1}. From different initial formation potentials, a reduction of the CD by IEX generally corresponded to a lower sDBP-FP. The degree of the reduction was source water dependent and varied with the resin condition. For example, water B was observed to show a reduction of 81% of the CD and 43% of the sDBP-FP by IEX. On the other hand, CD and sDBP-FP reduction by IEX were 32 and 2% for water A. Virgin resin increased the reduction of the CD and the sDBP-FP to 82% and 63% for this water.

Again, a clustering was observed when coagulation was used alone or combined with IEX. In these cases, the CD was almost completely removed (< 0.3 meq g_{DOC}^{-1}) by coagulation and IEX&Coag with sDBP-FP from 143 to 150 mg g_{DOC}^{-1} and 76 to 93 mg g_{DOC}^{-1}, respectively. The difference between the sDBP-FP for coagulation with and without IEX pre-treatment was therefore linked to the removal of compounds of low charge. An example of an uncharged molecule with high impact on the reactivity is resorcinol with a sTHM-FP of 1588 mg g_{DOC}^{-1} (Bond et al., 2010). This suggests that for low CD water the proportion of the HPO fraction is more important for estimating the sDBP-FP. A considerable reduction of the CD and HPO fraction led to a lower sDBP-FP and therefore the use of both parameters were useful indicators for the reduction of the sDBP-FP by treatment.

A reduction of the proportion of size fraction P2 generally followed a reduction of the sDBP-FP (Figure 3.5c). In water B, for example, the raw water showed a sDBP-FP of 230 mg g_{DOC}^{-1} for a P2 proportion of 68%, which was reduced to 142 mg g_{DOC}^{-1} at 28% P2. However, for the P2 fraction, the clustering observed for the HPO and CD did not apply, with point ε of water C and δ of water B showing a lower and higher P2 proportion than the other waters. A clustering, however, was seen for the P1 fraction (Supplementary Information, Figure S 3.5). For the other size fraction (P3-P5) an increase in the respective size fraction corresponded generally to a decline in the sDBP-FP. This was explained by the relatively low concentration of the P2 fraction, which in turn increases the proportion of the other fractions (Supplementary Information, Figure S 3.5 b-d). A decline of the sDBP-FP was seen when the CD, and HPO and P2 fraction were reduced, suggesting that the reactive precursors are predominantly of this character.

3.5 Conclusion

Three different source waters from catchment areas with organic rich soils were treated with IEX, coagulation and the combined treatment to compare their NOM treatability. Comparison between pre-used and virgin IEX resin facilitated the evaluation of resin deterioration associated with long-term continuous use. The results can be summarised as follows:

- Higher removal of the HPO was attributed to the resin having a higher affinity to hydrophobic compounds as well as there being a higher distribution of charged compounds in in the HPO fraction.
- Size fraction P2 was the dominant peak and showed the largest difference between waters. While size exclusion was the main reason for a lower removal of P1, charge density of the compounds in the LMW were suspected to be responsible in determining their removal efficiency.
- A higher CD in raw water resulted in higher CL removal. However, CL reduction was not close to the available exchange capacity of the resin indicating that exchange was limited to the sites close to the surface of the resin. CD reduction did not correspond to DOC removal when water was treated by pre-used resin, emphasising the importance of size distribution and resin state.
- The raw water composition exhibited a greater influence on removal when pre-used resin was applied, compared to virgin resin: A high DOC concentration of hydrophobic and charged character in the P2 size range limited the removal due to surface blockage.

- Treatability by the combined IEX and coagulation was excellent regardless of raw water characteristics. This knowledge is important when water companies have to decide a treatment technology targeting challenging waters. The combined treatment was able to reduce the DOC drastically and minimise the sDBP-FP to values that were 42-53% and 32-42% below those obtained for coagulation for sHAA-FP and sTHM-FP, respectively.

3.6 Acknowledgment

The authors would like to thank Scottish Water for sponsoring this research and allowing access to their sites and the staff of Scottish Water laboratories for their analytical support, as well as PWNT for providing pre-used resin.

3.7 References

Ailkenhead-Peterson, J.A., McDowell, W.H., Neff, J.C., 2003. Sources, Production, and Regulation of Allochthonous Dissolved Organic Matter Inputs to Surface Waters, in: Aquatic Ecosystems Interactivity of Dissolved Organic Matter. Academic Press, pp. 25–70.

Bazri, M.M., Mohseni, M., 2016. Impact of natural organic matter properties on the kinetics of suspended ion exchange process. Water Res. 91, 147–155.

Bhandari, V.M., Sorokhaibam, L.G., Ranade, V.V., 2016. Ion Exchange Resin Catalysed Reactions - An Overview, in: Industrial Catalytic Processes for Fine and Specialty Chemicals. Elsevier, pp. 393–422.

Bond, T., Goslan, E.H., Parsons, S.A., Jefferson, B., 2012. A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. Environ. Technol. Rev. 1, 93–113.

Bond, T., Goslan, E.H., Parsons, S.A., Jefferson, B., 2010. Disinfection by-product formation of natural organic matter surrogates and treatment by coagulation, MIEX and nanofiltration. Water Res. 44, 1645–1653.

Boyer, T.H., Singer, P.C., 2008. Removal of natural organic material by a magnetic ion exchange resin. Water Sci. Technol. Water Supply 8, 167–172.

Boyer, T.H., Singer, P.C., 2005. Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors. Water Res. 39, 1265–76.

Brezinski, K., Gorczyca, B., 2019. An overview of the uses of high performance size exclusion chromatography (HPSEC) in the characterization of natural organic matter (NOM) in potable water, and ion-exchange applications. Chemosphere 217, 122–139.

Cornelissen, E.R., Moreau, N., Siegers, W.G., Abrahamse, A.J., Rietveld, L.C., Grefte, A., Dignum, M., Amy, G., Wessels, L.P., 2008. Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions. Water Res. 42, 413–423.

Croué, J.-P., Korshin, G. V., Benjamin, M.M., 2000. Introduction, in: Characterization of Natural Organic Matter in Drinking Water. AWWA Research Foundation and American Water Works Association, pp. 1–10.

Drikas, M., Chow, C.W.K., Cook, D., 2003. The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth: An evaluation of magnetic ion exchange resin (MIEX) and alum coagulation. J. Water Supply Res. Technol. - Aqua 52, 475–487.

Drikas, M., Dixon, M., Morran, J., 2011. Long term case study of MIEX pre-treatment in drinking water; understanding NOM removal. Water Res. 45, 1539–1548.

EPA, 1994. Chapter 3: Factors That Favor Biofilm Growth, in: Control of Biofilm Growth in Drinking Water Distribution Systems. DIANE Publishing, Washington, pp. 9–16.

Fabris, R., Chow, C.W.K., Drikas, M., Eikebrokk, B., 2008. Comparison of NOM character in selected Australian and Norwegian drinking waters. Water Res. 42, 4188–4196.

Finkbeiner, P., Redman, J., Patriarca, V., Moore, G., Jefferson, B., Jarvis, P., 2018. Understanding the potential for selective natural organic matter removal by ion exchange. Water Res. 146, 256–263.

Golea, D.M., Upton, A., Jarvis, P., Moore, G., Sutherland, S., Parsons, S.A., Judd, S.J., 2017. THM and HAA formation from NOM in raw and treated surface waters. Water Res. 112, 226–235.

Gönder, Z.B., Kaya, Y., Vergili, I., Barlas, H., 2006. Capacity loss in an organically fouled anion exchanger. Desalination 189, 303–307.

Grefte, A., Dignum, M., Cornelissen, E.R., Rietveld, L.C., 2013. Natural organic matter removal by ion exchange at different positions in the drinking water treatment lane. Drink. Water Eng. Sci. 6, 1–10.

Harland, C.E., 1994. Ion Exchange: Theory and Practive, 2nd ed. The Royal Society of Chemistry, Cambridge.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). Water Res. 45, 879–885.

Humbert, H., Gallard, H., Jacquement, V., Croué, J.-P., 2007. Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water. Water Res. 41, 3803–3811.

Jeong, S., Nguyen, T.V., Vigneswaran, S., Kandasamy, J., Dharmabalan, D., 2015. Removal of natural organic matter at the Gunbower water treatment plant in northern Victoria, Australia. Desalin. Water Treat. 3994, 1–9.

Kawahigashi, M., Fujitake, N., Yajima, H., Sumida, H., 2011. Particle Sizes of Standard Humic Substances Calculated as Radii of Gyration, Maximum Diameter and Hydrodynamic Radii. Humic Subst. Res. 8, 13–18.

Kitis, M., Harman, I.B., Yigit, N.O., Beyhan, M., Nguyen, H., Adams, B., 2007. The removal of natural organic matter from selected Turkish source waters using magnetic ion exchange resin (MIEX). React. Funct. Polym. 67, 1495–1504.

Klučáková, M., 2018. Size and Charge Evaluation of Standard Humic and Fulvic Acids as Crucial Factors to Determine Their Environmental Behavior and Impact. Front. Chem. 6, 1–8.

Koreman, E., Galjaard, G., 2016. NOM-removal at SWTP Andijk (Netherlands) with a New Anion Exchange, called SIX. Gewässerschutz - Wasser - Abwasser 239, 50.1-50.13.

Li, Q., Elimelech, M., 2004. Organic fouling and chemical cleaning of nanofiltration membranes: Measurements and mechanisms. Environ. Sci. Technol. 38, 4683–4693.

Losty, E., Goslan, E., Jarvis, P., Jefferson, B., 2018. Formation of disinfection by-products following different treatment processes, in: UKWIR Disinfection By-Product Conference. Cranfield.

Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment : A review. Adv. Colloid Interface Sci. 159, 189–197.

Mergen, M.R.D., Jefferson, B., Parsons, S.A., Jarvis, P., 2008. Magnetic ion-exchange resin treatment: Impact of water type and resin use. Water Res. 42, 1977–1988.

Metcalfe, D., Rockey, C., Jefferson, B., Judd, S., Jarvis, P., 2015. Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process. Water Res. 87, 20–28.

Pivokonsky, M., Naceradska, J., Kopecka, I., Baresova, M., Jefferson, B., Li, X., Henderson, R.K., 2016. The impact of algogenic organic matter on water treatment plant operation and water quality: A review. Crit. Rev. Environ. Sci. Technol. 46, 291–335.

Rahmani, S., Mohseni, M., 2017. The Role of Hydrophobic Properties in Ion Exchange Removal of Organic Compounds from Water. Can. J. Chem. Eng. 95, 1449–1455.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., Demarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water : A review and roadmap for research. Mutat. Res. 636, 178–242.

SenGupta, A.K., 2017. Ion Exchange in Environmental Processes. John Wiley & Sons, Inc., Hoboken, NJ, USA.

Sharp, E.L., Parsons, S.A., Jefferson, B., 2006. Seasonal variations in natural organic matter and its impact on coagulation in water treatment. Sci. Total Environ. 363, 183–194.

Sillanpää, M., Levchuk, I., Marquez, J., 2018. Removal of natural organic matter (NOM) from water by ion exchange - A review. Chemosphere 192, 90–104.

Spellman, F., 2010. Basic Water Chemistry, in: Spellman's Standard Handbook for Wastewater Operators. CRC Press, pp. 61–82.

Tan, Y., Kilduff, J.E., 2007. Factors affecting selectivity during dissolved organic matter removal by anion-exchange resins. Water Res. 41, 4211–4221.

Valdivia-Garcia, M., Weir, P., Frogbrook, Z., Graham, D.W., Werner, D., 2016. Climatic, Geographic and Operational Determinants of Trihalomethanes (THMs) in Drinking Water Systems. Nat. Sci. Reports 6, 1–12.

Wang, C., Zhang, X., Wang, J., Liu, S., Chen, C., Xie, Y., 2013. Effects of organic fractions on the formation and control of N-nitrosamine precursors during conventional drinking water treatment processes. Sci. Total Environ. 449, 295–301.

3.8 Supplementary Information

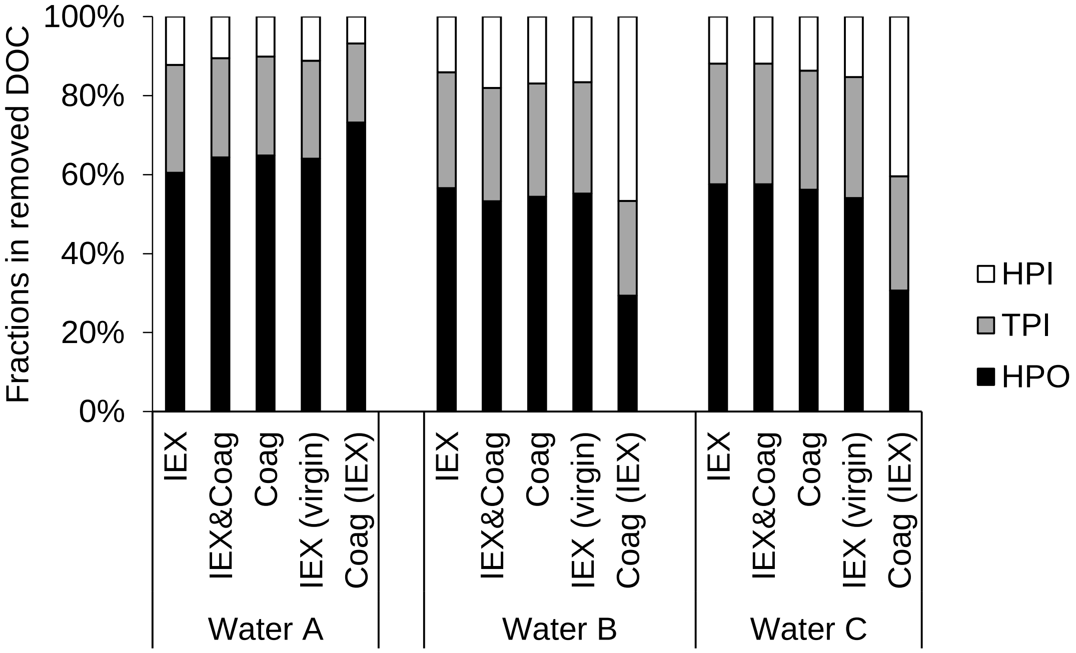


Figure S 3.1: Proportions of the different hydrophobicity fractions in the removed DOC for the different treatment steps.

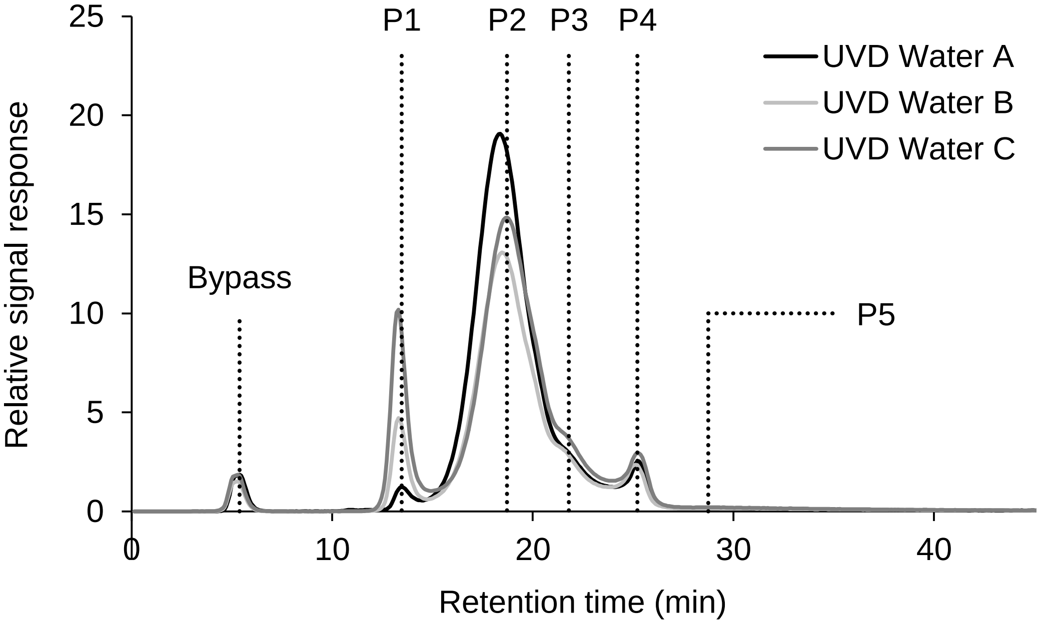


Figure S 3.2: LC-UVD traces for different raw waters. P1 to P5 are retention times as described in LC-OCD chromatogram (Figure 3.2); by-pass: detection of DOC from restricted flow that bypassed the column.

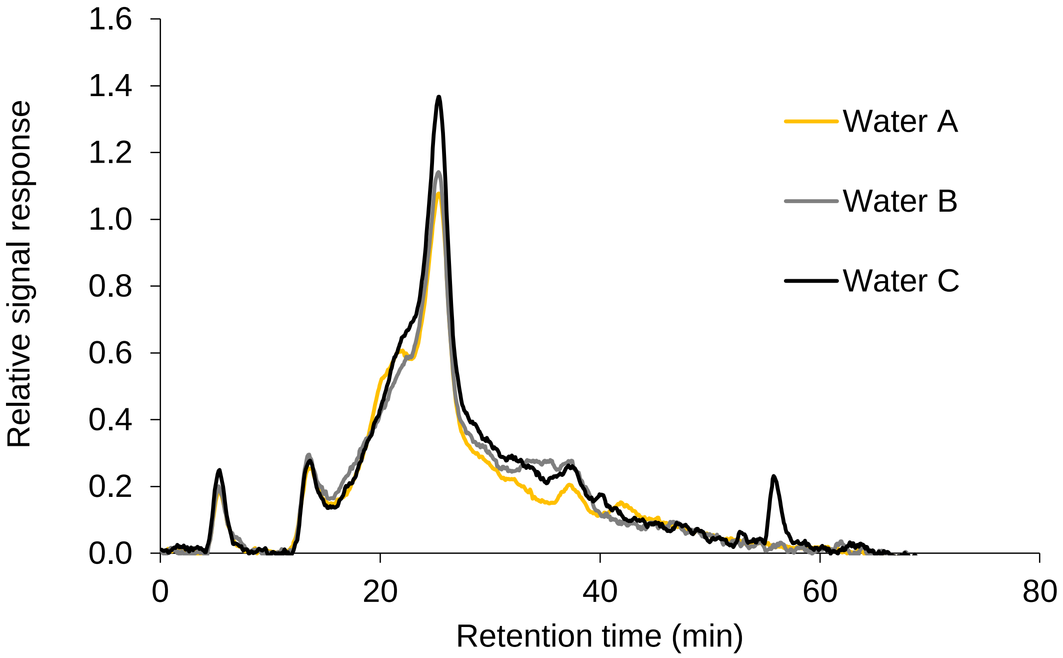


Figure S 3.3: LC-OCD traces for different waters after IEX&Coag treatment.

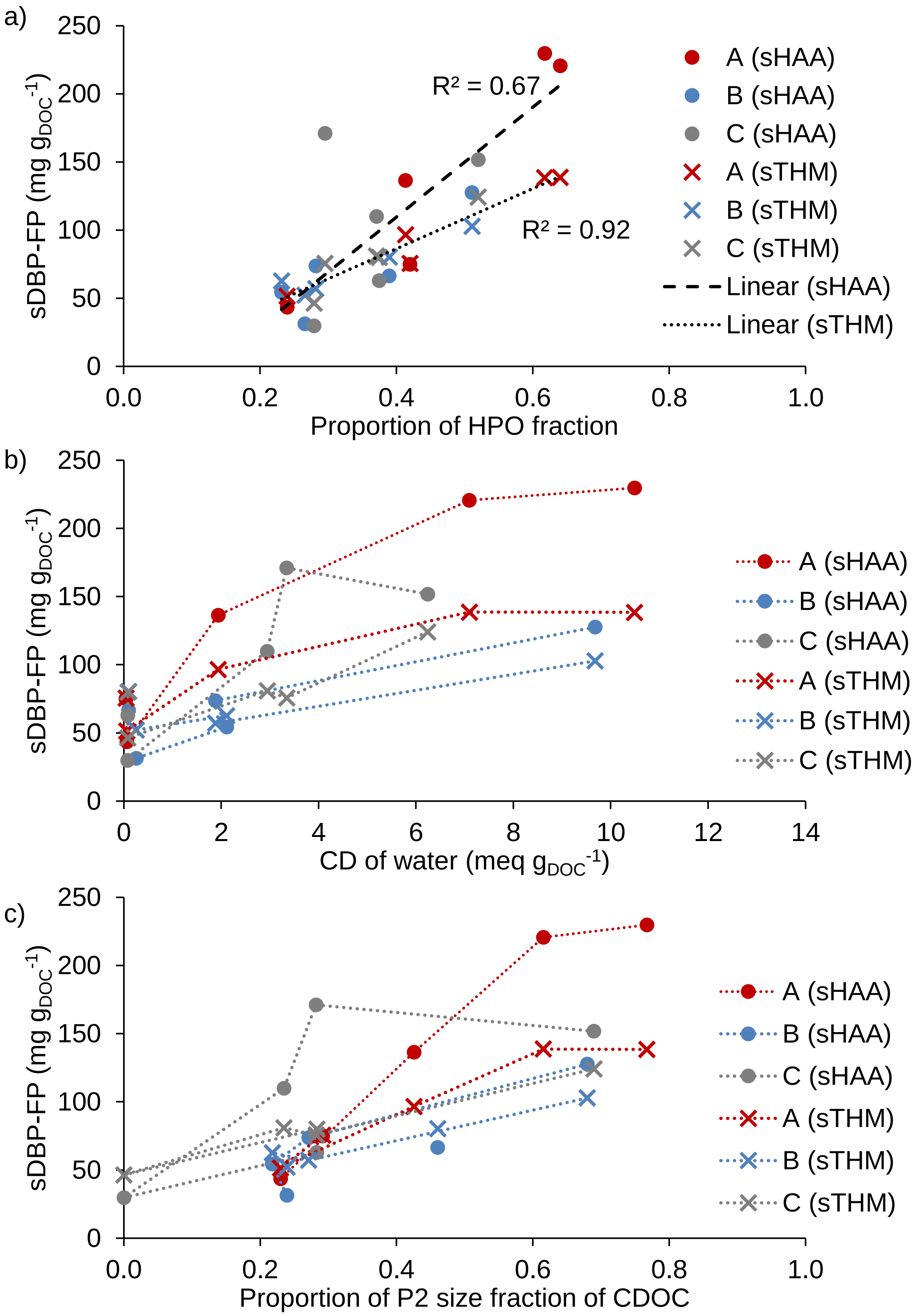


Figure S 3.4: Relationship between the sHAA and sTHM-FP and the water parameter a) HPO proportion, b) CD and c) Proportion of the P2 size fraction of the CDOC separated for the three waters.

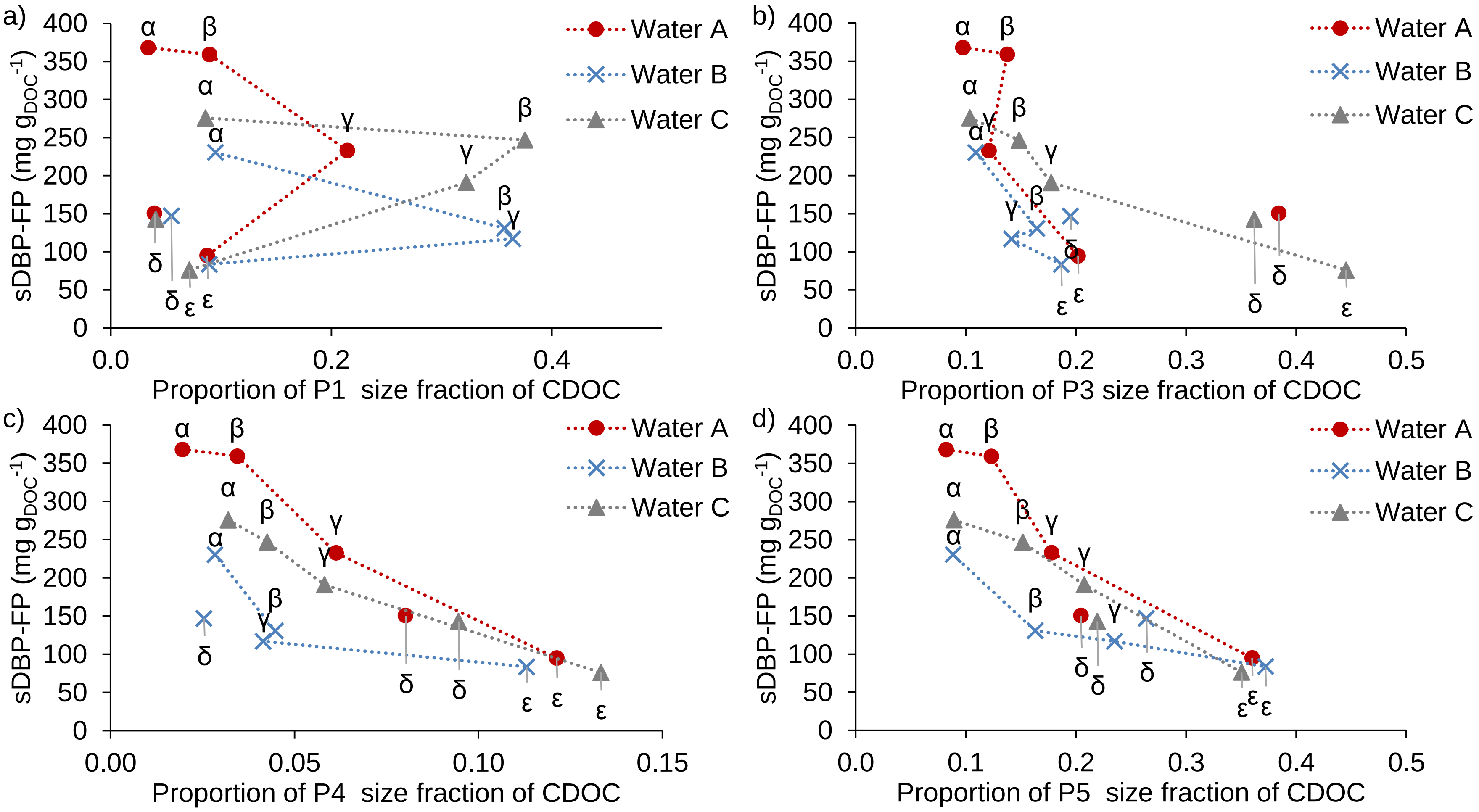


Figure S 3.5: Relationship between the sDBP-FP and the proportion of the size fraction a) P1, b) P3, c) P4 and d) P5; the different treatment stages are indicated by α = raw water, β = IEX, γ = IEX (virgin), δ = coagulation, ε = IEX&Coag.

Table S 3.1: Number-average molecular weight of peak 2 for waters at different treatment steps.

	Number-average molecular weight M_n (g mol^{-1})		
	Water A	Water B	Water C
Raw	630	605	552
SIX	903	817	781
SIX (virgin)	837	1011	588
Coag	381	578	370
SIX+Coag	407	688	-

Table S 3.2: Matrix showing Kendall's tau correlation coefficient (for non-parametric data) r, for hydrophobicity (HPO, TPI, HPI), size fraction proportions (P1 to P5) and charge density (CD) regarding raw, IEX treated (virgin and pre-used resin), coagulated and IEX&Coag treated water; ** Correlation is significant at the 0.01 level (1-tailed), *Correlation is significant at the 0.05 level (1-tailed).

	HPO%	TPI%	HPI%	P1%	P2%	P3%	P4%	P5%	CD
HPO%	-								
TPI%	0.23	-							
HPI%	-0.90^{**}	-0.35^{*}	-						
P1%	-0.34^{*}	0.00	0.32	-					
P2%	0.75^{**}	0.33^{*}	-0.75^{**}	-0.26	-				
P3%	-0.33^{*}	-0.32	0.39^{*}	-0.23	-0.49^{**}	-			
P4%	-0.50^{**}	-0.33	0.56^{**}	-0.01	-0.66^{**}	0.63^{**}	-		
P5%	-0.58^{**}	-0.38^{*}	0.68^{**}	0.03	-0.62^{**}	0.59^{**}	0.65^{**}	-	
CD	0.39^{*}	0.25	-0.45^{**}	0.19	0.43^{*}	-0.75^{**}	-0.65^{**}	-0.63^{**}	-

4 INTERACTIONS BETWEEN ORGANIC MODEL COMPOUNDS AND ION EXCHANGE RESIN

P. Finkbeiner[a], G. Moore[b], T. Tseka[c], T.T.I. Nkambule[c], B. Jefferson[a], P. Jarvis[a]*

[a]Cranfield Water Science Institute, Building 52a, Cranfield University, Cranfield, Bedford, MK43 0AL.
[b]Scottish Water, Castle House, 6 Castle Drive, Dunfermline, KY11 8GG.
[c]Nanotechnology and Water Sustainability Research Unit, University of South Africa, (UNISA), Johannesburg, Florida, 1709, South Africa.

4.1 Abstract

Ion exchange (IEX) can successfully remove natural organic matter (NOM) from surface water. The removal mechanism, however, is not well understood due to the complexity and variability of NOM in real source waters. The use of model compounds with a range of physical and chemical characteristics were therefore used to improve the understanding of NOM removal by IEX resins. 15 model compounds were used to evaluate the influence of hydrophobicity, size and charge of organic molecules on the removal by ion exchange. Three different resins, comprising polystyrene and polyacrylic resin of macroporous and gelular structure, showed that charge density (CD) was the most important characteristic that controlled the removal, with CD of >10 meq mg_{DOC}^{-1} resulting in high removal (≥89%). Size exclusion of compounds with high MW was evident with increasing concentration. The hydrophobicity of the resin and model compound was particularly important for removal of neutral molecules such as resorcinol, which was best removed by the more hydrophobic polystyrene resin. Relationships were identified that provided explanations of the interactions observed between NOM and IEX resin in real waters.

4.2 Introduction

The removal of natural organic matter (NOM) from surface water is known to be of importance, primarily for reduction of the formation of disinfection by-product (DBPs) in drinking water (Zhang et al., 2015). Ion exchange (IEX) has been shown to successfully reduce the concentration of NOM, particularly when used in combination with coagulation (Metcalfe et al., 2015). The removal of specific organic compounds by IEX facilitates an improved performance of coagulation, resulting in the reduction of the specific DBP formation potential (sDBP-FP) (Finkbeiner et al., 2018).

Exchange of NOM onto IEX resin occurs through the release of a counter ion into solution (Supplementary Information, Figure S 4.1a) (SenGupta, 2017). However, it has not been clearly shown how the physical structure of the IEX resin influences NOM removal. While some studies suggest that macroporous resins remove more NOM than gelular resins due to their larger pore diameter (Bolto et al., 2002), others have shown a better performance of gelular resins, attributed to the higher degree of swelling and thus access to exchange sites (Cornelissen et al., 2008). There is also inconsistency in the way that the chemical structure of a resin influences removal behaviour. While styrene resins were ascribed a higher selectivity for NOM (Sillanpää et al., 2018), others have seen no differences between resin types when investigating three acrylic and six styrene resins (Cornelissen et al., 2008).

These differences reflect the role that the NOM properties have on removal, where charge, hydrophobicity and size have all been shown to influence removal (Bazri and Mohseni, 2016; Finkbeiner et al., 2018; Rahmani and Mohseni, 2017). The most important removal pathway is the electrostatic attraction between functional groups on the resin and the negatively charged moieties of NOM molecules, evidenced by the stoichiometrical release of chloride (Boyer and Singer, 2008b). Each exchange is associated with an increase in Gibbs free energy (ΔG) when a larger ion on the exchanger resin is replaced by a smaller ion from the solution, described by equation (4.1), based on Coulomb’s law (SenGupta, 2017):

$$\Delta G_{el} = -\frac{Ne^2}{4\pi\varepsilon_0\varepsilon_D}\left(\frac{1}{r_R+r_B} - \frac{1}{r_{R0}+r_A}\right) \tag{4.1}$$

where N is the Avogadro constant, e is the elementary charge, ε_D is the vacuum permittivity, ε_D is the dielectric constant of the ion exchanger, r_R is the charge radius of the hydrated fixed ion and r_A or r_B that of the counter ions, where A refers to chloride and B to the ion that is exchanged.

The most common anionic groups in NOM are the carboxylate ion with a hydrated radius of 0.304 nm (Degtyarenko and Nieminen, 2010)) and the deprotonated hydroxyl ion (no data available for hydrated radius). During removal, these groups exchange with the larger chloride ion (r = 0.332 nm (Conway, 1981)) on the resin phase. A higher number of charged groups on a molecule increases its charge density (CD) and a direct correlation between CD and NOM removal has been reported previously (Boyer et al., 2008). However, hydrophobic adsorption of NOM has also been reported to occur in addition to direct ion exchange from coulombic attractive forces. Increased removal of organic compounds with higher hydrophobicity has been shown in several studies (Humbert et al., 2007; Rahmani and Mohseni, 2017). The removal of neutral compounds was attributed to hydrophobic adsorption phenomena (Cornelissen et al., 2008). (Supplementary Information, Figure S 4.1b). The sorption of the non-polar moiety onto the hydrophobic resin, leads to an increase in entropy which overcompensates the endothermic desolvation, resulting in an overall negative free energy change, making the process favourable (SenGupta, 2017). Another important parameter is the molecular weight of organic compounds. Large molecules can experience size exclusion and cannot penetrate into the resin interior leading to reduced removal (Finkbeiner et al., 2018).

The attribution and differentiation of these interactions between IEX resin and sorbent is difficult in a diverse mixture such as NOM. Accordingly, model compounds can be used to elucidate such interactions as different individual structures can represent the chemical features required for comparison, without the complexity and unknown structure associated with NOM in real water sources. Humic acid, tannic acid and resorcinol have been used as surrogates for hydrophobic NOM, while amino acids and sugars have been used to represent charged hydrophilic (glutamic acid, aspartic acid) and neutral hydrophilic compounds (mannose, xylose, glycine, leucine, serine) (Bond et al., 2010; Mergen, 2008). Other studies have investigated the removal of aromatic molecules on a layered hydroxide media using benzoic acid and derivatives with different numbers of carboxylic acids on the benzene ring (e.g. phthalic acid, trimesic acid, mellitic acid) and found a positive influence of multiple charge on removal (Liang and Butler, 2010). However, there have been no studies that have considered the combined influence of charge, hydrophobicity and molecular weight when selecting model compounds. This is particularly the case when considering the role of concentration (by mass, molecule and charge), competition and resin property. The aim of this work was to therefore determine the key features of NOM that control removal and ultimately allow for the screening of real water sources to determine their treatability by IEX. This was achieved through investigation of 15 model compounds, spanning a wide spectrum of molecular structure. Three resins of different chemical and physical structure were selected to understand the role of the resin type on the removal efficiency.

4.3 Materials and Methods

4.3.1 Model compounds

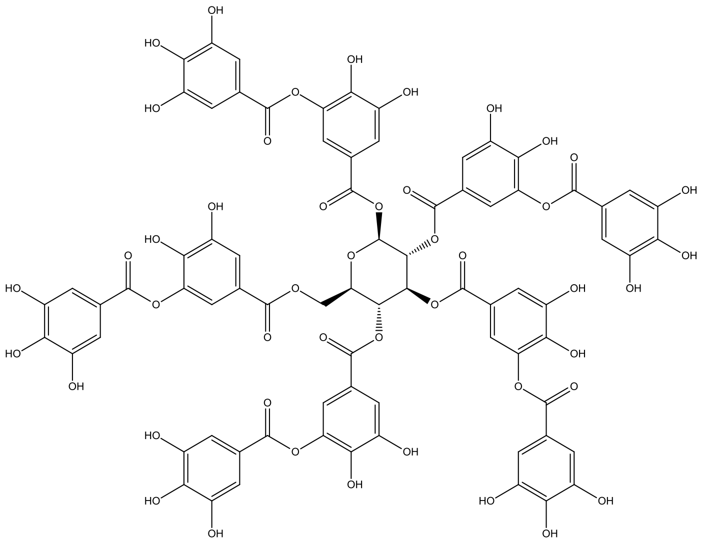
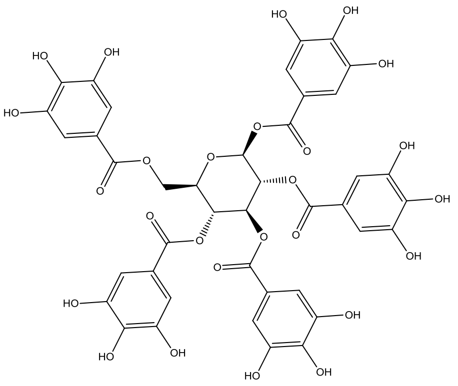
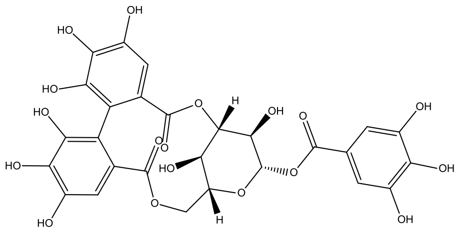
15 model compounds of different hydrophobicity, molecular weight and charge were selected to cover a diversity of physicochemical properties, as well as representing constituents of raw water, including humic substances (humic und fulvic acids), breakdown products (often referred to as building blocks), carbohydrates, carboxylic acids and amino acids (Table 4.1). Glucose and xylose were selected as model compounds for neutral small aliphatic molecules; glutamic acid as a surrogate for amino acids with one positively and two negatively charged groups. Resorcinol, a breakdown product of fulvic acids, is an aromatic compound with almost no charged functionality at neutral pH (Christman and Ghassemi, 1966). Aromatic compounds with increasing numbers of carboxylic acid group(s) were chosen to compare the impact of the number of

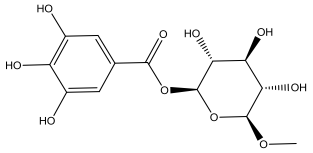
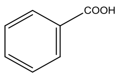
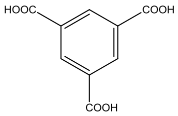
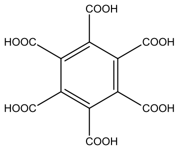
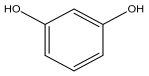
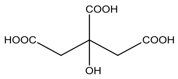
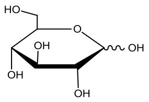
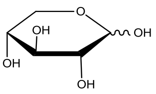
charged moieties. These were benzoic acid, trimesic acid and mellitic acid. Citric acid represented a charged aliphatic low molecular weight acid. Large hydrophobic components of low charge density were represented by tannic acid. Smaller derivatives of this large molecule with a comparable fundamental structure were studied to show differences in molecular weight and hydrophobicity: pentagalloyl glucose (PGG), monogalloyl glucose (MGG) and corilagin. Additionally, three different mass-average molecular weights (M_w) between 1.2-15 kDa of the synthetic polymer poly(acrylic acid) sodium salt (PAA) were used to study the influence of size for a charged aliphatic macromolecule.

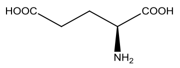
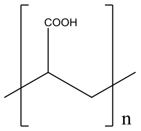
A solution of 10 mg_{DOC} L^{-1} was prepared for each model compound. Additionally, solutions of equivalent molar concentration (0.119 mM) and equivalent charge load (0.707 meq L^{-1}) were prepared. The working solutions were buffered with 20 mg L^{-1} $NaHCO_3$ and adjusted using HCl and NaOH to give a final of pH 7.

Mixtures of benzoic acid, resorcinol and tannic acid were prepared at concentrations of 10 mg_{DOC} L^{-1} and 0.119 mM of each compound and 20 mg L^{-1} $NaHCO_3$ was added before pH adjustment.

Table 4.1: Chemical structure and physicochemical properties of the model compounds

Name (constituent)	Structure	Log $K_{ow}$$^{(b)}$	CD $^{(a)}$ (eq g_{DOC}^{-1})	MW (Da)	pKas
Tannic acid (humic sub-stance)		6.2 [HPO]	0.56	1701 [P2]	7.51 7.91 8.20 8.46 8.69 8.87 8.93 8.94 9.20 9.43 9.49 9.58, *
Penta-galloyl-glucose (humic substance/ building block)		3.6 [HPO]	1.08	941 [P2]	7.45 7.85 8.15 8.45 8.76 8.85 8.88 11.31 11.69 11.75 **
Corilagin (building block)		0.1 [TPI]	4.00	636 [P3]	7.10 7.25 7.50 7.67 8.08 11.50 11.95 11.97 ***

Mono-galloyl-glucose (building block)		-1.3 [HPI]	0.49	332 [P3/P4]	8.08 11.24 12.23 13.10 13.77 14.48 15.05
Benzoic acid (arom. CA)		1.87 [HPO]	11.88	122 [P4]	4.08
Trimesic acid (arom. CA)		0.5 [TPI]	27.71	210 [P4]	3.14 3.85 4.55
Mellitic acid (arom. CA)		-0.9 [HPI]	41.23	342 [P3/P4]	0.27 1.14 1.89 3.95 4.73 5.72
Resorcinol (neutral arom.)		0.8 [TPI]	0.08	110 [P4]	9.26 10.73
Citric acid (aliph. CA)		-1.7 [HPI]	41.23	192 [P4]	3.05 4.67 5.39 13.92
Glucose (carbohydrates)		-2.6 [HPI]	0.00	180 [P4]	11.30 12.69 13.58 14.51 15.12
Xylose (carbohydrates)		-2.5 [HPI]	0.00	150 [P4]	11.31 12.79 13.76 14.97

Glutamic acid (amino acids)		-3.7 [HPI]	33.27	147 [P4]	1.88 4.27
Poly (acrylic acid) sodium salt	 n≈14, 28, 85, 158	n.a.	n.a.	1000 [P2] 8000 [P1] 15k [P1]	n.a.

(a) Charge density calculated based on pKa values estimated with Chemicalize.com (May 10, 2018), (b) PubChem XlogP3 values, n.a. = not available; CD = charge density, Log K_{ow} = octanol-water partition coefficient, MW = molecular weight, aliph = aliphatic, arom. = aromatic, CA = carboxylic acid; data in [..] is expected hydrophobicity and size fraction of compound: HPO = hydrophobic, TPI = transphilic, HPI = hydrophilic; P1-P5 refer to LC-OCD fractions (Chapter 3); *, **, *** further pKa values for tannic acid* (9.71, 10.45, 11.22, 11.62, 11.62, 11.92, 12.16, 12.63, 13.03, 13.50), pentagalloylglucose** (12.31, 12.67, 12.96, 13.26, 13.67), corilagin*** (12.44, 12.90, 13.41).

4.3.2 Resin preparation and jar tests

Three strong base anion exchange resins were selected based on their application for NOM removal and the differences in their structure (Supplementary Information, **Error! Reference source not found.**). The macroporous polystyrene Dowex Tan-1 resin had a bead size of 420 to 1200 µm and a capacity of 0.7 eq L^{-1}. The gelular Lewatit S5128 resin had a polyacrylic backbone with a bead size of 400 to 1600 µm and a capacity of 1.25 eq L^{-1}. The third resin was the magnetic macroporous MIEX®Gold resin which was of polyacrylic nature with a bead size of 0.15-0.18 µm and a capacity of 0.52 eq L^{-1}.

Table S 4.1: Properties of the three ion exchange resins.

Resin Name	Type	Structure	Size	Water content	Mean size	Total capacity	
			(mm)	(%)	(mm)	(eq L^{-1})	(eq L^{-1})
Lewatit S5128	PA	Gelular	0.4-1.6 [(a)]	57-64[(a)]	0.767 [e]	1.25 [(a)]	1.15 [e]
Dowex Tan-1	PS	Macro-porous	0.42-1.2 [(b)]	70-82[(b)]	0.685 [e]	0.7 [(b)]	0.68 [e]
MIEX® Gold	PA	Macro-porous	0.15-0.18 [(c)]	n/a	0.165 [e]	0.52 [(c)]	0.51 [e]

PS = Polystyrene, PA = Polyacrylic, [e] = experimental value, [(a)] (Lanxess, 2015), [(b)] (Dow, n.d.), [(c)] (S. Golubovic, IXOM, personal communication, 28/03/2019).

Prior to use, each virgin resin was rinsed using 20 times the resin volumes (RV) of deionized water to remove any preservatives or contaminants from manufacturing. The resin was regenerated with sodium chloride solution (20 RV, 100 g L^{-1} NaCl) in stirred suspension for 30 min at 150 rpm. The resin was separated from the brine and rinsed with deionized water (10-20 RV). To remove excess NaCl from the resin pores, the resin was stirred for another 30 min in 20 RV of deionized water at 150 rpm. The required volume of resin was measured in a measuring cylinder then transferred into a 1 L beaker where excess water was removed.

Previous research has shown that less than 1.5% of the resin capacity is utilised during ion exchange of NOM and that the resin surface area is more important for removal than the overall capacity (Chapter 3.4). Therefore resin concentrations of equivalent surface areas were used, normalised to 20 mL L^{-1} of the Lewatit resin, a concentration typical of that used in practice. This resulted in a resin volume of 4 mL L^{-1} for MIEX and 20 mL L^{-1} for Dowex (see Supplementary Information for calculations of resin volume). The required volume of the conditioned resin was mixed with 500 mL of the model compound solutions in a 1 L glass beaker and stirred with a paddle jar tester. After a contact time of 15 min at a stirring speed of 150 rpm, the resin was allowed to settle. For

MIEX resin the settling was assisted by strong neodymium magnets (15 mm radius, pull force 118 N). Each test was carried out in triplicate and one control without resin was run. Samples were taken after the 15 min experimental time.

4.3.3 Analyses

Prior to analysis, all samples were filtered through a 0.45 µm filter. Dissolved organic carbon (DOC) analysis was carried out using a non-purgable organic carbon method on a total organic carbon (TOC) analyser (TOC-V_{CPH}, Shimadzu). Results were reported as an average of triplicate experiments (instrumental error of the TOC analyser: 5%).

Model compound mixtures were quantified on an Agilent 1200 Series high performance liquid chromatography (HPLC) equipped with a degasser (G1379B, Tokyo, Japan) and ALS autosampler (G1329A, Waldbronn, Germany). A sample volume of 0.1 mL was injected onto a Gimini C6-Phenyl column (5 µm, 110 Å, 150 x 4.6 mm). Phosphate buffer, pH 2.1 and methanol were used as the mobile phase. A gradient elution with a flow rate of 1 mL min^{-1} was involved, increasing the initial methanol proportion of 0% after 10 min to 30% within 2 min. The column temperature was set to 30°C and analytes were detected with a diode array detector (G1215B, Waldbronn, Germany). Due to interferences in the detector, tannic acid removal was calculated from the initial and final DOC concentration which was corrected by the calculated DOC concentration of the other compounds in the mixture.

Chloride concentrations were measured by a Dionex ion chromatography system (ICS-1600, Thermo Scientific) with an electrical conductivity detector. The instrument was equipped with a Dionex IonPac^{TM} AS14A column and an AG14A pre-column.

A zetasizer (Malvern Nano Series, Worcestershire, UK) was used to measure the charge load of the model compound solutions according to the method described elsewhere (Chapter 3.3). In short, a stirred 15 mL sample (pH 7) was titrated with polydiallyldimethylammonium chloride (PDADMAC). The required volume of PDADMAC to reach the point of zero charge was used to determine the charge density (CD). The theoretical CD was calculated based on the molar concentration of the model compound and its proportion of ionised groups at pH 7 according to their logarithmic dissociation constant (the pKa) estimated by chemicalize.com (May 10, 2018). If not otherwise stated, the reported CD are the theoretical values for the model compounds.

Determination of the sDBP-FP was carried out as detailed in Chapter 3.3. In short, the model compound solutions (DOC = 1 mg L^{-1}) were chlorinated with NaOCl and incubated for 7 days at 25°C. Trihalomethanes (THMs) were quantified with gas chromatograph mass spectrometry (GC-MS) using a headspace method, and haloacetic acids (HAAs) were extracted and derivatised prior to analysis on a GC-MS.

The determination of total resin capacity was an adjusted silver nitrate titration method from Harland (1994) and has been described in Chapter 3.3.

4.3.4 Calculation of the change in free energy

For the calculation of the change in free energy for ion exchange, equation (4.1) was used. The challenge of calculating the change in free energy for the exchange of anions, is the limited literature providing dielectric constants (ε_0) of ion exchangers. Hence, ε_0 values are not available for the used resins in this work. An early study investigated the dielectric properties of quaternary ammonium ion-exchange beads using a QAE-Sephadex A-25 resin and found a dielectric constants of 58 for the ion exchanger in the chloride form (Ishikawa et al., 1984). This value was used for the calculations in this study.

Furthermore, there is limited information about the hydrated radius of functional groups. While the hydrated radius of chloride and carboxylate have been reported to be 0.332 and 0.304 nm, respectively (Conway, 1981; Degtyarenko and Nieminen, 2010), values are missing for deprotonated hydroxyl groups of organic compounds and quaternary ammonium moieties on the polymeric resin. The latter one was approximated with the hydrated radius of the tertramethyl ammonium ion of 0.367 nm (Bluhm and Li, 2003). The hydrated radius of deprotonated hydroxyl groups was assumed to be in a similar range as the carboxylate ion, and hence for both a value of 0.304 nm was used. These simplification allow an estimation of the change in free energy, but absolute values have to be taken with care.

4.4 Results and Discussion

4.4.1 Increased removal at higher charge density

At a model compound DOC concentration of 10 mg L^{-1}, a steep increase in removal with increasing CD was observed for all three resins (Figure 4.1). For example PGG had a CD of 1.07 meq g_{DOC}^{-1} and was removed by 74-82%. In comparison, benzoic acid with a CD of 11.88 meq g_{DOC}^{-1} was removed by 90-93%. This was explained by the higher free energy of the exchange of benzoic acid that occurred due to the increased proportion of charged groups on the molecule. To illustrate, the change in free energy ΔG was -1.70 J mg_{DOC}^{-1} for benzoic acid, while this was -0.15 J mg_{DOC}^{-1} for PGG (assumptions and approximation for the calculations are detailed in the Supplementary Information). Tannic acid, PGG, MGG and corilagin, which share a glucose ring with differing amounts of gallic acid esters, followed the same trend of increasing removal with CD. MGG had the lowest CD of the set (0.49 meq g_{DOC}^{-1}) and had a removal efficiency of 29%, while corilagin which had a CD that was 4.0 meq g_{DOC}^{-1} was reduced by 80% when using the Lewatit resin. This was also linked to the increase in free energy which favours ion exchange of the respective organic compound.

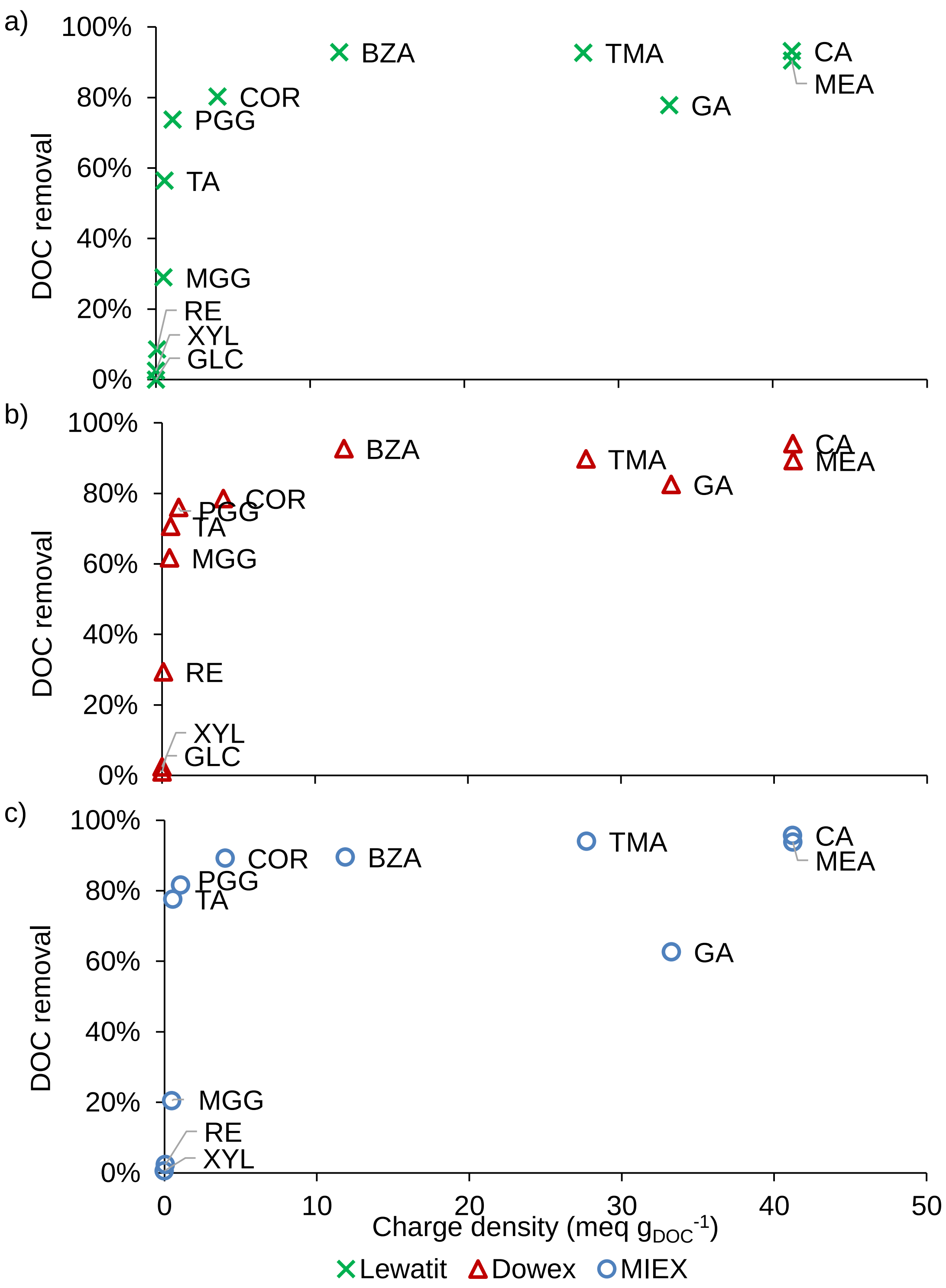


Figure 4.1: Removal of model compounds as a function of their charge density for a) Lewatit, b) Dowex and c) MIEX resin; BZA = benzoic acid, CA = citric acid, COR = corilagin, GA = glutamic acid, GLC = glucose, MEA = mellitic acid, MGG = monogalloyl glucose, PGG = pentagalloyl glucose, RE = resorcinol, TA = tannic acid, TMA = trimesic acid, XYL = xylose.

While large gains in removal were seen when CD was slightly increased from 0.4 to 4.0 meq mg_{DOC}^{-1}, there was little or no change above 11.88 meq g_{DOC}^{-1}, where ≥89% removal was seen for all resins (with the exception of glutamic acid). For instance the removal for citric acid (CD 41.23 meq g_{DOC}^{-1}), trimesic acid (CD 27.71 meq g_{DOC}^{-1}) and benzoic acid was 93% in all cases when the Lewatit resin was used. The results suggest that a maximum removal was reached in the range between 5 to 10 meq g_{DOC}^{-1}. Above this threshold a high level of removal by IEX was apparent but no further increase with higher CD was observed. In comparison, where the CD of natural surface waters has been measured, removal has not been seen to directly correlate to the CD (Chapter 2 and 3). However, when virgin resin was used, three surface waters that had CDs ranging between 6.2 to 10.5 meq g_{DOC}^{-1} resulted in a DOC removal of 86-89% when using Lewatit resin, a result consistent with that seen for the model compounds of high CD (Chapter 3).

In the present analysis the exception to the trend was glutamic acid, which had a high CD of 33.27 meq g_{DOC}^{-1} while its removal was less than for other compounds of similar CD. This was attributed to the zwitterionic nature of the compound. Repulsive forces, originating from the positive charge carried on the nitrogen atom of the amino acid, were believed to result in less favourable exchange. The proximity of the oppositely charged ammonium group to the carboxylate moiety was thought to inhibit the exchange of this second anionic group on the molecule. This in turn, would cause a negative charge on the outer periphery of the resin. Furthermore, Donnan ion exclusion could restrict glutamic acid molecules from entering the resin due to the positive charge on the molecule (SenGupta, 2017).

Resorcinol was removed by 9 and 29% by the Lewatit and Dowex resin, whereas MIEX resin showed no considerable removal (2%). At pH 7, the molecule is present almost entirely in the protonated form and of no charge. Hence the removal must originate from a different mechanism than ion exchange. Hydrophobic effects, and π-π interactions have been proposed as alternative removal mechanisms for some compounds (Zhang et al., 2015). Sorption of a hydrophobic compound to the resin results in an increase in entropy and hence an increase in ΔG. The Dowex resin had stronger interactions with the resorcinol due to the more hydrophobic and aromatic styrenic resin backbone compared to the polyacrylic resins, explaining the increased removal.

The removal of tannic acid was principally driven by its CD (0.56 meq g_{DOC}^{-1}). However, differences in removal were observed for the Lewatit and Dowex resin at 57 and 71% respectively. This was attributed to the hydrophobic/aromatic interaction of the molecules with the resin backbone. However, the MIEX resin showed a higher removal for tannic acid (78%) than the other two resins. This was unexpected as the resin has a polyacrylic structure which is less favourable for compounds of high log K_{ow} (octanol-water partition coefficient, Table 4.1) values. However, this resin has been developed to target high molecular weight organic compounds through having comparatively larger pore sizes than other resins used for DOC removal (Gibson and Golubovic, 2015). This would allow tannic acid easier access to more exchange sites in the resin.

The neutral uncharged compounds, glucose and xylose were not removed by any resin. These compounds possess no charge that could electrostatically interact with the resin. They are also very hydrophilic molecules (log Kow -2.5 to -2.6) and so have very low adsorption potential.

4.4.2 Impact of compound concentration on its removal

Solutions of equivalent molar concentration were prepared for eight selected compounds that were well removed by IEX. Additionally, five compounds with CDs >10 meq mg_{DOC}^{-1} were used to prepare solutions of equivalent charge load. Tannic acid was also included here to be representative of a large hydrophobic compound. An increase in charge load (CL) or concentration showed no considerable change in removal for the small molecules: resorcinol, benzoic acid, trimesic acid, mellitic acid and citric acid (Figure 4.2). For example, 93% of benzoic acid was removed at 0.13 and 0.70 meq L^{-1}. Glutamic acid was less well removed with increasing CL, decreasing from 78 to 72% for the Lewatit reisn. Pore blockage was not thought to be responsible for this decrease because twice as many of the similar sized benzoic acid molecules were removed (0.64 mM) in comparison to glutamic acid (0.26 mM). These observations were explained by the attachment of only one carboxylic group onto the resin for glutamic acid. As this compound is aliphatic, the second unattached negatively carboxylic group at the opposite end of the molecule acts to restrict further exchange due to repulsive electrostatic forces.

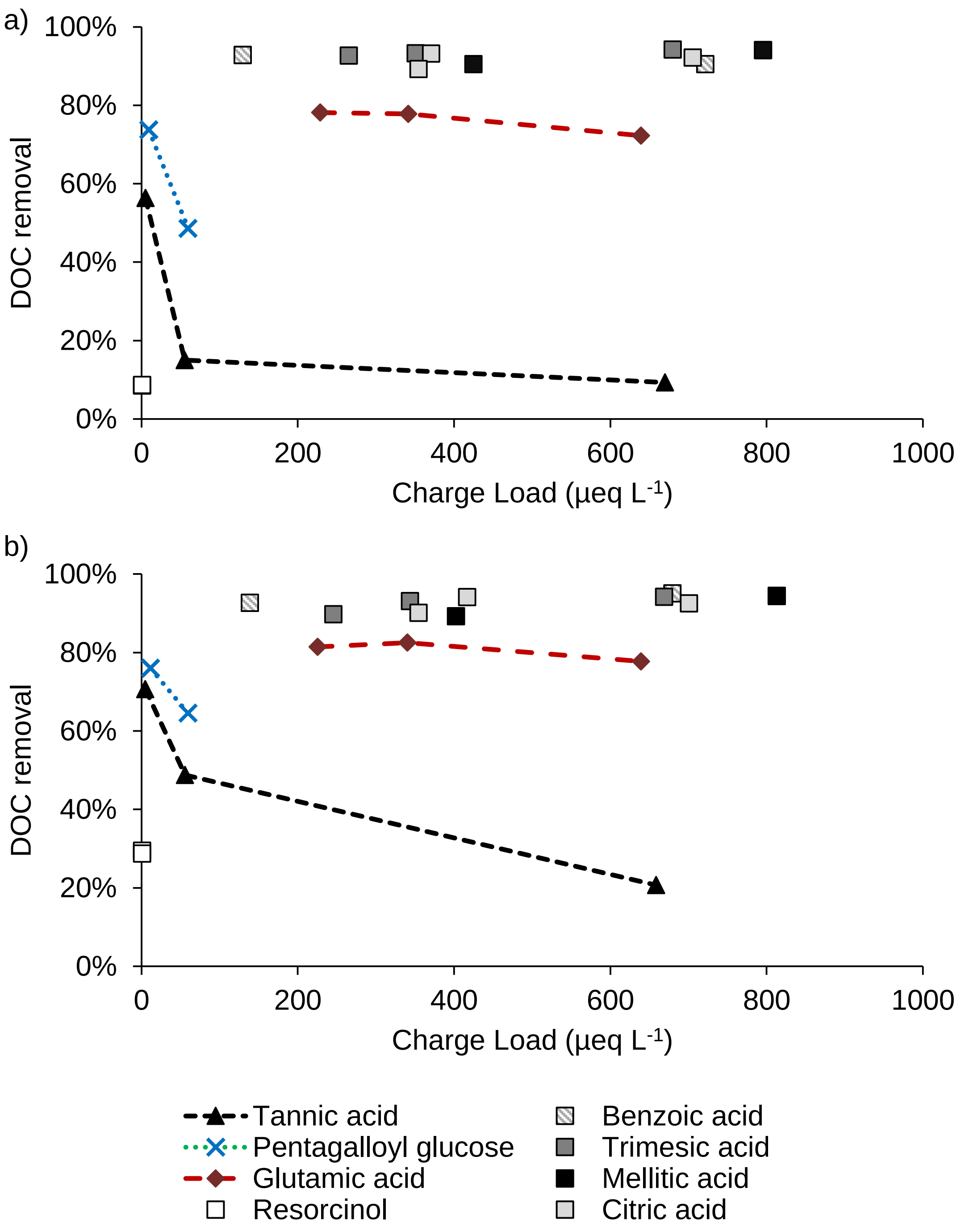


Figure 4.2: Removal of model compounds at different initial concentrations expressed as charge load for a) Lewatit and b) Dowex resin.

A greater change in removal was observed for larger compounds with increasing charge concentration. For example, when the charge load of PGG was increased from 10 to 60 µeq L^{-1} the removal dropped from 74 to 49% and from 76 to 65% for Lewatit and Dowex resin, respectively. A similar trend was observed for tannic acid: where the Lewatit showed a decrease in removal from 56 to 9% across the gradient of 5 to 670 eq L^{-1}. This was congruent with the hypothesis that compounds of higher MW were restricted to the outer surface of the resin due to sterically hindered pore diffusion (Ghoussoub et al., 2018; SenGupta, 2017). As a result, reduced removal was observed as the surface area was occupied. The diameter of tannic acid has been estimated to be 3 nm (Vinu et al., 2012), therefore size exclusion effects were important for the gel type resin with pores of <2-4 nm (Bhandari et al., 2016; Harland, 1994). Also the macroporous resins consist of gel phases that are fragmented by large pores and hence size exclusion can also occur in these resins (Harland, 1994; SenGupta, 2017). These results were consistent with the improved tannic acid removal seen when using the MIEX resin, known to have larger pores.

4.4.3 Molecular weight as a limiting factor

To further study the influence of size while reducing the impact of other physicochemical factors, solutions of PAA of different mass-average molecular weight (M_w) were used. PAA was less well removed with increasing size of the polymer chain for all resins (Figure 4.3a). For a M_w of 1.2 kDa, the concentration of the PAA was reduced by 83, 78% and 81% for Lewatit, Dowex and MIEX resin, respectively. The removal of PAA of 8 kDa was similar when MIEX resin was used (80%). However, the other two resins resulted in removal of 60%, suggesting that size exclusion started to take effect between a M_w of 1.2 and 8 kDa for these resins. While the Lewatit and Dowex showed similar removal efficiencies for low M_w compounds, the gel type resin had a much lower removal of 28% for the solution containing the largest polymer (15 kDa) compared to the macroporous resin that had a removal of 53%. Macroporous resins, such as the Dowex resin, have a much wider pore structure ranging between 20-100 nm (De Dardel, 2019), compared to the microporous gel-type resins <2-4 nm like the

Lewatit resin (Figure 4.3b, c), allowing access of the large molecules into the resin. Similarly, the macroporous MIEX resin removed 67% of PAA. The improved removal of MIEX resin over Dowex resin of the large PAA molecule was in agreement with the high removal of tannic acid. This was explained by the smaller bead size of MIEX and its larger pore size and was consistent with the reported improved DOC removal of the higher molecular weight compounds by MIEX (Gibson and Golubovic, 2015).

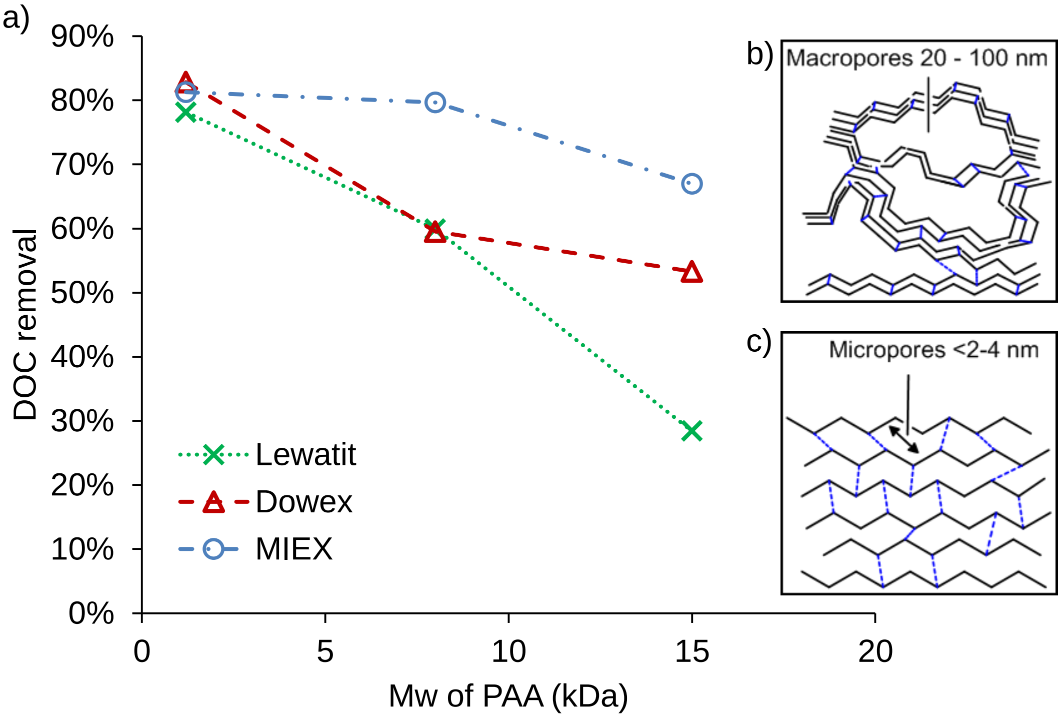


Figure 4.3: a) Comparison of the removal of PAA (poly(acrylic acid) sodium salt) at different mass-average molecular weight by Lewatit, Dowex and MIEX resin, b) structure of the macroporous resin such as Dowex and MIEX, c) structure of gel-type resin such as Lewatit; (b) and c) were adapted from De Dardel (2019)).

4.4.4 Stoichiometric exchange of NOM for chloride

The released chloride concentration was plotted against the theoretically exchanged charge load to evaluate whether a stoichiometric exchange took place (Figure 4.4). The data points were clustered around the stoichiometric exchange line, with the exception of glutamic and tannic acids. This indicates that most organic compounds were removed following a stoichiometric exchange. The higher values obtained for tannic acid were partly due to an underestimation of the CD calculated from its pKa value (1.1 meq g_{DOC}^{-1}). This was supported by empirical determination of the CD of tannic acid by titration with PDADMAC which was determined to be 3.2 meq g_{DOC}^{-1}, a result close to previously reported values (Mergen, 2008). When this CD value was used, the data points were located much closer to the stoichiometric exchange prediction (diagonal line).

The CL reduction for the removal of glutamic acid was distinctly higher than the chloride release. This further supported the view that glutamic acid only binds with one carboxyl group to the resin. When the CL reduction for the exchange of glutamic acid was based on only one negatively charged group, this corresponded very well with the released chloride equivalence (circular data points). Comparable observations were made for the MIEX resin. For all resins, mellitic acid at a set concentration of 0.41 meq L^{-1} resulted in a stoichiometric exchange for all six acidic functional groups. At high initial charge loads (ca. 0.8 meq L^{-1}), however, a lower than expected chloride release was observed, which was equivalent to an exchange of between 4 and 5 carboxylate groups. Accordingly, it was considered that not all of the available anionic groups attached to the resin exchange sites, an observation consistent with that seen for the aliphatic glutamic acid molecule.

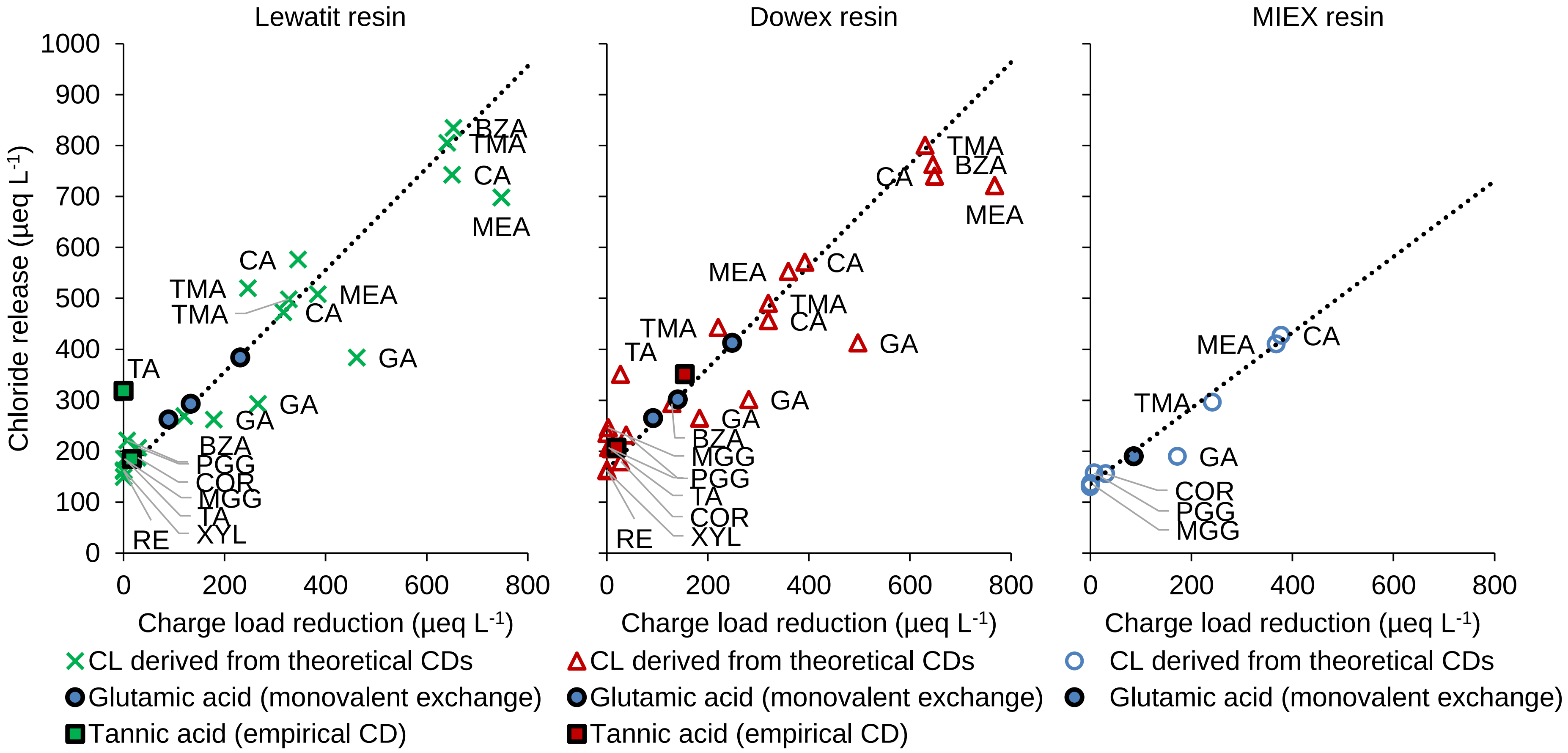


Figure 4.4: Chloride release from as a function of the theoretically removed charge density (CD), where the dotted line indicates a stoichiometric exchange of the charged groups of the molecules for chloride (chloride release for bicarbonate was taken into account, for MIEX it was estimated by a linear regression through the data points excluding GA); chloride release of 319 µeq L^{-1} for TA removal in a) probably an outlier related to experimental error; BZA = benzoic acid, CA = citric acid, COR = corilagin, GA = glutamic acid, GLC = glucose, MEA = mellitic acid, MGG = monogalloyl glucose, PGG = pentagalloyl glucose, RE = resorcinol, TA = tannic acid, TMA = trimesic acid, XYL = xylose.

4.4.5 Competition for exchange sites between contaminants

The influence of competing organic molecules was studied using solutions containing tannic acid, resorcinol and benzoic acid to represent a range of compound characteristics. For mixture 1, where compounds were present at equal DOC concentration, the concentration of benzoic acid showed a rapid decline in the first few minutes and levelled off at concentrations of 0.65, 0.45 and 2 mg L^{-1} after 15 min for Lewatit, Dowex and MIEX resin, respectively (Figure 4.5a). The same trend was observed for mixture 2, where there was a fixed molar concentration of 0.119 mM for each chemical (Figure 4.5b). The efficient removal of benzoic acid, even in the presence of a high concentration of tannic acid, indicated that ion exchange of benzoic acid was not inhibited by other components. This was explained by the ability of small aromatic anions to occupy exchange sites between voluminous anions on the resin. For MIEX resin, the removal kinetics showed a faster rate of removal of benzoic acid in the first few minutes of contact time compared to the other two resins. For instance within 1 min the benzoic acid concentration of mixture 1 was reduced by more than 50% by the MIEX resin, whereas Lewatit and Dowex resin required 2.5 min to achieve the same reduction. The smaller diameter and larger pore sizes of the MIEX resin beads were responsible for a faster intraparticle diffusion and enhanced the ion exchange rate (Harland, 1994; SenGupta, 2017). The pseudo first order adsorption rate constant was calculated to be 0.32, 0.37 and 0.55 min^{-1} for Lewatit, Dowex and MIEX resin in mixture 1 and 0.30, 0.29 and 0.39 min^{-1} in mixture 2. When approaching equilibrium, however, the overall removal of benzoic acid by MIEX was lower than for the Lewatit and Dowex resin and agrees with observations for the single compound solutions, ascribed to the lower overall capacity of the MIEX resin (Figure 4.1). The presence of competing molecules slightly decreased the removal of benzoic acid by MIEX resin. The removal was reduced to 86 and 81% in mixture 1 and 2, respectively, compared to the removal of 90% in the single compound mixture. This was attributed to the high concentration of the large tannic acid molecule as resorcinol was virtually not removed and hence did not compete for or shield exchange sites.

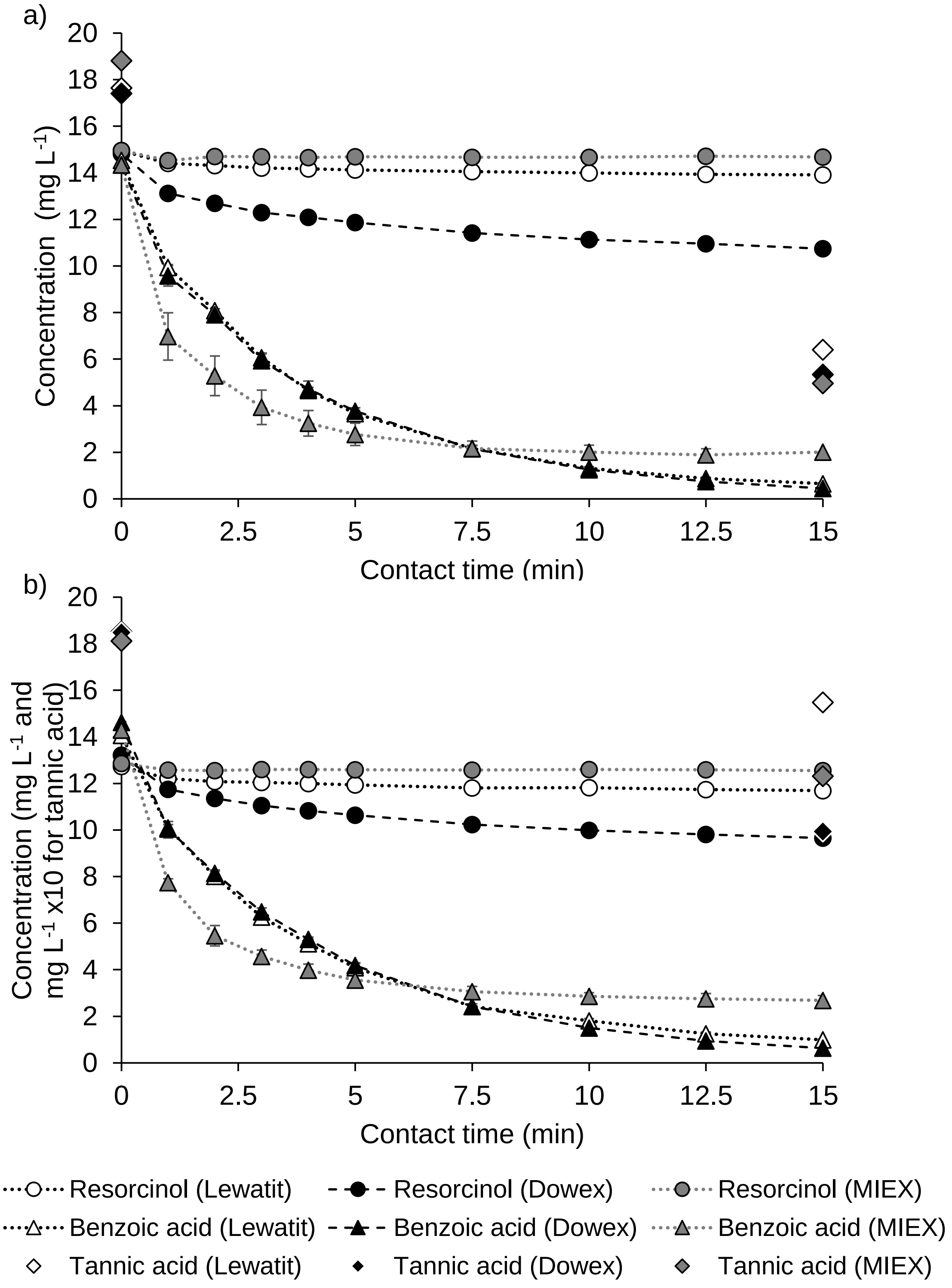


Figure 4.5: Removal over time for compound mixtures of tannic acid, resorcinol and benzoic acid at a) 10 mg L^{-1} DOC and b) 0.119 mM of each compound; tannic acid concentration calculated from DOC measurements.

The removal of tannic acid by the Dowex resin was shown to be influenced by its initial concentration, but only slightly by the presence of competing compounds. The level of removal was 69 and 46% in mixture 1 and 2 respectively, while in the individual compound solutions it was 71 and 49% (Supplementary Information, Table S 4.2). Interestingly, there was a higher removal of tannic acid by Lewatit resin in mixture 1 of 64% compared to 56% in the single compound experiment. This was explained by the hydrophobic interactions between the tannic acid and sorbed aromatic benzoic acid molecules on the resin, favouring the removal of tannic acid. In mixture 2, which had a mass concentration of 202 mg L^{-1}, the compound was removed by 16%. The beneficial effect of benzoic acid was cancelled out by the high relative rejection of tannic acid. The removal of tannic acid by MIEX resin showed a decline when competing compounds were in the solution. Rather than enhancing the removal of tannic acid from the increase in the hydrophobicity of the resin from the sorbed benzoic acid, in this case the competition for exchange sites reduced the sorption of tannic acid to the resin. For mixture 1, the removal was 74% compared to 78% in the single compound experiment. Again, this was ascribed to the overall lower exchange capacity of MIEX resin (0.51 eq L^{-1}) compared to the other two resins (0.68-1.15 eq L^{-1}). While the total exchange capacity was not exhausted, the relative occupation of the resin was much higher for the MIEX resin compared to Dowex and Lewatit resin, particularly if removal was limited to the exchange sites near the surface of the resin.

Resorcinol was removed by up to 8 and 28% for Lewatit and Dowex resin, respectively. The highest removal rate was achieved in the first minute and then declined quickly. The removal in the mixtures showed a similar magnitude as for the pure compound solutions, and therefore was not considerably impacted by the presence of other compounds.

4.4.6 The sDBP-FP of individual compounds and mixtures

To evaluate the impact of the removal on the specific disinfection by-product formation potential (sDBP-FP), the trihalomethane (THM) and haloacetic acid (HAA) concentration of the model compound solutions after chlorine exposure were measured. Trimesic, mellitic and glutamic acid as well as the sugars glucose and xylose showed a negligible sDBP-FP (Figure 4.6). Tannic acid, PGG and MGG shared a similar sTHM-FP between 33 and 39 mg g_{DOC}^{-1} and all three had a high HAA-FP of 103, 139 and 197 mg g_{DOC}^{-1}, respectively. Citric acid was equally important for both sHAA- and sTHM-FP with values of 117 and 145 mg g_{DOC}^{-1}, predominantly dichloroacetic acid. Resorcinol had a low sHAA-FP (31 mg g_{DOC}^{-1}) and mainly trichloroacetic acid was formed. However, a very high sTHM-FP of 1142 mg g_{DOC}^{-1} was observed. This type of compound was of considerable importance due to both its high formation potential and its low removal by IEX. There was no correlation between the sDBP-FP and the physicochemical properties of the compounds (Supplementary Information, Figure S 4.2), suggesting that the properties that control their removal by IEX do not relate to sDBP-FP.

The sTHM-FP of mixture 1 was 438 mg g_{DOC}^{-1} (Table 4.2). This value increased considerably after treatment and was attributed to the high residual resorcinol concentration and its high sTHM-FP. The Dowex resin gave the highest removal of resorcinol and had the smallest increase in sTHM-FP (69%, 741 mg g_{DOC}^{-1}). Less effective removal of resorcinol by Lewatit and MIEX resulted in an increased sTHM-FP which was 86 and 117% higher than before treatment, respectively. However, the sHAA-FP was reduced by 60-64% for all resins and was attributed to the removal of tannic acid, which was a high HAA former. The sHAA-FP was higher than it would be expected based on their concentration and their individual formation potential. The observed value was 61 mg g_{DOC}^{-1} higher than anticipated, whereas after treatment (when benzoic acid was mostly removed) the discrepancy was below 11 mg g_{DOC}^{-1}. The explanation for this observation was unclear, but this suggests that there may be reactive intermediaries that enhance the formation of some DBPs when more complex mixtures are considered. This may also offer explanation for why such variability in DBPs is seen in real water sources before and after IEX treatment.

In mixture 2, the DOC concentration of tannic acid was very high and the proportion of resorcinol was relatively small, hence the sTHM-FP of the untreated water was comparatively low (155 mg g_{DOC}^{-1}). Also the increase of the sTHM-FP after treatment was not as high as seen for mixture 1. The sHAA-FP in the untreated solution was 151 mg g_{DOC}^{-1} and therefore higher than in mixture 1, which was also explained by the increased tannic acid concentration.

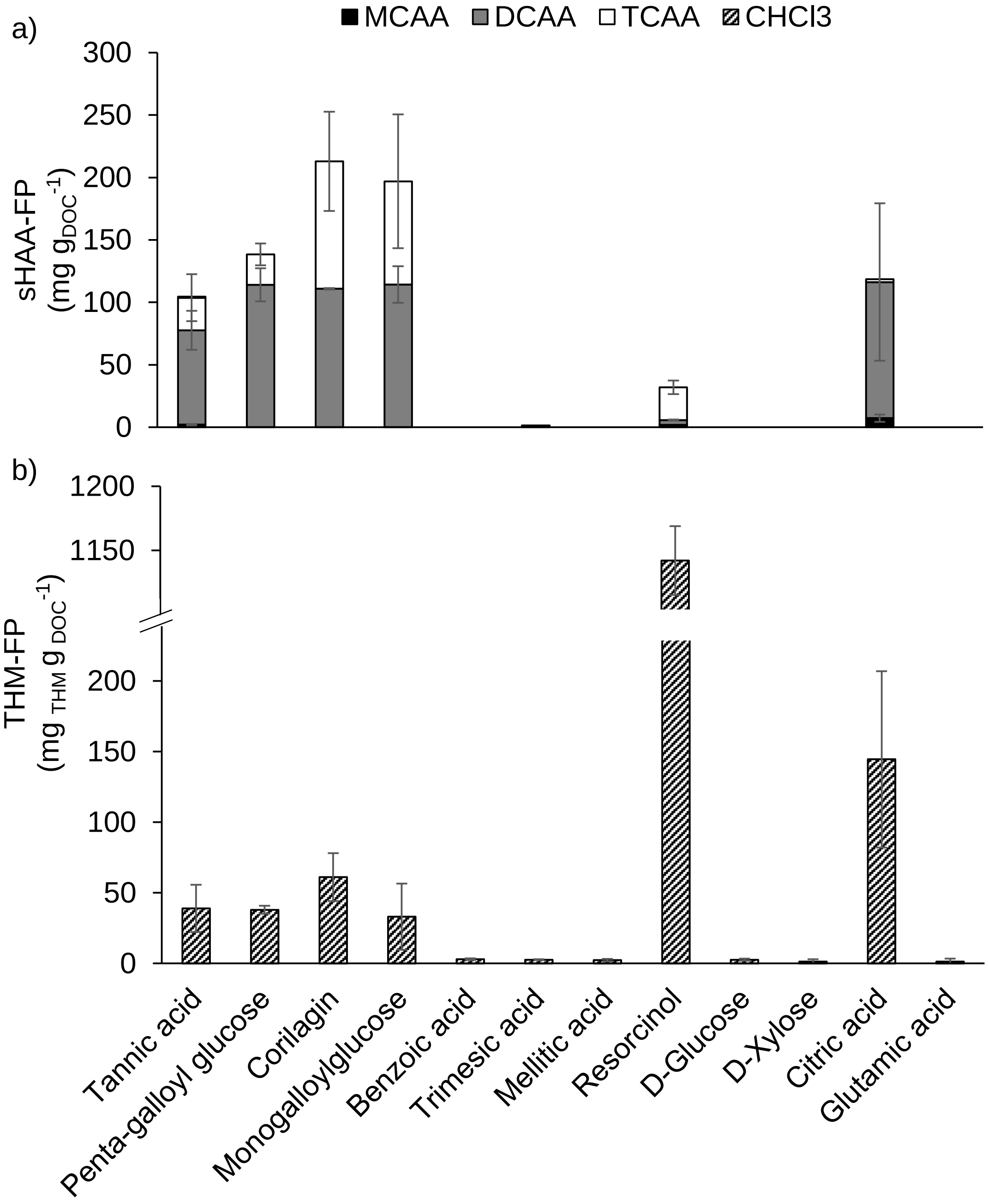


Figure 4.6: Specific DBP-FP of the model compounds: a) sHAA-FP and b) THM-FP; MCAA = Monochloroacetic acid, DCAA = Dichloroacetic acid, TCAA = Trichloroacetic acid, $CHCl_3$ = Chloroform.

Table 4.2: sHAA- and THM-FP of mixture 1 and 2 before and after treatment with the different resins; expected values were calculated from the sHAA- or sTHM-FP of each individual compound and their proportion of the overall DOC of the solution.

	sDBP-FP	Resin	measured (mg g_{DOC}^{-1})		expected (mg g_{DOC}^{-1})	
			untreated	treated	untreated	treated
Mixture 1	sHAA-FP	Lewatit	105	42	44	49
		Dowex		40		50
		MIEX		37		42
	sTHM-FP	Lewatit	438	813	394	811
		Dowex		741		798
		MIEX		952		816
Mixture 2	sHAA-FP	Lewatit	151	-	89	96
		Dowex		132		95
		MIEX		108		93
	sTHM-FP	Lewatit	155	239	116	131
		Dowex		194		155
		MIEX		201		157

4.4.7 Link to real water application

The influence of charge, hydrophobicity and MW were independently evaluated using the known structure and physicochemical properties of model compounds.

Studying individual compounds showed that hydrophobic character noticeably improved selectivity at low CD, especially for resins with a styrene backbone. This was shown by the removal of uncharged hydrophobic molecules. In real water the concentration of neutral compounds is very hard to establish as bulk charge density measurements provides only information about the overall charge load. Similarly, when real waters are split into fractions of different hydrophobicity, there is no information provided about the charge of the compounds present in this fraction. For individual compound experiments, a direct correlation between CD and DOC removal was observed, while for real waters this observation has not been seen (Chapter 3), presumably as a result of the removal of uncharged compounds. At high CD the importance of hydrophobicity diminished, whereas at

CD < 5-10 meq mg_{DOC}^{-1} hydrophobic interactions and MW contributed to the selectivity.

However, compounds with multiple charged groups do not necessarily exchange all of their anionic groups, resulting in a higher charge removal than sites occupied on the resin. This explains the high CL removal efficiency seen for waters of high CD (Chapter 3). Furthermore, glutamic acid showed that oppositely charged groups on a molecule inhibited its removal, an aspect that has not been considered in investigations treating real water. These observations are thought to be another aspect of the missing correlation between CD and DOC removal in real waters.

Molecular weight was an important factor for the removal of NOM, where reduced removal has been observed at an increased concentration of molecules around 1 kDa (Chapter 3). However, these molecular weights have been assessed using liquid chromatography organic carbon detection (LC-OCD) which take their estimated value from reference materials of known size, resulting in some inaccuracy. The model compounds therefore provide further insight into the removal of different size fractions by knowing their exact molecular weight. Furthermore, it was shown that the removal of molecules such as tannic acid (1701 Da) and PGG (940 Da) was lower at elevated concentrations and supporting the proposition that these compounds block resin pores, consistent with observations seen for real waters. These compounds would typically be found in the 1 kDa fraction when using LC-OCD.

The use of model compounds identified that the sDBP-FP and its reduction depended on the composition of the mixture. The ratio of different compounds defined the resulting sHAA- and sTHM-FP, and apparent synergistic effects were observed. This provides an answer to the question as to why IEX treatment resulted in a reduction of sDBP-FP for real water sources in some cases, while in others no change was observed (Chapter 2 and 3).

It was shown that the charge, hydrophobicity and size of a compound were influential in its removal and therefore the model compound investigation confirmed the hypothesis that all three factors have to be accounted for in order to allow for a comprehensive evaluation of the treatability of a water.

4.5 Conclusion

The model compounds were shown to be removed based on their physicochemical properties and the following conclusions can be drawn:

- The charge density was found to be the most indicative factor explaining compound removal. Removal increased rapidly between a CD of 0.4 to 4.0 meq g_{DOC}^{-1} and reached a maximum at 5 to 10 meq g_{DOC}^{-1} with consistently high removal observed for CD above this threshold (≥89%), with the exception of zwitterions. At high CD the hydrophobicity of a compound was not influential on its removal.
- The exchange of glutamic acid was inhibited due to its zwitterionic character. Exchanged glutamic acid bound with only one of the two carboxylic acid groups to the resin.
- Aromatic neutral compounds were removed according to the extent of hydrophobic interactions with the resin, emphasising the importance of hydrophobicity at low CD. The maximum removal of resorcinol was achieved with a macroporous polystyrene resin.
- An increase of concentration of small compounds did not impact the removal efficiency considerably. However, large compounds such as tannic acid experienced a reduced removal at high concentration due to pore blockage.
- The presence of competing anionic organic compounds was shown to be either beneficial or detrimental for the removal of tannic acid, depending on the resin structure.
- Resorcinol was the compound with the highest sTHM-FP and was important for mixtures that contained this molecule. It was removed more effectively by the hydrophobic Dowex resin, resulting in higher reactive precursor reduction than seen for the polyacrylic resins.

4.6 Acknowledgements

The authors would like to thank Scottish Water for their financial support to conduct this research. The resins used in this study were kindly provided by PWNT, DOW and IXOM. Furthermore, the authors would like to thank Adel Abrar from Phenomenex for his support in developing a method for the HPLC analysis.

4.7 References

Bazri, M.M., Mohseni, M., 2016. Impact of natural organic matter properties on the kinetics of suspended ion exchange process. Water Res. 91, 147–155.

Bhandari, V.M., Sorokhaibam, L.G., Ranade, V.V., 2016. Ion Exchange Resin Catalysed Reactions - An Overview, in: Industrial Catalytic Processes for Fine and Specialty Chemicals. Elsevier, pp. 393–422.

Bolto, B., Dixon, D., Eldridge, R., King, S., Linge, K., 2002. Removal of natural organic matter by ion exchange. Water Res. 36, 5057–5065.

Bond, T., Goslan, E.H., Parsons, S.A., Jefferson, B., 2010. Disinfection by-product formation of natural organic matter surrogates and treatment by coagulation, MIEX and nanofiltration. Water Res. 44, 1645–1653.

Boyer, T.H., Singer, P.C., 2008. Stoichiometry of Removal of Natural Organic Matter by Ion Exchange. Environ. Sci. Technol. 2008, 42, 608–613.

Boyer, T.H., Singer, P.C., Aiken, G.R., 2008. Removal of Dissolved Organic Matter by Anion Exchange : Effect of Dissolved Organic Matter Properties. Environ. Sci. Technol. 42, 7431–7437.

Christman, R.F., Ghassemi, M., 1966. Chemical Nature of Organic Color in Water. J. - Am. Water Work. Assoc. 58, 723–741.

Conway, B.E., 1981. Ionic Hydration in Chemistry and Biophysics. Elsevier Scientific Publishing Company, Amsterdam.

Cornelissen, E.R., Moreau, N., Siegers, W.G., Abrahamse, A.J., Rietveld, L.C., Grefte, A., Dignum, M., Amy, G., Wessels, L.P., 2008. Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions. Water Res. 42, 413–423.

De Dardel, F., 2019. Ion Exchange, URL http://dardel.info/IX/index.html (accessed 06 February 2019).

Degtyarenko, I.M., Nieminen, R.M., 2010. Dynamics of Biomolecules From First Principles, in: Nanoclusters: A Bridge across Disciplines. Elsevier, Oxford, pp. 557–573.

Finkbeiner, P., Redman, J., Patriarca, V., Moore, G., Jefferson, B., Jarvis, P., 2018. Understanding the potential for selective natural organic matter removal by ion exchange. Water Res. 146, 256–263.

Ghoussoub, Y.E., Fares, H.M., Delgado, J.D., Keller, L.R., Schleno, J.B., 2018. Antifouling Ion-Exchange Resins. ACS Appl. Mater. Interfaces 10, 41747–41756.

Gibson, A., Golubovic, S., 2015. MIEX Gold resin: Demonsatrtion at Aireys Inlet. Water J. Aust. Water Assoc. 42, 50–52.

Harland, C.E., 1994. Ion Exchange: Theory and Practive, 2nd ed. The Royal Society of Chemistry, Cambridge.

Humbert, H., Gallard, H., Jacquement, V., Croué, J.-P., 2007. Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water. Water Res. 41, 3803–3811.

Liang, X., Butler, E.C., 2010. Effects of natural organic matter model compounds on the transformation of carbon tetrachloride by chloride green rust. Water Res. 44, 2125–2132.

Mergen, M.R.D., 2008. Impact of magnetic resin on DOC removal and downstream water treatment processes. PhD Thesis, Cranfield University.

Metcalfe, D., Rockey, C., Jefferson, B., Judd, S., Jarvis, P., 2015. Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process. Water Res. 87, 20–28.

Rahmani, S., Mohseni, M., 2017. The Role of Hydrophobic Properties in Ion Exchange Removal of Organic Compounds from Water. Can. J. Chem. Eng. 95, 1449–1455.

SenGupta, A.K., 2017. Ion Exchange in Environmental Processes. John Wiley & Sons, Inc., Hoboken, NJ, USA.

Sillanpää, M., Levchuk, I., Marquez, J., 2018. Removal of natural organic matter (NOM) from water by ion exchange - A review. Chemosphere 192, 90–104.

Vinu, A., Ji, Q., Hill, J.P., Ariga, K., 2012. Mesoporous Nanoarchitectonics, in: Manipulation of Nanoscale Materials: An Introduction to Nanoarchitectonics. The Royal Society of Chemistry, Cambridge.

Zhang, Y., Zhao, X., Zhang, X., Peng, S., 2015. A review of different drinking water treatments for natural organic matter removal. Water Sci. Technol. Water Supply 15, 442–455.

4.8 Supplementary information

4.8.1 Calculation of resin concentration

Resin analysis: The mean size of the resin beads was obtained from a Mastersizer (Mastersizer 3000, Malvern). The void volume of the resin was determined by an adjusted method described by Harland (1994). A volume of 25 mL conditioned resin in the chloride form was filled in a measuring cylinder and DI water was added to give a total volume of 50 mL. The content of the measuring cylinder was filtered through a Buchner funnel by applying a vacuum. The volume of the supernatant was subtracted from of the filtrate volume and divided by the resin volume to give the void percentage.

The average bead size and void volume for Lewatit resin was 767 µm and 26%, respectively. For uniform spherical beads this equates to a resin surface area of 11.57 m^2. For the same area of Dowex resin with a bead size of 685 µm and a void volume of 29% a volume of 19 mL L^{-1} is required. For practical reasons a volume of 20 mL L^{-1} was chosen. For MIEX resin that had a bead size of 165 µm and 23% void volume, the required volume was 4 mL.

4.8.2 Supplementary figures

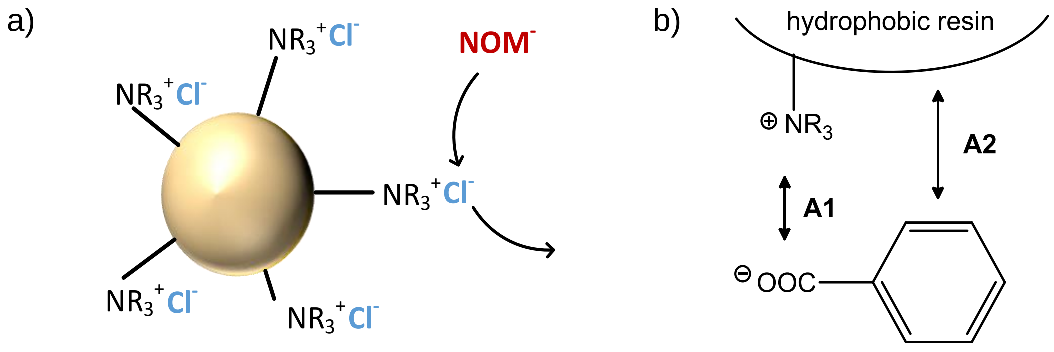


Figure S 4.1: Schematic of ion exchange of chloride on a strong base anion exchanger for negatively charge NOM (natural organic matter), b) attractive forces between resin and benzoic acid exemplary for organic molecules: A1 electrostatic and A2 hydrophobic interact

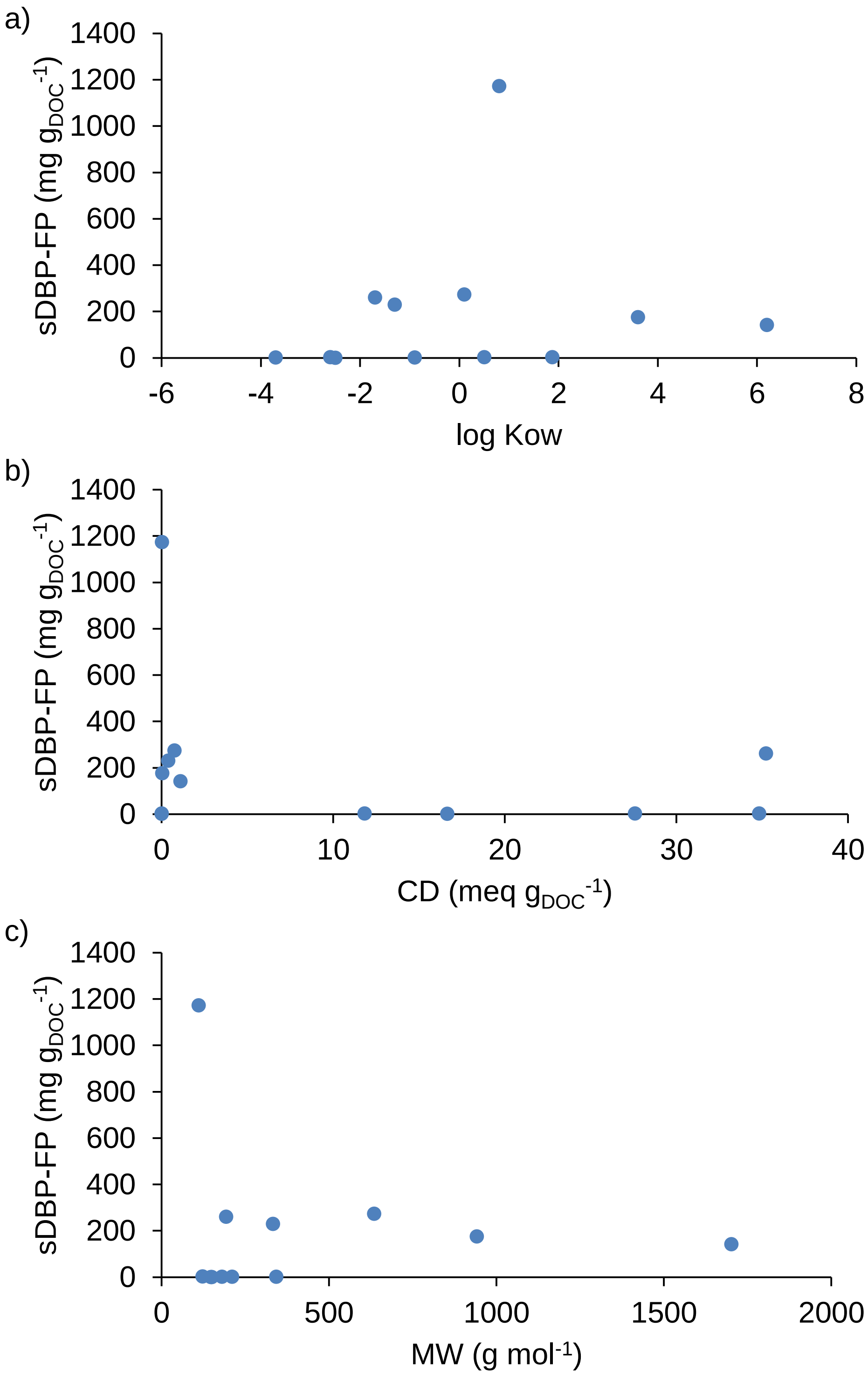


Figure S 4.2: sDBP-FP as a function of physicochemical properties a) hydrophobicity (expressed as logK$_{ow}$), b) charge density (CD) and c) molecular weight (MW).

4.8.3 Supplementary Tables

Table S 4.2: Comparison for removal of tannic acid in single compound solution and mixtures calculated from initial and final DOC concentration.

	Removal in mixture		**Removal in single compound solution**	
	10 mg L^{-1} of DOC per compound	0.119 mM of each compound	10 mg L^{-1} of DOC per compound	0.119 mM of each compound
Lewatit	64%	16%	56%	15%
Dowex	69%	46%	71%	49%
MIEX	74%	32%	78%	-

4.8.4 References

Bluhm, L.H., Li, T., 2003. The Role of Analogue Ions in the Ion-Pair Reversed-Phase Chromatography of Quaternary Ammonium Compounds. J. Chromatogr. Sci. 41, 6–9.

Conway, B.E., 1981. Ionic Hydration in Chemistry and Biophysics. Elsevier Scientific Publishing Company, Amsterdam.

Degtyarenko, I.M., Nieminen, R.M., 2010. Dynamics of Biomolecules From First Principles, in: Nanoclusters: A Bridge across Disciplines. Elsevier, Oxford, pp. 557–573.

Dow, n.d. Product Information DOWEX^{TM} TAN-1, URL https://www.lenntech.com/Data-sheets/Dowex-TAN-1-L.pdf (accessed 11 February 2016).

Ishikawa, A., Hanai, T., Koizumi, N., 1984. Dielectric properties of quaternary ammonium ion-exchange beads dispersed in aqueous phases. Colloid Polym. Sci. 262, 477–480.

Lanxess, 2015. Product Information Lewatit ® s 5128, URL https://www.lenntech.com/Data-sheets/Lewatrit-S-5128-L.pdf (accessed 02 March 2016).

5 DISCUSSION:
ION EXCHANGE - A WAY FORWARD

The thesis explored the removal of natural organic matter by ion exchange (IEX) at different scales, using real waters and solutions containing model organic compounds. The implication of the key findings are evaluated to inform decisions about the implementation of IEX for removal of natural organic matter (NOM).

5.1 When should IEX be used in the drinking water process?

A key observation of this work was that IEX upstream of coagulation improved the overall dissolved organic carbon (DOC) removal. Hence IEX can increase the performance of a treatment facility, where coagulation cannot provide the required final water quality. It was shown that different hydrophobic water sources in Scotland containing high DOC values (up to 11.4 mg L^{-1}) were effectively treated by the combined process (Chapter 2 and 3).

To decide whether IEX is a viable option as a pre-treatment, raw water characteristics have to be considered. Across the thesis, the charge of the organic compounds in the water has been identified as a key parameter for the IEX process. In the case of highly charged compounds (above 5-10 meq mg_{DOC}^{-1}) consistent removal was observed irrespective of other characteristics. However, with moderately charged compounds (0.4-4.0 meq mg_{DOC}^{-1}), the molecular weight (MW) and hydrophobicity influenced the removal profile (Chapter 4). Accordingly, a major implication of this work is that raw water characterisation that combines charge density, hydrophobicity and MW is critical to fully understand the potential efficacy of IEX alone or in combination with coagulation. The associated guide can be described as:

1. IEX should be used on water that contains at least a moderate level of charge, > 4 meq mg_{DOC}^{-1}. Below this level the appropriateness of IEX as a pre-treatment will be progressively poorer as the charge density decreases.

2. IEX was most effective at removing low-medium MW charged compounds. In fact, it was more effective than coagulation for this application and will therefore be suitable without coagulation for water rich in such compounds if the DOC is low.
3. IEX removal of large MW charged compounds is restricted as they experience size exclusion or blockage of exchange sites on an IEX resin. These compounds are better removed by coagulation. The critical MW is related to the IEX resin but a threshold of 8 kDa can be used as a general guide (Chapters 3 and 4). If the water contains a very high proportion of high MW compounds, then a pre-treatment may be preferred. For example, a low dose of coagulant will preferentially remove the HMW compounds.
4. The resin dose should be matched to the charge load (and proportion of HMW organics) to ensure consistent removal. This should replace the current practice of keeping the resin dose constant or to change it based on variation in DOC or UV_{254}.

IEX or coagulation could be used depending on the influent raw water quality: for waters of low DOC range and high charge, the preferable method would be IEX. On the other hand, when the NOM is primarily high MW, coagulation would be the better choice. For high DOC water sources, the combination will ensure very high overall removal and robust compliance to DBP regulations.

While IEX can be regarded as an option to improve water quality, coagulation cannot be dispensed with in the treatment train for the investigated water due to the requirement to remove suspended particles and residual DOC. An IEX-membrane configuration (without coagulation) was tested and found to be unfeasible due to a high increase in the TMP. The membrane fouling increased by >200 kPA within 8h. This phenomenon was thought to be as a result of fouling by large organic molecules that were not removed by SIX when the water was not coagulated. These molecules can attach to the membrane and are not released by the periodical backwashes (BWs). Conversely, the formation of a cake layer by the coagulant could be easily removed using regular BWs. The understanding of the synergies between coagulation and membrane filtration are an interesting subject that should be explored in further research.

It would also be possible to consider operating ion exchange after coagulation. In this case, the pre-coagulation could remove the bulk of the DOC, especially the large molecular weight fraction. This would allow SIX to operate as a polishing step that reduces the DOC further, ensuring that removal limitations or fouling are kept to a minimum as a result of the pre-treatment. A lower incoming DOC load for the SIX process would require lower resin concentrations and fewer regeneration cycles. Whether this set-up leads to a reduction of the sDBP-FP (compared to coagulation alone) as observed for SIX+CCMF has to be investigated.

Translation of the results to other types of organic matter contained in different water sources (for example effluent organic matter or algal organic matter) is currently inhibited by a lack of appropriate characterisation. This characterisation is strongly recommended prior to the use of IEX.

5.2 How can the efficiency of NOM removal by IEX be estimated?

In order to estimate water treatability by IEX, it is important to determine water quality characteristics. The results from this research have shown that the treatability of NOM by IEX requires a combination of different analytical measurements.

Charge measurements provide information about the charge load and CD of the organic matter. As elucidated in the model compound work, charge was the most important parameter for high CD water sources (Chapter 4). However, CD alone cannot be used to estimate treatability due to the interrelationship with other physicochemical parameters (Chapter 2 and 3). The measurement of the MW distribution of NOM was another important consideration. In determining the treatability of a water, the medium MW fraction (P2) was an important size fraction due to its dominance in the investigated waters. While being generally well removed, high concentrations of these compounds can limit the removal of DOC (Chapter 2 and 3). The occupation of the resin with organic compounds of this size range was linked to pore blockage, limiting access to other exchange sites. This was seen for the high DOC source water (water A) as well as for the model compounds, where an increased concentration of tannic acid was detrimental to its relative removal (Chapter 3 and 4). Knowing the proportion of this size fraction would allow the resin dose to be adjusted appropriately to maintain resilient treatment. Similarly, the concentration of the HMW fraction offers information on the overall removal efficiency, based on the size exclusion effects, pore blocking and covering of exchange sites by molecules of the P1 size fraction.

Estimations of DOC removal can be made by measuring the CD, the P1 and P2 size fraction and the hydrophobicity. Highly charged compounds were found to be well removed (Chapter 4) and the reduction of charge in waters of high CD was seen to be large (Chapter 3). Therefore a generally high removal can be expected for highly charged compounds and this was estimated to be >90% (Figure 5.1). The removal of NOM fractions in real water was of the order: hydrorophobic (HPO), transphilic (TPI) and hydrophilic (HPI) (Chapter 2 and 3). This was also the case for the model compounds tannic acid (HPO) and MGG (HPI). Both were of low to moderate charge, however they were quite different in their hydrophobicity. Therefore, for low to moderate charge in the fractions, a removal of 75, 50 and 35%, for HPO, TPI and HPI, respectively, is proposed. High molecular weight compounds were generally less well removed. In the real waters the removal of this fraction (P1) ranged between 12 and 39% (Chapter 2 and 3). The high MW model compound poly(acrylic acid)sodium salt (15 kDa; classified as a P1 compound), was removed by between 28 and 67%, depending on the nature of the resin (Chapter 4). This led to the estimation of high MW compounds in the P1 fraction to be removed by about 30%. The medium MW fraction (P2) was removed by up to 93% for highly charged raw waters (Chapter 3). When no resin limitation was present, these compounds were expected to be removed similarly for other waters and a removal of about 90% is suggested. When this fraction has a lower charge the removal would correspondingly be reduced. This was the case seen for tannic acid and PGG which were reduced by 73% (Chapter 4). Both of these compounds are low to moderately charged and found in the P2 MW band. Hence, the medium MW compound removal was estimated to be 75% for IEX.

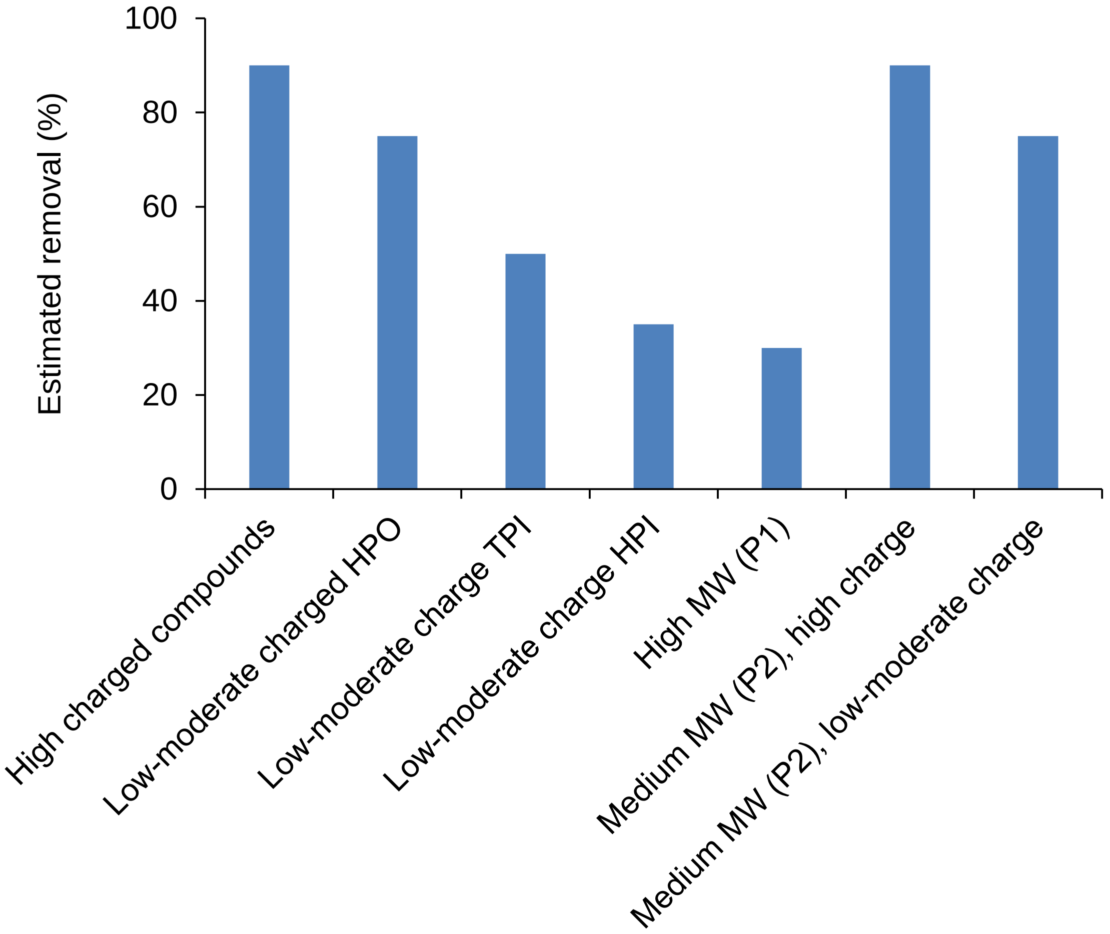


Figure 5.1: Estimated removal for different NOM components.

The model compound work clearly showed that hydrophobic and aromatic interactions have an influence on the removal of low charged molecules. While the removal of resorcinol by acrylic resins was low, the polystyrenic resin showed higher removal of up to 29% (Chapter 4). Hydrophobic and aromatic interaction between organic molecules in solution and the polystyrene resin increased the attraction and facilitated the removal. For hydrophobic compounds or those containing an aromatic structure, a removal that is 2 to 3 times higher is estimated for a styrene resin compared to an acrylic resin. Hence the knowledge of resin properties helps to estimate DOC removal by IEX.

Overall, the highest removal of NOM by IEX is expected to be seen for a highly charged water, low in the P1 MW size fraction and with a high proportion of the HPO fraction treated using polystyrene resin. A removal of >90% is estimated under the premise that no limitations occur as result of occupation of exchange sites by the P2 fraction. This also requires the resin to be effectively regenerated to ensure that accessible exchange sites are made available.

5.3 What are the benefits of using IEX?

One of the important observations from this work was that the use of IEX as a pre-treatment step enabled a synergistic effect in terms of DOC removal and sDBP-FP reduction. Therefore, IEX effectively increases the final water quality and improves the performance of a treatment process, which was regarded as the main advantage of its application compared to conventional coagulation. IEX is regarded as a valuable pre-treatment option to reduce DOC loads further than coagulation alone and enable DBP targets to be met.

This was demonstrated by the higher DOC removal in the combined process (up to 94%) compared to individual coagulation or IEX, and a resulting average residual DOC of 0.7 mg L^{-1} (Table 1, Chapter 2 and 3). The pilot plant trial showed that more than 80% of the DOC measurements were below 1 mg L^{-1} compared to 17% for coagulation (Chapter 2). Additionally, the combined process showed a higher robustness (slope = 1.25) than IEX (0.16) or coagulation (0.93), demonstrated in a more stable final water quality with changing raw water. Hence the IEX&Coag treatment was suitable for a fluctuating water source. The robustness of the IEX process can be improved by having more flexibility of the resin dose through adjustment based on the raw water quality. Additionally, IEX can be easily taken out of the treatment train by simply discontinuing the dosing of the resin to the raw water.

Compared to a conventional full scale plant, the IEX process combined with coagulation provided considerably lower DOC values as well as much lower DBP values. Pre-treatment with IEX and subsequent coagulation targeted the reactive DBP precursors. Even at high DOC concentration and when the proportional DOC reduction from IEX was low, the combined process generally reduced the sDBP-FP further than coagulation managed by itself (at a higher dose). The average specific HAA- and THM-FP of 39 and 42 mg g_{DOC}^{-1} for the final water in the pilot plant demonstrate the benefit compared to coagulation with 66 and 64 mg g_{DOC}^{-1} (Chapter 2) and similar values were obtained in the jar tests.

One can argue that the ceramic membrane combined with in-line coagulation is able to reduce the DOC load and the sDBP-FP sufficiently. However, the additional removal of reactive DBP pre-cursors by IEX can be important when stricter regulations are enforced, for example the proposals for regulation of HAA9 in the new EU drinking water directive. The combined treatment is able to provide greater resilience to DBP failures than coagulation alone and result in improved water quality for the water companies who target increasing compliance. The question whether IEX can be dispensed of needs to be assessed for the raw water quality, water quality targets and the resilience required for future scenarios.

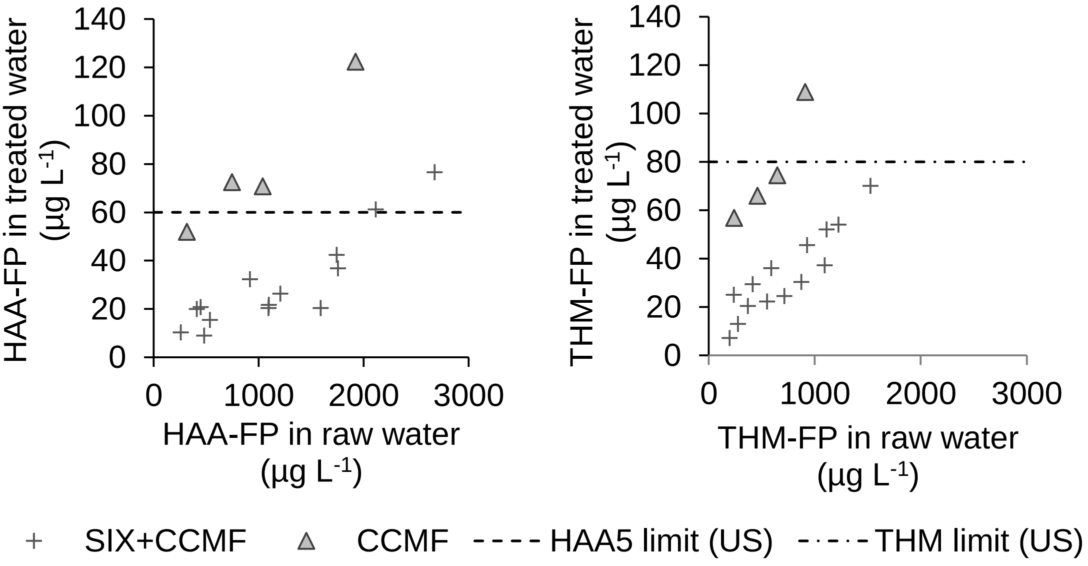


Figure 5.2: HAA- and THM-FP after SIX+CCMF and CCMF treatment as a function of the raw water DBP-FP, including the current regulated limits for HAA5 and THM in final water (formation potential tests are performed with excess of chlorine and

therefore represent the maximum DBP concentration possible; values do not represent expected DBP levels and serve for comparison only).

Furthermore, IEX pre-treatment enabled the reduction of coagulant use. The coagulant dose (Al^{3+}) was up to 42% lower than that required for coagulation alone (Chapter 2 and 3). Facilitated by the reduction of the DOC load in the IEX stage and the lower coagulant dose required for the residual DOC, this in turn decreases the sludge production of the process by about 50% (Table 1). The DOC removal for a highly treatable water is expected to be around 90% for IEX (CD > 10 meq mg_{DOC}^{-1}, low in P1, hydrophobic character). As a result the commensurate reduction in downstream coagulant dose may lead to sludge volume reductions around 90%. However, this should be balanced with the production of another waste stream, the regeneration brine. As a waste stream with a high salt content, this can be difficult to dispose of, particularly for WTWs that do not have a sewer connection.

Economically, incorporating IEX in the treatment increases the costs of chemicals. As an example, the amount of salt required for regenerating the resin would be approximately 0.06 £ m^{-3} higher than the costs saved for the lower coagulant dose when considering treatment of water source containing a DOC concentration of 6.6 mg L^{-1}. However, this does not take into account the improved DOC removal achieved by the combined process, so the final water quality is not comparable.

Other factors that should also be taken into account include costs for the treatment or disposal of the regenerant brine solution is an issue that has to be addressed if discharge into a river, sea or sewer system is not available. In these cases, the costs of tankering the brine for disposal or treatment using membranes or coagulation need to be considered. These increased costs need to be evaluated alongside the benefits of improved water quality depending on the individual circumstances of the location.Overall, the results show that IEX is a highly favourable treatment process for treatment of NOM laden water sources. IEX is regarded as a valuable pre-treatment option to reduce DOC loads further than coagulation alone and allow to meet DBP targets. For WTWs that have seen increases in the concentration of NOM in the receiving waters, conventional coagulation and clarification processes can often struggle to remove sufficient DOC from the water. In these cases, IEX can be retrofitted into the treatment flowsheets to enable more robust removal of DBP precursors when used as a pre-treatment to coagulation. Where new WTWs are being considered, IEX can be a pre-treatment to emerging processes such as ceramic membranes, either with or without in-line coagulation, depending on the raw water quality characteristics. This option has the potential to significantly reduce the footprint of new WTWs as well as providing high quality drinking water.

Table 5.1: Average values for different treatment (Chapter 2 and 3) and estimated values for highly IEX-treatable water source, based on the findings of the thesis.

	Pilot plant (Chapter 2)			**Jar tests (Chapter 3)**			**Proposed *****
	IEX	Coag.	IEX& Coag	IEX	Coag.	IEX& Coag	IEX& Coag
DOC removal (%)	45	73	84	75	78	92	95
Coagulant dose ($mg_{Al^{3+}}$ mg_{DOC}^{-1})	0	0.75	0.47	0	0.49	0.32	0.32
Robustness*	0.16	0.93	1.25	n.a.	n.a.	n.a.	n.a.
Residual DOC (mg L^{-1})	2.6	1.3	0.7	2.4	1.9	0.7	0.3
Sludge mass (g m^{-3})**	0	16.5	8.1	0.0	13.2	6.6	1.0
sHAA-FP (mg g_{DOC}^{-1})	185	66	39	155	68	35	n.a.
sTHM-FP (mg g_{DOC}^{-1})	119	64	42	91	79	50	n.a.

*Robustness evaluated by steepness of the slope in the linear region of the cumulative probability curve between 15 and 85% (Chapter 1); **Sludge mass calculated with following assumptions: no suspended solids, $M_{PACl} = M_{Al2Cl(OH)5}$ = 174.5 g mol^{-1}, DOC in raw water = 6.6 mg L^{-1}, DOC removal by IEX was 45% (average in pilot plant), residual DOC after combined treatment = 0.7 mg L^{-1}; n.a. = not applicable. ***Proposed removal of highly treatable source water (CD > 10 meq mg_{DOC}^{-1}, low in high molecular weight organics, hydrophobic character) with expected removal of 90% by IEX and overall reduction by 96%.

6 CONCLUSIONS
AND FUTURE WORK

6.1 Conclusions

6.1.1 Treatability

- Dissolved organic matter (DOC) and disinfection by-product formation potential (DBP-FP) for a fluctuating water source were shown to be successfully reduced by ion exchange (IEX) combined with coagulation.
- The combination of IEX and coagulation resulted in a synergistic effect, showing lower DOC concentrations in the treated water and higher removal of reactive DBP precursors than the individual processes. IEX removed organic compounds that enabled enhanced removal of high DBP forming organic matter in the coagulation stage.
- The combined process consistently demonstrated high quality treated water, independent of water type of varying initial DOC concentration and composition.

6.1.2 Physicochemical properties

- Charge density (CD) was identified as the most important parameter for the removal of organic molecules using model compounds, but could not be correlated to DOC removal by used resin for real waters due to the interlinked influences of hydrophobicity and size. However, when virgin resin was used to treat real waters of elevated CD, a high removal was observed that was in line with the model compound work.
- Medium and low molecular weight molecules were well removed, however compounds of the weight fraction around 1 kDa, occupy easily accessible exchange sites, blocking resin pores, when the organic loading is high.
- Size exclusion was the limiting factor for high molecular weight organic compounds.

- The hydrophobicity of the resin and organic compounds was important, especially for uncharged molecules, even in waters containing charged compounds.
- The resin structure had an impact on the removal. A more hydrophobic and aromatic resin enhanced non-electrostatic interactions between the exchanger and organic molecules.
- The combination of charge, molecular weight and hydrophobicity were important in understanding the treatability of a water source by IEX.
- Organic molecules can compete for exchange sites or assist sorption processes depending on their nature and the resin characteristics.

6.2 Future work

This work has shown that the aggregation of charge, hydrophobicity and molecular weight improve the understanding of the removal of natural organic matter (NOM) by IEX. However, further research is needed to expand the understanding of this process:

- The evaluation of water treatability can be enhanced by quantifying the CD of the different size and hydrophobicity fraction. Size analysis of the hydrophobicity fractions would further support the understanding of selective DOC removal by IEX.
- To further understand the interaction between organic compounds and the resin, additional resin characterisation should be undertaken. Surface analysis such as X-ray diffraction or photoelectron spectroscopy could be used to identify differences between used and virgin resin. Additionally, it is of interest to measure the porosity of the resins. Porosimetry can be used to show differences in pore size distribution between resins and allow the study of changes to the available pore volume and diameter of used resin.
- Investigation of compound mixtures with a higher number of different molecules should be carried out in order to show possible multicomponent interactions.

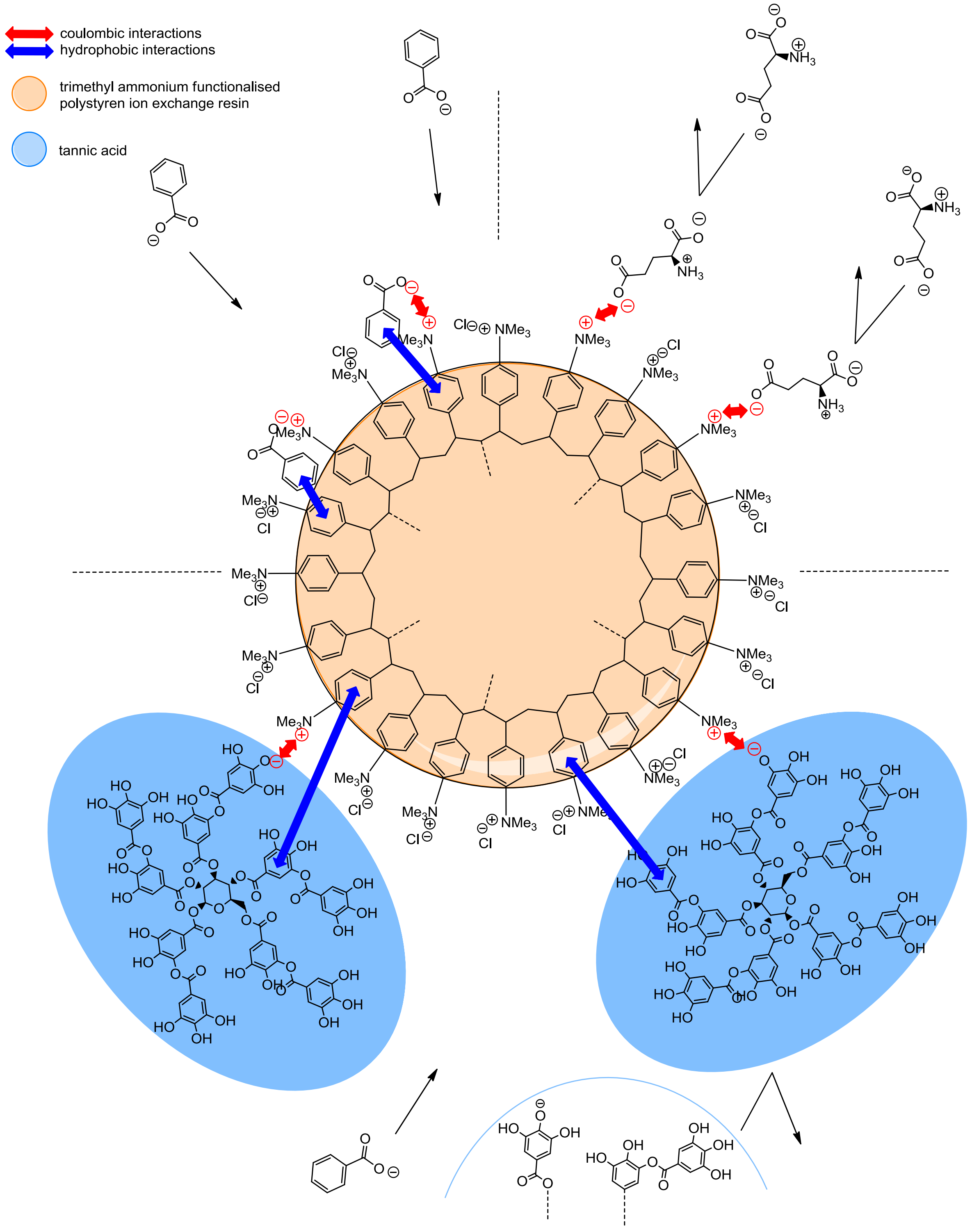
- Regeneration is a crucial aspect of the IEX process. Insufficiently regenerated resin has been seen to significantly reduce removal efficiency and can lead to fouling. Hence understanding the relationship between NOM character on the resin and its regenerability can provide information on irreversible and reversible resin blinding.
- Brine management, resulting from IEX regeneration, requires consideration in order to reduce or recover waste streams. An option for energy recovery is the application of reverse electrodialysis which converts salinity gradient energy to electrical energy, through selective ion mixing (Tufa et al., 2018).
- Understanding the relationship between IEX treatment and emerging and non-regulated disinfection by-products is required to determine the potential of IEX for more widespread control of DBPs. This could be considered for compounds such as the haloacetonitriles, iodinated-DBPs, brominated-DBPs and the total organic halides (TOX).
- A combination of resins with different properties could provide improved removal of NOM. Combining different pore sizes and resins of different chemical structure (styrene and acrylic) could facilitate a broader removal of NOM by IEX.
- The polymeric IEX resins are a potential source of microplastic (MP) in water. The origin of resin beads found in river systems has been suggested to be from industrial water purification processes that use ion exchange (Mani et al., 2019). Therefore, the risk of resin carry-over and contamination of drinking water, brine solution or sludge with MPs requires attention.

6.3 References

Mani, T., Blarer, P., Storck, F.R., Pittroff, M., Wernicke, T., Burkhardt-Holm, P., 2019. Repeated detection of polystyrene microbeads in the lower Rhine River. Environ. Pollut. 245, 634–641.

Tufa, R.A., Pawlowski, S., Veerman, J., Bouzek, K., Fontananova, E., Velizarov, S., Crespo, J.G., Nijmeijer, K., Curcio, E., 2018. Progress and prospects in reverse electrodialysis for salinity gradient energy conversion and storage. Appl. Energy 225, 290–331.

APPENDIX



Figure_Apx 1: Interaction between organic molecules and polystyrene ion exchange resin with quaternary ammonium groups.